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AND TECHNOLOGY

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INTRODUCTION

The new classification guide of the Atomic Energy Commission places the majority of information on reactor technology and related subjects in the "Confidential" category. Much of the material in back issues of the Journal of Nuclear Science and Technology and its predecessors, the Journal of Metallurgy and Ceramics and the Journal of Reactor Science and Technology, falls into this category. In order to make such information readily available to those possessing a suitable clearance, articles from these earlier issues are being reissued as Gray Area Journals as follows:

TID-2501 JMC, Issues 1 thru 6 (TID-65 thru 69), July 1948 - January 1951
TID-2502 RST, Vol. 1, Issues 1 thru 3 (TID-71 thru 73), April 1951 - December 1951
TID-2505A Cumulative Index to all "back issue" JMC and RST Gray Area material
TID-2506 NST, Vol. 1, Issues 1 thru 3 (TID-2016 thru 2018), February - Vol. 1A, Issue 1

Due to the many changes which have taken place on the editorial staff of the Journal during its history, it has been considered inadvisable to specify individual credits for material from early issues. In this regard, the present editors would like to acknowledge the fine work of former editors, Bruce S. Old, George L. Weil and Frank R. Ward, through whose efforts most of the material was originally obtained.
Preparation and Properties of the Aluminum-Uranium Alloys

By H. A. Saller
Battelle Memorial Institute

Abstract

The constitution diagram of aluminum - uranium is replotted on a weight per cent basis. In spite of slight age hardening no significant solid solubility of uranium in aluminum is indicated. A eutectic between aluminum and UAl₃ occurs at approximately 13 weight per cent uranium. UAl₃ is produced by peritectic reaction between UAl₃ and liquid of 18 per cent uranium. UAl₃ also occurs.

Melting and casting of alloys are described as well as the forging and rolling characteristics. Tensile and hardness properties of variously heat treated rolled and forged samples containing from 2.43 to 16.8 per cent uranium are tabulated. Creep data for a 17.3 per cent uranium alloy sample and thermal conductivity of forged bars containing 12.5, 22.7 and 30.5 per cent uranium are also included.

INTRODUCTION

Aluminum-uranium alloys have long been of interest to pile designers as a possible means of distributing active material in a medium of relatively low cross section. These alloys, when clad with aluminum, also offer good corrosion resistance.

The constitution diagram of the aluminum-uranium system was first investigated by Kaufmann and Gordon of MIT. As the interest in the low-uranium alloys became greater, this portion of the diagram was investigated more completely. The final diagram is shown in Figure 1, replotted on a weight per cent basis to permit a closer examination of the aluminum-rich portion of the system.

It will be noted that no significant solid solubility of uranium in aluminum was indicated. This conclusion was based on microscopic examination of heat-treated samples and diffusion studies of alclad alloys. The slight age hardening, which was observed in some alloys, would indicate that some solubility is possible. It is believed, however, that the results obtained by the first two methods were more accurate, and that no significant solid solubility of uranium in aluminum does exist.

A eutectic between aluminum and UAl₃ occurs at approximately 13 weight per cent uranium. There is a peritectic reaction between UAl₃ and liquid of 18 per cent uranium, which produces UAl₃. This peritectic offers a possible means of controlling the type and amount of compound which will occur in cast alloys. As will be noted later, this phenomenon was used to produce rollable structures through the method of chill casting. The compound UAl₃ also occurs in the system.

Since alloys containing less than 35 per cent uranium were of greatest interest for pile designs, the major portion of the investigation was directed...
toward the casting, rolling, and alcladding of these alloys. As the various alloys were produced and fabricated, their physical properties were determined.

**PREPARATION OF ALLOYS**

**Melting and Casting**

Alloys of aluminum and uranium were prepared by open melting in either graphite or clay-graphite crucibles, using gas-air or induction heating. The uranium was added as pure metal, the oxide, or the tetrafluoride, with recoveries exceeding 90 per cent.

For alloys prepared from pure uranium, the aluminum was melted and heated to 800°C. The uranium was then added in small pieces with considerable stirring.

Attempts to add uranium oxide directly to molten aluminum gave negligible recoveries. A number of trial heats were made using an exothermic mix, briquettes of oxide and aluminum, and oxide or tetrafluoride plus cryolite. Since the oxide or fluoride plus cryolite mixture appeared most promising, further tests were made to determine the effect of holding time, holding temperature, and the amount of cryolite in the mixture. Results are given in Table 1.

The melting method finally used consisted in melting the aluminum under a layer of cryolite, then adding the cryolite-oxide or fluoride mix with constant stirring. The bath was stirred for one minute out of every five, during the holding period. The flux was then removed from the low-melting alloys by allowing it to freeze around a carbon rod. Alloys with a melting point close to that of the flux were allowed to freeze in the crucible. The slag and metal could then be separated, the metal remelted and cast.
Table 1. Recovery of uranium when added as oxide or fluoride to aluminum.

<table>
<thead>
<tr>
<th>Addition</th>
<th>Holding time, (min)</th>
<th>Holding temp., (°C)</th>
<th>Per cent uranium</th>
<th>Recovery per cent*</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Charge</td>
<td>In alloy</td>
</tr>
<tr>
<td>Exothermic mix†</td>
<td>60</td>
<td>1100/1200</td>
<td>8.7</td>
<td>2.7</td>
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<tr>
<td>Briquette, oxide and Al</td>
<td>5</td>
<td>850</td>
<td>8.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Briquette, plus flux</td>
<td>30</td>
<td>1100</td>
<td>8.8</td>
<td>9.1</td>
</tr>
<tr>
<td>Oxide plus cryolite</td>
<td>20</td>
<td>1100</td>
<td>10.0</td>
<td>8.9</td>
</tr>
<tr>
<td>55% cryolite and oxide</td>
<td>20</td>
<td>1100</td>
<td>10.0</td>
<td>7.2</td>
</tr>
<tr>
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<td>9.6</td>
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<td>1100</td>
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<td>8.0</td>
</tr>
<tr>
<td>55% cryolite and oxide</td>
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<td>1300</td>
<td>10.0</td>
<td>10.1</td>
</tr>
<tr>
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<td>1100</td>
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<td>9.5</td>
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<tr>
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<td>60</td>
<td>1300</td>
<td>10.0</td>
<td>10.7</td>
</tr>
<tr>
<td>65% cryolite and oxide</td>
<td>20</td>
<td>1100</td>
<td>20.0</td>
<td>18.3</td>
</tr>
<tr>
<td>65% cryolite and oxide</td>
<td>20</td>
<td>1100</td>
<td>20.0</td>
<td>18.4</td>
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<td>1100</td>
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<tr>
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<td>10.1</td>
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<tr>
<td>65% cryolite and fluoride</td>
<td>20</td>
<td>1100</td>
<td>10.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

*Calculated from analysis and total weight of recovered metal or product.
† Mix contained oxide, granular Al, NaNO₃, and Mg powder.
‡ Recovery low because of poor separation of slag and metal.

Alloys used for the first rolling experiments were cast into ingots 6 in. x 8 in. x 1 1/2 in. in a tilting steel mold. This type of mold was employed both to give a large amount of chill to the metal and to simulate commercial practice for pouring aluminum-sheet ingots. Eventually, the 35 per cent alloy was cast into ingots 4 in. x 6 in. x 1 1/2 in., using a steel mold with walls 1 1/2 inch thick. Pouring temperatures ranged from 700 to 1100°C, depending upon the uranium content of the alloy. The mold temperature did not exceed 150°C. This careful control of mold and pouring temperatures to give an extremely rapid cooling rate was found of great importance in the rolling of the 35 per cent alloy. As will be discussed more completely under fabrication and metallography, the
structure of the 35 per cent alloys was greatly affected by cooling rate during casting. This structure then had a marked effect upon fabrication.

Fabrication and Alcladding

In order to produce alloy sheet covered on all sides with aluminum, it was necessary to forge, roll, and clad the alloys.

Forging was accomplished at temperatures of 550 to 600°C on alloys containing up to 20 per cent uranium. Alloys in the range of 20 to 30 per cent uranium could be forged, but with great difficulty and low recoveries. Higher alloys were not forged successfully.

The hot-rolling qualities of the alloys were quite like the forging characteristics. Since the use of alloys containing 35 per cent uranium were desired for pile construction, it was necessary to develop methods of rolling these alloys.

From a consideration of the constitution diagram, it was observed that, during solidification of a 35 per cent uranium alloy, a large amount of $\text{UA}_1$ was formed. This compound then reacted with the liquid to form $\text{UA}_2$. If this peritectic could be suppressed, the amount of $\text{UA}_2$ formed would be lower. This would then cause less aluminum to be combined with uranium, and should reduce the volume of compound. Since the compounds were quite refractory, any reduction in their volume should improve the rolling qualities.

This method was only partially successful, but, by combining rapid cooling and the use of an aluminum jacket, the higher alloys (up to 40 per cent uranium) were rolled quite easily. The jacketing procedure consisted of fitting the alloy into a frame of 25 aluminum, then folding a sheet of aluminum over the core and frame to form a cover. The frame was folded over at the back, but the sides were left open. There was very little corrosion of the alloy core during heating. Scratch brushing of all contacting surfaces just before assembling was necessary to insure good bonding. Details of this jacketing method are shown in Figure 2. In cases where complete cladding was not desirable, the alloy core was coated with magnesium oxide before assembling. This coating prevented welding, and made it possible to strip the core from the jacket.

After the cast structure had been broken down by hot working, the alloys could be cold rolled quite easily. Even in alloys containing 35 per cent uranium, cold reductions of 50 to 60 per cent were made without annealing. Further cold reductions were possible by using intermediate anneals.

Alloys which could be broken down by hot rolling, unjacketed, were clad by the same jacketing technique employed for fabricating the higher alloys. In some cases, the alloys were rolled part of the way in one jacket, then cut and rejacketed in order to produce the desired ratio of core to cover in the final sheet.

![Metallography](image)

Metallography

The alloys of aluminum-uranium were polished quite easily with the techniques normally employed for polishing aluminum. Most of the alloys were etched with $\text{NaOH}$ or other standard aluminum etchants. Typical cast structures are shown in Figure 3. These samples were taken from sheet ingots, and were cooled quite rapidly. The alloy containing 9 per cent uranium showed a normal hypoeutectic structure. The apparently large amount of primary aluminum was caused by the high density of the compound. In the 18.1 per cent alloy, there were a few small crystals of $\text{UA}_1$ in the eutectic matrix. More of the $\text{UA}_1$ crystals can be observed in the 29.1 per cent alloy.
In Figure 4 are shown a rolled sample and the bond on an alclad sheet. It may be noted that cold rolling did not break up the large compound particles.

In connection with the use of rapid quenching to suppress the peritectic and improve fabricating qualities, it was necessary to develop methods of differentiating between UA\textsubscript{1}, and UA\textsubscript{2}. In Figure 5 are shown structures obtained in a 35 per cent alloy cooled at quite different rates. In the chillcast sample, the compound crystals (UA\textsubscript{1}) occur in long chains, but are not completely continuous. During fabrication, these crystal chains can be broken up without cracking. In the slow-cooled sample, the peritectic reaction has had time to approach completion, and long massive needles of compound

Figure 3. Structures of cast aluminum uranium alloys. NaOH etch. 100x
(UA\textsubscript{1}) have formed. Such a structure cracks very easily during fabrication. The structures obtained in these samples were, of course, the two extremes of those obtained from actual ingots. An etch consisting of chromic and acetic acids used electrolytically caused UA\textsubscript{1} to be colored yellow, while UA\textsubscript{3} was blue-gray. These results were confirmed by means of x-ray analysis.

In producing slab ingots for cladding experiments, a metallographic examination was used quite successfully to predict rolling qualities. Samples containing a large proportion of UA\textsubscript{1} would roll, while those containing only UA\textsubscript{3} would crack badly.

**PHYSICAL PROPERTIES**

**Tensile Testing**

Tensile tests were run on both 0.080-inch sheet stock and one-inch round forged bars of various uranium contents. Sheet specimens, containing 2.4 to 16.8 per cent uranium, were tested in the following conditions: as cold rolled, annealed three hours at 550°C, water quenched after three hours at 550°C, and aged six hours at 175°C after quenching. The solution and aging temperatures used were based on other aluminum alloys. Results of these tests are shown in Table 2. In the hard-rolled condition, the alloys showed a maximum of 28,000 psi tensile strength with a yield strength of 20,000 psi. These properties were found in the 9 per cent alloy. After annealing or quenching from 550°C, all alloys showed a decrease in yield and tensile strengths. In the quenched or annealed samples, there was an increase in strength with an increase in uranium content up to 9 per cent. Above this point, the strengths remained constant. The quenching treatment gave properties quite similar to those obtained by furnace cooling, indicating little, if any, solubility of UA\textsubscript{3} in aluminum. Aging the quenched alloys gave no significant change in properties.

Tensile properties of 12.5, 22.7, and 30.5 per cent uranium alloys are given in Table 3. These properties were obtained from standard 0.505-inch specimens machined from forged bars which had been annealed one-half hour at 370°C. The modulus of elasticity was determined by preloading the specimens to 1100 pounds (about 5500 psi). The specimens were then reloaded to 5000 psi, with elongations measured by Tuckerman strain gauges on both sides of the specimen. The sensitivity of the readings thus obtained was 0.000002 inch/inch.
Table 2. Tensile properties of uranium-aluminum alloy sheet.

<table>
<thead>
<tr>
<th>Composition, per cent uranium</th>
<th>Cold reduction, per cent</th>
<th>Per cent elongation</th>
<th>Yield strength.* (psi)</th>
<th>Tensile strength.* (psi)</th>
<th>Per cent elongation</th>
<th>Yield strength.* (psi)</th>
<th>Tensile strength.* (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As Rolled</td>
<td></td>
<td></td>
<td>Annealed 3 hr at 550°C</td>
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<td></td>
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<tr>
<td>2.43</td>
<td>58</td>
<td>7.5</td>
<td>19,300</td>
<td>21,800</td>
<td>24.8</td>
<td>4,870</td>
<td>11,650</td>
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<tr>
<td></td>
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<td>8.5</td>
<td>18,350</td>
<td>22,200</td>
<td>16.5</td>
<td>4,950</td>
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<td>3.10</td>
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<td>10.8</td>
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<td>22,400</td>
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<td>34.5</td>
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<td>Water quenched, 3 hr at 550°C</td>
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<td>23.7</td>
<td>9,250</td>
<td>18,850</td>
</tr>
<tr>
<td>14.3</td>
<td>45</td>
<td>23.5</td>
<td>8,600</td>
<td>18,000</td>
<td>26.0</td>
<td>7,650</td>
<td>17,050</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.8</td>
<td>8,100</td>
<td>17,700</td>
<td>22.8</td>
<td>7,950</td>
<td>17,450</td>
</tr>
<tr>
<td>16.3</td>
<td>45</td>
<td>22.6</td>
<td>8,750</td>
<td>17,900</td>
<td>21.5</td>
<td>8,250</td>
<td>17,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.2</td>
<td>8,030</td>
<td>17,900</td>
<td>23.0</td>
<td>9,050</td>
<td>18,500</td>
</tr>
<tr>
<td>16.8</td>
<td>45</td>
<td>27.7</td>
<td>8,250</td>
<td>18,000</td>
<td>21.0</td>
<td>8,450</td>
<td>17,800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.0</td>
<td>8,350</td>
<td>17,700</td>
<td>21.5</td>
<td>8,600</td>
<td>17,900</td>
</tr>
</tbody>
</table>

* Yield strength based on an offset of 0.2 per cent.
Age Hardening and Solubility of Uranium

A series of rolled alloys containing 0.16, 0.22, 0.85, 0.92, 1.65, and 3.71 per cent uranium were solution treated for 24 hours at 580°C and quenched. The samples were approximately 1/2 in. x 1 in. x 0.080 in. The microstructures of these alloys were examined and compared with those obtained before solution treatment. Results of this study indicated that the solubility of uranium in aluminum was considerably less than 0.16 per cent.

In order to determine the effect of age hardening on the alloys, a series of samples containing 2.4 to 16.8 per cent uranium were solution treated for three hours at 550°C, and then aged at 175°C for times of 2, 4, 6, and 8 hours. Hardness readings obtained on the various samples are shown in Table 4. There was some slight increase in hardness with an increase in aging time for the low uranium contents (up to 5 per cent). The higher alloys showed no change in hardness. This apparent indication of solid solubility was not considered to be conclusive enough to overrule the results of other tests, which indicated no significant solid solubility.

Samples of alclad sheet containing 14 per cent uranium were aged for times up to 150 days at about 550°C. The cladding was then machined off in thin layers, and examined for uranium, at Argonne Laboratory, by means of a very sensitive alpha counter. There was no evidence of diffusion or solution of the uranium into the cladding even in the layers adjacent to the core.

High-Temperature Testing

Since the proposed use of these alloys in piles would involve some loading at elevated temperatures, the tensile properties at 150 and 300°C were determined. Creep data were obtained on one alloy at 150°C.

Tensile tests were run on alloys containing 11.3 and 17.3 per cent uranium. The specimens were annealed for one hour at 370°C prior to testing. Results of these tests, together with data for pure aluminum, are given in Table 5. At 150°C, the tensile and yield strengths were about 20 to 25 per cent lower than at room temperature, but were still nearly twice the values for pure aluminum. Yield strength could not be obtained at 300°C, but the tensile strengths were about three times as high as those obtained for pure aluminum. The elongations observed were about one-half of those obtained for pure aluminum.

A specimen of 17.3 per cent uranium alloy, annealed one hour at 370°C, was tested for 2000 hours at 150°C. It was tested by the step-up load-
Table 3. Tensile properties of forged aluminum
uranium alloys.

<table>
<thead>
<tr>
<th>Composition, % uranium</th>
<th>Average modulus of elasticity x 10^8 (psi)</th>
<th>Tensile strength (psi)</th>
<th>Yield strength (psi)</th>
<th>0.2% Offset Elongation (%)</th>
<th>Reduction of area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.0</td>
<td>13,000</td>
<td>5,000</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>12.5†</td>
<td>10.4</td>
<td>22,500</td>
<td>10,800</td>
<td>20</td>
<td>34</td>
</tr>
<tr>
<td>22.7 (a)</td>
<td>10.9</td>
<td>18,600</td>
<td>11,600</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>22.7 (b)</td>
<td>11.3</td>
<td>23,500</td>
<td>14,500</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>30.5</td>
<td>11.3</td>
<td>26,100</td>
<td>14,850</td>
<td>10.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

*Estimated to be correct within ±3 per cent.
†Single specimens were used except in the 22.7 per cent uranium alloy.

Table 4. Hardness data on aluminum uranium alloy sheet.

<table>
<thead>
<tr>
<th>Composition, % uranium</th>
<th>Load, psi</th>
<th>Creep Rate, % per cent elongation/hr</th>
<th>Stress, psi</th>
<th>Total deformation, % per cent elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>3000</td>
<td>0.00004</td>
<td>4480</td>
<td>0.134</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>0.00035</td>
<td>3410</td>
<td>0.420</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.00027</td>
<td>2621</td>
<td>4.21</td>
</tr>
</tbody>
</table>

From a log-log plot of stress versus creep rate, the stresses to produce selected rates of creep were as follows:

<table>
<thead>
<tr>
<th>Creep Rate, %/hr</th>
<th>Stress, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>4480</td>
</tr>
<tr>
<td>0.0001</td>
<td>3410</td>
</tr>
<tr>
<td>0.00001</td>
<td>2621</td>
</tr>
</tbody>
</table>

From a log-log plot of stress versus creep rate, the stresses to produce selected rates of creep were as follows:

Thermal Conductivity

Specimens for thermal conductivity were prepared from forged bars (annealed one-half hour at 370°C), containing 12.5, 22.7, and 30.5 per cent uranium. The conductivities were determined by the Bureau of Standards' method described in Research Paper RP668, April 1934. The results are shown in Figure 6 compared to values for pure aluminum taken from the Metals Handbook.

Table 4. Hardness data on aluminum uranium alloy sheet.

<table>
<thead>
<tr>
<th>Composition, % uranium</th>
<th>2 hr</th>
<th>4 hr</th>
<th>6 hr</th>
<th>8 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.43</td>
<td>25</td>
<td>27-29</td>
<td>29-31</td>
</tr>
<tr>
<td>2</td>
<td>3.10</td>
<td>29-31</td>
<td>32-33</td>
<td>36-36</td>
</tr>
<tr>
<td>3</td>
<td>4.95</td>
<td>41-42</td>
<td>43-44</td>
<td>45-47</td>
</tr>
<tr>
<td>4</td>
<td>7.00</td>
<td>53-54</td>
<td>55-56</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>9.00</td>
<td>57-59</td>
<td>60-61</td>
<td>59-61</td>
</tr>
<tr>
<td>6</td>
<td>11.3</td>
<td>61-62</td>
<td>64-65</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>14.3</td>
<td>58</td>
<td>58-59</td>
<td>58-59</td>
</tr>
<tr>
<td>8</td>
<td>16.3</td>
<td>58-59</td>
<td>60-62</td>
<td>62-63</td>
</tr>
<tr>
<td>9</td>
<td>16.8</td>
<td>58-59</td>
<td>60-62</td>
<td>61-62</td>
</tr>
</tbody>
</table>

*Quenched from 550°C after holding for 3 hours.

The conductivity decreased with increasing alloy content, which seems correct for this system. From a consideration of all the data obtained, the following values for thermal conductivities were obtained:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Conductivity in Watts cm⁻¹ °C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 % U</td>
<td>200</td>
</tr>
<tr>
<td>22.7 % U</td>
<td>300</td>
</tr>
<tr>
<td>30.5 % U</td>
<td>400</td>
</tr>
</tbody>
</table>

*Estimated to be correct within ±3 per cent.
Table 5. High temperature properties of aluminum-uranium alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile strength, Room Temperature (psi)</th>
<th>Yield strength, 0.2% set (psi)</th>
<th>Per cent elongation</th>
<th>Tensile strength, 150°C (psi)</th>
<th>Yield strength, 0.2% set (psi)</th>
<th>Per cent elongation</th>
<th>Tensile strength, 300°C (psi)</th>
<th>Per cent elongation</th>
<th>Reduction in area, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2SO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>13,000</td>
<td>5,000</td>
<td>45*</td>
<td>7,500</td>
<td>3,500</td>
<td>65</td>
<td>2,500</td>
<td>90</td>
<td>–</td>
</tr>
<tr>
<td>11.3% U</td>
<td>19,700</td>
<td>11,320</td>
<td>28</td>
<td>14,125</td>
<td>9,200</td>
<td>31</td>
<td>8,630</td>
<td>31</td>
<td>57</td>
</tr>
<tr>
<td>17.3% U</td>
<td>20,080</td>
<td>11,480</td>
<td>28</td>
<td>14,700</td>
<td>10,000</td>
<td>27</td>
<td>8,780</td>
<td>34</td>
<td>60</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>13,650</td>
<td>7,020</td>
<td>35</td>
<td>8,210</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>13,300</td>
<td>6,480</td>
<td>35</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

* Elongation in 2 inches, others in 1 inch.

Note: Tests on metal annealed at 370°C for one hour. 2SO values from "Alcoa Aluminum and Its Alloys".

Figure 6. Thermal conductivity of uranium-aluminum alloys. (0-4547)
Coefficient of Linear Thermal Expansion

Thermal-expansion specimens, 0.500 inch in diameter by 3.25 inches long, were prepared from forged alloys containing 12.5, 22.7, and 30.5 percent uranium. The apparatus used for thermal expansion was similar to that used at the Bureau of Standards, and is described in the Bureau of Standards Journal of Research, Volume 1, page 775, 1928.

Table 6. Coefficient of linear expansion of uranium-aluminum alloys (per°C)

<table>
<thead>
<tr>
<th>Temperature range, (°C)</th>
<th>0%*</th>
<th>12.5%</th>
<th>22.7%</th>
<th>30.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x 10^{-6}$</td>
<td>$x 10^{-6}$</td>
<td>$x 10^{-6}$</td>
<td>$x 10^{-6}$</td>
</tr>
<tr>
<td>20–100</td>
<td>24.0</td>
<td>20.0</td>
<td>20.0</td>
<td>19.4</td>
</tr>
<tr>
<td>20–200</td>
<td>25.9</td>
<td>21.1</td>
<td>21.2</td>
<td>20.8</td>
</tr>
<tr>
<td>20–300</td>
<td>26.7</td>
<td>22.1</td>
<td>21.9</td>
<td>21.3</td>
</tr>
<tr>
<td>20–400</td>
<td>27.2</td>
<td>23.1</td>
<td>22.5</td>
<td>21.6</td>
</tr>
<tr>
<td>20–500</td>
<td>27.9</td>
<td>23.5</td>
<td>22.7</td>
<td>22.1</td>
</tr>
<tr>
<td>100–500</td>
<td>24.4</td>
<td>23.2</td>
<td>22.6</td>
<td></td>
</tr>
</tbody>
</table>


Heating and cooling curves were run over the temperature range from 50 to 500°C. Data obtained during heating and cooling were similar. The coefficients obtained for different temperature ranges are given in Table 6. Similar values for pure aluminum are included for comparison. In obtaining these values down to 20°C, some interpolation was necessary.

ACKNOWLEDGMENTS

The author wishes to express appreciation to Dr. H. W. Russell, of Battelle Memorial Institute, under whose supervision the investigation of the problem was carried out. The assistance of Dr. L. W. Eastwood, of Battelle Memorial Institute, and Mr. L. H. Grenell, formerly of the Battelle staff and now with Western Cartridge and Brass Company, is gratefully acknowledged.

This article is based on Battelle Topical Reports S-M-5, S-C-8, and S-C-12.

REFERENCES

1 The Project Handbook, Volume I, Chapter IX, pages 58 and 59.

2 MIT Progress Report for the Month of September, 1946, CT-3550, pages 12 and 12A.
Forming Uranium Dioxide Washers and Rods

By Robert McKechnie and Alan U. Seybolt

Both pressed discs and washers, and small extruded rods were made of UO₂. These shapes were not of very high density, varying from about 8 g/cc for the flat shapes to 7 g/cc for the extruded rods; theoretical density of UO₂ is about 10.3 g/cc.

It was found necessary to incorporate organic “binders” to secure satisfactory forming characteristics. Sintering in a hydrogen atmosphere at about 1800°C produced reasonably strong and hard bodies, readily handled without dusting or breakage.

UO₂ is wet by sodium at temperatures near 500°C, and low density UO₂ bodies tend to disintegrate into powder due to some unknown action of the sodium. However, if the UO₂ sintered density is near 8 g/cc or over, several days exposure to hot sodium appears to have no effect other than wetting the oxide.

It appears feasible to produce pellets or washers of UO₂ in automatic compacting machines.

INTRODUCTION

An outstanding advantage of the possible use of uranium oxide as a fuel element in enriched nuclear reactors is that much less fuel processing is involved as compared to the utilization of a metal fuel. Hence, not only cost and fabrication time is reduced, but the amount of material loss, both temporary and permanent, is lessened. All that is required is to decompose the metal salt to the oxide (mostly U₂O₃), reduce to UO₂, and press and sinter. The great difference in complexity of operations is obvious.

Another advantage of the use of oxide is that in contact with an iron or nickel container, there is no possibility of the formation of the iron-uranium or nickel-uranium eutectic because of accidental overheating of the pile; these eutectics form in the neighborhood of 700°C.

Two fuel element shapes being considered for the Schenectady pile are (1) flat “washers” of the order of 0.485 inch outside diameter and 0.285 inch inside diameter and about 0.030 inch thick, and (2) uranium rods of the order of one inch long and 0.050 inch in diameter.

The object in this work was twofold: one, to find suitable conditions for making thin oxide washers and rods which would not be dusty or otherwise difficult to handle, and two, to make some observation on the reaction of UO₂ with sodium at about 500°C. It is planned to use sodium as a pile coolant, and the sodium will be used both inside and outside the fuel slugs. Hence the inherently poor thermal conductivity of the oxide is of no concern.

EXPERIMENTAL PROCEDURE

Raw Materials

The first experiments were made with uranium oxide prepared by oxidizing some scrap uranium metal in the air at 650°C and then reducing to UO₂ in
a hydrogen atmosphere at 1000°C. Later, a supply of UO$_2$ was obtained from the Mallinckrodt Chemical Company. It was necessary to use UO$_2$ rather than U$_2$O$_3$, because the latter is readily reduced to UO$_2$ by metallic sodium, while UO$_2$, as far as is known, is stable in the presence of sodium. The composition of UO$_2$ was verified by x-ray diffraction, giving a pattern which agreed with the established structure.

Block sodium from du Pont was used in the few experiments conducted on the behavior of the sintered oxide bodies in liquid sodium.

Fabrication of Washers

The first experiments were made on solid discs about one inch, and one and one-half inches in diameter and with thicknesses varying from 0.030 inch to about 0.200 inch. When it became evident that disc forming would not prove particularly difficult, a cored die shown in Figure 1 was made and used throughout most of the work. This die was used to produce washers of any desired thickness 0.766 inch OD and 0.390 inch ID, a size suggested by the pile design group. The thickness desired, as stated above, was about 0.030 inch. However, to obtain suitable pressing and sintering conditions, thicker pieces were generally made because of greater ease in fabrication. As soon as pressing conditions were more or less standardized, washers were made with one and two gram charges, resulting in thicknesses of 0.030 and 0.060 inch respectively.

Pressing Experiments

A hand operated 20 ton Elmes press was used for all disc and washer forming except where otherwise noted.

The UO$_2$ was pressed with and without various additions to aid in securing a good compact. It was found that when the discs were about 0.10 inch thick or thicker, no additions were required other than a certain moisture content; very dry powder baked in an oven could not be compacted. However, in order to produce a thin oxide disc about 0.030 inch thick, organic compounds had to be added. At first, stearic acid in ether was used, but in order to secure a good pressing, enough of this material was required to cause subsequent blistering during the sintering operation. Later, 2 per cent carbowax (a product of Union Carbide and Carbon) dissolved in water was found to be a very satisfactory addition. It allowed the formation of a "green" compact which could be easily handled, and yet caused no difficulty during sintering.

Various pressures were used, and fairly early in the work 10 tons per sq in. was chosen as the best pressure for good forming; higher pressures caused the appearance of laminations and difficulty in ejection.

No difficulty was experienced in changing from the simple solid disc or tablet to the cored washer shape, and the same technique described above for powder preparation and pressure was satisfactory. Figure 1 shows the unassembled die and a washer made from the die. From left to right are the die body, the upper punch, the core, and the lower punch. Because of the thin section required, there was no advantage in using the so-called double acting principle where the die body is floating over the lower punch.

As pressed density at 10 tons per sq in. varied from about 5 to 6 g/cc, the theoretical density of UO$_2$ is about 10.3 g/cc.

Some improvement in green density and possibly in final density could be expected from a proper grading of the particle size of the UO$_2$ powder. However, no attempt was made to check the screen analysis of the oxide used, mainly because necessary equipment was not at hand. The use of other people's equipment would have posed a difficult decontamination problem. The powder was all 200 mesh or finer. In any case, the actual final density was not of prime importance as long as a form sufficiently strong and hard to be handled was obtained.

Sintering Experiments

The sintering was done in a molybdenum-wound tube furnace ordinarily using dry hydrogen of about -50°C dew point, but there was no indication that very dry gas was necessary. Several experiments were done with undried hydrogen with satisfactory results. X-ray diffraction checks of the structure before and after sintering demonstrated no appreciable deviation from the composition UO$_2$.

Some investigation of the effect of temperature on density demonstrated the desirability of sintering temperature of about 1800°C. This temperature
Sodium Experiments

A few pressed and sintered UO₂ washers were placed in a static sodium pot at 500°C for periods of about 10 days. It was at first found that the compacts disintegrated to powder; other than this no useful fact was found because of the difficulty of separating the oxide powder from the sodium. This disintegration occurred in the case of discs of comparatively low density.

Later, when washers of about 8 g/cc density were subjected to the sodium, no break-up was observed. The surface of the washers was thoroughly wet with sodium; this was a desirable feature from the pile heat transfer standpoint.

No prolonged tests of this nature have been carried out as yet, but it is suspected that the oxide may not remain in one piece if in contact with the hot sodium for periods of the order of weeks or months.

There was no indication of any bulk chemical reaction between sodium and the oxide unless the wetting is argued to be evidence of a chemical reaction.

Fabrication of Rods

a. Extrusion Experiments. The oxide rods desired were to be about one inch long and from 0.030 inch to about 0.050 inch in thickness. The obvious method for preparing such shapes was to extrude a slurry of the oxide through a die. After some experiments with a die arrangement designed to be used with various sized die holes, it was decided to take advantage of the equipment of the Ceramic Section of the Research Laboratory. One feature of their die design was the use of a quite long bearing area, which appeared to assist in maintaining a reasonably straight extruded length.

The UO₂ was mixed with polyvinyl alcohol gel to give a paste of about the consistency of putty. The extruded wire or rod coming out of the die was laid in one of several grooves in a plaster slab and there allowed to air dry to a hardness where it could be picked up and placed in the molybdenum firing boat. The following diameters were extruded: 0.125 inch, 0.1084 inch, 0.065 inch, and 0.030 inch. As would be expected the thicker rods extruded straighter than the thin ones, but otherwise there seemed to be no appreciable difference in either final properties or ease of fabrication.

Fortunately, straightness was desired only over lengths of about one inch, and from this standpoint, the rods appeared to be adequate. The appearance of the four sizes of extruded and sintered UO₂ is shown in Figure 2.

b. Sintering Experiments. The rods were given the same sintering treatment as described previously for the washers.

As might be expected because the pressure was low compared to a regular pressing operation, the as-pressed and final density was lower than in the case of the washers. No measurements were made of the as-extruded and air dried density, but the sintered density was about 7 g/cc. While this is comparatively low, the density was sufficiently high to allow good handling properties, which was the main consideration.

Pressing in a Pill Machine

In order to examine the feasibility of a mass production method for the fabrication of oxide washers, some experiments have been performed using a hand operated laboratory pill press. Since a die for pressing 7/16 inch discs was available, the first tests were made with this die. The die consists of three parts: a fixed bottom sleeve, a moving bottom plunger which moves in the sleeve, and a mov-
ing top plunger. The plungers are cam-operated and can be adjusted to give a desired thickness of pressed part; compacting pressure is thus a derived quantity depending upon weight of charge and thickness of sample. The compression ratio actually used was about 3:1.

Two types of organic binder were used: carbowax in water and lucite in mesityl oxide solvent. In this work, the powder was screened after adding the binder to give better die loading properties. The results with carbowax were not very satisfactory because of nonuniform filling and hence attention was turned to the lucite binder. The steps taken were as follows: (1) UO$_3$ powder was mixed with 3\% lucite in solution and dried (under hood); (2) The mix was ground in a mortar and the -40 mesh portion saved; (3) The -40 mesh was sieved again and the -40 - 250 mesh portion was used for the experimental pressings. Extreme care was used in driving off the mesityl oxide in order not to make the mix sticky.

The sweep fill of an automatic machine was simulated by placing the die in the load position of the cycle and then filling the die by dragging excess powder across the cavity using a spatula. The charge was easily accomplished since the powder flowed quite readily. Powder prepared in the above manner pours in about the same way as dry sand.

The green compacts pressed in the pill press using the lucite binder showed very good strength with no laminations. A green density of about 6 g/cc was obtained. Thicknesses varied ±3 mils with a weight variation of ±0.02 grams. Closer tolerances can be expected on shifting to automatic machine.

The sintering step is as described previously except that the pieces are heated to 350°C over about five hours. The temperature is then rapidly raised to 1650°C. The sintered density for these pills was about 8.2 g/cc.

**GENERAL DISCUSSION**

The production of simple shapes of UO$_3$ by powder metallurgy methods appears to be a fairly straightforward procedure providing small amounts of suitable organic binders are added to aid good pressing properties. No great effort has been made to secure densities near theoretical because this has appeared unnecessary, or even undesirable. There seems to be no reason why much higher densities could not be obtained if required.

For the proposed use in the pile, it appears that the production of a fairly liquid oxide-sodium "mush" would be desirable if this could be accomplished without the use of too much sodium. Such
a mush, or semiliquid condition, would be preferable from the standpoint of conducting heat from the inside of the fuel slugs to the circulating cooling sodium on the outside of the slugs.

On the other hand, it has been considered desirable to form the oxide into shapes approximating the shape of the fuel cavity in the slugs for ease of handling. It would be very awkward and messy to have to introduce loose powder into the fuel slugs. Therefore, methods have been worked out as described above for producing fairly hard and coherent shapes. It is not expected that the oxide will remain in the original form for very long, and very likely it would be undesirable for this to happen as explained previously.

It was hoped that sufficient data would be at hand to establish how much residual carbon from the added binders was retained after the hydrogen sintering operation. However, because of inadequate sampling and unsatisfactory carbon analyses, such data cannot be cited at present. The actual carbon content is probably not very important as long as it is known, and is consistent in amount from point to point in the pile. This, of course, assumes a low carbon content of the order of 0.1 per cent, or less, and evidence to date indicates that there need be no great concern on this score.

ACKNOWLEDGMENTS

The authors wish to express their thanks to the painstaking work of John Hartwell who performed many of the operations described, and to the Ceramic Section of the Research Laboratory for their cooperation in oxide extrusion.

Figure 2. Extruded UO$_2$ rods after sintering at 1600°C.
The Binary Alloys of Uranium

By Robert W. Buzzard and Harold E. Cleaves
National Bureau of Standards

A condensed summary of the available information on several binary alloy systems of uranium was prepared in connection with a current research project at the National Bureau of Standards. At the suggestion of Dr. Bruce Old, Chief, Metallurgy and Materials Branch, Research Division, U.S. Atomic Energy Commission, this summary has been expanded to include all binary alloys of uranium for which information is accessible to the authors. The assistance of Dr. J. C. Warner, Carnegie Institute of Technology, and Dr. H. D. Young, Argonne National Laboratories, in securing some of the information included in this summary is gratefully acknowledged.

A more detailed survey of the uranium alloy systems is being compiled by Dr. Warner for inclusion in Volume 12, Division IV of the National Nuclear Energy Series.

The diagrams presented herein are those proposed by the various investigators but redrawn to a uniform scale. Much of the information on which these diagrams are based is the product of investigations whose aim was specific information on alloy characteristics rather than the establishment of the alloy diagrams. Hence these diagrams are mainly tentative, subject to the revision that future data may require. The broken lines indicate approximate limits proposed by the investigation but for which substantiating data are lacking.

URANIUM-ALUMINUM (Figure 1)

The U-Al system has been fairly well established with the exception of the liquidus. The system contains three compounds: UA₁₄, UA₁₃, and UA₁. There are two eutectics in the system, one between gamma U and UA₁₄ at 1105°C, and one between UA₁₃ and Al at 640°C.

The gamma U eutectoid has been assumed from phase rule considerations. The metallographic evidence for the solubility of Al in gamma U is conclusive and alloys in the gamma solubility range can be precipitation hardened. The beta-gamma transformation temperature is lowered somewhat but the alpha-beta transformation temperature does not appear to be affected by the presence of Al.

UA₁₄ is stable up to the melting point (approximately 1590°C); having a diamond cubic structure, a₀ = 7.72Å (Angstrom units). UA₁₃ and UA₁ decompose by a peritectic reaction, UA₁₄ at 1350°C and UA₁₃ at 730°C. UA₁ has a simple cubic structure a₀ = 4.26Å. The structure of UA₁₃ has not been determined. References: 1-15.
URANIUM-ANTIMONY

Alloys containing 0.5, 2.6, and 5.0 wt per cent antimony were made from biscuit metal in beryllia-lined alundum crucibles at 1200, 1205, and 1325°C, respectively. The structure of the 0.5% alloy consisted of a eutectic at the grain boundaries, precipitation of fine particles within the grains and an angular phase. The 2.6% alloy showed segregation. The 5% alloy had the same phase as the 0.5% alloy plus a needle-like phase.

The 5% alloy disintegrated in less than 24 hours in boiling distilled water. The approximate loss in weight of the 0.5% alloy was 5.5 mg/cm²/hr. Further data is not available. References: 16, 17.

URANIUM-ARSENIC

Two compounds of arsenic-uranium have been identified: UAs and U₂As. UAs has a cubic structure (a₀ = 5.75Å) with an x-ray density of 10.77 g/cm³. Further data is not available. References: 18, 19, 20, 21, 22, 23, 81.

URANIUM-BERYLLIUM (Figure 2)

The major portion of the U-Be system has been fairly well established; only the metal-rich ends and the liquidus line remaining doubtful. The system contains one compound of an approximate composition of UBe₆. The composition of the compound...
is uncertain by ±3%. There are two eutectics in the system, one at 1060°C between gamma U and the compound and one at 1200 to 1250°C between the compound and Be.

The solubility of Be in gamma U has been assumed because of the lowering of the solidus and the appearance of the eutectic in the microstructure. The fact that the beta-gamma and alpha-beta transformation temperatures are lowered indicates some solubility of Be in alpha U and beta U. While these solubilities have not been determined, they are known to be less than 10 atomic per cent. The liquidus between 16 and 90 atomic per cent Be has not been determined. A 90 atomic per cent Be alloy gives a diffraction pattern corresponding to a simple cubic structure, \( a = 5.09 \text{Å} \). Precision parameter measurements indicate that the solid solubility of uranium in beryllium is exceedingly small, even at 1150°C. References: 1, 11, 14, 15, 24-30.

URANIUM-BISMUTH (Figure 3)

The U-Bi system has been partially established. The system contains two compounds: UBi and UBi

\[ \text{X-ray studies have shown the presence of two phases other than U and Bi in the system but the complicated structures have not been worked out.} \]

The melting point and transitions of U were unchanged by Bi. The solid solubility limits of the phases in each other have not been determined. Little evidence of solid solubility was found in the

\[ \text{Figure 2. Uranium-Beryllium} \]
U-Bi system. There appears to be an immiscibility gap between 4.9 and 43% Bi. At 4.9% Bi the two liquid phases appear immiscible, the heavier phase consisting of U containing 4% Bi and the upper layer containing 43 to 50% Bi. Bi distills from a 50% alloy at 1650°C.

UBi melts above 1400°C and UBi₂ decomposes peritectically at about 980°C. The pyrophoric nature of the alloys and the peritectic decomposition of UBi₂ make it quite difficult to obtain satisfactory photomicrographs in the range between UBi and UBi₂; so this region is somewhat uncertain. References: 1, 5, 8, 15, 26, 31–38.

URANIUM-CADMIUM

The high vapor pressure of cadmium prevents its addition to molten uranium. Two heats were made in which a slug of biscuit metal was soaked in molten cadmium at 650°C, for one- and two-hour periods. In neither case was any evidence of alloying noted. Reference: 39.

URANIUM-CALCIUM

Very little work has been done in the U-Ca system. Compacts of U-Ca powders, annealed at 800°C...
for 24 hours, did not alloy. The samples were not pyrophoric and appeared to be a simple mixture of calcium and uranium with no reaction layers identified. Reference: 40.

URANIUM-CARBON (Figure 4)

The U-C system has been fairly well established up to 67 atomic per cent carbon. Two compounds...
UC and UC₂ have been identified. The possibility of the existence of a higher carbide than UC has been investigated but no evidence that a higher carbide exists has been obtained.

It is reported that the solid transformation temperatures of U are not affected by the presence of carbon, but other evidence is presented to show that carbon is soluble in gamma U to about 2 atomic per cent, in beta U to about 0.6 atomic per cent carbon and in alpha U to less than 0.2 atomic per cent carbon. Carbide inclusions in cast metal go into solution on prolonged annealing, indicating that the solubility of carbon in liquid uranium is less than in gamma U, which implies a peritectic reaction between UC and the liquid to form the solution of C in gamma U.

The crystal structure of UC has been found to be cubic (NaCl type), a₀ = 4.948 ± 0.001 Å, the calculated density is 13.68 g/cm³ and the melting point 2250°C. The variability of the UC x-ray spacing with oxygen and nitrogen impurities indicates that the carbon may be replaced by either nitrogen or oxygen in the UC structure. UC₂ is tetragonal, with 2 molecules per unit cell; a = 3.449 ± 0.001 Å, c = 5.987 ± 0.001 Å, c/a = 1.735, calculated density 11.68 g/cm³ and the melting point 2350 to 2400°C. References: 1, 2, 5, 8, 22, 24, 26, 31, 35, 36, 41–58.

URANIUM-CERIUM

Melts containing nominal amounts of 5.5 and 28.2% cerium were made. Investigators agree the system consists of almost complete insolubility in both the liquid and the solid states. References 16, 17, 59, 60, 61, 62, 63, 64.

URANIUM-CHROMIUM (Figure 5)

Only the uranium rich end of the U-Cr system has been established. The liquidus has not been established above 20 atomic per cent chromium. Since the main interest of study was the uranium rich alloys, the melting point and possible solid modifications of chromium were not investigated.

There appears to be a compound in the region 40 to 45 atomic per cent chromium and a second compound around 70 atomic per cent chromium. The second compound decomposes peritectically and there are some indications of a compound between these two which also decomposes peritectically. Two eutectics exist, one in the neighborhood of 20 atomic per cent chromium and the other around 50 atomic per cent.

The maximum solubility of chromium in gamma U is estimated to be 4 atomic per cent chromium. The gamma-beta transformation of uranium is lowered by chromium. The solubility of chromium in beta U is less than 2.5 atomic per cent. There is little or no solubility of chromium in alpha U. Likewise there is little or no solid solubility of uranium in chromium. References: 1, 65–70.

URANIUM-COBALT (Figure 6)

The U-Co system has been fairly well established. The system contains three compounds: U₃Co, UC₀ and U₃Co₂. There are two eutectics in the system, one at 734°C and the other at 1053°C.

Cobalt alloys are very hard and brittle and show no unusual resistance to corrosion.

There is no detectable solid solubility of either cobalt in uranium or uranium in cobalt.

The uranium liquidus is lowered rapidly by the addition of cobalt to a minimum of 734°C at the eutectic composition, 34 atomic per cent cobalt. The compound U₃Co (14.3 atomic per cent cobalt) separates as a primary phase in alloys with less than 34% cobalt. U₃Co is a highly crystalline material formed by a peritectic reaction at 822°C. The compound is body-centered-tetragonal structure, a = 10.34 ± 0.02 Å, c = 5.20 ± 0.02 Å, calculated density 17.7 g/cm³, unit volume 550 Å³. The compound UC₃, decomposes peritectically at 805°C. UCo₃ has a body-centered cubic structure, a = 6.343 ± 0.001 Å unit cell volume 255 4 Å³, a calculated density 15.4 g/cm³. U₃Co₃ has a face-centered cubic structure, a = 6.9783 ± 0.004 Å with a calculated density of 13.83 g/cm³. References: 39, 65, 71.

URANIUM-COLUMBIUM (Figure 7)

Information on U-Cb system is incomplete. The principal emphasis has been concentrated on the uranium rich alloys.

The maximum solubility of Cb in alpha U and beta U is less than 0.3 per cent above 600°C. The beta phase probably decomposes eutectoidally at a temperature 100°C to the gamma eutectoid temperature. Columbium raises the freezing point of uranium and lowers the gamma-beta transformation. X-ray data of quenched alloys show the existence of alpha U in low columbium alloys and gamma phase in those containing 9 or more per cent Cb. Cb additions in excess of 2% increase the room temperature stability of the gamma phase.

With increasing Cb, the transformation of gamma to the alpha plus Cb rich phases becomes increas-
ingly sluggish. Retention of gamma U by quenching is extremely difficult in alloys of less than 1 wt per cent Cb. References: 16, 61, 62, 63, 72–77.

URANIUM-COPPER (Figure 8)

The U-Cu system is relatively complete, although the portion of diagram between 7.76 and 83.3 atomic per cent copper is somewhat tentative. The system contains one compound: UCu₄. This compound forms a eutectic containing 92 atomic per cent copper, melting at 1850°C. A monotectic is formed at 5.4 atomic per cent copper and 1080°C. At this temperature uranium separating from liquid containing 5.4 atomic per cent copper, shifts the composition of the liquid to 77.6 atomic per cent copper. The boundary of the miscibility gap has not been determined but a 61.6 atomic per cent quenched from 1700°C indicated miscibility at this temperature.

The alpha-beta U and the beta-gamma U transformation temperatures are not affected by the presence of copper, indicating negligible solubility of copper in solid uranium. There is no evidence of solubility of uranium in solid copper.

The compound UCu₄ has been established from x-ray data. Some microscopic evidence of solubility of uranium in UCu₄ down to 80.9 atomic per cent copper has not been substantiated. The compound UCu₄ has a face-centered-cubic structure, with four molecules per unit cell, \(a_0 = 7.019 \pm 0.002\)
A) an x-ray density of 10.61 g/cm³ and a measured density of 10.7 g/cm³. The compound oxidizes slowly in air and is extremely brittle. References: 1, 5, 8, 11, 22, 35, 36, 51, 52, 53, 56, 78, 79, 80, 82.

**URANIUM-GALLIUM**

The microstructures and hardness values of alloys containing two atomic per cent gallium have been investigated. References: 66, 83.

**URANIUM-GERMANIUM**

Alloys containing 5 and 10 wt per cent germanium were prepared using a procedure similar to that used in preparing manganese alloys. When the germanium was added, it appeared that a higher melting compound was formed. This caused the melt to freeze momentarily each time germanium was added. References: 39, 72.

**URANIUM-GOLD**

Alloys with 2 atomic per cent and 5–10 wt per cent of gold were prepared and studied. Some solubility of Au in alpha U was indicated. The 5% Au alloy, as cast, showed a definite two phase structure, the 10% alloy, as cast, showed light particles of a gold-rich phase in a eutectic matrix. The gold alloys do not appear to have any unusual corrosion properties. References: 39, 66, 83.

![Figure 6. Uranium-Cobalt](image-url)
URANIUM-HYDROGEN (Figure 9)

Hydrogen reacts with U according to the equation $2U + 3H_2 = 2UH_3$, the reaction being most rapid at 225°C.

Uranium hydride is a brownish black or brownish gray, fine, pyrophoric powder. The crystalline structure is cubic with eight uranium atoms per unit cell; $(a_o = 6.634 \pm 0.002 \text{ Å})$ with an x-ray density of 10.91 ±0.05 g/cm$^3$.

Above the decomposition temperature of the hydride, 435°C, the capacity of uranium to dissolve hydrogen increases with temperature. The increase is particularly marked in the liquid state. The equilibrium content of hydrogen in alpha U is about 2 ppm and changes little with temperature. The alpha-beta transformation at 660°C causes the solubility to increase from 2 to 8 ppm. The beta-gamma transformation increases the solubility to 15 ppm. Melting which occurs at 1132°C increases
the solubility to 17-18 ppm and the hydrogen content of the liquid metal continues to increase rapidly with temperature, reaching 30 ppm at 1250°C. In casting, a hydrogen content of 2 ppm is considered the danger limit. References: 1, 28, 48, 50, 53, 54, 58, 84-100.

URANIUM-INDIUM

Uranium-indium alloys with 5-10 wt per cent indium were prepared. No results were reported. Reference: 72.

URANIUM-IRIDIUM

Microstructures of an alloy containing 2 atomic per cent of iridium were studied. References: 66, 83.

URANIUM-IRON (Figure 10)

Data on U-Fe system is relatively complete. The system contains two compounds: \( \text{U}_2 \text{Fe} \) and \( \text{UFe}_5 \). There are two eutectics in the system, one between \( \text{U}_2 \text{Fe} \) and \( \text{UFe}_5 \) at 36 atomic per cent iron and 725°C and one between \( \text{UFe}_5 \) and iron at 1080°C. Phase rule considerations and microscopic examination confirm the existence of an eutectoid somewhat below 1 atomic per cent iron, the transformation occurring at 770°C.

Iron is soluble in gamma U up to a maximum of 1.5 to 2.0 atomic per cent at 815°C. The solubility of iron in alpha U and beta U appears negligible as does the solubility of uranium in alpha Fe. The solubility of U in gamma Fe is limited; its actual extent has not been determined but it is known to
be less than one-half atomic per cent uranium. The details in the delta iron region are doubtful but the solubility of uranium in delta iron appears negligible. The alpha-gamma transformation appears at 910°C but the data are somewhat inconsistent.

$\text{UFe}_2$ has been identified from x-ray and microscopic analysis and is stable up to the melting point, 1235°C. The compound has a diamond cubic structure, ($a = 7.004\, \text{Å}$) and an x-ray density of 13.2 $\text{g/cm}^3$. $\text{U}_6\text{Fe}$ has been identified from microscopic analysis and decomposes peritectically at 815°C. The crystal structure of this compound has not been established. References: 1, 9, 45, 65, 93, 101, 102.

**URANIUM-LEAD**

There is little information on the uranium-lead system. The alloys in general, appear to be pyrophoric and the microstructures are reported as complex. There is some evidence of liquid immiscibility, a normal 50 atomic per cent alloy having been reported to have formed two liquid layers. References: 1, 11, 28, 41, 103.

**URANIUM-MAGNESIUM**

Although some work has been done on the U-Mg system no definite conclusions are available. Attempts to prepare U-Mg alloys have met with little success. There is some evidence that the solu-

![Figure 9. Solubility of hydrogen in uranium in equilibrium with hydrogen at atmospheric pressure.](image-url)
bility of magnesium in uranium is extremely low and that at least one and possibly two compounds are formed. References: 1, 8, 40, 48, 55, 78, 79.

URANIUM-MANGANESE (Figure 11).

The U-Mn system is relatively complete. The system contains two compounds: $U_2Mn$ and $UMn_2$. There are two eutectics in the system. One eutectic is formed between $U_2Mn$ and $UMn_2$ at 21 atomic per cent manganese and 716°C. A second eutectic exists at 85 atomic per cent manganese between $UMn_2$ and Mn at 1035°C. The liquidus between 21-85 atomic per cent manganese has been plotted above many of the actually determined points. The liquidus between 85 to 100 atomic per cent manganese is fixed from two points, one of which lies considerably under the curve as plotted and, if considered, would reverse the curvature of the liquidus.

It has been established from microstructures that the maximum solubility of manganese in gamma uranium approximates 4 per cent. The solubility is less in the beta region and there is a eutectoid at 1 atomic per cent manganese at 626°C. There is no appreciable solubility of manganese in alpha uranium. The solubility of uranium in manganese has been investigated but the results are inconclusive.
The compound $U_xMn$ is formed by a peritectic reaction between beta uranium and liquid at 726°C. The compound is body-centered tetragonal, $(a = 10.265 \pm 0.01 \text{ Å}, c = 5.23 \pm 0.02 \text{ Å})$ with a calculated density of 17.8 g/cm$^3$. $UMn_2$ is stable with a melting point of 1120°C. The compound has a body-centered cubic structure $(a = 7.1484 \pm 0.001 \text{ Å})$ with a calculated density of 12.57 g/cm$^3$. References: 104, 105.

**URANIUM-MERCURY (Figure 12)**

The U-Hg system is apparently complete. The system contains the three compounds: $UHg_2$, $UHg_3$, and $UHg_4$. $UHg_4$ decomposes at 360°C to $UHg_3$ and Hg (vapor); $UHg_3$ decomposes at 390°C to $UHg_2$ and Hg (vapor); $UHg_2$ breaks down at 460°C into U + Hg (vapor). Because of the pyrophoric nature of the amalgams, all work was done in vacuum or in an inert atmosphere.

There appears to be some solubility of uranium in mercury and mercury in uranium but no mutual solubility between the compounds.

$UHg_2$ has a hexagonal structure $(a = 4.77 \text{ Å}, c = 3.21 \text{ Å})$ with a calculated density of 15.29 g/cm$^3$. $UHg_3$ has a hexagonal c.p. structure $(a = 3.30 \text{ Å}, c = 4.86 \text{ Å})$ with a calculated density of 14.88 g/cm$^3$. $UHg_4$ has a pseudo body-centered cubic structure $(a = 3.62 \text{ Å})$ with a calculated density of 14.59 g/cm$^3$. References: 1, 22, 36, 51, 52, 53, 56, 106.

![Figure 11. Uranium-Manganese](image-url)
The U-Mo system has been partially established. The system is characterized by a peritectic type of liquidus and solidus, extensive solubility of molybdenum in uranium, the lowering of the transformation temperatures of uranium and the absence of any intermetallic compound. In view of the very sluggish solid transformations the phase boundaries in some regions have been drawn somewhat arbitrarily. The liquidus temperatures have not been located with certainty above 1285°C. Little work has been done on the Mo-rich side of the system because of the difficulty in preparing these alloys. The existing data indicates that the region is as postulated in the tentative diagram.

Solubility of molybdenum in gamma U, as determined by x-ray studies, varies from 35.8 atomic per cent molybdenum at 1000°C to 29.9 atomic per cent at 700°C. There appears to be no appreciable solubility of molybdenum in alpha U. The lattice parameter of the Mo-phase corresponds to a solubility of approximately 1 atomic per cent of uranium in molybdenum at 900°C. Microscopic studies indicate one- and two-phase alloys in the general ranges so indicated, but the exact limits of these transformations have not been determined. The peritectic reaction occurs at 1285°C and extends from 25 to approximately 95 atomic per cent molybdenum.

X-ray diffraction patterns of the alloys in the gamma field show a body-centered cubic struc-
ture, the lattice parameter varying with the molybdenum content. The beta phase has been retained by quenching low molybdenum alloys, its diffraction pattern indicating a complicated and, as yet, undetermined structure. References: 1, 16, 37, 39, 56, 65, 66, 72, 73, 78, 79, 80, 107-117.

URANIUM-NICKEL (Figure 14)

The U-Ni system has been fairly well established. The diagram is based chiefly on thermal and microscopic studies since extensive segregation made interpretation of x-ray data somewhat
uncertain. The system contains four compounds: $\text{U}_3\text{Ni}$, $\text{UNi}$, $\text{UNi}_2$, and $\text{UNi}_4$. There are two eutectics in the system, one between $\text{U}_3\text{Ni}$ and $\text{UNi}$ at 37 atomic per cent nickel and 738°C; and one between $\text{UNi}_2$ and Ni at about 88 atomic per cent nickel and 1104°C.

The lowering of the gamma-beta transformation in uranium and the microstructure of the low nickel alloys indicates a eutectoid somewhere below 2 atomic per cent nickel. The solubility of uranium in nickel and the mutual solubility of the compounds has not been determined.

$\text{U}_3\text{Ni}$ decomposes peritectically at 780°C. X-ray diffraction patterns of a 15 atomic per cent nickel alloy indicate the existence of a face-centered cubic structure, $a = 4.876$ Å.

$\text{UNi}$ decomposes peritectically at 810°C and $\text{UNi}_2$ decomposes peritectically at 985°C. The peritectic reactions are clearly shown in the thermal data but the composition has been assigned on rather poor microscopic evidence. No definite evidence of the compound has been found in the x-ray patterns.

$\text{UNi}_4$ melts at about 1295°C. The composition has been determined with some certainty from microscopic examination. The x-ray diffraction pattern of a 90 atomic per cent nickel alloy indicates a hexagonal structure, $a = 4.70$ Å, $c = 7.24$ Å, presumably $\text{UNi}_4$. References: 1, 65, 118–121.
URANIUM - NITROGEN

No data are available on the solubility of nitrogen in uranium nor have the melting point or dissociation temperature of the compounds been determined. The reaction between massive uranium and nitrogen becomes rapid above 450°C. Nitrides formed below 750°C and above 800°C, although of apparently the same composition, differ in visual appearance. At the lower temperatures a dark adherent scale with a metallic lustre is formed; above 800°C the reaction is much more active, producing a matte, nonadherent powder. The sharp break in the reaction rate, presumably, is associated with beta-gamma transformation in the metal.

The uranium nitride phase with the lowest nitrogen content is the mononitride, UN. UN sinters at 2300°C and melts in an atomic hydrogen arc at about 2630 ± 50°C. This compound is face-centered cubic (a = 4.88 ± 0.001 Å) with a calculated density of 14.31 g/cm³. Between uranium and UN there are neither intermediate stoichiometric compounds nor extensive solid solubility. Between UN and UN₂, the system is inhomogeneous, consisting of two separate phases: UN and UN₁₉. The suggested structure of UN₂ is body-centered cubic, 10.678 Å, with a calculated density of 11.24 g/cm³. From UN₁₉ up to the dinitride UN₃, which is the third stoichiometric nitride of uranium, the system is homogeneous. With increasing nitrogen content the UN₁₉ crystal structure is transformed gradually, without discontinuity, into the UN₃ structure.

References: 1, 2, 8, 10, 28, 48, 81, 90, 94, 99, 100, 122, 123, 124, 125.

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URANIUM - OSMIUM

Microstructures and hardness of a uranium-osmium alloy containing 2 atomic per cent osmium were determined. References: 66, 83.

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URANIUM - OXYGEN (Figure 15)

The uranium-oxygen system is incomplete. The common oxides of uranium appear to be UO₂ and U₂O₃. Three other oxides or suboxides have been reported: UO, U₃O₅ and U₄O₉.

The solubility of O₂ in U is very small, even at temperatures above 2000°C. A solubility of 0.05 atomic per cent at the melting point of uranium, rising to 0.1 per cent at 1400°C and 0.4 per cent at 2000°C, is reported.

The solubility of oxygen in solid uranium is less, microstructures indicating a solubility of less than 0.003 weight per cent (0.04 atomic per cent).

X-ray evidence indicates that UO exists and that the next higher oxide stable at room temperature is UO₂. Further increase in the oxygen content decreases the UO₂ spacing, as though U were removed from the UO₂ structure. At compositions above UO₂, two phases appear, UO₃ with decreased spacing and U₃O₄. The U₃O₄ structure is related to the U₃O₅ structure and there is a gradual change in structure until the composition U₄O₈ is reached; only one phase is present between the composition UO₂ and U₄O₈. References: 6, 7, 9, 10, 47, 53, 123, 124, 126–139.

---

Lattice constants UN₁₀ to UN₃

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<th>Face-centered cubic (Psuedo-cell) (Angstrom units)</th>
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### Oxide structures

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<td>b = 6.50 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 4.21 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 15. Uranium-Oxygen**
**URANIUM-PALLADIUM**

Information on the uranium-palladium system is rather meager. Apparently there is a eutectic at about 40-45 atomic per cent palladium and 1000°C and a new phase at about 75 atomic per cent.

The temperatures of the alpha-beta and beta-gamma transformations of uranium appear unaffected by palladium. The solid solubility of palladium in uranium appears to be about 4 atomic per cent palladium at 980°C. References: 39, 59, 66, 83, 140, 141.

**URANIUM-PLATINUM**

Hardness and microstructures of alloys with 5 wt per cent and 2 atomic per cent platinum were determined. References: 65, 66, 67.

**URANIUM-RHENIUM**

Hardness and microstructure of an alloy with 2 atomic per cent of rhenium were determined. References: 66, 83.

**URANIUM-RHODIUM**

Little information available on this system as the tests were terminated because of poor corrosion resistance. References: 17, 66, 83.

**URANIUM-RUTHERIUM**

Investigation was terminated because of poor corrosion properties. References: 17, 63, 66, 83.

**URANIUM-SILICON (Figure 16)**

The uranium-silicon alloy system has been fairly well established. The system contains four terminal solid solutions: alpha, beta, and gamma uranium and delta silicon; six intermediate phases: epsilon, which contains about 23 atomic per cent silicon, (the structure and composition of this phase have not been satisfactorily ascertained) and \(\text{U}_2\text{Si}_3\), \(\text{U}_3\text{Si}_5\), \(\text{U}_5\text{Si}_3\), and \(\text{U}_7\text{Si}_3\). There are three eutectics in the system, one between gamma U and \(\text{U}_2\text{Si}_3\) at 985°C, the second between \(\text{U}_6\text{Si}_3\) and \(\text{U}_7\text{Si}_3\) at 1570°C and the third between delta Si and \(\text{U}_7\text{Si}_3\) at 1315°C.

The solubility ranges are very limited. Alpha U is stable up to 665°C and contains a negligible amount of silicon in solid solution. Beta U is stable between 665°C and 770 to 795°C, depending on the composition. Solubility of silicon in beta U is less than 1 atomic per cent. Gamma U is stable between 770-795°C and 1125°C. It contains a maximum of 1.75 atomic per cent silicon in solution at 980°C. Delta silicon melts at 1420°C and contains very little uranium in solid solution.

Epsilon, which forms by a peritectic reaction between gamma U and \(\text{U}_6\text{Si}_3\) at 930°C, contains 23 atomic per cent silicon. This phase has excellent resistance to corrosion. \(\text{U}_2\text{Si}_3\) melts at 1665°C and forms a eutectic with USi at 1570°C. USi forms a peritectic reaction between liquid and \(\text{U}_7\text{Si}_3\) at 1575°C. \(\text{U}_5\text{Si}_3\) forms by a peritectic reaction between liquid and USi at 1610°C. USi melts at approximately 1700°C. Its crystal structure is body-centered tetragonal, containing 4 molecules per unit cell, \((a = 3.97 \pm 0.03 \text{ A}, c = 13.76 \pm 0.08 \text{ A})\) with a calculated density of 8.98 g/cm³. USi is formed by a peritectic reaction between USi and liquid at 1510°C. Its crystal structure is simple cubic, \(a = 403 \text{ A}\). References: 1, 9, 10, 11, 123, 133, 136, 137, 142, 143.

**URANIUM-SILVER**

Silver alloys separated into two distinct phases: Ag and U. No alloying effect was observed. Silver was lost by vaporization. References: 39, 65.

**URANIUM-STRONTIUM**

The U-Th system has been partially established although the liquidus beyond 5 atomic per cent
Thorium has not been located. One eutectic has been established at approximately 5 atomic percent thorium and 1065°C. No evidence was found of the formation of intermetallic compounds or of solid solubility of one component in the other. Very little is known definitely as to the degree of solubility of U in Th; if any exists it is estimated to be less than 2 atomic percent. References: 61, 62, 146, 147.

**URANIUM-TIN (Figure 19)**

The U-Sn system has been partially established. The extremely pyrophoric nature of most of the alloys has handicapped the investigation but it is believed three compounds exist in the system: U₅Sn₄, U₃Sn₆, and USn₃.

The evidence indicates no solubility of tin in uranium. The transformation temperatures of uranium do not appear to be affected by tin. There appears to be no material solubilities of the intermediate phases. The solubility of uranium in tin is less than 0.005 atomic percent at 600°C.

The compounds U₅Sn₄ and U₃Sn₆ are proposed on the basis of thermal and microscopic data but oxidize so readily that positive identification has been impossible. Thermal data indicate that U₅Sn₄ is stable up to the melting point (approximately 1500°C) and that U₃Sn₆ decomposes peritectically at 1380°C.

USn₃ is not as pyrophoric as the lower tin alloys. It decomposes peritectically at 1350°C. USn₃ has a simple cubic structure, (a = 4.62Å) and a cal-

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**Figure 16. Uranium-Silicon**

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Figure 17. Uranium-Tantalum
URANIUM-TITANIUM

Little data are available for this system. The beta-gamma U transformation is lowered somewhat by small amounts of titanium, while the alpha-beta transformation is not appreciably altered. References: 39, 72, 73, 116, 149.

URANIUM-TUNGSTEN (Figure 20)

The U-W system consists of four phases: alpha, beta, and gamma uranium, and tungsten. No evidence was found of formation of intermetallic compounds. The liquidus line was established up to 2400°C.

The temperatures of the alpha-beta and betagamma uranium transformations are not altered by tungsten. The nature of the solidus transformation is in some doubt. The solidus line at 1135°C is about 10°C higher than the melting point found for uranium. The solidus transformation is tentatively described as a peritectic transformation.

The solid solubilities of tungsten in uranium and uranium in tungsten were found to be very limited. The solubility limits in both cases are probably less than one atomic per cent. References: 10, 17, 134, 136, 150.
URANIUM-VANADIUM

Investigation of these alloys was terminated because of their poor resistance to corrosion. References: 16, 63, 83, 151.

URANIUM-ZINC

Preliminary work in the U-Zn system indicated that alloys containing more than 20 atomic per cent uranium are difficult to prepare because of the distillation of zinc as the liquidus rises. Microscopic examination of high zinc alloys shows a eutectic, apparently between 90 and 100 atomic per cent zinc. No information is available concerning the second phase involved in this eutectic or the number of compounds existing in the system. References: 1, 4, 8, 22.

URANIUM-ZIRCONIUM

Exploration of this system is incomplete. Results indicate zirconium deplaces the solid state transformation considerably and that above 5 atomic per cent zirconium, two horizontals exist, one at approximately 675°C and the other at 605°C. These horizontals indicate the presence of two eutectoids. There appears to be no considerable solubility of zirconium in gamma uranium. References: 16, 17, 59, 60, 63, 141, 152, 153, 154, 155.

Figure 19. Uranium-Tin
Figure 20. Uranium-Tungsten
SUMMARY

The phase diagrams of the binary systems of uranium with aluminum, beryllium, carbon, chromium, cobalt, copper, iron, manganese, mercury, nickel, silicon, tantalum, tin, and tungsten have been established for the greater part, although information on some areas is incomplete.

Partial data exist for a number of other systems. Some alloys were studied principally in the hope of obtaining alloys with corrosion resistance superior to that of uranium itself. Only the alloys of uranium with columbium, molybdenum, silicon, and zirconium appear to have enhanced resistance to corrosion.

No substantial solubility of any metal in alpha uranium has been reported. However, a number of metals are soluble with gamma phase. Solubility of uranium in most solid metals appears to be negligible.

A considerable number of intermetallic compounds of uranium have been identified. Compounds of the type $U_M$ are usually exceedingly brittle although not hard enough to scratch glass.

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The Mechanical Properties of Beryllium

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It has been recognized since the early days of nuclear energy production that beryllium should be an ideal material for pile construction; first, because it is an excellent moderator; and second, because, being a metal, it might reasonably be expected to have mechanical properties which would allow its use as a structural material. That beryllium has to date not been so employed may be attributed largely to two factors; namely, the relative ease with which very pure graphite could be obtained during the war when time was such an important consideration, and the paucity of information available concerning the metallurgical and mechanical properties of beryllium. The situation with regard to both these factors has been appreciably improved as a consequence of research and development during the past several years. The present paper is a report of information concerning the mechanical properties of beryllium resulting from research carried out at MIT under the auspices of the Manhattan Project and the Atomic Energy Commission.

Beryllium metal available at the present time is produced chiefly by one or the other of two general techniques. In the first of these, BeF₂ is reduced with magnesium and the metal is made available in the form of lumps. The lump metal is then refined by vacuum melting and cast, also under vacuum, into billets. The billets are usually fabricated into useful shapes by extrusion, although rolling and forging techniques have also been used with some success. Lump metal can also be fabricated by powder metallurgy techniques as in the Brush "QT" process. In the second production technique the beryllium is obtained in the form of flakes by the electrolysis of beryllium chloride. The flake metal is processed by cold compression of the flakes into billet form, followed by hot extrusion of the compacted billet. The mechanical property testing to be described below has been carried out most extensively on extruded vacuum cast lump beryllium, but both extruded flake and metal fabricated by powder metallurgy methods have been investigated to some extent.

EXPERIMENTAL TECHNIQUES

Measurements made included tensile tests at temperatures up to 1000°C, and stress-rupture and creep tests at temperatures in the range of 500 to 1094°C. The degree of precision was in general confined only to that necessary to give good comparative data. For example, elongations were measured in such a way that the stretch taking place in the specimen billet region was included in the strain measurements. Thus the absolute values of elongation might be in error by a relatively large amount, but the comparative values from specimen to specimen were considerably more accurate.
is considered that the errors may be as high as 15 per cent on an absolute basis; the reproducibility of values is within about 2 to 3 per cent.

A schematic drawing of the apparatus used for high temperature tensile testing is shown in Figure 1. Measurement of strain was made by means of dial gages actuated by feeler rods seated at the base of the specimen threaded section. In some cases dial gage measurement of the displacement of the pulling crosshead of the Tinius-Olsen 20,000 lb standard tensile tester was considered sufficiently accurate for comparison purposes. Furnace temperature was controlled with Variacs and was held within ±5°C while the average differential from top to bottom of the specimen gage length was 3°C. At temperatures of 800°C and above the specimens were tested under an atmosphere of preheated helium in order to eliminate the excessive air corrosion which beryllium undergoes in this temperature range.

Stress-rupture tests above 700°C were conducted in the apparatus schematically illustrated in Figure 2. Vacuums of 10⁻⁴ mm of Hg or better were maintained during testing. Strain measurements were made by a dial gage indicating the specimen elongation as transmitted through the weight pan. This apparatus was limited to creep rates above 10⁻⁹ in./in./hr and loads below about 65 pounds. For slower rates of creep or heavier loads at relatively low temperatures use was made of a standard type creep apparatus available in the regular MIT creep laboratories. In this case strain was measured by telescopic observation of the movement of reference marks attached directly to the specimen at the ends of the gage length.

ROOM TEMPERATURE TENSILE PROPERTIES

Investigation of the room temperature tensile properties of beryllium have been carried out largely on vacuum cast extruded metal. The discussion, therefore, will be confined mainly to this type of beryllium although a brief comparison with the other types will be included.

For vacuum cast extruded beryllium, if the melting and casting conditions and the chemistry of the metal are kept reasonably constant, the room temperature tensile properties would be expected to be a function chiefly of the extrusion conditions and any subsequent annealing treatment. The effects of varying extrusion temperatures and annealing conditions were, therefore, the first factors investigated. It was later found, however, that, be-
Hence, a series of experiments was conducted to determine the extent of the surface effect on beryllium extruded at various temperatures. The results of these experiments will be described first, since some of the earlier results on the effect of varying annealing conditions may thus be better understood.

A group of tensile specimens was prepared from bars extruded with a 11 to 1 reduction at temperatures in the range 500 to 1208°C. For each extrusion temperature tests were performed in duplicate on specimens in the following conditions: (1) as extruded and machined, (2) as extruded, machined, and annealed at 600°C, and (3) as extruded, machined, and electrolytically etched to remove 0.010 inch of metal on the diameter of the specimen gage length. The results of these tests are listed in Table 1. Analysis of these data leads to several important conclusions. In the as-extruded and machined condition the ultimate strength drops off rapidly as the extrusion temperature is raised, and the per cent elongation is of the order of only a few tenths of one per cent for all extrusion temperatures. If, however, the surface of the specimen gage is removed to a depth of 0.005 inch (on the radius) before testing, for extrusion temperatures of 900°C and above the ultimate strength is raised appreciably and the elongation is markedly improved, particularly at the higher extrusion temperatures. For extrusion temperatures of 500 and 700°C the removal of the surface has little effect on the properties. Examination of the microstructures of the as-extruded material (Figures 3 to 6) reveals that extrusion at 500 and 700°C leaves the metal in a completely cold worked condition. Extreme distortion of the grains is evident as well as a pronounced fibering in the longitudinal direction. Partial recrystallization is seen in the structure of the 300°C extruded material, and for higher extrusion temperatures the metal is completely recrystallized. It seems apparent, then, that removal of the specimen surface has a large effect on the tensile properties, but only when the main body of the metal is in the recrystallized condition. In other words, the inherent properties of the recrystallized material are intermediate strength and relatively high ductility, but the damaged surface layer causes premature failure and does not allow these inherent properties to be realized. On the other hand, if the metal is in a severely cold worked condition throughout, it is inherently strong and very brittle and the surface damage resulting from machining, if present, has no appreciable effect on its tensile properties.

*ductility values are high for beryllium, but still low compared with most other metals.
Table 1. The effect of extrusion temperature and machining stresses on the tensile properties of beryllium.

<table>
<thead>
<tr>
<th>Extrusion temperature (°C)</th>
<th>Bar no.</th>
<th>As extruded and machined</th>
<th>As extruded, machined, and annealed at 800°C</th>
<th>As extruded, machined, and etched</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ultimate (psi)</td>
<td>Elong. (%)</td>
<td>Ultimate (psi)</td>
</tr>
<tr>
<td>500</td>
<td>345</td>
<td>347</td>
<td>Broke in threads</td>
<td>51,600</td>
</tr>
<tr>
<td>700</td>
<td>349</td>
<td>73,100</td>
<td>0.28</td>
<td>51,500</td>
</tr>
<tr>
<td>900</td>
<td>351</td>
<td>350</td>
<td>48,400</td>
<td>3.77</td>
</tr>
<tr>
<td>352</td>
<td>48,700</td>
<td>2.71</td>
<td>60,500</td>
<td>0.30</td>
</tr>
<tr>
<td>1060</td>
<td>354</td>
<td>355</td>
<td>45,800</td>
<td>2.79</td>
</tr>
<tr>
<td>358</td>
<td>44,300</td>
<td>2.15</td>
<td>50,200</td>
<td>1.29</td>
</tr>
<tr>
<td>1105</td>
<td>358</td>
<td>36,900</td>
<td>0.64</td>
<td>52,800</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>49,600</td>
<td>2.81</td>
</tr>
<tr>
<td>1208</td>
<td>359</td>
<td>34,800</td>
<td>0.44</td>
<td>54,000</td>
</tr>
<tr>
<td></td>
<td>50,200</td>
<td>3.80</td>
<td>Broke in threads</td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 1 for the specimens tested after annealing at 800°C indicate that such annealing also eliminates the effects of surface damage. In addition, the annealing recrystallizes the cold worked beryllium and thus raises the ductility and lowers the strength of the metal extruded at the lower temperatures. This effect will be discussed more thoroughly in the section below.

In order to investigate the effect of annealing on room temperature tensile properties, specimens were prepared from bars extruded with a 16 to 1 reduction at temperatures of 650, 730, 815, and

Figure 3. Transverse and longitudinal microstructure of vacuum cast Be as extruded at 500°C. Polarized light at 100×
Figure 4. Transverse and longitudinal microstructure of vacuum cast Be as extruded at 700°C. Polarized light at 100x

Figure 5. Transverse and longitudinal microstructures of vacuum cast Be as extruded at 900°C. Polarized light at 100x

Figure 6. Transverse and longitudinal microstructures of vacuum cast Be as extruded at 1060°C. Polarized light at 100x
900°C. Examination of the microstructures of these specimens revealed that the transition temperature between cold working and hot working during extrusion occurred somewhat below 815°C. Metal extruded at the two lower temperatures showed essentially completely cold worked structures, whereas metal extruded at 815 and 900°C showed largely recrystallized structures. The slight discrepancy in the location of the transition temperature as indicated by this work and the work previously noted may be explained by the fact that the temperatures given are furnace heating temperatures and not necessarily actual working temperatures. Billet size, extrusion equipment, and speed of handling would all affect the differential between this nominal temperature and actual working temperature.

For each extrusion temperature specimens were tested in the as-extruded condition and after annealing at 600, 750, and 900°C. These temperatures were chosen on the basis of previous work which indicated that the recrystallization temperature for severely cold worked beryllium is about 725°C. It was found as expected that the 600°C anneal produced no change in the microstructure of any of the specimens, the 750°C anneal caused virtually complete recrystallization in the cold worked metal, and the 900°C anneal resulted in appreciable grain growth in all specimens. These microstructural changes are illustrated in Figures 7 and 8 for the material extruded at 650 and 815°C. The strength and ductility properties of the annealed specimens are plotted as a function of anneal temperature in Figure 9.

In studying the curves of Figure 9, it should be remembered that this work was done prior to that demonstrating the effect of surface damage on the tensile properties. None of the specimens for which values are given in Figure 9 were etched to remove the damaged surface layer. Hence, all specimens tested in the as-extruded condition and even those given a 600°C anneal (this annealing temperature has been shown to be insufficient to relieve surface effects) were subject to the effect of surface damage. With this in mind the data in Figure 9 together with the evidence of Figure 7 and 8 may be appraised and found to justify the following conclusions: (a) annealing at 600°C and below causes no large change in the room temperature properties of beryllium regardless of whether it has been cold worked or hot worked during extrusion; (b) raising the annealing temperature to 750°C is sufficient to accomplish essentially complete recrystallization of severely cold worked material, accompanied by some decrease in strength and a marked improvement in ductility; (c) for metal extruded at temperatures high enough to produce recrystallized as extruded material annealing at 750°C effects no observable change in microstructure, but produces a noticeable improvement in strength and a large improvement in ductility, which changes may be attributed to the elimination of the effects of surface damage; (d) annealing at 900°C stimulates grain growth accompanied by lowering of the strength properties and improvement of the ductility compared with the values after annealing at 750°C.

In the case of extruded flake and material fabricated by powder metallurgy, the effect of variables on the room temperature properties have not been studied extensively. However, it has been found that for these materials the problem of grain growth is not encountered. Figure 10 indicates the grain size of cast and flake bars as extruded at 900°C and after annealing at 1000°C. A similar comparison is shown for Brush process "QT" metal (a powder product) as received and after annealing at 1000°C. It is evident that major grain growth has occurred only in the cast material. It is believed that the oxide film about the original flake or powder particles plus the presence of some porosity in the metals fabricated from the flake and powder products act to inhibit grain growth both during extrusion and annealing. The combination of relatively high strength and ductility obtainable with extruded and annealed flake metal as compared with similarly treated vacuum cast metal is shown by the following ranges of values obtained over a number of tests in the annealed condition (annealing temperature 800°C, extrusion temperature approximately 1060°C).

<table>
<thead>
<tr>
<th></th>
<th>Cast and extruded</th>
<th>Flake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportional limit (psi)</td>
<td>17,000/23,000</td>
<td>20,000/30,000</td>
</tr>
<tr>
<td>Ultimate strength (psi)</td>
<td>36,000/55,000</td>
<td>59,000/78,000</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>1.5/4.0</td>
<td>4.0/7.0</td>
</tr>
</tbody>
</table>

The improved properties of the flake material may be associated with its considerably smaller normal grain size.
Figure 7. Microstructures showing the effect of annealing on vacuum cast beryllium extruded at 650°C. Polarized light 35×
Figure 8. Microstructures showing the effect of annealing on vacuum cast beryllium extruded at 815°C. Polarized light 35×
Before any comparative evaluation of the various types of metal can be made the factor of directionality must be considered. In many cases a material cannot be applied in such a way as to concentrate maximum stresses in the ideal direction. For example, in the high flux pile, it has been planned to use beryllium slabs (in the reflector) containing slots for the passage of cooling water. Thermal gradients at operating temperatures will therefore produce high transverse stresses and the question of final use of beryllium in this structure will depend on its ability to withstand transverse stresses. It has been observed that in extruded beryllium the directional differences in tensile properties are
Table 2. Room temperature directional properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>Condition</th>
<th>Ultimate (psi)</th>
<th>Elong. (%)</th>
<th>Ultimate (psi)</th>
<th>Elong. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast and extruded</td>
<td>As extruded</td>
<td>32,730</td>
<td>0.36</td>
<td>19,400</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Annealed 800°C</td>
<td>39,970</td>
<td>1.82</td>
<td>16,550</td>
<td>0.18</td>
</tr>
<tr>
<td>Extruded flake</td>
<td>As extruded</td>
<td>46,600</td>
<td>0.55</td>
<td>29,125</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Annealed 800°C</td>
<td>63,650</td>
<td>5.0</td>
<td>25,500</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>1 hr plus</td>
<td>68,450</td>
<td>6.6</td>
<td>26,700</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>1000°C 1 hr</td>
<td>80,500</td>
<td>6.6</td>
<td>26,700</td>
<td>0.30</td>
</tr>
<tr>
<td>Brush QT Metal</td>
<td>Annealed 800°C</td>
<td>34,400</td>
<td>2.2</td>
<td>33,800</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

very pronounced. Table 2 shows results on 3-inch by 1/2-inch flats of extruded flake and extruded cast beryllium. Tests taken transverse to the extrusion direction (i.e., across the flat) show strengths generally less than half those in the longitudinal direction. Ductilities are similarly poor.

Extruded beryllium is characterized by two structural properties either or both of which could account for the directional differences in tensile properties. Figure 4 shows the gross longitudinal grain fibering introduced by the extrusion. In addition x-ray analysis has revealed that the extruded beryllium has a marked preferred orientation, the 0001 (basal) planes and a 1010 direction being lined up almost parallel to the extrusion axis. It has been found that the gross fibering is virtually eliminated by annealing at temperatures above 750°C, but that preferred orientation remains even up to 1000°C. Inasmuch as such annealing does not appreciably improve the transverse tensile properties, it seems apparent that the directional differences are associated largely with the preferred orientation and not with the gross fibering.

C.S. Barrett has indicated that slip in beryllium crystals at room temperature takes place on the 0001 planes and in a 2110 direction. Slip occurs when the resolved shear stress on this plane and in this direction attains a certain critical value. The resolved shear stress is given by the expression

$$
\tau = \frac{F \cos \phi \cos \alpha}{A}
$$

where \( \tau \) is the resolved shear stress, \( F \) the tensile load, \( A \) the cross sectional area of the specimen, \( \phi \) the angle between the normal to the slip plane and the tension axis, and \( \alpha \) the angle between the slip direction and the tension axis. It is seen that \( \tau \) is a maximum when both \( \phi \) and \( \alpha \) equal 45° and is zero when either angle is 90°. On this basis, consideration of the crystal orientation existing in the extruded beryllium readily explains, at least qualitatively, the directional differences in tensile properties. In a longitudinal test the angle \( \phi \) approaches 90°, hence the resolved shear stress \( \tau \) is small. Consequently large loads are needed to initiate slip and the proportional limit should be high. In a transverse test the allowed rotation of the basal planes (possibly within certain limits) around the extrusion axis locates a statistical number of slip planes in the optimum position for maximum resolved shear stress; thus the load required to produce slip is low and relatively low proportional limits should be observed. Tests show, in fact, that whereas the longitudinal proportional limit is in the range of 16,000/30,000 psi, the trans-
verse proportional limit is so low that no elastic region is observed within the limits of accuracy obtained. Figure 11 shows sample stress-strain curves in the longitudinal and transverse directions for cast and flake materials.

Similar considerations reveal that the relatively low ultimate strength in the transverse direction as compared to that in the longitudinal direction is consistent with the preferred orientation known to exist in the extruded metal. It has not been determined whether the test specimen failures were of the brittle cleavage type or of the shearing fracture type. In the latter case, however, fracture has generally been found to occur at a critical value of the resolved shear stress on the slip plane. Hence, just as in the case of the proportional limit, high

Figure 10. Effect of annealing at 1000°C on various types of beryllium. All photomicrographs 50 x using polarized light.
fracture strength would be expected in the longitudinal direction and low strength in the transverse direction. In the case of brittle cleavage of zinc and the hexagonal metals it has been observed that cleavage occurs when a certain critical normal stress acting on the cleavage plane is exceeded. The resolved normal stress $N$ is given by

$$N = \frac{F}{A} \cos^2 \phi$$

where $F$ and $A$ are as before and $\phi$ is the angle between the tension axis and the normal to the cleavage plane. For beryllium it is reasonable to suppose that the 0001 plane has the lowest critical normal stress for cleavage, since a beryllium crystal given a sudden blow with a hammer cleaves along the 0001 plane. Because this plane is almost parallel to the extrusion axis, in a longitudinal test $\cos \phi$ will be small and high fracture strength should again be expected; in a transverse test $\cos \phi$ and therefore $N$ will be large for a statistical number of crystals and the fracture strength should be relatively low.

Since the transverse weakness is thus indicated to be inherent in extruded beryllium, the powder process would seem at present to be the only practical one by which a nearly isotropic material may be produced. It is therefore of considerable interest to compare the directional properties of a block produced by powder metallurgy with the properties of an extruded flat. Table 2 includes values obtained from a 9 1/4 x 5 x 2 3/4-inch block of Brush process QT metal. Longitudinal samples

![Figure 11. Comparison of longitudinal and transverse stress-strain curves for beryllium.](image-url)
were taken in the 9 1/4-inch direction and the transverse samples were taken in the 5-inch direction. It should be emphasized that these results do not necessarily indicate the limits of properties available in powder materials since new and improved processes have been developed. Data are not yet available on the properties of these later materials, however. The significant point is that there is no large difference between longitudinal and transverse properties and the strength values are considerably better than those obtained in the transverse direction on extruded metal.

A further effect which must be considered in regard to the use of beryllium as a pile material is that of radiation damage. The work of Siegel indicates that after a total exposure of 50 Mwd/ct at 30°C no definite changes occur in length, elasticity, electrical resistivity, frequency of elastic vibration, damping capacity, hardness, or thermal conductivity. Work is underway at MIT to determine radiation effects, if any, on mechanical properties in tension and compression and on lattice parameters as indicated by x-ray methods.

HIGH TEMPERATURE PROPERTIES

Much of the present interest in beryllium centers about its possible use in combination with uranium as a fuel constituent operating at very high temperatures in the Daniels Pile. Tentative plans contemplate the possible use of Be-U fuel elements operating at a maximum temperature of about 900°C with the possibility of occasionally reaching 1100°C. From a structural standpoint the fuel rods would need to support only their own weight, but due to temperature gradients there is the possibility of larger stresses acting on the material. Considerable work has therefore been done on high temperature short time tensile tests, stress-rupture tests and creep tests.

![Figure 12. Variation of ultimate strength of beryllium with testing temperature in short time high temperature tensile tests.](image)
Figures 12, 13, and 14 show the effect of temperature variation on ultimate strength, elongation, and reduction in area in high temperature tensile tests on extruded cast metal and flake metal, all measurements being taken in the longitudinal direction. Points plotted in Figure 12 for ultimate strength are averages of all results to date on materials tested at elevated temperatures. They consist of averages of from 3 to 11 tests at each temperature and include results on 8 different bars. Agreement of individual values was very good for ultimate strength data, but ductility values showed considerable variation between bars and were difficult to plot statistically. Figures 13 and 14, therefore, give only schematically the plot of average elongation and reduction against temperature. Individual bars in some cases differed markedly from the values shown, but the trend of results is approximately as indicated.

The marked increase in ductility noted from 200 to 400°C may be associated with the occurrence of slip on planes other than the 0001 plane to which slip is presumably limited at room temperature. There has been no proof of this, however. The ductility decrease in the neighborhood of 600°C is probably related to the change in mechanism of fracture from intragranular to intergranular which is completed between 500 and 700°C. The increased elongations above 700°C were accompanied by the appearance of numerous small intergranular cracks, generally transverse, and existing even at some distance from the final fracture. Stretch thus occurred at least partially by actual separation of crystals and should not be considered true ductility.

The effect of annealing on the room temperature properties of material extruded above the recrystallization temperature has been discussed in a previous section. The drop off in strength in un-
Figure 14. Schematic variation of reduction in area of beryllium with testing temperatures in short time high temperature tensile tests.

The ductility of flake metal at elevated temperatures in an ordinary tensile test varies in a similar fashion to that of cast and extruded material. Bar to bar variations make an exact comparison of ductilities impossible. A very definite difference in strength values exists, however, as can be seen in Figure 12. At low testing temperatures flake metal has higher strength than the cast and extruded metal, while at testing temperatures between 450 and 800°C the opposite is true. At low temperatures grain boundary material must have higher strength than the grains themselves since fracture always occurs through the grains. At high temperatures (700°C and above) the boundary material is weaker than the grains, since fracture occurs at the boundaries. It seems reasonable, therefore, that the fine grain flake metal with a larger area of boundary material, should be the stronger of the two at low temperatures and the weaker at high temperatures. These results appear to apply only to a tensile test of ordinary duration since the stress-rupture strength of flake Be seems to be much greater than that of vacuum melted metal as is mentioned later.

Transverse tests at elevated temperatures show
little improvement in ductility over those at room temperature. Table 3 lists values obtained at testing temperatures up to 800°C in longitudinal and transverse tests from the same 3-inch by 1/2-inch flats of cast and flake metal noted in Table 2. For cast metal there is little change in transverse strength or ductility below 600°C. Flake metal shows a gradual decrease in strength over this same range. The strengths of flake metal in transverse and longitudinal directions are nearly equalized by 600°C, while in cast metal the transverse strength is still about 25 per cent below the longitudinal at 800°C.

The effect of strain rate has been investigated at three different temperatures: 350, 600, and 800°C. Summary curves for ultimate strength, elongation and reduction in area are shown in Figures 15, 16, and 17 for cast and extruded beryllium. Plotted points are averages of 3 to 4 tests at each strain rate. A marked effect of rate is noted on all three properties. The reason for the reversed trend in reduction values at 350°C as compared to those at 600 and 800°C is related to the mechanism of fracture. It has been found in previous work that under conditions producing transcrystalline fracture ductilities increase with decreasing strain rate, while under conditions producing intercrystalline fracture ductilities decrease with decreasing strain rate. Fractures on nearly all specimens tested between 300 and 500°C showed a small dark

Table 3. Directional effects on beryllium mechanical properties.

<table>
<thead>
<tr>
<th>Test temp.</th>
<th>Condition of test</th>
<th>Direction of test</th>
<th>No. of tests</th>
<th>Ultimate strength (psi)</th>
<th>Elong. (%)</th>
<th>Red. (%)</th>
<th>No. of tests</th>
<th>Ultimate strength (psi)</th>
<th>Elong. (%)</th>
<th>Red. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room</td>
<td>As extruded Longitudinal</td>
<td>4</td>
<td>46,600</td>
<td>0.55</td>
<td>-</td>
<td>3</td>
<td>32,730</td>
<td>0.36</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Room</td>
<td>Annealed 800°C for 1 hr Longitudinal</td>
<td>2</td>
<td>29,125</td>
<td>0.3</td>
<td>-</td>
<td>2</td>
<td>19,400</td>
<td>0.30</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Room</td>
<td>Annealed 800°C-1 hr Transverse</td>
<td>1</td>
<td>25,500</td>
<td>0.3</td>
<td>-</td>
<td>2</td>
<td>16,550</td>
<td>0.18</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Room</td>
<td>Annealed 1000°C-1 hr Transverse</td>
<td>1</td>
<td>26,700</td>
<td>0.3</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>As extruded Longitudinal</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>39,870</td>
<td>13.4</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>Annealed 800°C-1 hr Transverse</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>14,250</td>
<td>1.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>400°C As extruded Longitudinal</td>
<td>2</td>
<td>30,590</td>
<td>14.8</td>
<td>9.6</td>
<td>3</td>
<td>27,870</td>
<td>29.0</td>
<td>32.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C As extruded Transverse</td>
<td>2</td>
<td>22,840</td>
<td>1.9</td>
<td>0.3</td>
<td>2</td>
<td>14,500</td>
<td>3.0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C As extruded Longitudinal</td>
<td>2</td>
<td>13,570</td>
<td>10.6</td>
<td>7.2</td>
<td>2</td>
<td>25,850</td>
<td>29.0</td>
<td>32.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C As extruded Transverse</td>
<td>1</td>
<td>11,200</td>
<td>2.5</td>
<td>0.6</td>
<td>2</td>
<td>15,980</td>
<td>1.2</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800°C As extruded Longitudinal</td>
<td>2</td>
<td>4,760</td>
<td>9.1</td>
<td>4.2</td>
<td>3</td>
<td>9,270</td>
<td>25.6</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800°C As extruded Transverse</td>
<td>1</td>
<td>5,860</td>
<td>0.3</td>
<td>-</td>
<td>2</td>
<td>6,900</td>
<td>9.6</td>
<td>8.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 15. The effect of strain rate on the ultimate strength of beryllium at 350, 600, and 800°C as measured in high temperature tensile tests.

centrally located area in an otherwise bright fracture. Closer examination showed the dark area to be an intercrystalline fracture. By 600°C the fracture is completely intercrystalline. We may therefore assume that the change in mechanism of fracture occurs over the range of 300 to 600°C and that in this range both mechanisms are involved. This fits in well with previous indications from the strength relationships of flake and cast metal that the so-called "equicohesive" temperature at normal strain rates is in the vicinity of 450°C. Increasing temperature and decreasing strain rate both tend to produce intergranular rather than intragranular fractures. It is not unreasonable to expect, therefore, that at some temperature in the neighborhood of the "equicohesive" temperature (i.e., 450°C) a minimum in ductility might be found in the curve for some intermediate strain rate.

Stress rupture tests so far have been limited to extruded cast metal at high temperatures, particularly 1094°C. Data on similar material has been obtained by Battelle Memorial Institute at 927°C and 700°C in standard creep units. MIT data on creep at 500°C is the low limit of investigated temperatures. All this data has been assembled in Figure 18, showing a log-log plot of creep rate versus load and rupture time versus load. Reasonably good straight line plots are obtained for all temperatures. By reploting the intersections of these curves with a series of arbitrary rupture times and creep rates the family of curves in Figures 19 and 20 is developed. From these an approximation of loads to produce a given creep rate or rupture time at any temperature between 500 and 1100°C may be obtained.

Preliminary tests indicate that equivalent results are obtained in creep in either longitudinal
or transverse tests at 927°C. There is also a small amount of data to indicate very much higher creep strength in flake metal at 1094°C than in cast and extruded metal tested at the same temperature. This fact may be of value in connection with pile fuel material for use at very high temperatures.

As has been indicated previously in connection with grain growth there is believed to be an oxide film surrounding the flake particles. It is possible that this oxide is responsible for the improved stress-rupture properties of flake material. Work is underway at present to test out this thesis by the production of extruded powder compacts containing varying amounts of BeO up to 25 weight per cent. The stress-rupture properties will be studied as a function of BeO content in the hope that the role of oxide in high temperature strength may be further clarified.

THE EFFECT OF ALLOY ADDITIONS

It is apparent from the data listed so far that the beryllium available at present is a very brittle metal when compared with such metals as iron, copper, and aluminum. Extruded cast beryllium can be annealed to give elongations up to about 4 per cent at room temperature and extruded flake may go as high as 7 per cent. In an effort to improve the ductility, the effects of various alloy additions to beryllium have been studied. In one set of experiments several dilute binary alloys of beryllium with Ti, Zr, Mg, Ce, Ca, S, Se, and Al were made. These elements were chosen because of the possibility that they might deoxidize Be as mentioned in earlier work. In all cases additions of about 1 weight per cent of the alloying element

Figure 16. The effect of strain rate on the elongation of beryllium at 350, 600, and 800°C as measured in high temperature tensile tests.
were used, except that for Al a second alloy containing 3 per cent Al was also prepared. Table 4 reveals the results of the tensile tests on these alloys. No appreciable improvement in either the strength or ductility of Be is indicated for any of the additions. The effect of annealing is similar to that discussed in preceding sections for unalloyed beryllium, maximum elongations of 2 to 3 per cent being obtained after annealing just above the recrystallization temperature.

It was found by metallographic examination and x-ray parameter measurements that the extent of solid solubility of all the above elements in beryllium is exceedingly small, considerably less than the amounts added in preparation of the alloys. With the thought that elements which form extensive solid solubility phases with beryllium might have a beneficial effect on its tensile properties, measurements were made to determine the solid solubility limits in Be of U, B, Co, Th, Cb, Pd, Ge, Pt, Ru, Os, Rd, Cr, Ag, Cu, and Bi. Of these elements only Cu, Pd, Ni, and Ag showed appreciable solid solubility in beryllium. The solubility of Cu varied from 20 weight per cent at 500°C to 36 weight per cent at 1125°C. Pd dissolved in amounts of nearly 8 weight per cent at 600°C and 24 weight per cent at 1150°C; Ni dissolved in amounts of about 10 to 15 per cent, and Ag about 8 to 10 per cent at temperatures up to 1050°C. Accordingly tensile tests were made on extruded bars of binary alloys containing 15 weight per cent Cu, 32 weight per cent Cu, and 10 weight per cent Ni respectively. Tests on the 32 per cent Cu alloy were made both as extruded and as quenched from 1050°C. The results of the test are listed in Table 5. Although some increase in tensile strength may be noted for the 32 per cent Cu alloy the ductilities were very poor in all cases. Even after annealing at 800°C the highest elongations observed were of the order of only a few tenths of one per cent.
Table 4. The effect of alloying elements on the tensile properties of beryllium.

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Per cent added element</th>
<th>Extrusion temp., °C</th>
<th>Anneal temp.(°C), time (hr)</th>
<th>Breaking stress, psi</th>
<th>Per cent elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>L64-1</td>
<td>0.73 Ti</td>
<td>760</td>
<td>As extruded</td>
<td>43,200</td>
<td>0.42</td>
</tr>
<tr>
<td>L64-1</td>
<td>0.73 Ti</td>
<td>760</td>
<td>725 20</td>
<td>53,700</td>
<td>1.6</td>
</tr>
<tr>
<td>L64-2</td>
<td>0.73 Ti</td>
<td>760</td>
<td>725 20</td>
<td>53,600</td>
<td>1.1</td>
</tr>
<tr>
<td>L64-A</td>
<td>0.73 Ti</td>
<td>760</td>
<td>725 20</td>
<td>32,900</td>
<td>0.15</td>
</tr>
<tr>
<td>L64-B</td>
<td>0.73 Ti</td>
<td>760</td>
<td>750 5</td>
<td>51,400</td>
<td>1.2</td>
</tr>
<tr>
<td>L65-1</td>
<td>0.65 Zr</td>
<td>755</td>
<td>As extruded</td>
<td>37,200</td>
<td>0.2</td>
</tr>
<tr>
<td>L65-1</td>
<td>0.65 Zr</td>
<td>755</td>
<td>725 20</td>
<td>40,400</td>
<td>1.4</td>
</tr>
<tr>
<td>L65-2</td>
<td>0.65 Zr</td>
<td>755</td>
<td>725 20</td>
<td>48,400</td>
<td>2.2</td>
</tr>
<tr>
<td>L65-B</td>
<td>0.65 Zr</td>
<td>755</td>
<td>700 50</td>
<td>47,100</td>
<td>2.6</td>
</tr>
<tr>
<td>L69-1</td>
<td>0.05 Mg</td>
<td>730</td>
<td>As extruded</td>
<td>40,400</td>
<td>0.19</td>
</tr>
<tr>
<td>L69-A</td>
<td>0.05 Mg</td>
<td>730</td>
<td>725 20</td>
<td>42,700</td>
<td>2.3</td>
</tr>
<tr>
<td>L69-B</td>
<td>0.05 Mg</td>
<td>730</td>
<td>725 20</td>
<td>42,300</td>
<td>2.4</td>
</tr>
<tr>
<td>L70-1</td>
<td>0.60 Ce</td>
<td>750</td>
<td>As extruded</td>
<td>38,100</td>
<td>0.1</td>
</tr>
<tr>
<td>L70-1</td>
<td>0.60 Ce</td>
<td>750</td>
<td>725 20</td>
<td>40,400</td>
<td>0.18</td>
</tr>
<tr>
<td>L70-2</td>
<td>0.60 Ce</td>
<td>750</td>
<td>725 20</td>
<td>42,500</td>
<td>0.15</td>
</tr>
<tr>
<td>L70-A</td>
<td>0.60 Ce</td>
<td>750</td>
<td>750 5</td>
<td>44,500</td>
<td>1.5</td>
</tr>
<tr>
<td>L70-B</td>
<td>0.60 Ce</td>
<td>750</td>
<td>800 5</td>
<td>37,600</td>
<td>1.0</td>
</tr>
<tr>
<td>L71-1</td>
<td>1.45 Ca</td>
<td>760</td>
<td>As extruded</td>
<td>40,000</td>
<td>0.29</td>
</tr>
<tr>
<td>L71-1</td>
<td>1.45 Ca</td>
<td>760</td>
<td>725 20</td>
<td>49,400</td>
<td>1.4</td>
</tr>
<tr>
<td>L71-2</td>
<td>1.45 Ca</td>
<td>760</td>
<td>725 20</td>
<td>52,900</td>
<td>1.3</td>
</tr>
<tr>
<td>L71-A</td>
<td>1.45 Ca</td>
<td>760</td>
<td>725 20</td>
<td>37,600</td>
<td>0.88</td>
</tr>
<tr>
<td>L71-B</td>
<td>1.45 Ca</td>
<td>760</td>
<td>750 5</td>
<td>52,800</td>
<td>2.7</td>
</tr>
<tr>
<td>LA 3-1</td>
<td>0.05 S</td>
<td>765</td>
<td>As extruded</td>
<td>53,100</td>
<td>0.17</td>
</tr>
<tr>
<td>LA 3-1</td>
<td>0.05 S</td>
<td>765</td>
<td>725 20</td>
<td>49,100</td>
<td>1.2</td>
</tr>
<tr>
<td>LA 3-2</td>
<td>0.05 S</td>
<td>765</td>
<td>725 20</td>
<td>38,800</td>
<td>0.45</td>
</tr>
<tr>
<td>LA 3-A</td>
<td>0.05 S</td>
<td>765</td>
<td>750 20</td>
<td>47,400</td>
<td>3.0</td>
</tr>
<tr>
<td>L72-1</td>
<td>0.05-0.5 Se</td>
<td>740</td>
<td>As extruded</td>
<td>46,700</td>
<td>0.44</td>
</tr>
<tr>
<td>L72-1</td>
<td>0.05-0.5 Se</td>
<td>740</td>
<td>725 20</td>
<td>42,000</td>
<td>0.44</td>
</tr>
<tr>
<td>L72-2</td>
<td>0.05-0.5 Se</td>
<td>740</td>
<td>725 20</td>
<td>46,900</td>
<td>0.26</td>
</tr>
<tr>
<td>L72-A</td>
<td>0.05-0.5 Se</td>
<td>740</td>
<td>750 5</td>
<td>33,400</td>
<td>0.86</td>
</tr>
<tr>
<td>L72-B</td>
<td>0.05-0.5 Se</td>
<td>740</td>
<td>800 5</td>
<td>47,100</td>
<td>2.7</td>
</tr>
<tr>
<td>L61-1</td>
<td>0.62 Al</td>
<td>685</td>
<td>As extruded</td>
<td>50,800</td>
<td>0.18</td>
</tr>
<tr>
<td>L61-1</td>
<td>0.62 Al</td>
<td>685</td>
<td>725 20</td>
<td>47,700</td>
<td>1.9</td>
</tr>
<tr>
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<td>0.62 Al</td>
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<td>725 20</td>
<td>45,500</td>
<td>2.4</td>
</tr>
<tr>
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<td>0.62 Al</td>
<td>685</td>
<td>725 20</td>
<td>50,000</td>
<td>3.0</td>
</tr>
<tr>
<td>LA 2-1</td>
<td>3.00 Al</td>
<td>675</td>
<td>As extruded</td>
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<td>0.57</td>
</tr>
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<td>LA 2-1</td>
<td>3.00 Al</td>
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<td>3.00 Al</td>
<td>675</td>
<td>725 20</td>
<td>47,200</td>
<td>2.7</td>
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</table>
Table 5. Tensile results on binary beryllium alloys.

<table>
<thead>
<tr>
<th>Composition, wt per cent</th>
<th>Treatment</th>
<th>Ultimate tensile strength in psi</th>
<th>Elongation* (%)</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Cu</td>
<td>As extruded</td>
<td>49,400</td>
<td>0.19</td>
<td>One phase alloy, completely recrystallized.</td>
</tr>
<tr>
<td>15 Cu</td>
<td>As extruded</td>
<td>53,700</td>
<td>0.19</td>
<td>Fine grained, same as above.</td>
</tr>
<tr>
<td>15 Cu</td>
<td>As extruded + 5 hr at 800°C (slow cool)</td>
<td>51,900</td>
<td>0.19</td>
<td>One phase alloy, completely recrystallized, fine grained.</td>
</tr>
<tr>
<td>15 Cu</td>
<td>As extruded + 5 hr at 800°C (slow cool)</td>
<td>54,800</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>15 Cu</td>
<td>As extruded + 3 hr at 750°C (slow cool) + 15 min at 1050°C (quenched)</td>
<td>6,100</td>
<td>-</td>
<td>One phase alloy, recrystallized, large grained.</td>
</tr>
<tr>
<td>15 Cu</td>
<td>As extruded + 3 hr at 750°C (slow cool) + 15 min at 1050°C (quenched)</td>
<td>7,700</td>
<td>-</td>
<td>Same as above.</td>
</tr>
<tr>
<td>32 Cu</td>
<td>As extruded + 15 min at 1050°C (quenched)</td>
<td>5,100</td>
<td>-</td>
<td>One phase alloy, few globules of white compound, completely recrystallized, fine grained.</td>
</tr>
<tr>
<td>10 Ni</td>
<td>As extruded</td>
<td>57,300</td>
<td>0.25</td>
<td>One phase alloy, completely recrystallized, fine grained.</td>
</tr>
<tr>
<td>10 Ni</td>
<td>As extruded + 5 hr at 800°C (slow cooled)</td>
<td>60,600†</td>
<td>3.22</td>
<td>One phase alloy, completely recrystallized, fine grained. Crack in center containing iron.</td>
</tr>
<tr>
<td>10 Ni</td>
<td>As extruded + 5 hr at 800°C (slow cooled) + 15 min at 1050°C (quenched)</td>
<td>33,100</td>
<td>0.14</td>
<td>One phase alloy, recrystallized, large grained. Few cracks near outer edge.</td>
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<tr>
<td>10 Ni</td>
<td>As extruded + 15 min at 1050°C</td>
<td>23,800</td>
<td>0.11</td>
<td>One phase alloy, recrystallized, large grained. Crack in center containing iron.</td>
</tr>
</tbody>
</table>

*Elastic elongation. None of the samples underwent plastic deformation.
†Broke in grips.
Figure 18. A compilation of stress-rupture and creep data for beryllium plotted on a log-log scale.

Stress rupture tests were run at 1094°C on an alloy of Be with about 2 weight per cent of U, an alloy of possible interest for pile fuel material. Results were not entirely consistent, but the 2 per cent alloy was generally superior to unalloyed Be. A plot of the data for the alloy and for unalloyed Be is shown in Figure 21 on the usual log-log basis. The form of the creep curves encountered was somewhat unusual, having two "steady state" rates of creep instead of the usual single "steady state". This is illustrated in Figure 22 for a 1.62 per cent U alloy loaded at 84.3 psi at 1094°C (2000°F). The primary rapid creep period of about 20 hours was followed by a 50-hour period of creep at 0.00031 in./in./hr. There was then an abrupt change in slope and creep continued at a lower rate of 0.00012 in./in./hr until the final short stage of rapid stretch to rupture at 174 hours. No explanation of this peculiarity is offered here. A Be-U alloy of this sort would be subject to damage by fission fragments resulting from the uranium fission. In this connection the size of the Be₅U compound particles is of considerable importance. It is believed that for particles over 100 microns in diameter the fission fragments remain within the compound particle and therefore do not affect the beryllium matrix. In the case of particles under one micron in diameter the fission fragments may be expected to penetrate into the Be matrix and this may cause undesirable property effects. Any appreciable degree of solid solubility of uranium in beryllium might be expected to aggravate fission fragment effects in the matrix. Solubility work indicates, however, that U fortunately is practically insoluble in Be at low temperatures.
Figure 19. A semi-logarithmic plot for beryllium showing load to produce rupture in 10,100, or 1000 hours at temperatures between 500 and 1100°C.
Figure 20. A semi-logarithmic plot for beryllium showing load to produce creep rates of 1.0, 0.1, 0.01, and 0.001 per cent per hour at temperatures between 500 and 1100°C.
SUMMARY

The overall picture indicates that present methods are still far from producing a beryllium of any large degree of ductility at room temperature. Properties of flake and cast extruded materials show a high degree of directionality which should be considered in any engineering applications. Of the two, the flake metal shows better mechanical properties, but has the drawback of poor corrosion resistance and higher cost. Materials produced by powder metallurgy methods eliminate the directionality factor. The latest developments along these lines have not been tested, but the best of the earlier samples investigated indicate that considerably better properties can be developed in powder products than in the transverse direction in any extruded material. Corrosion resistance of powder materials tested so far has been inferior, but improvement should be possible. It is the authors' opinion that serious consideration should be given to powder products where multidirectional stresses are involved.

For high temperature uses up to 700°C beryllium shows considerable promise, particularly where weight saving or specific nuclear properties are desired. Above 700°C corrosion in air becomes a serious factor and protective atmospheres are necessary. Directional factors must be considered in high temperature applications also.

It seems unlikely that any major improvement in room temperature properties will be produced by methods of extreme purification or by alloying. Future efforts should be directed towards refinement of methods of working and treatment to produce optimum properties in the ranges indicated, towards methods of eliminating as much as possible the directionality factor, and towards improvement of physical properties and corrosion resistance at elevated temperatures.
ACKNOWLEDGMENTS

The authors wish to acknowledge the early testing work of H. R. Bethke and R. C. Fellinger; the Be solubility determinations carried out by E. Gordon; the cooperation of S. V. Arnold and B. J. Bergson of the fabrication group; the preparation of photomicrographs by H. P. Roth; and the laboratory assistance of C. E. Latham-Brown and D. A. Kadish as well as many others of the MIT Metallurgical Project.

REFERENCES

4. Ibid., p. 317.
8. MIT Progress Reports (A-1), October and November 1945, (CT-3353 and CT-3379).

Figure 22. Stress-rupture curves for Be-U alloy showing anomaly of two steady state creep rates.
The Solubility of Uranium and Thorium in Liquid Metals and Alloys

By E. E. Hayes and P. Gordon
Massachusetts Institute of Technology

INTRODUCTION

Among the various schemes being considered for the adaptation of atomic energy to power production, one involving the use of a liquid reactor pile has seemed to offer considerable practical possibilities. In such a pile it is proposed that the uranium, or thorium, fuel be dissolved in a liquid solvent which would serve as the medium for transmission of the nuclear power generated. It has been recognized that a liquid metal or alloy would be an ideal solvent provided one could be found which is capable of holding appreciable quantities of uranium or thorium in liquid solution at sufficiently low temperatures. To the end of finding a metal or alloy which would fulfil these conditions, the present investigation of the solubilities of uranium and thorium in various liquid metals and alloys was undertaken.

SUMMARY OF RESULTS

Of the twenty-two metals or alloys tried as solvents for uranium, it was found that pure bismuth and pure aluminum dissolve the largest quantities of uranium at the lowest temperatures. Typical values for bismuth are 1.6 atomic per cent (1.8 wt per cent) uranium at 550°C, and 3.1 atomic per cent (3.5 wt per cent) at 650°C. The aluminum alloy is solid below about 650°C, whereas the bismuth alloy is liquid at temperatures considerably below this, although with lesser amounts of uranium in solution.

Fifteen solvents were tried for thorium. In this case pure aluminum gave the best results. At 650°C, aluminum dissolves 3.7 atomic per cent (24.8 wt per cent) thorium.

Aluminum was tried as a solvent in a ternary system involving both uranium and thorium and was found to dissolve considerable amounts of both elements. At a temperature of 650°C, the solubility of uranium and thorium in aluminum can be represented by the empirical formula:

$$2(\text{wt per cent } U) + \text{ wt per cent } \text{Th} = 25$$

EXPERIMENTAL DETAILS

The general technique used for determining the liquidus lines of the various binary and ternary alloys was as follows: The alloy being studied was heated to a solution temperature in the single phase region, cooled to some temperature below this and held for a period of several hours. A sample of the liquid in the alloy at this temperature was then withdrawn for chemical analysis. The alloy was then cooled to a lower temperature, allowed to soak, sampled, and this process repeated at several temperatures down to the point of solidification.

Several of the steps in this procedure will bear more complete description. The melting was carried out in the vertical resistance wound furnace shown in Figure 1. Beryllia lined alundum crucibles large enough to give a melt 4 inches deep and 1 3/4 inches in diameter were used for most alloys. The vertical muffle of the furnace was provided with a cover through which argon was introduced as a protective atmosphere. In addition, as shown in Figure 2, the cover contained a tube through which metal was added and the sampling
done. There was also provision for the insertion of a protected chromel-alumel thermocouple and a stirring rod. The latter was fashioned by cementing alundum paddles to a 3/16-inch alundum rod and firing the assembly with a slip coat of beryllia. (See Figure 3.)

In making a run, the metal or alloy in which the uranium or thorium was to be dissolved was premelted and held at about 930°C if possible. Some of the more volatile alloys had to be held at lower temperatures. The uranium or thorium, after careful cleaning and removal of oxide, was then quickly added to the melt through the large sampling tube. In this way the metal was immediately covered by the molten solvent and oxidation was kept at a minimum. The melt was stirred for two to three hours. It was found desirable in some melts to add the uranium (or thorium) in increments of 5 weight per cent until the maximum solubility was reached. The solubility could be roughly determined by the resistance to the stirring rod. When this point was attained, the stirring was stopped and the melt held at temperature for about two hours in order to allow any excess solid to settle out. The supernatant liquid was then sampled for chemical analysis. After lowering the temperature of the melt a predetermined amount, a time of two hours was again allowed for settling and another sample taken. This procedure was repeated at successively lower temperatures until samples had been obtained at five or six temperatures over a range of 200–500°C depending on the particular alloy being studied.

The sampling was accomplished by vacuum-sucking the molten metal up into a pyrex glass tube inserted about 1/4 inch below the surface of the liquid. The thick walled capillary upper section of the tube (see Figure 3) served to freeze the metal as it was drawn up, and a constriction at the lower end helped to hold the sample in the tube until it solidified.

A microexamination of some sectioned melts showed complete settling of the uranium or thorium, except for the eutectics of aluminum-uranium...
and aluminum-thorium, thus indicating that the samples did not contain any appreciable amount of suspended solid particles. A comparison of several reruns of melts also indicate that the samples were taken under nearly equilibrium conditions.

Some significant departures from the above procedure were made in the case of several of the melts. For the sodium-thorium melt the crucible and stirring rod were made of a very low carbon iron. (It had been reported by Grube and Botzenhardt [Z. Electrochem. 48: 424–425, 1942] that 75 weight per cent thorium would dissolve in sodium at 160°C; the implication was that the use of carbon-free iron crucibles was important in obtaining this solubility). The sodium was melted.
in the crucible over a hot plate in a dry box with an argon atmosphere. Westinghouse powdered thorium was then added to the molten sodium and after cooling was quickly transferred to the vertical furnace. The melt was vigorously stirred at about 650°C for 4 hours and then allowed to cool at 300°C at which temperature a sample was taken. Another departure from the general procedure was for the gallium-uranium melt. Since only 50 grams of gallium were available for this melt a very small BeO crucible was used. This necessitated making a much smaller stirring rod which was accomplished using only BeO components. The standard sampling tubes used for other melts would not work with gallium since gallium would not freeze in the small capillary because of its low melting point. Small quartz buckets (0.2 cc capacity) at the end of a quartz rod were employed instead. The results of the gallium-uranium melt are subject to some doubt due to difficulties which were encountered in sampling. The surface tension of the gallium was found to be extremely strong and the quartz bucket could be inserted completely underneath the surface of the melt and yet not have any metal in the bucket when it was taken out. When the bucket was agitated, however, the bucket would fill with metal. As a result, the chemical analyses were somewhat variable due to some precipitated uranium which was probably included in the sample. It can be definitely stated, however, that gallium will dissolve less than 0.9 atomic per cent uranium at 700°C and less than 0.03 atomic per cent at 40°C.

The third departure from the general procedure made use of a thermal analysis to find the eutectic temperature of an alloy. The transition elements, iron, nickel, and chromium, are known to form eutectics with uranium at temperatures as low as 725°C (U-Fe eutectic). Because of the high uranium content of these alloys, they might be useful liquid reactors provided the eutectic temperatures could be lowered somewhat by the addition of other elements. One attempt was made to do this. Since antimony lowers the melting point of iron rapidly, an alloy containing 10 per cent antimony, 10 per cent iron, and 80 per cent uranium by weight was prepared. A thermal analysis indicated that the antimony lowers the U-Fe eutectic from 725°C to 695°C. Though this is not a striking decrease, it is thought that such alloys offer possibilities worthy of further investigation.

DISCUSSION OF RESULTS

A complete list of comparative data for the binary and ternary alloys investigated is given in Tables 1, 2, 3, 4 and Figure 4. The values shown in these tables are interpolated figures obtained from solubility curves which were determined by the chemical analyses of the samples. The actual experimental data of the sample temperatures and chemical analyses are given in Table 5 and 6. The significant features of the results may be summarized as follows:

1) Uranium dissolves only to a very limited extent in liquid zinc, antimony, lead, indium, thallium, and gallium.

2) Aluminum and bismuth each dissolve uranium to an appreciable extent. In aluminum, the solubility of uranium varies from 1.7 atomic per cent (13.5 wt per cent) at 650°C, to 4.2 atomic per cent (28.0 wt per cent) at 900°C. The alloy is solid below about 650°C. In bismuth, the solubility of uranium increases from 0.9 atomic per cent (1.0
tried were magnesium, silver, silicon, and zinc in the case of the aluminum-uranium alloys, and tin, cadmium, sodium, and aluminum in the case of the bismuth-uranium alloys.

3) The addition of third elements to the uranium-aluminum or uranium-bismuth alloys invariably decreases the uranium solubility. Third elements

4) The addition of 10 wt per cent antimony to

Table 1. Weight per cent solubility of uranium in liquid metals and alloys.

| T°C  | Al   | 68% Al 8% BI | 72% Al 8% BI | 76% Al 12% BI | 88% Al 32% BI | Zn  | 1.5% Al 98.5% Bi | Bi  | Sn  | 60% Bi 40% Sn | 80% Bi 20% Sn | 40% Bi 60% Sn | 8% Sn | 8% Sn | Zr  | Ba  | Pb  | Sb  | Bi  | Ag  | In  | Ti  | Ge  |
|------|------|--------------|--------------|---------------|---------------|-----|----------------|-----|-----|----------------|----------------|----------------|-------|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| 900  | 28.0 | 14.1         | 6.1          | 13.8          | 4.5           | 2.9 | .6             | .05 | .17 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 850  | 25.5 | 7.6          | 5.0          | 4.6           | 8.5           | 10.5| 3.2            | .4  |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 800  | 23.0 | 4.4          | 3.2          | 3.6           | 18.7          | 16.5| 8.0            | 1.8 | .8  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 750  | 20.5 | 2.5          | 1.9          | 2.8           | 17.9          | 15.0| 6.0            | 1.2 | .06 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 700  | 17.3 | 1.9          | 1.9          | 1.1           | 2.3           | 4.5 | 13.0           |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 650  | 15.5 | 1.5          | 1.5          | 1.6           | 7.1           | 19.0| 12.0           | 10.5| 6.5 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 600  | 14.0 | 1.6          | 9.4          | 7.8           | 3.2           |     | 2.5            | 1.4 | .4  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 550  | 10.5 |             | 1.8          |               | 1.8           | 1.0 | .05            | 1.0 | .05 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 500  |     |              | .32          |               | .9            | .04 |                |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 450  |     |              |              |               |               |     |                |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |

Table 2. Atomic per cent solubility of uranium in liquid metals and alloys.

| T°C  | Al   | 68% Al 8% BI | 72% Al 8% BI | 76% Al 12% BI | 88% Al 32% BI | Zn  | 1.5% Al 98.5% Bi | Bi  | Sn  | 60% Bi 40% Sn | 80% Bi 20% Sn | 40% Bi 60% Sn | 8% Sn | 8% Sn | Zr  | Ba  | Pb  | Sb  | Bi  | Ag  | In  | Ti  | Ge  |
|------|------|--------------|--------------|---------------|---------------|-----|----------------|-----|-----|----------------|----------------|----------------|-------|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| 900  | 4.2  |              | .14          |               | 1.5           | 12.3| 3.1            |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 850  | 3.7  |              | .9           | .6            | 1.2           | 6.9 | 9.3            | 2.2 | .2  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 800  | 3.3  |              | .5           | .4            | 1.0           | 3.0 | 3.1            | 7.1 | 1.2 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 750  | 2.8  |              | .3           | .2            | .8            | 2.8 | 2.7            | 5.3 | .8  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 700  | 2.3  |              | .21          | .02           | .2            | 1.6 | 2.2            | 4.2 | .4  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 650  | 1.7  |              | .17          | .016          | .2            | 1.8 | 1.9            | 3.1 | .2  |                      |                |                |       |       |     |     |     |     |     |     |     |
| 600  | .5   |              | .05          | .4            | 1.4           | 1.3 | 1.1            | 2.2 | .07 |                      |                |                |       |       |     |     |     |     |     |     |     |
| 550  | .7   |              |              |               |              | 1.6 | .06            |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 500  |     |              | .32          |               | .9            | .04 |                |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |
| 450  |     |              |              |               |               |     |                |     |     |                      |                |                |       |       |     |     |     |     |     |     |     |

ND - NOT DETECTED * LESS THAN 0.3 AT 40°C
Table 3. Weight per cent solubility of thorium in liquid metals and alloys.

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<th>35% Mg</th>
<th>65% Al</th>
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ND = NOT DETECTED

Table 4. Atomic per cent solubility of thorium in liquid metals and alloys.

<table>
<thead>
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<th>T °C</th>
<th>AI</th>
<th>65% Al</th>
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ND = NOT DETECTED

the iron-uranium eutectic composition lowers the eutectic temperature from 725°C to 695°C.

5) Liquid antimony, lead, indium, and thallium dissolve thorium only to a very limited extent.
6) In contradiction to the results reported by Grube and Botzenhardt, sodium is found to dissolve practically no thorium at 300°C.

7) Of the alloys investigated, aluminum is the best solvent for thorium, dissolving 3.7 atomic per cent (24.8 wt per cent) at 650°C and 6.4 atomic per cent (37 wt per cent) at 850°C.

8) Bismuth and tin dissolve small amounts of thorium.

9) As in the case of uranium, the addition of magnesium, silicon, silver or zinc to aluminum or sodium or cadmium to bismuth decreases the solubility of thorium in each case.

10) Aluminum will dissolve considerable amounts of both uranium and thorium together. Figure 4 shows a partial ternary diagram of the uranium-thorium-aluminum alloys investigated. The dotted lines are approximate isothermal lines on the liquidus surface. The solid line (AB) indicates the range of compositions which are liquid to a temperature of 650°C.

Table 5. Experimental data on uranium solubility and thorium solubility.

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* Data from equilibrium diagram in: M. Hansen, "Aufbau der Zweistofflegierungen" (1936).
† ND: not detected.
### Table 5. Experimental data on uranium solubility and thorium solubility. (Continued)

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* Above liquidus line.
Table 5. Experimental data on uranium solubility and thorium solubility. (Continued)

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* Bad Samples.
† ND: not detected.
‡ Not determined chemically.
Table 5. Experimental data on uranium solubility and thorium solubility. (Continued)

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*ND: not detected.
†These values are higher than original wt per cent U in charge—no good.
‡Only these samples considered as indicating maximum solubility. True values, however, may be lower.
Table 5. Experimental data on uranium solubility and thorium solubility. (Continued)

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Table 6. Experimental data on solubility of uranium and thorium in aluminum.

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<td></td>
<td>870</td>
<td>17.5</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>821</td>
<td>15.7</td>
<td>19.0</td>
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<tr>
<td>Al</td>
<td>920</td>
<td>8.9*</td>
<td>23.0*</td>
</tr>
<tr>
<td></td>
<td>867</td>
<td>9.0*</td>
<td>23.1*</td>
</tr>
<tr>
<td></td>
<td>835</td>
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<td>23.2*</td>
</tr>
<tr>
<td></td>
<td>780</td>
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<td>23.1</td>
</tr>
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<td></td>
<td>734</td>
<td>8.4</td>
<td>22.1</td>
</tr>
<tr>
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<td>674</td>
<td>7.6</td>
<td>18.5</td>
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<tr>
<td></td>
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<td>16.6</td>
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</tr>
<tr>
<td></td>
<td>663</td>
<td>11.0</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>644</td>
<td>9.8</td>
<td>9.9</td>
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<tr>
<td>Al</td>
<td>642</td>
<td>3.6</td>
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</tr>
<tr>
<td>Al</td>
<td>638</td>
<td>10.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

* Above liquidus line.
Figure 4. Schematic sketch of Al-U-Th alloy diagram.

ACKNOWLEDGMENT

The authors wish to acknowledge the work of Mr. G. Bitsianes who designed the original apparatus used in this investigation and developed the described stirring and sampling techniques which were essential in this work. Appreciation is also extended to Mr. E. B. Read under whose direction all the analytical work was done and to Dr. A. R. Kaufmann who supervised the entire program.
The Influence of Pile Radiations on Solid Materials

By Frederick Seitz, Carnegie Institute of Technology

This article represents a revision and digest of reports M-4075 and M-3990, based on lectures given at the training program of Clinton Laboratories (1946-47)

The theory of the influence of bombardment by neutrons and fission fragments on the properties of solids is summarized. The results are used as a basis for reviewing the experimental observations concerning the changes induced in metals and insulators that have been exposed to pile radiations. It is pointed out that the atoms that are knocked-on by close collisions with fast neutrons and fission fragments are responsible for secondary effects which represent an important part of the influence of the primary radiations. Equations are given for estimating the fraction of the energy of one of the primary particles which is expended in excitation and ionization of the electrons in the medium through which these particles are passing and the fraction which is expended in transmitting kinetic energy to the atoms as a whole. Of the latter fraction about one half induces lattice vibrations and the remaining half produces permanent displacements of the atoms in typical materials of construction. Quantitative estimates are given of the number of atoms that are permanently displaced by fission neutrons and fission fragments in several interesting materials; graphite, beryllium, beryllium oxide, and aluminum. In addition the changes induced in uranium metal by fission fragments are summarized in detail. It is found that the theoretical calculations are in good agreement with the experimental results that have been observed to date, particularly for graphite and beryllium oxide in which the effects do not reverse automatically at normal operating temperatures. It is suggested that the changes induced in metals such as aluminum and beryllium are reversed almost at once during exposure and that most of the effects observed in uranium metal are caused by the fission products, which behave like foreign atoms, and by the thermal agitation that accompanies the passage of fission fragments.

1. INTRODUCTION

Early in 1943

Wigner pointed out that the carbon atoms would receive very heavy neutron bombardment during an extended period of operation and that one should expect many of them to be displaced permanently from their normal positions. This, in turn, would bring about a change in the physical properties of the moderator which might have marked influence on the operation of the pile. As a result of this observation, experiments were started on the changes that actually occur when graphite and similar materials are irradiated...
ated either with neutrons alone or with more complex pile radiations. The initial work was started by M. Burton and a very able group that was assembled at the Metallurgical Laboratory of the University of Chicago; however, the interest in the subject is so widespread that it has since been taken up at a number of laboratories.

The most rudimentary measurements leave no doubt that Wigner's initial observation was correct, for the properties of many solid materials are changed appreciably when subject to the radiations found in reactors.

It is evident that the subject has interest for two reasons: First, the development of the technology of piles requires accurate knowledge of the manner in which materials of construction will behave when subject to radiation; second, a study of the behavior of suitably chosen materials may provide fundamental information concerning the internal properties of solids. To date, the greatest pressure for study has come from the purely technological side. This is reflected in the fact that most of the solids investigated are not those whose fundamental properties are understood most completely at present, but are instead substances which have interest for immediate pile construction. Fields of technology usually make most rapid progress when studies of materials of practical interest are coupled with investigations of idealized substances under specially selected conditions in which the practical goals are ignored. It is to be hoped that the near future will see emergence of increasing emphasis on the more fundamental aspects of the subject.

The principal radiations that occur in piles are as follows:

a. Gamma Rays

This radiation is produced by the fission products during the course of their transition from unstable to stable states. Gamma rays usually follow the emission of beta particles. About 5 Mev of gamma rays are produced for each fission. This represents about 3 per cent of the fission energy.

b. Beta Particles

These are produced by the fission products in the transition from the neutron-rich states in which they are produced. The total energy per fission that is dissipated in the beta decay process is about 23 Mev. However, about 16 Mev of this appears in the form of neutrinos which are lost from the pile and produce a negligible amount of irradiation effect.

c. Neutrons

Approximately two neutrons are produced in each fission process. These have in total about 5 Mev of kinetic energy which is available for producing radiation effects.

d. Fission Fragments

The fragments produced during fission have an energy of about 165 Mev which is divided almost equally between the two halves. It is to be noted that these particles have by far the greatest amount of energy available for producing disturbance.

Simple addition of the energies associated with each of these products of fission shows that the total energy of fission is almost exactly 200 Mev. It is to be noted that any one of the massive fragments (neutrons and fission products) may produce fast ions by collision. These ions become missiles which are capable of producing further disturbance.

Although bombardment with gamma rays and beta particles can produce significant changes in the physical properties of solids, interest thus far has been focussed on the influence of neutrons, fission fragments, and the charged atoms that are produced by collisions with these particles. In most of the substances of practical interest studied so far the influence of neutrons and fission fragments greatly outweighs the effects of other radiations when the substance is exposed to all. For this reason, we shall omit further reference to gamma and beta radiation. It may be emphasized in passing, however, that materials which are placed in regions of a pile where they receive only gamma and beta radiation can deteriorate or at least become altered at an appreciable rate. For example, glasses may become deeply discolored and plastics may become brittle.

2. PRIMARY EFFECTS OF NEUTRONS

Neutrons are both scattered and absorbed by matter. In most materials the migration of neutrons through a layer of matter involves the superposition of both effects. Neutrons having energies in a particular range are often absorbed very strongly by special materials; for example,
Cadmium has a very large cross section for absorption of neutrons having thermal energies. In such cases the absorption completely overthrows scattering. From the standpoint of physical properties the most important influences of neutrons are: (a) the effects related to their ability to displace atoms from their normal equilibrium positions by a knock-on process; (b) the radioactivity which they induce in the materials.

The displacement effect is particularly important for fast neutrons since these produce knock-on atoms having sufficient kinetic energy to produce additional displacements. This effect is now known to be of practical importance and merits considerable attention. The induced radioactivity appears to be of secondary interest, except in the case of fissionable materials. In this case, the secondary displacements produced by the fission fragments are exceedingly great.

It is interesting to consider the kinetic energies which are imparted to atoms by fast neutrons in knock-on collisions in which the overall kinetic energy is conserved. If the atom is at rest and the neutron has energy \( E_n \), the kinetic energy which the neutron imparts to the atom when it is deflected through an angle \( \theta \) in a moving coordinate system in which the center of gravity of the neutron and atom is at rest is

\[
\Delta E = E_n \frac{4mM}{(m + M)^2} \sin^2 \frac{\theta}{2}
\]

(2.1)

Here \( m \) is the mass of the neutron and \( M \) that of the knock-on atom. If the collision cross section is isotropic, which can usually be assumed to good approximation, the average energy lost per collision is:

\[
\overline{\Delta E} = E_n \frac{2mM}{(m + M)^2} = E_n \frac{2A}{(1 + A)^2}
\]

(2.2)

in which \( A = M/m \) is the mass number of the atom struck by the neutron. Table 1 contains the energies received on the average from neutrons possessing 2 Mev of energy. In the same table is given the energy of an electron possessing the same velocity as the knocked-on particle.

The most important conclusion to be drawn from this table is that in all cases except that of hydrogen the knocked-on atom has a velocity of the same order of magnitude as that of the valence electrons in most substances. As we see in the next section, this means that these atoms will dissipate their energy either by knocking on other atoms or by exciting the valence electrons of the material in which they reside.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \Delta E ) (kev)</th>
<th>Energy of equivalent electron (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Be</td>
<td>360</td>
<td>21.7</td>
</tr>
<tr>
<td>C</td>
<td>380</td>
<td>12.7</td>
</tr>
<tr>
<td>N</td>
<td>265</td>
<td>11.1</td>
</tr>
<tr>
<td>O</td>
<td>221</td>
<td>7.5</td>
</tr>
<tr>
<td>Al</td>
<td>140</td>
<td>5.2</td>
</tr>
<tr>
<td>U</td>
<td>17</td>
<td>0.039</td>
</tr>
<tr>
<td>FP*</td>
<td>93,400</td>
<td>507</td>
</tr>
<tr>
<td></td>
<td>66,600</td>
<td>259</td>
</tr>
</tbody>
</table>

* Represents a pair of fission products having masses of 100 and 140 and initial kinetic energies of 93.4 and 66.6 Mev. These data are given for purposes of comparison.

3. ENERGY LOSS OF MOVING CHARGED ATOM

When a charged atom moves through matter it can dissipate its energy in two ways:

a) As a result of excitation of the electrons in the surrounding matter. This possibility originates in the Coulomb interaction between the charges on the moving ion and the electrons in the surrounding material.

b) As a result of close collisions in which the moving ion transmits momentum to the nuclei of the stationary atoms in sufficient amount to give the latter appreciable kinetic energy. These are sometimes called elastic collisions since the kinetic energy of motion of atoms is conserved.

Both of these processes can occur if the moving atom is uncharged, however the first process is then limited to encounters in which the moving atom actually passes through a stationary atom, for the moving atom will not be able to exert forces at long distances if it is uncharged. The
second process is of practical interest to us only in collision between the moving and stationary atom which are so close that it is immaterial whether the moving atom is ionized or not.

We shall summarize the principal facts concerning the two processes:

a. Energy Loss by Excitation and Ionization of Stationary Atoms

When the moving ion has a velocity that is large compared with the velocities of the electrons in the stationary atoms, the rate at which it dissipates energy by excitation or ionization in traveling unit distance, \(-dE/dx_e\), is

\[-\frac{dE}{dx_e} = \frac{4\pi e^2 \varepsilon^2}{mv^2} N_e \ln \frac{mv^2}{E} \]  (3.1)

Here \(e\) is the electronic charge, \(z\) is the charge on the moving ion, \(v\) is its velocity, \(m\) is the mass of the electron, \(N_e\) is the number of electrons per unit volume and \(E\) is an energy of the order of the average ionization energy of the electrons on the stationary atoms — a quantity that can be determined most reliably from experiment, except in the most simple atoms. It is to be observed that the mass of the moving ion does not appear in this expression. This means that the charge and velocity of the moving ion are the quantities of primary importance for exciting the stationary atoms. If the moving charge were an electron, for which \(z\) would be unity, equation (3.1) would be modified slightly by the presence of a factor inside the \(\ln\) term which results from the fact that it is not possible to distinguish between the moving and ionized electron.

Since the velocity of the moving atom is of primary interest, it is convenient to express this velocity in indirect form by stating the energy that an electron having the same velocity would have, namely \(mv^2/2\). We shall designate this quantity by \(\varepsilon\) in all of the following discussion. Evidently \(\varepsilon\) is related to the kinetic energy \(E\) of the moving atom by the equation

\[\varepsilon = (M/M_e)E\]

in which \(M\) is the mass of the moving atom.

Equation (3.1) is valid in the form given only when \(\varepsilon\) is large compared with the ionization energy of any electron in the stationary atoms. It frequently happens that \(\varepsilon\) is large compared with the ionization energy of the electrons in the outer shells, but is smaller than the ionization energies of electrons in inner shells. In such cases the electrons which have ionization energies larger than \(\varepsilon\) should be excluded in evaluating \(N_e\) and \(E\) should be taken as the average ionization energy of the remaining electrons. This rule is conveniently included by writing equation (3.1) in the form

\[-\frac{dE}{dx_e} = \frac{4\pi e^2 \varepsilon^2}{mv^2} Z' n_e \ln \frac{mv^2}{E'} \]  (3.2)

in which \(n_e\) is the number of stationary atoms per unit volume, \(Z'\) is the number of electrons per atom capable of being excited or ionized and \(E'\) is the average ionization energy of the electrons that can be excited or ionized. \(Z'\) is large compared with \(n_e\) and \(Z\), the atomic number of the stationary atom, as \(\varepsilon\) increases from zero to a value larger than the ionization energy of the most tightly bound electron in the stationary atom.

Table 1 shows that the atoms knocked on by the average fast fission neutron have a value of \(\varepsilon\) that is small compared with the ionization or excitation energy of all electrons in most atoms except the valence electrons. It follows that the moving atoms will not dissipate an appreciable amount of energy in exciting any electrons other than those in the valence shells. The knocked-on hydrogen atoms which may have an energy as large as 500 ev (see Table 1) are a possible exception.

Since the atoms knocked on by fission neutrons can only excite the valence electrons, it follows that the dissipation of energy from this source will be dependent upon the manner in which the valence electrons are attached to the stationary atoms; if the stationary atoms are bound into a solid, the case of principal interest to us, it will depend upon whether this solid is a metal or an insulator. Equation (3.2) cannot be used in the form given for the cases that are of major concern since this is derived with the assumption that \(\varepsilon\) is large compared with \(E'\). Instead, it is necessary to return to first principles and derive new expressions which are more nearly valid when \(\varepsilon\) and \(E'\) are more nearly equal. The mathematical methods of present-day collision theory are very unreliable under these conditions; however, it is possible to obtain results which are at least of qualitative interest. We shall consider the case of a typical metal and a typical insulator.

1) Metal.—In a typical metal, the conduction electrons form a degenerate Fermigas, and possess kinetic energies ranging from zero to a
value $\epsilon_0$ which is of the order of several electron volts if the slight effects of temperature are neglected. Values of $\epsilon_0$ for several metals are given in Table 2.

Table 2. Kinetic energy $\epsilon_0$ of fastest conduction electrons at absolute zero of temperature.

<table>
<thead>
<tr>
<th>Metal</th>
<th>n</th>
<th>$\epsilon_0$(ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>1</td>
<td>4.72</td>
</tr>
<tr>
<td>Sodium</td>
<td>1</td>
<td>3.12</td>
</tr>
<tr>
<td>Beryllium</td>
<td>2</td>
<td>14.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>2</td>
<td>4.26</td>
</tr>
<tr>
<td>Aluminum</td>
<td>3</td>
<td>11.7</td>
</tr>
</tbody>
</table>

The quantity $n$ listed in the second column is the number of conduction electrons per atom. Approximate expressions for the manner in which the conduction electrons dissipate the energy of a moving atom can be derived in the three cases in which $\epsilon$ is small compared with $\epsilon_0$, is comparable to $\epsilon_0$ and is large compared with $\epsilon_0$. These expressions are as follows:

a) $\epsilon \ll \epsilon_0$ (very slow atom)

$$-\frac{dE}{dx} = \frac{12\pi n e^2 Z^2}{\epsilon}$$  \hspace{1cm} (3.3)

b) $\epsilon \sim \epsilon_0$

$$-\frac{dE}{dx} = \frac{1.08\pi Z^2 e^4 n}{\epsilon}$$  \hspace{1cm} (3.4)

c) $\epsilon > \epsilon_0$

$$-\frac{dE}{dx} = \frac{\pi Z^2 e^4}{\epsilon} n (\ln \epsilon/\epsilon_0 + 1.077)$$  \hspace{1cm} (3.5)

In these equations $Z$ is the atomic number of the moving atom and all of the other quantities have the designations given in previous parts of this section. It is to be emphasized that these results are valid when the moving atom is neutral. They are not altered substantially if the moving atom is ionized. We see from these approximate results that the moving atom dissipates its energy most strongly when $\epsilon$ is comparable to $\epsilon_0$. For smaller values of $\epsilon$ the dissipation by electron excitation decreases approximately linearly with $\epsilon$, whereas it decreases as $1/\epsilon$ when $\epsilon$ increases above $\epsilon_0$. It is interesting to note that equation (3.5) has a close resemblance to equation (3.2) for sufficiently large values of $\epsilon$, which shows that the stopping effect of conduction electrons could be included at least approximately with those of bound electrons for very fast particles in a semi-empirical description of the dissipation by electron excitation.

2) Insulator. — The determination of the dissipation of energy of a moving atom by the electrons in an insulator is an inherently more complex problem than the problem of dissipation by completely free electrons, particularly when the velocity of the moving atom is comparable to the velocity of the valence electrons in the insulator. It may be treated approximately under the following simplifying assumptions:

a) It is assumed that the valence electrons in the insulator possess discrete levels, so that the assemblage of atoms in the insulator can be treated as if it were a collection of isolated atoms with discrete levels to which the valence electrons are tightly bound.

b) It is assumed that the velocity of the moving atom is sufficiently slow that the velocity parameter $e = mv^2/2$ is comparable to the first excitation potential of the insulator.

The calculations based on these assumptions lead to the following conclusions:

a) The dissipation of energy $-dE/dx$ is greatest when the velocity parameter $e$ is approximately equal to the first excitation energy of the electrons in the insulator.

b) The dissipation falls off as $C/e$, where $C$ is a constant, for large values of $e$ when the moving atom is neutral. $C$ is replaced by a function of the type $\ln e/B$, where $B$ is a constant, if the moving atom is charged.

c) The energy loss falls very rapidly (transcendently) when $e$ drops below about one-eighth of the excitation energy of the electrons in the insulator.

b. Energy Loss by Elastic Encounters with Other Atoms

We are now in a position to consider the dissipation of the kinetic energy of a moving atom by collisions in which it transfers energy elastically
to the atoms of the medium through which it is passing. The simplest case to treat is that in which the stationary and moving atom are of the same species. This is the case for example when a carbon atom is knocked on in graphite and transfers part of its energy to other carbon atoms by elastic collision.

The rate at which the energy is dissipated is found to be

\[ -\frac{dE}{dx} = \frac{2\pi Z^4 e^4}{M v^2} N_0 \ln \frac{E}{E^*} \]  

(3.6)

where \( Z \) is the atomic number of the atoms, \( M \) is their mass, \( E \) is the kinetic energy of the moving atom, \( v \) is its velocity, and \( E^* \) is of the order of one-hundredth of an electron volt.

Table 3. Values of \( E^* \) for several elements (expressed in ev).

<table>
<thead>
<tr>
<th>Element</th>
<th>( E^* ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.00510</td>
</tr>
<tr>
<td>C</td>
<td>0.00500</td>
</tr>
<tr>
<td>Al</td>
<td>0.00373</td>
</tr>
</tbody>
</table>

We shall have cause in the following discussion to be interested in those collisions in which the initially stationary atom received sufficient energy to be displaced permanently from its initial environment. If we designate by \( E_d \) this energy, which should be of the order of 25 ev for typical materials, we find that the corresponding dissipation is

\[ -\frac{dE}{dx} \mid_{c,d} = \frac{2\pi Z^4 e^4}{M v^2} N_0 \ln \frac{E}{E_d} \]  

(3.7)

The ratio of the total energy dissipated by collisions to that dissipated in collisions for which the energy transferred is greater than \( E_d \) is

\[ \frac{dE}{dx} \mid_{c,d} = \ln \frac{E}{E^*} / \ln \frac{E}{E_d} \]  

(3.7a)

This ratio is usually near to 2 for the values of \( E \) of most interest to us. Consequently about half the energy expended in elastic collisions displaces atoms permanently and the remainder excites lattice vibrations.

The foregoing equations may be generalized readily to cover the case in which the two colliding atoms have different atomic numbers. If \( Z_1 \) and \( Z_2 \) are respectively the values of the atomic numbers of the two atoms, the total rate of energy loss is found to be

\[ -\frac{dE}{dx} = \frac{2\pi Z_1^4 e^4}{M_1 v^2} N_0 \ln \frac{E}{E_1^*} \]  

(3.7b)

where \( E_1^* \) is independent of atomic numbers and is related to \( E^* \) in (3.6) by the equation

\[ E_1^* = \frac{1}{4} \frac{E^*}{Z_1^4 M_2} \left( \frac{M_1 + M_2}{M_1 M_2} \right)^2 \]  

(3.8)

Here \( M_1 \) and \( M_2 \) are the masses of the two atoms of atomic number \( Z_1 \) and \( Z_2 \).

We shall eventually be interested in the average energy \( \bar{E} \) transferred to a stationary atom by the moving atom having energy \( E \) in those elastic collisions in which the energy transferred is greater than \( E_d \), the critical value needed to dislodge the stationary atom permanently. The result is found to be

\[ \bar{E}_{c,d} = E_d \ln \frac{E}{E_d} \left( \frac{4M_1 M_2}{M_1 + M_2} \right)^2 \]  

(3.8a)

which reduces to

\[ \bar{E}_{c,d} = E_d \ln \frac{E}{E_d} \]  

(3.9)

when the colliding atoms have equal mass.

Although most of the foregoing results for dissipation of energy by the two interesting means are correct only in order of magnitude they are of considerable value for estimating the relative importance of the various modes. For example, in the range of velocity for which \( \epsilon \) is greater than \( \epsilon_0 \) the ratio of the energy loss arising from collisions to that arising from excitation of free electrons is (see equations 3.5 and 3.6)

\[ \frac{dE}{dx} \mid_c / \frac{dE}{dx} \mid_e = \frac{Z^3}{n} \ln \frac{E/E^*}{E_d} \]  

(3.10)

In a light metal, such as aluminum, this ratio is small compared with unity, that is of the order of 0.01, for values of \( E \) of the order of 100 kev. The ratio is greater for the heavy elements since it increases approximately as the first power of \( Z \).
Similarly, when $\epsilon$ is very small compared with $\epsilon_0$, the ratio is
\[
\frac{dE/dx}_c = \frac{Z^{10/3}}{3n} \frac{m E^2}{M} \frac{\ln E/E^*}{\epsilon^2} \approx 1.33
\] (3.11)

This ratio becomes large compared with unity when $\epsilon$ decreases sufficiently, showing that the knock-on encounters eventually account for the major part of the loss of energy when the atoms move sufficiently slowly.

In a similar way, comparison of $dE/dx)_e$ and $dE/dx)_d$ for an atom moving through an insulator shows that the loss by electron excitation predominates until $\epsilon$ falls below $\Delta E_e/\epsilon$, where $\Delta E_e$ is the first excitation energy of the valence electrons in the insulator. The dissipation by electron excitation then ceases for all practical purposes and dissipation by elastic collisions predominates.

4. NUMBER OF DISPLACED ATOMS PER FISSION NEUTRON

We are now in a position to consider the number of atomic displacements resulting from the collisions which a fission neutron makes with the atoms of a moderator in the course of being slowed down to thermal velocities. This calculation can be made under the following assumptions:

a) The fission neutron has an initial energy of 2 Mev. All of this energy is lost to the moderator by elastic collision. In practice the neutron may lose energy in other ways; however, this is the principal mode.

b) A threshold energy $E_t$ is needed to displace an atom permanently from its position in the lattice. $E_t$ will be taken as 25 ev for beryllium metal, beryllium oxide, graphite, and aluminum, the materials which will be employed as examples in the ensuing discussion.

c) In the case of the lighter metals (aluminum, beryllium), it is assumed that the atoms which are knocked-on by the neutrons dissipate all of their energy by exciting the conduction electrons until they reach a velocity for which $\epsilon$, the energy of an electron having the same velocity satisfies the equation
\[
\frac{dE/dx}_e = \frac{Z^{10/3}}{3n} \frac{m E^2}{M} \frac{\ln E/E^*}{\epsilon^2} \approx 1
\] (4.1)

d) In the case of the lighter insulators, it is assumed that all of the energy of the knocked-on atoms is dissipated by electron excitation until $\epsilon$ decreases to a value at which
\[
\epsilon = 1/8 \Delta E
\] (4.2)
in which $\Delta E$ is the mean excitation energy of the valence electrons.

e) In both metals and insulators it is assumed that when $\epsilon$ is less than the critical values defined by equations (4.1) and (4.2) the energy of the knocked-on atoms is dissipated entirely by elastic collisions with other atoms.

The average energy transmitted to an atom by a 2 Mev neutron is
\[
\frac{2 \Delta E}{(1 + A)^2}
\] (4.3)
in which $A$ is the atomic weight of the atom. The coefficient $2 \Delta E/(1 + A)^2$ takes the following values for beryllium, carbon, and aluminum.

Table 4.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$2A/(1 + A)^2$</th>
<th>$\Delta E$ (kev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.180</td>
<td>360</td>
</tr>
<tr>
<td>C</td>
<td>0.142</td>
<td>285</td>
</tr>
<tr>
<td>Al</td>
<td>0.071</td>
<td>140</td>
</tr>
</tbody>
</table>

Thus, the fastest carbon atoms have an energy of the order of 285 kev, whereas the fastest aluminum atoms have an energy of about 140 kev.

We may now determine the energy at which a moving atom ceases to dissipate most of its energy in the excitation of electrons and starts to create secondary atoms. Using equation (4.1) we find that in the case of aluminum, the threshold value $\epsilon_t$ of $\epsilon$ is
\[
\epsilon_t = 2.6 \times 10^{-2} E_R = 0.35 \text{ ev}
\] (4.4)

This corresponds to a threshold kinetic energy $E_t$ of
\[
0.35 \times \frac{M}{m} = 0.35 \times 49,680 = 17,500 \text{ ev}
\]
in which $M/m$ is the ratio of the atomic to the electronic mass.
Graphite is neither a good metal nor a good insulator. Optical evidence suggests that its ability to absorb light increases in passing from the visible to the ultraviolet part of the spectrum. As a reasonable estimate, we shall assume that $\Delta E = 4$ ev, corresponding to $\epsilon_t \sim 0.5$ ev and take the threshold kinetic energy to be $E_t = 10,000$ ev. A somewhat lower value is obtained if graphite is treated as if it were a metal possessing one valence electron ($E_t \sim 7000$ ev).

Beryllium oxide is an ideal insulator and probably possesses a value of $\Delta E$ which is 10 ev or larger, corresponding to $\epsilon_t = 1.25$ ev or $E_t = 20,000$ ev for a beryllium atom. This is to be contrasted with the value $E_t = 2300$ for metallic beryllium computed with the use of (4.1). This relatively large difference in the values of $E_t$ for the insulator and metal containing beryllium may be a spurious result of the conditions (4.1) and (4.2) adopted for determining the cut-off energy; however, it suggests that there may be a striking difference in the behavior of light insulators and light metals under the effect of neutron bombardment. This point will be discussed further below. For simplicity, we shall treat BeO to begin with as if only the beryllium atoms could be displaced.

We see then that in all of the light materials, the fastest knocked-on atoms have energy much in excess of the threshold at which electron excitation ceases. This means that a large part of the energy of the fast neutrons appears in the form of electron excitation. The neutron whose knocked-on atoms possess the energy

$$E_{n,t} = E_t \frac{(A + 1)^2}{2A}$$

(4.5)

Until the neutron has slowed to the energy $E_{n,t}$, the atoms which it knocks on in a given material produce on the average the same number of displacements, for all of them will ultimately reach the energy $E_t$ at which they produce only displacements. The number of primary atoms knocked on by the neutron that is being slowed to energy $E_{n,t}$ is

$$N_t = \frac{\ln[2(\text{MeV})/E_{n,t}]}{\xi}$$

(4.6)

where $\xi$, the average change in $\ln E$ per collision is

$$\xi = 1 - \frac{r}{1 - r} \ln r, \quad r = \frac{A - 1}{A + 1}$$

(4.7)

Values of $\xi$ and $N_t$ for the materials under consideration are given in the last two columns of Table 5.

Once the neutron energy falls below $E_{n,t}$, the knocked-on atoms produced by it will dissipate all of their energy in colliding elastically with other atoms, according to the picture adopted. We shall assume that these knocked-on atoms behave in about the same way as a number $M$ of knocked-on atoms having energy $E_t$, where

$$M = \frac{E_{n,t}}{E_t} = \frac{(1 + A)^2}{2A}$$

(4.8)

We must now consider the number of permanent displacements produced by an atom which starts with an energy $E_t$ and dissipates this energy in elastic collisions. In the first place, we note that atoms having energy in the neighborhood of several kilovolts spend about half their energy in displacing other atoms permanently and about half in exciting lattice vibrations (see equation 3.6). Moreover, the atoms which are permanently

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\epsilon_t$ (ev)</th>
<th>$E_t$ (kev)</th>
<th>$E_{n,t}$ (kev)</th>
<th>$\xi$</th>
<th>$N_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium metal</td>
<td>0.14</td>
<td>2.3</td>
<td>12.8</td>
<td>0.209</td>
<td>24.1</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>1.25</td>
<td>20</td>
<td>111</td>
<td>0.209</td>
<td>13.9</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.5</td>
<td>10</td>
<td>70.4</td>
<td>0.158</td>
<td>21.1</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.35</td>
<td>17.5</td>
<td>245</td>
<td>0.0724</td>
<td>29.0</td>
</tr>
</tbody>
</table>
displaced, that is receive energy in excess of $E_d$, receive on the average the energy

$$\bar{E} = E_d \frac{E_t}{E_d}$$  \hspace{1cm} (4.9)$$

(see equation 3.9). This energy is about 125 ev for each of the materials under consideration if we choose $E_d = 25$ ev. These 125 ev secondary atoms will behave like rigid spheres in collisions with other atoms and on the average they displace about 1 tertiary atom from the lattice. Thus, each atom possessing energy $E_t$ will produce

$$2 \times \frac{E_t/2}{E_d \ln(E_t/E_d)}$$  \hspace{1cm} (4.10)$$

secondary and tertiary atoms that are permanently displaced. Thus, the total number of atoms displaced by the initial 2 Mev neutron is

$$N_d = (N_t + M) \times \frac{E_t}{E_d \ln(E_t/E_d)}$$  \hspace{1cm} (4.11)$$

Table 6 contains values of $N_d$ for the materials under consideration.

<table>
<thead>
<tr>
<th>Material</th>
<th>$N_t$</th>
<th>$M$</th>
<th>$(N_t + M)$</th>
<th>$E_t/E_d \ln(E_t/E_d)$</th>
<th>$N_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium metal</td>
<td>24.1</td>
<td>5.6</td>
<td>29.7</td>
<td>15.3</td>
<td>454</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>13.8</td>
<td>5.6</td>
<td>19.4</td>
<td>133</td>
<td>2580</td>
</tr>
<tr>
<td>Graphite</td>
<td>21.1</td>
<td>7.0</td>
<td>28.1</td>
<td>66.7</td>
<td>1874</td>
</tr>
<tr>
<td>Aluminum</td>
<td>29.0</td>
<td>14.1</td>
<td>43.1</td>
<td>140</td>
<td>6034</td>
</tr>
</tbody>
</table>

It is to be noted that $N_d$ depends upon $E_t$ principally through the coefficient $E_t/E_d \ln(E_t/E_d)$ appearing in (4.11), that is, depends essentially on the first power of $E_t$. The coefficient $(N_t + M)$ varies relatively slowly with this parameter. It follows that $N_d$ is relatively sensitive to the choice of $E_t$ and that the final values could be altered appreciably by more accurate calculations. In particular the large difference in $N_d$ for metallic beryllium and beryllium oxide may be partly the result of incorrect choice of the parameter $E_t$ for the two cases. On the other hand the large difference in $N_d$ for beryllium metal and aluminum probably is more significant since $E_t$ was determined from the same general equation in these two cases.

The calculation of the number of displaced atoms for BeO is somewhat in error because we have assumed that this material behaved as if the cross section for scattering of neutrons by oxygen were negligible. A correction for the influence of oxygen may be made and shows that the value of $N_d$ should be raised by about 20 per cent. However, the error involved in the determination of $N_d$ is undoubtedly larger than this.

Let us now examine the fraction $f_m$ of the moderator atoms that are displaced during the course of a period of operation. We shall assume that the moderator behaves homogeneously in slowing down the fission neutrons. Actually, the portion of the moderator near the fissioning material will receive greater bombardment than that farther away; however, a correction for this can be made when the pattern of slowing down is known.

Suppose that a fraction, $F$, of the fissionable material has been consumed and that the ratio of the number of moderator atoms to fissionable atoms is $R$. Moreover, let us designate the number of neutrons produced per fission as $v$. We shall assume that all of these neutrons are slowed down in the moderator and take $v$ to be somewhat lower than the actual value in order to correct for fast leakage and absorption. Under these assumptions $f_m$, the fraction of displaced moderator atoms, is
If the pile is a natural uranium-graphite pile in which the ratio of the number of graphite atoms to the number of uranium atom is 90 and if 10 per cent of the \( v_3' \) has fissioned, we have

\[
R = \frac{90}{0.007}
\]

\[
F = 0.1
\]

in which 0.007 is the fraction of natural uranium in the form of \( v_3' \). Taking \( \nu = 2 \) and \( N_d = 1874 \), we obtain

\[
f_m = 0.029
\]

Thus, about 3 per cent of the carbon atoms will be displaced on the average.

5. DISPLACEMENTS PRODUCED BY FISSION FRAGMENTS

Fission fragments possess a large amount of kinetic energy which is dissipated in collisions with the atoms of the medium in which the fissionable material is dispersed. This material is metallic uranium in the case of a natural uranium metal pile, but could be another solid. At start we shall focus attention on the effects produced in metallic uranium.

A fission fragment differs from an atom that has been knocked on by a neutron primarily as a result of the fact that the former has a higher energy. We note from the values presented at the bottom of Table 1 that typical fission fragments have, at least at start, velocity parameters of several hundred electron volts. This means that they may excite electrons that are more tightly bound than the valence electrons in the materials through which they pass. It also means that electrons which are attached to the fission fragments with a binding energy of less than several hundred electron volts will be stripped away as the fragment moves through matter. As a result the fission particles will be more highly charged than knocked-on atoms. These differences will have a quantitative effect on the manner in which the fission fragment dissipates its energy; however, the processes will remain qualitatively the same as for knocked-on atoms, namely electron excitation and elastic collisions.

The equation presented in section 3 for the dissipation of energy as a result of elastic collisions is (equation 3.7)

\[
\frac{dE}{dx} = N_0 \frac{2\pi e^4 Z_1^2 Z_2^2 M_1}{E^2 M_2} \ln \frac{E}{E^*}
\]

in which \( E \) is the kinetic energy of the moving fragment, \( M_1 \) is the mass, \( M_2 \) is the mass of the stationary atom and \( Z_1 \) and \( Z_2 \) are the atomic numbers of the colliding atoms, the first of which is the fission fragment. The derivation of this equation involved the assumption that the two atoms are neutral. Actually, the fission fragment will carry a charge during the greater part of its range since its velocity corresponds to that of an electron having energy of the order of 500 ev. The use of (5.1) thus, underestimates the number of elastic collisions since it assumes too small an interaction between the atoms, particularly when the atoms are at large distances from one another. The principal influence of the error lies in the value of the \( \ln \) term which is relatively insensitive to the basic assumptions made.

The fraction of the elastic collisions which produce permanent displacements is given by the ratio (cf. equation 3.7a).

\[
\frac{\ln E/E_d}{\ln E/E^*}
\]

Near the start of the range of the fission fragment, which possesses an energy in the vicinity of 80 Mev this ratio is about 0.6, so that about 60 per cent of the collisions lead to permanent displacements, according to equation (5.2). Actually, this is probably an overestimate of the ratio since we have neglected the long-range character of the interaction that results from the fact that the fission fragment is charged.

The average energy obtained by that fraction of atoms which receives energy greater than \( E_d \) is

\[
E_d \frac{\ln E}{E_d} \frac{4M_1M_2}{(M_1 + M_2)^2}
\]

If we assume that \( E_d \) is 25 ev, as in the previous calculations, we find that the average energy
transferred is about 375 ev for fission fragments near the start of the range in a moderately heavy material, and is not strongly sensitive to the relative mass.

The expression to be used for estimating the loss of energy associated with electron excitation is somewhat more difficult to ascertain. Since the velocity parameter, is of the order of several hundred volts for the fission fragment it will be able to excite inner shells as well as the valence electrons. Moreover, each shell can be excited in what we may regard as two ways: By collisions in which the moving atom passes through the atom to be excited, and by collisions in which the moving atom passes at larger distances. The second type of collision depends upon the electrostatic charge of the moving atom. If the atom were uncharged the energy dissipation for a given shell would take the form

\[
\frac{dE}{dx} = \frac{2\pi e^4}{mv^2} Z_i^2 n_e G(\epsilon)
\]

(5.3)

in which \(Z_i\) is the atomic number of the fission fragment, \(n\) is the number of electrons in the atomic shell and \(G\) is a function which is more or less constant when \(\epsilon\) is larger than the excitation energy of the shell under consideration and drops rapidly when \(\epsilon\) decreases appreciably below the excitation energy. An expression of this type is to be used for each shell of electrons, the total dissipation for electron excitation being the sum of terms for all shells. The corresponding expression for more distant collisions, which depend upon the fact that the moving atom is charged, will be of the same general form, \(Z_i\) being replaced by \(Z^*\), the ionization charge, and \(G\) being replaced by another function of the same form. We shall combine both of these effects and assume that the dissipation caused by excitation of all shells is governed by an expression of the type

\[
-\frac{dE}{dx} = \frac{2\pi e^4}{mv^2} Z_i^2 N_p B(\epsilon)
\]

(5.4)

in which \(B\) is taken to be 32 at start of the range. Under these assumptions the ratio of the dissipation caused by exciting collisions and that caused by elastic collisions is

\[
\frac{dE}{dx}_e = \frac{M_e}{m} \frac{B(\epsilon)}{Z_i^2 \ln E/E^*}
\]

(5.5)

If the stopping material is uranium we may take \(M_e/m = 239 \times 1840, Z_i = 92\). Substituting these values and taking \(E\) to be 80 Mev, we find that the ratio is

\[
\frac{dE}{dx}_e \left/ \frac{dE}{dx}_c \right. = 75
\]

(5.6)

Thus, about 1.33 per cent of the energy of the fission fragment is dissipated in elastic collisions during the initial portion of the range. Actually, we are interested in the average value of (5.5) over the entire range in which electron excitation is important. Detailed analysis shows that \(B(\epsilon)\) varies with \(\epsilon\) in the approximate manner

\[
B(\epsilon) = \frac{\epsilon}{\epsilon_0} B(\epsilon_0)
\]

(5.7)

in which \(B(\epsilon_0)\) is the value of \(B\) at the start of the range, when the fission fragment has its highest energy. Thus, if we treat the in term in the denominator of (5.5) as if constant through the greater part of the range, the average of (5.5) is

\[
\frac{1}{m} \frac{B(\epsilon_0)}{Z_i^2 \ln E/E^*}
\]

(5.8)

This average value is just half the initial value, and shows that about 2.66 per cent of the energy of the fission fragment is dissipated in producing displacements during the large fraction of the range in which electron excitation is appreciable. Near the end of the range, the majority of the energy is dissipated in elastic collisions because electron excitation ceases. If we assume that the critical value of \(\epsilon = mv^2/2\) for termination of electron excitation is \(\epsilon_1 = 1.0\) ev, the fraction of the initial energy of the pair of fission fragments below \(\epsilon_1\) is about 0.30 per cent (see Table 1) for initial values of \(\epsilon\) for a pair). Thus, the total fraction of the kinetic energy of the fission fragments expended in elastic collisions is about 2.66 + 0.30 = 2.96 per cent.

We saw above that the average knocked-on primary atom produced by the fission fragment has an energy of about 375 ev, particularly near the beginning of the range of the fragments. We may expect each atom of this type to produce about 3 secondaries so that the total number of atoms displaced per fission pair is about
in which the factor 1/2 enters because about 50 per cent of the elastic encounters of the fission fragment stimulate lattice vibrations instead of displacing atoms. The fact that the atoms displaced near the end of the path have only about 125 ev of energy is compensated by the fact that they produce fewer secondary knocked-on atoms.

Consider a specimen of uranium metal in which one tenth of the $^{238}$U has been consumed. In this case a fraction of 0.0007 of the atoms have undergone fission so that each atom of metal will have been displaced

$$7 \times 10^{-4} \times 2.53 \times 10^4 = 17.7$$

(5.10)
times. It is evident that the metal will have been subject to considerable rearrangement.

If the fissionable material were distributed in a solid containing light atoms instead of uranium the total number of displacements would be smaller; for example, if the material were carbon, $Z_a$ would be 6 instead of 92, so that the $Z_a^2$ in the denominator would be about 230 times smaller. This is partly compensated by the fact that $M_e$ is about 20 times smaller and $B$ is about 12 instead of 32. Inserting these numbers in (5.5) we find that the ratio is

$$\frac{dE}{dx}_{el} = 162$$

(5.11)

so that only about 0.62 per cent of the energy of the fission fragment is dissipated in elastic collisions during the initial part of the range. This is about four times larger than the amount of energy dissipated in elastic collisions near the end of the range when electron excitation ceases. If we assume that $\epsilon_t$ is 0.5 ev the fraction of the initial energy of each of the fission fragments for which $\epsilon$ is less than $\epsilon_t$ is (see Table 1) 0.1 and 0.2 per cent. Thus, the average fraction of the total energy spent purely in producing elastic collisions near the end of the range is 0.15 per cent. The total fraction of energy spent in producing elastic collisions is 0.62 + 0.15 = 0.77 per cent instead of 2.96 per cent as for uranium.

We shall determine the number of displaced atoms produced per fission in graphite by assuming that this 0.77 per cent is dissipated in various ways in the same manner as the fraction of the energy of the 2 Mev neutron which is dissipated in elastic collisions. The energy of the neutron spent in this way is $(N_f + M)E_t = 28.1 \times 10 = 281$ kev. The corresponding number of displacements was found to be 1874 (see Tables 5 and 6). In the case of the fission fragments the energy dissipated per fission in an elastic manner is 160,000 \times 0.0077 = 1230 kev. It follows that about 8300 displacements occur per fission in graphite. This is about 0.33 times as many as in metallic uranium.

The fraction of the kinetic energy dissipated in elastic collisions is found to be about 0.99 per cent in beryllium oxide, if it is assumed that $\epsilon_t = 1.25$ ev, as in previous calculations. The corresponding number of displacements is found to be about 10,500 per fission.

6. EXPERIMENTAL IRRADIATION STUDIES

Considerable experimental work has been carried out on the influence of exposure to pile radiations on the properties of solid materials. The great majority of this work has had very practical objectives in mind. Nevertheless the experiments made it possible to draw a number of general conclusions. We shall review each of the materials which have been subject to extensive study.

a. Graphite

This material has been examined most thoroughly to date because of its great importance for the Hanford development. The majority of this work has been carried on by Burton, Franck, Maurer, and their numerous coworkers, Allen, Novick, Neubert, Shapiro, Van Dyken, Royal, and others. The general properties of graphite are as follows:

Graphite is a material having properties intermediate between those of a metal and an insulator. The electrical conductivity is about 100 times lower than that of the good metals. It has a characteristic layer-lattice structure. The layers are plane hexagonal networks of carbon atoms which are separated equidistantly. Each layer is identical with that below it; however, only every second layer can be made to coincide by displacement normal to the planes. The spacing between neighboring planes is 3.35 A. The spacing between al-
ternate planes is designated by $A_3 = 6.71 \text{ Å}$. The spacing between atoms in the plane network is expressed in terms of a parameter $A_1$, which is related to the nearest interatomic spacing $d$ by the equation $d = A_1/3$. The measured value of $A_1$ is $2.456 \text{ Å}$.

Graphite is found naturally in a very highly crystalline state. However, such material is usually so strongly contaminated with impurities that its properties usually have only qualitative interest. Practically none of the studies of interest to the plutonium project were carried out with the use of natural graphite because the material becomes strongly active and is difficult to handle.

Artificial graphite is made by sintering and extruding carbon prepared from petroleum coke. The sintering is carried out in several stages and involves heating to temperatures in the vicinity of 3000°C for several weeks. The bar being sintered is saturated with pitch between heating stages in order to provide material for crystal growth. The final bars, which exhibit a high degree of preferred orientation, the planes lying along the extrusion axis, have a density of about 1.7. This density is to be compared with the ideal density of 2.3. Zachariasen has shown that the final material consists of nearly perfect coherent crystalline domains which are in the form of plates about 50 Å high and about 500 Å in diameter. The graphite planes are normal to the short dimension. It may be concluded that plates of this type cluster together to form a more or less porous network, there being considerable empty space between the plates. The voids are sufficiently large to permit water and gases to permeate through a block of material.

The thermal conductivity of graphite is very high, being of the order of 0.4 cal/°C sec cm, comparable to some of the best metals. Since the electrical conductivity is low, it may be concluded that the high thermal conductivity is the result of rapid transmission of thermal vibrations through the lattice, as in diamond.

Experimental studies of the influence of irradiation have been made on materials exposed to pile radiations in three different locations:

1) Materials in Intimate Contact with Uranium Metal.—This material receives an accelerated exposure because of the high flux of fast neutrons near the metal.

2) Materials Exposed in Temperature-Controlled Test Holes.—In some cases the temperature is maintained as low as 30°C.

3) Materials Taken from Blocks of Normal Pile Graphite.—All of the materials are commonly given a thermal anneal at temperatures up to 1000°C after measurements have been made on their properties in order to determine the ease with which effects induced by irradiation can be reversed.

The influence of radiation upon the various properties of graphite may be summarized as follows:

1) Thermal Conductivity.—The thermal conductivity decreases very much as a result of neutron bombardment. For example the thermal conductivity of specimens maintained in the temperature range from 40 to 60°C drops by a factor of about 9 when it is in a location approximately midway between slugs of metal in which 1 per cent of the $^{235}U$ has undergone fission. The corresponding factor is about 28 when 10 per cent of the $^{235}U$ has undergone fission. If the temperature is between 110 and 130°C the corresponding factors are 4.5 and 14, respectively. Two conclusions may be drawn: The initial rate of change of properties is more rapid than that which occurs later; specimens irradiated at elevated temperatures are affected at a slower rate than those irradiated at low temperatures. Experiments carried out with the purpose of exploring the first of these conclusions further show that the rate of change eventually approached a value that is practically constant. In any case we may conclude that neutron bombardment has a pronounced influence upon the thermal conductivity. Since this conductivity is associated with the transmission of vibrational waves, we may conclude that the changes are such to produce more effective scatterings.

A portion of the conductivity that is lost by irradiation can be regained by annealing the specimens. Specimens irradiated for a relatively short time will regain practically all of their conductivity when annealed at 1000°C, whereas those irradiated for a longer period regain a smaller fraction.

2) Electrical Resistivity.—The electrical resistivity, like the thermal resistivity, increases during exposure. During the initial stages both increase by comparable magnitude; however the electrical resistivity eventually levels off at a value 5 to 6 times its initial value. In addition it is found that the electrical resistivity can be reduced by annealing more easily than the thermal resistivity can. Maurer has found that the Hall coefficient of irradiated graphite changes sign during irradiation. This indicates that both the
mean free path and the density of the conduction electrons change during irradiation. Apparently a rise in the density of free electrons eventually compensates for the decrease in mean free path and yields a more or less constant increase in resistivity.

3) Dimensions.—The dimensions of the graphite are changed during irradiation. On a macroscopic scale it is found that the dimensions normal to the direction of extrusion, that is in a direction normal to the graphite planes, expand by about 0.5 per cent when about 10 per cent of the $U^3$ has undergone fission. This expansion varies approximately linearly with time. Recovery is almost complete if the specimens are heated to 1000°C.

Zachariasen has found that the changes in dimension are closely related to changes which take place on an atomic scale. For example, he has found that $A_1$ increases between 3 and 5 per cent when 10 per cent of the $U^3$ has undergone fission. $A_1$ decreases slightly during the same period of operation.

In connection with the study of dimensional changes, Zachariasen has found that the degree of perfection of the coherent domains is decreased during irradiation even though the size of the domains is unchanged. In effect the graphite planes become "blistered" or warped as irradiation proceeds. Zachariasen has expressed the blistering in two ways: In terms of the root mean square displacement of the planes from the average position, and in terms of the number of blisters per carbon atom. He finds that the root mean square displacement is approximately 0.38 A at the end of a period in which about 10 per cent of the $U^3$ has changed and that there are about 0.005 to 0.01 blisters per carbon atom at the end of this period. It is found that the amplitude of blistering decreases by only about 50 per cent as the result of an annealing treatment at 1000°C. If it is assumed that each blister represents about one displaced atom, it may be concluded that Zachariasen's results support the conclusion that of the order of 1 per cent of the graphite atoms are displaced during the period of time in which 10 per cent of the $U^3$ has reacted.

More recently, Lukesh has repeated Zachariasen's measurements and has made a careful determination of the contraction of the graphite lattice in the planar nets of the graphite lattice (concentration of $A_1$ parameter). Using this information and Pauling's semi-empirical relation between the carbon-carbon separation and the number of electrons per bond, Lukesh has calculated the number of vacant lattice sites which exist within the net after definite amounts of exposure. In doing this he assumed that the vacancies do not coagulate and that interstitial carbon atoms do not have an appreciable influence on the atomic spacing near lattice vacancies. Although these assumptions represent the introduction of substantial approximations, they are well in keeping with the semi-quantitative character of all of the work on graphite. Lukesh finds that the graphite behaves as if about 8 per cent of the carbon atoms have been displaced at the time 10 per cent of the $U^3$ has undergone fission, in place of the value of 3 per cent computed in this article. The difference between the two values is probably not highly significant and does not imply that the foregoing calculations need extensive revision.

4) Mechanical Strength.—The mechanical strength of graphite appears to increase during the early stages of irradiation and eventually to reach a saturation value, if it does not actually decrease. The peak strength is 2 or 3 times the initial value. Measurements of the changes in mechanical strength actually are fairly difficult because large fluctuations are observed from specimen to specimen. These fluctuations are presumably related to the fact that graphite possesses many voids and the observed strength of a given specimen is determined by the voids rather than by the properties of the individual grains of graphite.

5) Stored Energy.—Energy is stored in graphite during irradiation (Szilard effect). The amount of stored energy is usually measured in two different ways. In the first the stored energy is determined by measuring the amount of heat released when an irradiated specimen is heated to the vicinity of 1000°C. This is usually done by the use of the Sykes technique, which measures the relative heat capacity of an irradiated and an unirradiated specimen, the evolved heat being treated as a negative contribution to the heat capacity of the irradiated specimen. In the second method, the graphite is burned and the heat of combustion is measured. Stored energy appears as a contribution to the heat of combustions. Measurements of this type have usually been carried out by Rossini at the National Bureau of Standards. It is evident that the two methods measure rather different quantities: The heat capacity technique
measures that stored energy which can by released below the temperature to which measurements are carried; the heat of combustion technique measures the total stored energy. The value determined by the second method should be larger than that determined by the first by the amount of stored energy which cannot be released below the temperature to which the Sykes experiment is carried.

The results obtained by measuring stored energy are as follows:

a) It is found that specimens which have been irradiated in regions of the pile where 10 per cent of the \( ^{235}U \) has reacted possess about 200 cal/gram of stored energy if they have been maintained between 40 and 60°C, whereas they contain about 100 cal/gram if the temperature is 110 to 130°C. These values are determined by the heat of combustion method.

b) If the specimens are annealed at 1000°C before being burned, the stored energy is about 30 cal/gram when the temperature lies in the range 40 to 60°C and about 25 cal/gram when the temperature is about 110 to 130°C.

c) The rate at which energy is stored eventually reaches a more or less constant value which is appreciably less than the initial rate. Experiments carried out for long durations also show that the fraction of stored energy which can be released below 1000°C gradually decreased, more and more being "tightly stored." As a matter of fact there are indications that the absolute amount of energy which can be released below 1000°C eventually decreases.

Considerable thought has been given to the mechanism by which the changes in the properties of graphite are brought about. The following picture, which is principally due to Franck and Burton appears to correlate the known facts:

The primary and secondary atoms which are displaced from the lattice as a result of neutron bombardment eventually become lodged between the planes of the lattice. Single atoms in this position are sufficiently mobile at operating temperatures that they migrate until they form pairs of atoms, the energy gained by pair formations being of the order of 90,000/Na cal per pair, where Na is Avogadro's number. This value is chosen because the heat of formation of a \( \text{C}_2 \) molecule is 90,000 cal. It is possible that further aggregation takes place; however it is believed that most of the energy of cohesion of such clusters is represented by the energy of the \( \text{C}_x \) units.

During an annealing step at 1000°C the interstitial clusters diffuse to the edge of the crystal where the carbon atoms join the ends of the crystal planes to add to the size of the crystal. The vacant lattice sites produced by irradiation do not diffuse at an appreciable rate at 1000°C and as a result remain in the interior of the crystal. It is believed that the atoms in the interstitial clusters do not fall into these vacancies and heal the lattice with any appreciable frequency because an activation energy is needed for an interstitial atom to join with a vacancy. The need for an activation energy is probably characteristic of a valence crystal in which the energy of a group of atoms is strongly dependent upon the relative orientation of atoms.

In connection with the diffusion of carbon atoms through the interstices of the graphite lattice, it is to be noted that graphite absorbs appreciable quantities of halogen atoms, such as chlorine, at moderately low temperatures. X-ray evidence shows that these atoms diffuse between the planes and occupy lattice-like positions there. The ease with which the halogen atoms enter and leave the lattice indicates that the planes of graphite behave as if chemically saturated so that migration through the region between planes is relatively easy.

It is to be emphasized that detailed proof of the foregoing mechanism has not yet been given in the sense that alternative mechanisms have been examined carefully and discarded either on the basis of careful calculation or decisive experiments. For this reason this picture is still to be regarded mainly as a good working hypothesis which has a great many points of reasonableness in its favor.

Estermann has used the foregoing picture of the mechanism as a basis for calculating the number of displaced atoms at the end of a period of irradiation. He assumes that the energy required to remove an atom from the lattice to form a vacancy plus a free atom is \((250,000 - N_a)\) cal/mol where 250,000 cal/mol is the energy required to break 3 graphite C-C bonds (twice the heat of sublimation) and \(N_a\) is the unknown energy gained by relaxation of the carbon atoms near the vacancy. Thus if \(n\) atoms are displaced, the energy \(E_S\) per mol that is stored satisfies the equation
\[ E_s = \frac{n}{N_a} (250,000 - N_a x - 45,000) \text{cal/mol} \quad (6.1) \]

in which the 45,000 cal/mol is the energy gained per atom as a result of the formation of C\(_2\) pairs.

If we assume that after an annealing operation at 1000°C the interstitial atoms migrate to the surface to form additions to the planes of the crystallites and that an energy of 125,000 cal/mol is gained by adding a free atom to the surface, the stored energy \( E_s (1000^\circ) \) after the annealing operation satisfies the equation

\[ E_s (1000^\circ) = \frac{n}{N_a} (250,000 - N_a x - 125,000) \text{cal/mol} \quad (6.2) \]

Taking the ratio of both sides of the two equations, we find

\[ \frac{205,000 - N_a x}{125,000 - N_a x} = \frac{E_s}{E_s (1000^\circ)} \quad (6.3) \]

Taking the value \( E_s = 102.12 \text{cal/mol} \) and \( E_s (1000^\circ) = 20.12 \text{cal/mol} \) for a typical case, Estermann finds

\[ N_a x = 105,200 \text{cal/mol} \]

\[ \frac{n}{N_a} = 0.012 \quad (6.4) \]

This example actually corresponds to a case in which approximately 10 per cent of the U\(^{235}\) was consumed and indicates that the average number of displacements is of the order of a few percent, in agreement both with Zachariasen's measurements and the results obtained from the theoretical analysis of section 4.

The changes in the other properties of graphite may be understood at least qualitatively in terms of this general picture. For example, the decrease in thermal and electrical conductivity is exactly what would be expected from the distortion which accompanies displacements. Similarly, it is not surprising that the presence of interstitial carbon atoms causes the lattice to swell in a direction normal to the graphite planes; a similar swelling occurs when the halogens diffuse between the planes. It is to be noted that Zachariasen has found that the transverse expansion disappears on annealing at 1000°C whereas the blistering is cut only to half. This result is in qualitative agreement with the notion that the interstitial atoms diffuse out during the annealing process whereas the vacancies remain, thereby leaving a portion of the disorder that causes the lattice planes to warp.

It is more difficult to understand the increase in mechanical strength that is observed at least during the early stages of irradiation. The increase in disorder should cause a decrease in ductility of the graphite. In the case of metals a decrease in ductility is usually accompanied by a loss in strength since the applied stresses are not relieved by plastic flow in the regions near cracks where stress concentration occurs. Two explanations of the effect are possible. In the first place it is possible that some of the knocked-on atoms find their way to the cracks which cause stress concentration, decrease the curvature of the surfaces, and thereby decrease the stress concentration. It is also possible that the process of rupture involves splitting of crystallites between crystal planes and that this splitting becomes more difficult when interstitial atoms are present to form a partial bridge between planes. In this connection it should be mentioned that the elastic modulus measured normal to the planes appears to increase at first and then decrease as irradiation continues, in close correlation with the changes in breaking strength.

Fuchs, Kierstead, Nagy, and Wohlberg of Argonne Laboratories have studied the influence of impregnation with uranium oxide on the change in properties of graphite. Specimens were impregnated with varying amounts of the oxide extending to about 7 weight per cent. Both natural uranium and uranium enriched to 30 per cent of U\(^{235}\) were used in the work. The specimens were exposed to the neutrons in the central experimental tube of the Argonne heavy water reactor for about one week. The relative values of the change in electrical resistivity observed in the specimens containing about 6 per cent of natural and enriched oxide are listed in Table 7.

The pure specimen was presumably affected only by the fast neutrons, whereas the other specimens received an additional effect because of the presence of fissioning atoms. According to the figures in the table, this additional effect is about 2 times
the effect produced by fast neutrons in the graphite containing natural uranium and is about 80 times the effect of fast neutrons in the graphite impregnated with enriched material. Since the material impregnated with enriched uranium contains about 42 times as much $^{235}U$ as the graphite impregnated with natural uranium, we would expect the change associated with fission fragments alone to be 42 times greater in the former. This is the general range of the increased effect if we assume that the influence of fission fragments is about 2 for the specimens impregnated with natural uranium in

Table 7. Relative changes in resistivity of pure and impregnated graphite. (7-day exposure at Argonne)

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure graphite</td>
<td>1</td>
</tr>
<tr>
<td>Impregnated with 6 weight per cent of natural uranium</td>
<td>3</td>
</tr>
<tr>
<td>Impregnated with 6 weight per cent of 30 per cent enriched uranium</td>
<td>60</td>
</tr>
</tbody>
</table>

terms of the relative units employed in the table.

It is interesting to calculate the relative influence of fast neutrons and fission fragments in the material impregnated with 6 weight per cent of natural uranium oxide. This specimen contains approximately $0.06 \times \frac{12}{270} = 0.0027$ times the atom-fraction of $^{235}U$ atoms contained in natural uranium. Since each fission pair produces 25,300 displacements in uranium (equation 5.9) and only about 8300 in graphite, it follows for a period of time in which 10 per cent of the $^{235}U$ is consumed, the fraction of graphite atoms displaced would be

$$17.7 \times 0.0027 \times \frac{8300}{25,300} = 0.015 \quad (6.5)$$

Equation 6.5

in which 17.7 is the number of times the average uranium atom in a slug of natural uranium would be displaced in the corresponding period of operation. In the same period of time a fraction of about 0.03 of the atoms in a specimen of graphite placed in an average position in the pile would be displaced. That is, the effects caused by fast neutrons in the pure specimens placed in the average position would be about two times larger than those due to fission in the impregnated specimens placed in fuel channels.

An independent calculation may be made in the following way. The cross section for fission of $^{235}U$ by thermal neutrons is about 200 times larger than the cross section for displacement of a carbon atom by one of the fast neutrons. Of the atoms in the graphite impregnated with 0.06 weight per cent of natural uranium oxide, a fraction of $1.9 \times 10^{-3}$ are $^{235}U$. Since the thermal flux is about five times larger than the fast flux which produces appreciable displacements of carbon atoms in the central test hole of the Argonne pile, it follows that about 50 carbon atoms are displaced by fast neutrons for each fission that occurs. Now the calculations of section 4 indicate that in each collision with a carbon atom, a fast neutron expends 10 kev (see $E_i$ in Table 5) in producing elastic collisions among the atoms. The corresponding energy per fission is 1230 kev according to the calculations of section 5. It follows that the ratio of displacements produced by fission and by fast neutrons is $1230/50 \times 10 = 2.4$. Hence the impregnated material should undergo displacements at a rate that is about 3.4 times faster than the unimpregnated material as a result of the combined effect of fast neutrons and fission. This result is also in reasonable agreement with the observations given in Table 7.

Hunter\(^{*}\) has reported results which he believes are in contradiction with those just quoted for impregnated graphite, or at least lead to results which he believes contradict the theoretical calculations which give the agreement just quoted. Hunter exposed specimens of graphite containing 23 weight per cent of $^{235}U$ in the Clinton pile and measured the change in thermal conductivity as time progressed. The specimens were maintained at a temperature in the vicinity of 800°C during the exposure and the change in thermal conductivity was determined by measuring the temperature drop within the specimen. Since the specimens are at this high temperature, the only data available with which his results may be compared are those obtained from specimens of pure graphite which have been subject to neutron irradiation at lower temperatures and have then been annealed near 800°C.

The amount of fissible material in Hunter's specimens is so high that practically all of the internal heating of the material is caused by fission.

In a typical case which we shall discuss for
comparison, Hunter finds that the thermal conductivity has dropped by a factor of 2 after 1 kilowatt hour of heat has been produced within one cubic centimeter of the specimen. This degree of exposure is on the lower end of the range studied by Hunter, but we shall consider it since the opportunity for reversal of exposure is less than in the specimens exposed for longer times. Some of his specimens received ten times this exposure. Since each fission releases about 160 Mev of thermal energy at once, the release of 1 kilowatt hour of energy corresponds to about $1.4 \times 10^{17}$ fissions per cc. Each fission causes the displacement of about 8300 carbon atoms in graphite, according to the calculations of section 5. Hence $1.4 \times 10^{17}$ fissions should displace about $1.2 \times 10^{21}$ atoms per cc or about 1.2 per cent.

**b. Aluminum**

Since the aluminum tubes which bear the water and uranium in the pile are subjected to very intense neutron bombardment and are kept relatively cool, they provide a very interesting subject for investigation. Tests of the mechanical, electrical, and thermal properties of these tubes at various times have given no indication that substantial permanent changes, comparable to those observed in graphite, occur. Koehler and his co-workers carried out very sensitive measurements of internal friction on single crystals of aluminum that had been irradiated and found no effects that lay outside experimental error. It may be concluded that the changes induced in aluminum do not leave a permanent record. It is doubtful if the calculations for aluminum carried out in section 4 can be so seriously in error that they would overestimate the number of displaced atoms by a factor of ten or a hundred. Apparently we must conclude that the effects associated with the production of displacements are annealed even at room temperature.

Since the primary effect of displacement is to produce interstitial atoms and vacancies, we may conclude that either one or both of the two products are sufficiently mobile at room temperature to cause reunion in a relatively short space of time. Let us suppose that atoms are displaced at a rate

$$R_d = \sigma n_v$$  \hspace{1cm} (6.6)

per unit volume in which $n_v$ is the density of atoms in the material and $\sigma$ is determined by the pile flux and the characteristic properties of the material. We saw in section 4 that about 13 per cent of the aluminum atoms in a cooling tube would be displaced in the period of operation in which 10 per cent of the $U^{235}$ is consumed. If this time is taken to be about 200 days or $2 \times 10^7$ sec, $\sigma$ is $0.13/2.10^7 = 6.5 \times 10^{-9}$ sec$^{-1}$. If the fraction of displaced atoms is $n/n_0$, each vacancy must make $n_0/n$ jumps from one lattice site to another before meeting a displaced atom. Thus the rate of recombination satisfies the equation

$$R_r = \frac{n^2}{n_0} \nu$$  \hspace{1cm} (6.7)

in which $\nu$ is the frequency with which vacancies jump from one lattice position to the next. We may express this frequency in the form

$$\nu = 10^{13} \exp(-Q/RT) \sec^{-1}$$  \hspace{1cm} (6.8)

in which the factor $10^{13}$ sec$^{-1}$ is the characteristic oscillational frequency of the atoms in the lattice and $Q$ is the activation energy for diffusion of the vacancies. There is evidence to show that $Q$ is about half the activation for self diffusion in the lattice and may be taken as about 17,000 cal for aluminum. If we assume that the water temperature is near 350$^\circ$K, $\nu$ is found to be about $10^8$ sec$^{-1}$. Equating $R_d$ and $R_r$, we find that at equilibrium

$$\frac{n}{n_0} = \sqrt{\frac{\sigma}{\nu}} = 2 \times 10^{-8}$$  \hspace{1cm} (6.9)

This fraction of displaced atoms is undoubtedly too small to produce effects that are easily observed. We may conclude that the rapid rate of self diffusion within the aluminum is sufficient to explain the absence of permanent effects.

**c. Beryllium Metal**

Beryllium metal appears to resemble aluminum in the sense that permanent effects caused by neutron bombardment are either very small or are absent. The calculations of section 4 suggest that one reason for this may be that the number of atoms which become displaced in beryllium metal under a given set of conditions is small compared to the number that would be displaced in graphite. This however is probably only part of the story.
since elementary reasoning shows that back diffusion probably is important in this case as well. The activation energy for self diffusion in beryllium has apparently not been measured. We may assume that the value is in the vicinity of 50,000 cal. since metals having similar melting points possess values in this range. We shall assume that $Q$ in equation (6.8) is half this or 25,000 cal, and obtain

$$n_0 \sim 10^{-3} \tag{6.10}$$

This value probably is on the borderline of easy observation. It is to be observed that when the density of displaced atoms has this value, about $10^6$ seconds or ten days is required for an average vacancy to find an interstitial atom. Thus any observed effects should dissipate in a measurable time.

d. Beryllium Oxide

Beryllium oxide is a highly insulating solid having the wurzite lattice. This lattice may be viewed as a hexagonal close-packed array of oxygen ions in the interstices of which are distributed beryllium ions which also have a close-packed arrangement. The density of the crystal is about 2.87.

The behavior of beryllium oxide under neutron bombardment has been the object of considerable experimental investigation because of the interest in this material for the purpose of the power pile. The initial investigations were stimulated by Farrington Daniels at the Argonne Laboratory and have been carried out recently under the direction of O. C. Simpson. The materials studied are pure sintered beryllium oxide having several values of density and beryllium oxide impregnated with uranium oxide. The results of the experiments carried out to date are as follows:

1) Thermal Conductivity.—The thermal resistance of the pure material appears to rise by a factor of about 1.6 during the course of a period of time in which about 3 per cent of the $^{235}$U in neighboring metal slugs has been transformed. The results show that the rate of rise of resistance gradually decreases with time of exposure, but probably attains a finite constant value.

Material impregnated with 2 per cent and 10 per cent of $\text{UO}_2$ in which the $^{235}$U has been enriched to 30 per cent shows a rapid change in resistivity at first and the ultimate attainment of a constant rate. The samples containing 10 per cent of uranium oxide have a slightly higher initial resistance than those containing 2 per cent of oxide, the former being about 20 per cent higher than the latter. It should be noted that the fractional change in thermal resistance is somewhat larger in the material containing the smaller amount of oxide, attaining a value between 5 and 6. The difference in the ratio is about 15 per cent for the two types of materials. Small differences are found in specimens sintered to low and high density; these differences being of the order of 20 per cent in the two cases. The high density material exhibits the greater change in general.

The calculations of section 4 suggest that the number of displacements produced in graphite and in beryllium oxide in the process of slowing down a neutron from fission energy to thermal energy should be nearly equal. Actually, if beryllium oxide and graphite are placed in regions of equal fast flux, the number of displacements in the former will be larger than that in the latter by a factor

$$\left(\frac{\sigma_{\text{Be}}}{\sigma_{\text{C}}}\right) = \frac{133}{66}$$

in which $\sigma_{\text{Be}}$ and $\sigma_{\text{C}}$ are the scattering cross sections and the ratio 133/66 is the relative number of atoms displaced per knocked on atom (see Table 6). We shall take the ratio of cross sections to be 1 in order to include the influence of oxygen, so that the multiplicative factor is 2.0. Now the beryllium oxide specimens studied in the investigation are not placed near the uranium slugs so that they receive about as many displacements as they would in an average position in the pile. This means that we should expect about 6 per cent of the atoms to be displaced in the course of a period of time in which 10 per cent of the $^{235}$U is transformed, in comparison with the value of 3 per cent for a specimen of graphite at an average position. The experiments actually show that the thermal resistance of pure beryllium oxide rises by only a factor of 1.6 in the time in which the resistivity of graphite increases by a factor between 15 and 20. Moreover the rate of increase of resistance in beryllium oxide ap-
pears to be about one-tenth as large as the corresponding rate for graphite in the more or less steady-state condition in which the rate of change is nearly constant. A part of the difference between the two materials probably rests upon the fact that the initial thermal conductivity of graphite is about 3 times larger than the value for BeO so that the initial mean free path of the thermal waves responsible for the thermal conductivity may be greater in graphite. In this case we might expect the ultimate rise in resistance of graphite to be greater. However even the introduction of this factor of 3 leaves a difference of a factor of about 10 in the relative behavior of graphite and beryllium oxide. We must conclude either that each displaced atom has a more predominant effect upon the thermal conductivity of graphite or that the number of displaced atoms is a decade or so less than the calculations of section 4 indicate to be the case. It is possible, for example that we have chosen $\epsilon_0$ to be much larger than it should be.

The ratio of $^{238}U$ to nonfissionable atoms in the material containing 10 per cent of enriched uranium oxide is about $0.01 \times \frac{30}{0.07} = 0.4$ times as great as the corresponding ratio in natural uranium. The specimens of beryllium oxide are placed in fuel-free water holes where the flux of thermal neutrons is about 2 times as large as in the fuel-containing tubes. As a result, the fraction of fissioning atoms in the specimens is about $2 \times 0.4 = 0.8$ times as great as in the slugs of metal for any given period of time if we assume that the thermal neutron density is about the same in the metal and in the specimens. Now we saw in section 5 that each atom is displaced about 17.7 times in the metal slugs during a period of time in which 10 per cent of the $^{238}U$ is used. This factor should be decreased by about $25,250/10,500 = 2.4$ if the materials in which the fissioning atoms are dispersed is composed of beryllium oxide (see section 5). Thus we should expect about $17.7 \times \frac{0.8}{2.4} = 5.9$ or about 590 per cent of the beryllium atoms to be displaced by fission fragments in the impregnated material or about 100 times as many as are displaced by direct neutron bombardment. Actually the change $R$ in thermal resistivity appears to increase only about $5/0.8 = 8$ times as rapidly in the impregnated as in the pure material. It should be noted that this estimate of the relative number of displacements is essentially independent of the value taken for $\epsilon_0$.

The ratio of displacements for impregnated and pure material can also be derived by considering the relative values of fast and slow neutron flux in the vicinity of the specimens being irradiated. The discrepancy between the calculated value of the ratio of displaced atoms in impregnated and pure material and the value deduced from experiment is not entirely surprising if it is recalled that the theoretical value implies that each atom of beryllium oxide would be displaced more than once during an irradiation period in which 10 per cent of the $^{235}U$ in the metal slugs would have reacted. We would expect some type of saturation to be reached in the change of resistance before this stage is reached since a reverse reaction would cause some of the lattice structure to be retained. This saturation might well have been observed in the specimens containing 10 per cent of uranium oxide if the irradiations had been extended three or four times longer so that 10 or more per cent of the $^{235}U$ in the metal had reacted instead of only about 3 per cent.

It is doubtful, however, if all of the discrepancy can be ascribed to attainment of a limiting density of displacements, for the experiments show that the thermal resistance rises by almost the same amount, even during the initial stages of irradiation, in beryllium oxide containing 2 per cent and 10 per cent of enriched oxide. This is true even during a period of time in which only a few per cent of the atoms of the beryllium oxide would have been displaced. Since the Chicago measurements show that the initial resistivities of the two types of specimen are essentially the same, and are closely like the resistivity of the pure material, it is not possible to ascribe the differences and similarities in behavior of the various specimens to difference in the starting resistance $R_0$. It is possible however that the enriched materials attain an elevated temperature during exposure and this temperature permits the displaced atoms to aggregate into clusters which are less effective in scattering the thermal waves than the isolated atoms are. In this case we would expect the more highly impregnated material to reach a higher temperature and thus achieve a more nearly annealed state. The fact that the resistance actually does not saturate during the observed period of exposure prohibits us from concluding that the temperatures reached are sufficiently high to permit a complete reversal of the effect of irradiation. It is evident that further investigation of the properties of beryllium oxide would be very desirable.
It is to be noted that when 10 per cent of the U\textsuperscript{235} has undergone fission the specimen impregnated by 10 per cent of enriched uranium oxide contains about 0.05 atom per cent of impurity in the form of fission products.

2) Elastic Modulus.—The elastic modulus of pure beryllium oxide changes by an almost negligible amount during the course of extensive irradiation in which approximately 10 per cent of the U\textsuperscript{235} in the slugs is used. On the other hand the modulus of the impregnated material decreases by about 30 per cent in the corresponding period, the decrease being about the same for the specimens impregnated with 2 per cent and 10 per cent of the oxide.

Concurrent with the drop in modulus is a decrease in breaking strength of the order 30 per cent, also observed to this order of magnitude only in the impregnated material.

c. Uranium Metal

At the present time there are a few qualitative observations which indicate that the uranium metal that has been in the Hanford pile has undergone very large changes. The principal facts are these: The slugs become very hard and brittle; they can be cut with a Carboloy tool only with the greatest of difficulty; and are relatively easily broken by application of a bending impact. In addition the slugs develop surface blisters which seem to imply that the material has undergone considerable internal rearrangement, somewhat analogous to recrystallization, without a change in density. Unfortunately the observations carried out to date are restricted to those properties which can be measured at a safe distance with relatively crude apparatus.

It is possible to speculate on the changes which would be anticipated on the basis of what is known about the properties of materials. There are two factors which serve to alter the properties of the metal: First the extensive rearrangements produced by atomic displacement; and second the introduction of the fission fragments, which behave like foreign elements into the lattice structure. The atomic displacements will have two effects. They will introduce a certain degree of lattice disorder which will have effects similar to those observed as the result of atomic displacement in graphite; they will rearrange the atoms and possibly alter such things as the size of grains and the shape of the tiny cracks and flaws which seem to play a very important role in determining the mechanical properties of the materials. The second of these effects becomes particularly important when each atom becomes displaced a number of times, as is possible, according to the calculations of section 5 if ten per cent of the U\textsuperscript{235} has undergone fission. The fission products also become important when an appreciable fraction of the U\textsuperscript{235} has reacted for they then begin to represent an appreciable component of the material from the chemical viewpoint. For example, they represent 0.14 atomic per cent of the composition when one-tenth of U\textsuperscript{235} has undergone fission. This is comparable to an amount of impurity that can have a very pronounced influence on the properties of steel.

To begin with let us consider the influence of atomic rearrangements. Since uranium has a melting point near that of beryllium, we may assume that the activation energy for the migration of vacant lattice sites is of the order of 26,000 cal. This corresponds to a jump-frequency of about 10 sec\textsuperscript{-1} for a specimen that is at about 200°C, the temperature near the center of a slug. Actually there is another contribution to the jump frequency which should be considered at this point. Each fission fragment passing through the lattice has the effect of heating the atoms in the immediate vicinity of its path to a very high temperature for a very brief period of time; during this transient heat pulse the atoms may be able to undergo a number of jumps. A straightforward calculation of this effect shows that when the pile activity is such that 10 per cent of the U\textsuperscript{235} would transform in 200 days, \( \nu \) is about 10\textsuperscript{-2} sec\textsuperscript{-1} from this source. The calculations show that only the fraction of the energy of the fission fragment (about 1 per cent) which is transferred through elastic encounters appears as heat in the sense that is of interest here. The energy transferred to the electrons comes into equilibrium so slowly that it produces a negligible amount of local heating. If the rate of jumping of vacancies because of the ambient temperature of the slug is less than 10\textsuperscript{-2} sec\textsuperscript{-1} the rate associated with the thermal pulses associated with the passage of fission fragments will completely determine the jump-frequency. In fact if the activation energy for jumping is 26,000 cal, the purely thermal effect becomes important only when the slug temperature is above about 125°C.

We may now determine the equilibrium density of displaced atoms at 200°C using equation (6.9). If 18 displacements are produced in about 200 days, \( \alpha \) will have the value 9.0 \( \times \) 10\textsuperscript{-7}. If we take \( \nu \) as 10 sec\textsuperscript{-1}, we obtain
\[ \frac{n}{n_0} = 3.10^{-4} \] (6.11)

From our estimate of the limit placed upon \( \nu \) by the passage of fission fragments, it follows that \( \frac{n}{n_0} \) is constant below 125°C and will have the value 0.003.

Corresponding values at other temperatures are given in Table 8.

**Table 8. Equilibrium fraction of displaced atoms.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \frac{n}{n_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>3.0 \times 10^{-4}</td>
</tr>
<tr>
<td>200</td>
<td>3.0 \times 10^{-4}</td>
</tr>
<tr>
<td>350</td>
<td>1.0 \times 10^{-5}</td>
</tr>
<tr>
<td>500</td>
<td>3.0 \times 10^{-7}</td>
</tr>
</tbody>
</table>

According to these results the displaced atoms will be present in sufficient concentration to influence the internal properties of the crystal grains only below a temperature of the order of 200°C. Since the outer portions of a slug may be at a much lower temperature a layer of material that is hardened by the presence of displaced atoms could occur.

As long as only a small percentage of the atoms are displaced it is probable that the grain structure and system of microscopic flaws which influence the mechanical properties will not be appreciably altered. In this case it is probable that the regions hardened by displacement will be brittle. However it is possible that the flaws will eventually be "dissolved" as the result of a large amount of atomic redistribution. In this case it is possible that the brittleness would be replaced by an increase in strength without loss in hardness.

The foreign atoms introduced into uranium as a result of fission may be expected to exert an influence upon the mechanical properties of the metal. In fact we may expect them to have effects similar to those produced by the addition of comparable amounts of impurities in steel and similar metals.

The impurity elements in a metal may be classed in three ways, namely metals, nonmetals, and gases. Table 9 shows the approximate manner in which fission products are distributed among their three categories.

It may be seen that the majority of the residual fission products are metals. These range from those such as zirconium which have approximately the same atomic diameter as tuballoy to those such as cesium and cobalt which are respectively both much larger and much smaller. It is well known that metallic impurities of the order of magnitude of 0.06 atom per cent will influence the hardness and notch strength of standard structural metals, particularly if the specimen is given a heat treatment that will assist aging. This effect should be particularly marked in the present case in which an appreciable fraction of the foreign atoms will be forced into interstitial positions where there is little room for them. The observed hardness and brittleness of the Hanford slugs could be caused by this effect alone.

It is improbable that the 0.003 per cent of nonmetallic impurities will induce any significant changes in the mechanical properties of the metal that are not produced more markedly by the larger percentage of metallic impurities. The nonmetals, such as oxygen and sulfur, usually have their most important influence when they are able to aggregate at grain boundaries and form brittle compounds which weaken the intergranular bond. In this location they are able to produce very important effects even when present in exceedingly small quantities. For example, it is believed that metals such as chromium are made brittle by amounts of oxygen of the order of 0.01 per cent. It seems highly improbable that one of these striking effects will occur in the present case, for in the first place the nonmetallic impurities are distributed over several species (Xe, Br, and I are the most prominent); and in the second place, it is unlikely that sufficient diffusion will occur to allow the nonmetals to occupy a location at which they can

**Table 9. Approximate distribution of fission products among three categories.** (Residual values after conversion of 10 per cent of \( ^{235}U \) followed by about 100 days of standing)

<table>
<thead>
<tr>
<th>Type of fission product</th>
<th>Atomic percentage of metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic</td>
<td>86</td>
</tr>
<tr>
<td>Nonmetal</td>
<td>2</td>
</tr>
<tr>
<td>Gas (Kr and Xe)</td>
<td>12</td>
</tr>
</tbody>
</table>

[Atomic percentage of metal]
cause appreciable harm. The rate of diffusion will be discussed below.

It is now well established that gaseous impurities can cause important embrittlement in steel. For example, 0.001 atom per cent of hydrogen by diffusion to internal cracks can open these cracks and rupture the material. The amounts of Kr and Xe listed in Table 9 lie in the range where they could have important consequences if they are able to diffuse to suitable cracks. The rare gases are of particular interest since they are probably practically insoluble in any metal. Seltz has found for example that helium is soluble to less than about one part in 10⁵ in uranium.

Measurements of the diffusion coefficient of the various fission products carried out at Ames and Pittsburgh during the war on material which was heated after irradiation indicates that the diffusion coefficients correspond to activation energies above 40,000 cal. If these values prevail during operation it is improbable that sufficient diffusion occurs to cause any important aggregation of fission products even when the temperatures are near 350°C. The rates would be significant however if operation took place near 1000°C as is contemplated in high-temperature piles. It is possible however that diffusion is much more rapid during operation because a high density of vacancies prevails. A calculation carried out by the writer shows that it is not entirely improbable that the rare gases will diffuse to internal cracks in dangerous quantities because of this effect.

The effects observed to date on the Hanford slugs can be explained without recourse to the mechanism of gaseous embrittlement. The great increase in hardness and loss of strength are exactly what would be expected from the presence of the fission products if it is assumed they are dispersed interstitially. Similarly it may prove possible to explain the blistering in terms of atomic migration which takes place both as a result of ambient temperature and the displacements produced by the fission fragments.

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PRODUCTION OF THORIUM METAL

I. Purification of Thorium Nitrate and the Subsequent Production of Thorium Oxalate

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Institute for Atomic Research, Iowa State College, Ames, Iowa
Report ISC-33

ABSTRACT

Commercial thorium nitrate is purified by solvent extraction and an oxalate precipitation. This is the beginning step in the production of pure thorium metal by the Iowa State College Institute for Atomic Research. A review is given of the preliminary experimental work which preceded the present pilot-plant process. The operation and equipment of this pilot plant are described in detail.

INTRODUCTION

The principal steps involved in the production of cast thorium metal by the Iowa State College process are:

1. Preparation of a solution of commercial thorium nitrate, calcium nitrate, and nitric acid, and the extraction of the thorium nitrate from this solution by a solvent mixture of tributyl phosphate and dibutyl ether, thus effecting a separation of the thorium nitrate from the bulk of the impurities present in the commercial salt.

2. Re-extraction of the thorium nitrate from the solvent by distilled water.

3. Precipitation of thorium oxalate from acid solution by the addition of oxalic acid, and the filtration and drying of the precipitate.

4. Calcination of the thorium oxalate to thorium dioxide at a temperature of 650°C.

5. Hydrofluorination of the thorium dioxide to thorium fluoride by anhydrous hydrogen fluoride at a temperature of 550°C.

6. Reduction of the thorium fluoride by metallic calcium employing zinc chloride as a booster.

7. The boiling off of the zinc from the crude thorium-zinc alloy, and the casting of the thorium in graphite molds.

This paper is concerned with steps (1) through (3). Subsequent papers will consider the succeeding steps.†

In thorium metal to be used for nucleonic purposes, it is desirable that the concentration of impurities having high capture cross sections, i.e., rare earths, boron, cadmium, etc., be kept as low as possible. Commercial thorium salts that were available in quantities that would permit their use as raw materials for metal production were sufficiently low in most elements, but

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they contained on the average 50 ppm total rare earths. From work done elsewhere on uranium¹ and plutonium² separations involving liquid-liquid solvent extraction of their nitrates, it appeared that a similar technique could be applied to effect a separation of rare-earth impurities from thorium nitrate. This proved to be so, and a pilot-plant production-scale extraction system was built and operated that reduced the total rare-earth content of the processed thorium nitrate to less than 1 ppm.

The system used as feed an aqueous nitric-acid solution of thorium nitrate with calcium nitrate as salting-out agent and originally used methyl isobutyl ketone (hexone) as the organic solvent. A solvent mixture containing 20% tributyl phosphate and 80% dibutyl ether was later substituted for hexone.

PRELIMINARY EXPERIMENTAL WORK

The preliminary experimental work included consideration of the feasibility of the process, selection of salting-out agents and solvents, and determination of concentrations of solutions for optimum extraction. Determination of physical data relating to the solutions involved and the development of analytical methods were also undertaken. Details on these may be found in reports listed in the references.

Among the salting-out agents considered were ammonium, calcium, copper, silver, aluminum, and manganous nitrates. Calcium nitrate was selected over the other nitrates because of a combination of factors. It was relatively cheap and readily available in tonnage lots, it was quite soluble, and it possessed good salting-out properties, also, less than 1% of the calcium nitrate was extracted by the solvent under column conditions. This amount would be reduced in the oxalate-precipitation step, and any calcium nitrate remaining would not be serious since calcium was used as a reducing agent in the fluoride-reduction step.

Solvents considered included hexone, nitromethane, cyclohexanone, isophorone, naphthyl methyl ether, diethyl oxalate, acetophenone, diethyl cellosolve, and tributyl phosphate. Hexone was first selected because, while others of the solvents extracted thorium to a greater degree, hexone was available in quantity, it was soluble only to the extent of 2% in water, its density was low enough (0.80), its viscosity was low enough (0.55 centipoise) to make operation of a countercurrent extraction system possible, and its flash point was fairly high (75°F. by A.S.T.M. open cup), also, the rare earths were extracted to a lesser degree with hexone than with some of the other solvents considered.

Table 1 shows the effect on the extraction of thorium of variations in calcium-nitrate concentration, thorium-nitrate concentration, and nitric-acid concentration for one batch extraction with equal volumes of solvent and of feed. These data were obtained from experiments in which the liquids were equilibrated by shaking in a separatory funnel and sampled for analysis after gravity separation.

Table 2 shows the extraction of tracer rare earths from solutions of 3M calcium nitrate con-
PURIFICATION OF THORIUM NITRATE

Table 2. Extraction of tracer rare earths from 3M Ca(NO$_3$)$_2$ - HNO$_3$ - Th(NO$_3$)$_4$ solutions by hexone.

<table>
<thead>
<tr>
<th>Th(NO$_3$)$_4$ molarity</th>
<th>HNO$_3$ molarity</th>
<th>% thorium extracted</th>
<th>% rare earths extracted</th>
<th>Ratio of thorium to rare earths</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0</td>
<td>54</td>
<td>0.11</td>
<td>490</td>
</tr>
<tr>
<td>0.00</td>
<td>1</td>
<td>—</td>
<td>0.03</td>
<td>—</td>
</tr>
<tr>
<td>0.21</td>
<td>1</td>
<td>35</td>
<td>0.10</td>
<td>350</td>
</tr>
<tr>
<td>0.43</td>
<td>1</td>
<td>42</td>
<td>0.31</td>
<td>140</td>
</tr>
<tr>
<td>0.86</td>
<td>1</td>
<td>56</td>
<td>1.1</td>
<td>51</td>
</tr>
<tr>
<td>0.00</td>
<td>3</td>
<td>—</td>
<td>0.14</td>
<td>—</td>
</tr>
<tr>
<td>0.21</td>
<td>3</td>
<td>56</td>
<td>0.14</td>
<td>400</td>
</tr>
<tr>
<td>0.86</td>
<td>3</td>
<td>54</td>
<td>0.47</td>
<td>115</td>
</tr>
</tbody>
</table>

operation. The high thorium-nitrate concentration meant a poorer rare-earth separation as shown in Table 2, but was necessary to insure an adequate capacity for the extraction system. Higher concentrations of either the thorium nitrate or the salting-out agents were not feasible because the freezing point of the feed solution selected was about 15°C and any additional salt would tend to cause crystallization at room temperature. To improve the separation of rare earths, a scrubbing section was planned in which the enriched solvent would contact a solution which was 3M in calcium nitrate and 3M in nitric acid. Rare earths that were salted out into the solvent in the extraction column would tend to pass back into the aqueous phase when in contact with the scrubbing solution.

Hexone proved to be unstable in contact with strong nitric acid. It could only be used for a short period of time before being discarded, because as the decomposition proceeded there was a tendency for the hexone to react violently. To replace the hexone, solvents that had good extracting properties, but which had been rejected on the basis of high densities or viscosities, were diluted with lighter inert solvents. Tributyl phosphate and isophorone were diluted with n-dibutyl ether—each mixture proved to work satisfactorily. Isophorone discolored in the presence of nitric acid, and so it was discarded in favor of the tributyl phosphate. A mixture of 20% tributyl phosphate and 80% dibutyl ether, by volume, was used in the pilot plant system. Table 3 gives values for the extraction of thorium nitrate by mixed solvents in one batch extraction and shows the effect of dilution upon the extracting power. Table 4 gives an indication of the rare-earth separation possible with the mixed solvent. The data were obtained by using macro amounts of neodymium and analyzing for it spectrophotometrically.

DESCRIPTION OF THE EXTRACTION SYSTEM

A sketch of the plant layout is shown in Fig. 1. The limited space, as well as cost considerations, required a simple, compact system. The installation is located in an enclosure built in the north stairwell of the Chemistry Building at Iowa State College and in adjoining space at the basement.
Table 3. Extraction of thorium nitrate from $3M\ Ca(NO_3)_2 - 0.15M\ HNO_3 - 0.44M\ Th(NO_3)_4\cdot4H_2O$ with mixed solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density</th>
<th>Ratio of organic to feed</th>
<th>% thorium extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% butyl phosphate</td>
<td>0.87</td>
<td>1</td>
<td>82</td>
</tr>
<tr>
<td>50% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% butyl phosphate</td>
<td>0.82</td>
<td>2</td>
<td>93</td>
</tr>
<tr>
<td>75% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% butyl phosphate</td>
<td>0.81</td>
<td>2</td>
<td>72</td>
</tr>
<tr>
<td>80% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% butyl phosphate</td>
<td>0.79</td>
<td>2</td>
<td>44</td>
</tr>
<tr>
<td>90% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% isophorone</td>
<td>0.85</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>50% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90% isophorone</td>
<td>0.91</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>10% butyl ether</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Extraction of neodymium from $3M\ Ca(NO_3)_2 - 0.44M\ Th(NO_3)_4\cdotHNO_3$.

<table>
<thead>
<tr>
<th>HNO_3 conc. molarity</th>
<th>Rare-earth concentration (moles per liter)</th>
<th>Distribution coefficient $K_{\text{solvent/aqueous}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous phase</td>
<td>Solvent phase</td>
</tr>
<tr>
<td>1</td>
<td>0.0126</td>
<td>No detection*</td>
</tr>
<tr>
<td>2</td>
<td>0.0132</td>
<td>No detection</td>
</tr>
<tr>
<td>3</td>
<td>0.0128</td>
<td>No detection</td>
</tr>
<tr>
<td>4</td>
<td>0.0133</td>
<td>No detection</td>
</tr>
</tbody>
</table>

* Minimum detection, 0.0006 moles per liter.

and attic levels. An open space 65 ft high and 6 ft by 9 ft in cross section was available for the columns and auxiliary equipment. Steel gratings at the floor levels of the building support the equipment and serve as platforms for the operators.

The columns proper are of 3-in. pyrex-glass pipe, in 6-ft lengths, with $\frac{3}{4}$-in. Teflon gaskets between the lengths. The extraction column is divided into two sections by a pyrex tee with a 1-in. diameter side arm. The lower extracting section is 19 ft in height, and the upper scrubbing section is 6 ft. This extraction column is column A in the flow sheet shown in Fig. 2. It is fitted with inlet pipes through which scrubbing solution is introduced at the top of the column, feed solution at a point 6 ft below the top, and organic solvent at the bottom; and outlet pipes through which raffinate stripped of thorium is removed at the bottom of the column, and organic solvent enriched with thorium is removed at the top. Col-
Fig. 1. Thorium-nitrate solvent extraction plant layout.
umn B, the stripping column, is 18 ft high and is arranged so that the enriched organic solvent from column A is introduced at the bottom of the column and distilled water at the top. The aqueous product solution is removed at the bottom of the column, and the organic solvent, stripped of thorium, at the top. All of the piping and fittings used in these lines are standard \( \frac{1}{2} \) in., type 304 stainless steel, except for the upper 5 ft of the line carrying the enriched solvent from the top of column A to the bottom of column B. This section is made of 1-in. stainless steel tubing, to smooth out surges and prevent the trapping of air between slugs of enriched solvent which might interfere with smooth operation of column B. Both columns are packed with \( \frac{1}{4} \)-in. unglazed-procelain Berl saddles, supported at the bottom of each 6-ft section by \( \frac{1}{4} \)-in. stainless steel mesh, permitting the replacement of a single section without unpacking the entire column. The packed height of column A is 21 ft and of column B is 15 ft.

The four liquids fed to the columns, namely, feed solution, scrubbing solution, organic solvent, and distilled water, each flow from a constant-head tank through a control panel, equipped with a rotometer and a needle valve for each line, and into the columns. The feed and scrubbing solutions are pumped to the respective constant-head tanks from two 50-gal stainless steel storage tanks. A \( \frac{1}{2} \)-in. overflow line maintains the liquid level constant and returns the overflow to the storage tanks. A 50-gal stainless steel tank serves as reservoir for the organic solvent, from which the solvent is pumped to its constant-head tank. The overflow is returned to the reservoir through the overflow line. The stripped solvent from column B is also returned to this reservoir for recirculation through the system.

The solution make-up tanks for the feed and scrubbing solutions are two 100-gal stainless steel tanks equipped with stainless steel stirrers, located so that the solutions may be fed by gravity to the storage tanks. Filters containing 200-mesh stainless steel screens are placed in each line. The raffinate and product solutions leave the bottom of columns A and B, respectively, and are drawn off through interface control systems. The raffinate is sent to a 50-gal stainless steel drum for recovery of the calcium nitrate. The product solution may be diverted into any one of three 50-gal stainless steel process tanks.

In each of the columns the organic phase is dispersed and passes up through the aqueous phase, agglomerating at the top and separating from the aqueous phase. The position of the interface between the phases is regulated by adjusting the rate at which the aqueous phase leaves the bottom of the column. A needle valve in a by-pass line from the bottom of the column provides the coarse adjustment, and an inverted U-loop, whose height may be varied, provides the fine adjustment. Up or down movement of the loop causes a corresponding change in the position of the interface in the column. A helical coil of \( \frac{1}{8} \)-in. Saran tubing in one leg of the loop permits the neces-
sary up or down movement. Adjustments in the height of the loop are made manually by the operator.

The product solution receivers are equipped with stainless steel stirrers to aid in precipitation of the oxalate, and are piped to an 18-in. stainless steel filter press having fifteen 1-in. frames. The discharge from the filter press may be returned to any one of the receivers until the filtrate is clear, after which it may be diverted to a reservoir where it is held until the filter press is full. In the event that a cloth should break, any thorium oxalate passing into the filtrate would be held in the reservoir, the contents of which could then be refiltered. If the contents of the reservoir remain clear, they are discharged to the drain through a limestone neutralizer. The press is piped so that the cake may be washed free of acid and then blown dry with air. Fiberglass cloths with 18-in. square filter-paper sheets on each face are the filter media used.

The raffinate receiver also has a stirrer to facilitate neutralization of the calcium-nitrate solution. Beyond the receiver the calcium-nitrate recovery system is of iron, since the neutralized solution has a pH of about 9. The receiver is piped to a monte-jus operating on 75 lb/sq in. air, by means of which the slurry is moved up to the solution make-up level of the plant after filter-aid has been added. Here the slurry is stored until it has passed through an 18-in. filter press, after which part of it is used in feed and scrubbing solution make-up while the balance is evaporated in an open steam-jacketed evaporator to the point where it will crystallize as the tetrahydrate upon cooling. This solid salt is also used in solution make-up.

OPERATION

In the preparation of the feed and scrubbing solutions, the recovered calcium-nitrate solution is the starting material. It has a specific gravity of between 1.36 and 1.45, and contains about 7.5 lb of calcium nitrate tetrahydrate. This is too dilute to be used directly in make-up, so sufficient solid calcium nitrate is added to bring the concentration up to the required point. The solid calcium nitrate is obtained by heating the solution until a boiling point of 132°C is reached, the boiling point of calcium nitrate tetrahydrate. The calcium nitrate is usually used for make-up in the molten form to facilitate its solution. It melts at a temperature of 42°C. Calculated quantities of concentrated nitric acid and thorium nitrate tetrahydrate are then added. A feed solution 0.63M in thorium nitrate, 3M in calcium nitrate, and 3M in nitric acid requires, for 80 gal, 234 lb of thorium nitrate, 151 lb of calcium nitrate as salt, 497 lb of calcium nitrate as solution, and 223 lb of nitric acid. The corresponding scrubbing solution would require no thorium nitrate, 17 lb of calcium nitrate as salt, 716 lb of calcium nitrate as solution, and 223 lb of nitric acid. The solutions, after thorough mixing, are run down to the column storage tanks as needed.

About 30 gal of the solvent mixture is kept in the system at a time. This quantity contains 47.8 lb of tributyl phosphate and 149 lb of dibutyl ether, and has a density of 0.81.

At the start of operations, the constant-head tanks are filled by starting the respective pumps. After an overflow is evident from each tank, column A is filled with scrubbing solution. The organic-solvent valve is then opened to give the operating flow rate, as indicated by the rotometer, and as the solvent reaches the top of the column both the feed and the scrubbing solution valves are set at their operating flow rates. The raffinate outlet valve is adjusted to give a steady raffinate flow from the column, and the interface is brought to a point within a few inches of the top of the column and maintained there by manipulation of the U-loop. As the enriched solvent passes over into column B, the distilled-water valve is opened until the distilled water is flowing at its proper rate. The product-solution valve is then opened and the position of the interface is adjusted with the U-loop, so that stripped solvent is returned to the solvent storage tank. Flow rates for a typical production run are 6.5 gph of feed solution, 3.5 gph of scrubbing solution, 34 gph of organic solvent, and 4 gph of distilled water. Solutions leaving the columns do so at the rates of 6 gph for the product solution, 8 gph for the raffinate and 34 gph for the solvent. These solutions have the following composition: product solution, 1.55 lb of thorium per gal, 3.2M nitric acid; raffinate, 0.026 lb of thorium per gal, 0.2M nitric acid; stripped organic solvent, 0.075 lb of thorium per gal, 0.6M nitric acid. The extraction for this run was about 99%.

Table 5 gives data obtained from the early experimental runs with hexone as the solvent, and indicates the variation in thorium extraction with different solvent/feed ratios. A ratio of hexone
to feed of about 2 was used in production runs on the basis of these data. This ratio gave a high extraction with a satisfactory thorium throughput.

Table 5. Variation in thorium extraction with different solvent/feed ratios.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed rate, gph</th>
<th>Solvent/feed</th>
<th>% thorium extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>7.75</td>
<td>0.7</td>
<td>31.5</td>
</tr>
<tr>
<td>5</td>
<td>5.5</td>
<td>1.0</td>
<td>68.6</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>1.75</td>
<td>93.4</td>
</tr>
<tr>
<td>14</td>
<td>8</td>
<td>2.0</td>
<td>99.7</td>
</tr>
<tr>
<td>9</td>
<td>7.5</td>
<td>2.14</td>
<td>99.3</td>
</tr>
<tr>
<td>17</td>
<td>7</td>
<td>2.28</td>
<td>99.3</td>
</tr>
</tbody>
</table>

A solvent/feed ratio of 5.2 gave a corresponding extraction when the tributyl phosphate-dibutyl ether mixture was substituted for hexone.

Table 6 gives similar data on the extraction into the water phase from the solvent. The concentration of nitric acid remaining in the solvent was used as an indication of the degree of stripping, since the thorium concentration follows it closely.

Table 6. Variation in stripping of enriched solvent with different solvent/water ratios.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Water rate, gph</th>
<th>Solvent/water</th>
<th>Nitric acid in solvent, molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>2.5</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>3.25</td>
<td>3</td>
<td>0.10</td>
</tr>
<tr>
<td>9</td>
<td>3.75</td>
<td>4</td>
<td>0.99</td>
</tr>
<tr>
<td>11</td>
<td>3.5</td>
<td>4.3</td>
<td>1.01</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>5</td>
<td>1.04</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>6</td>
<td>1.79</td>
</tr>
</tbody>
</table>

A solvent/water ratio of between 4 and 5 was used with hexone, although this was too high for thorough stripping of the thorium, in order that a satisfactorily concentrated product solution could be obtained. With the tributyl phosphate-dibutyl ether solvent, a ratio of 8.5 was used.

The raffinate contains some unextracted thorium nitrate, some nitric acid, most of the calcium nitrate, and any rare earth or other nitrates that were present as impurities in the salt. When about 40 gal of raffinate has collected, it is neutralized by slowly adding lime (CaO). In the resulting basic solution, thorium, rare earths, and other metal impurities are precipitated as hydroxides, but the calcium nitrate remains in solution. A filter-aid is added, and after filtration the calcium nitrate solution is ready for feed and scrubbing solution make-up. There is very little loss of calcium nitrate from the system.

The cake removed from the filter press is processed to recover the thorium content. A diatomaceous earth was originally used as filter-aid, which required dissolving the hydroxides and filtering off the filter-aid. Since the substitution of a cellulose type of filter-aid, the cake is simply ignited and the hydroxides converted to oxides. These are dissolved and the resulting solution is given a preliminary extraction step before being run through the regular extraction system.

After 40 gal of product solution has collected in a receiver, the outlet line from the column is diverted to another receiver and a sample of the solution is taken for analysis by a rapid method. This consists of measuring the specific gravity and obtaining a reading with a dipping-type refractometer. Data relating the concentration of thorium and of nitric acid to these measurements were obtained and plotted as nomographs (Figs. 3 and 4). An analysis can be made in a few minutes and is sufficiently accurate for the purpose. Based on the thorium concentration obtained, a 10% excess of oxalic acid is added, and the slurry stirred for 1 to 2 hr. The thorium oxalate is then filtered, washed with distilled water, and dried by blowing air through it. The precipitate may be thixotropic, depending upon the thorium and acid concentrations at the time of precipitation. Unless the cake is quite dry when it is removed from the press, it is very difficult to handle. It becomes sticky and pasty when being dumped from the press, and sets up into a solid mass in the drums in which it is transported to the drying oven, making it troublesome to remove. A ratio of moles of acid to moles of thorium of about 4 gives a satisfactory crystalline precipitate, but below this value the thixotropic results. Product solutions leaving the columns with thorium concentrations below 0.9 lb/gal, or above 1.65 lb/gal, seem to fall in the thixotropic region. Using fil-
Purification of Thorium Nitrate

A spectrographic analysis of the commercial thorium nitrate revealed the presence of the following quantities of rare earths, calculated on a thorium metal basis:

- Cerium: 24 ppm
- Lanthanum: 8 ppm
- Neodymium: 6 ppm
- Praseodymium: 3 ppm
- Samarium: 0.8 ppm
- Yttrium: 1 ppm
- Gadolinium: 0.5 ppm
- Dysprosium: 0.1 ppm

An analysis made on the column product solution failed to detect the presence of any of the above elements. The smallest quantities of these elements that could be detected at that time were:

- Cerium: 0.4 ppm
- Lanthanum: 0.05 ppm
- Neodymium: 0.2 ppm
- Praseodymium: 0.1 ppm
- Samarium: 0.2 ppm
- Yttrium: 0.05 ppm
- Gadolinium: 0.04 ppm
- Dysprosium: 0.05 ppm

Fig. 3. Nomograph of thorium in product solution.
Fig. 4. Nomograph of nitric acid in product solution.
These figures represent the maximum quantities of the elements that could be present; the actual values could be much less.

A later analysis, made after the change to the tributyl phosphate–dibutyl ether solvent, gave the following results from a sample in which the rare earths were concentrated 14,000 times relative to the thorium present:

- Cerium 0.23 ppm
- Lanthanum 0.34 ppm
- Neodymium No Detection, <0.006 ppm
- Yttrium No Detection, <0.005 ppm
- Dysprosium No Detection, <0.002 ppm
- Gadolinium No Detection, <0.002 ppm

The total of rare earths present is something less than 1 ppm.

**SUMMARY**

The Ames laboratory process for purifying thorium nitrate and producing thorium oxalate has been described in detail. The process consists of a liquid–liquid countercurrent solvent extraction of a nitric-acid solution of commercial thorium nitrate with a solvent mixture consisting of 20% tributyl phosphate and 80% dibutyl ether, using calcium nitrate as a salting-out agent. The purified thorium nitrate is re-extracted from the solvent by distilled water, and subsequently precipitated as thorium oxalate by oxalic acid. The total concentration of rare earths is reduced to less than 1 ppm of thorium.

Assuming an ample supply of thorium nitrate, the present purification pilot plant is adequate for the production of 25 tons of finished virgin metal a year.

**REFERENCES**


Various phases of the work are described in detail in the following reports of the Iowa State College Institute for Atomic Research.

PRODUCTION OF THORIUM METAL

II. Production of Thorium Oxide and Thorium Fluoride

By R. H. Giffen and H. A. Wilhelm
Institute for Atomic Research, Iowa State College, Ames, Iowa

Report ISC-34

ABSTRACT

Thorium oxide and thorium fluoride are produced at the Iowa State College Institute for Atomic Research as a step in the production of thorium metal. Thorium oxalate of high purity is dried and calcined to the oxide, which is subsequently hydrofluorinated at an elevated temperature to produce anhydrous thorium fluoride.

A review is given of both the experimental work leading up to the present pilot-plant process and the current developmental work for improving this process. The operation and equipment of this pilot plant are described in detail.

INTRODUCTION

This paper is the second in the "Production of Thorium Metal" series. The first paper included the purification of commercial thorium nitrate and the subsequent precipitation of thorium oxalate. The present paper includes the conversion of thorium oxalate to thorium oxide and the subsequent hydrofluorination of the oxide, which produces anhydrous thorium fluoride suitable for reduction to the massive metal.*

Early in the history of the Manhattan District, Iowa State College, undertook the task of producing metallic thorium. In August, 1943, it was found that massive thorium metal could be produced by reducing anhydrous thorium fluoride with calcium metal. Various methods for producing pure, anhydrous thorium fluoride were investigated. After a preliminary research program, the process described in this paper was adopted. A small pilot plant for this process was designed, constructed, and operated by the research group during the latter months of the late war.

Under contract with the Atomic Energy Commission, the Ames laboratory has designed and constructed a larger pilot plant that is now producing a more uniform product with increased efficiency.

The Ames laboratory is currently conducting a study of the reactions involved in this process for producing anhydrous thorium fluoride. The results of this research are expected to provide the necessary data for the design of large-scale plants and their operation for maximum efficiency and quality of product. Alternative processes are

also being studied, and improvements will be incorporated in the production process as they are developed.

HISTORICAL

Thorium had previously been prepared in small quantities by the reduction of its chloride or oxide by alkali or alkaline-earth metals, and by electrolysis in a fused-salt medium. The product of these preparations was a powder of impure metal that had to be sintered by heat and pressure to form a cohesive mass.

Early in the history of the Manhattan District, the group at Iowa State College found that massive thorium metal could be produced by reducing anhydrous thorium fluoride with metallic calcium. For large scale production, the metallothermic reduction of thorium fluoride appeared to be more economical than the electrolytic method, and a suitable process for producing anhydrous thorium fluoride was sought.

Several different processes for making thorium fluoride were tested before the present process was adopted. The main criteria for process selection were the purity and bulk density of the product and the economic aspects of the process itself. A high bulk density was required for making more metal per reduction, and it was subsequently found that the reduction yield and quality of metal produced were higher with a high-bulk-density fluoride.

Thorium fluoride, precipitated from an aqueous solution of thorium nitrate by hydrofluoric acid, could not be completely dehydrated and was very bulky. Even in a vacuum at 500°C, some water of crystallization remains bound to the thorium fluoride. Water of crystallization develops excessive pressures during reduction and is therefore dangerous.

In a medium of molten sodium and potassium chlorides, thorium sulfate and a mixture of sodium and potassium fluorides react to form anhydrous thorium fluoride. The precipitate may be washed free of reactants and medium by leaching with water. The process was considered to be impractical for large-scale production.

Most of the preliminary work was concentrated on hydrofluorination reactions at some elevated temperature. The reactions were carried out in a graphite apparatus, as illustrated in Fig. 1. The material being tested is placed in the graphite cups to a depth of \( \frac{1}{2} \) in., and the cups are stacked as shown in the figure. Thorium carbonate, hydroxide, oxalate, and oxycarbonate were hydrofluorinated. Thorium hydroxide gave a product with the highest bulk density. Later it was found that thorium oxide, which was formed at 650°C from thorium oxalate, reacted readily to hydrofluorination and gave a high-bulk-density product. The oxalate can be precipitated with higher purity than the hydroxide because of the gelatinous nature of the hydroxide precipitate, which tends to occlude impurities and prevent their being washed out.
Other processes suggested themselves to the research group, but they were eliminated for various reasons. Thus, the process wherein thorium oxide is reacted with anhydrous hydrogen fluoride at an elevated temperature was adopted and scaled up to pilot-plant production.

DESCRIPTION OF PROCESS AND EQUIPMENT

Drying Thorium Oxalate

The thorium oxalate is received from the purification plant, in the form of a filter cake, in 50 gal stainless steel drums. Each drum contains about 150 lb of wet thorium oxalate. The moist and occasionally thixotropic material is transferred from the drums to shallow stainless steel trays, each containing from 10 to 20 lb of wet thorium oxalate. These trays are placed on the shelves of a cabinet drier.

The drier consists of a rectangular box made of stainless steel sheet welded to a skeleton of angle iron and externally insulated with sheets of transite, as illustrated in Fig. 2. There are ten shelves, each of which can accommodate four trays.

Calcining Thorium Oxalate

The dried thorium oxalate is ignited in air at 650°C to convert the material to thorium oxide. The overall reaction may be written

\[
\text{Th}_2\text{(C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{ThO}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O},
\]

since the dried thorium oxalate has been found to be a dihydrate.

The Monel calcining trays are 36 in. long, 7 1/4 in. outside diameter, and 5 in. deep. As illustrated in Fig. 3, these trays are placed in cylindrical furnaces that are 45 in. long and 8 in. inside diameter. The furnace is heated electrically by impressing 220 volts on a 10-ohm resistance winding. The temperature is maintained at 650°C by a thermocouple-controlled Wheelco model 224 Capacitrol. The gaseous products of ignition are swept out of the furnace by a small flow of compressed air, which also supplies the additional oxygen required for complete reaction.

If the thorium oxalate has not been washed free of nitric acid in the filter press, a reaction occurs in the Monel trays during the calcining process. Stainless steel trays are being substituted to avoid this potential source of product contamination.

The filter cake is left in the drier for at least 8 hr, but usually overnight, and is then removed and cooled in air. It is packaged in cardboard drums if storage is necessary, otherwise, the material is calcined immediately.
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Fig. 3. Calcining furnace.

Fig. 4. Hydrofluorination furnace.

1. HF in 2. HF out 3. Flue gas stack
4. Reaction Chamber 5. Tray shelves 6. Gas burners

Hydrofluorination of Thorium Oxide

Thorium oxide is hydrofluorinated to thorium fluoride in a gas-fired furnace at about 550°C. The overall reaction may be written

\[ \text{ThO}_2 + 4\text{HF} \rightarrow \text{ThF}_4 + 2\text{H}_2\text{O} \]

As illustrated in Fig. 4, the furnace contains a Monel reaction chamber which is 8 ft long, 12 in. wide, and 8 in. high. The chamber will accommodate four rectangular Monel trays, each of which will hold 45 lb of thorium oxide to give a total charge of 180 lb. The depth of the granular...
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solids in the trays is about 1 in. The shelves which support the trays are arranged so that the gas flows over the four trays, in series, before leaving the reaction chamber. The trays are placed into the chamber from one end, which is then sealed with a bolted rectangular flange carrying a gasket of sheet copper backed with asbestos.

The furnace walls are constructed of commercial fire brick. The temperature of the reaction chamber is controlled by means of thermocouples connected to a Brown Instrument Company three-point temperature indicator-recorder-controller. The instrument controls the amount of gas burned in the furnace by means of three solenoid valves in parallel with three pilot valves. Three thermocouples are located along the length of the reactor and are the sensing elements for the controller. From the temperature record in Fig. 5, the temperature is seen to be constant within 3% of the absolute temperature. The two curves were obtained from measurements made with test thermocouples placed inside the reactor along the top and bottom shelves, while the Brown potentiometer was set at a control temperature of 550°C.

Commercial anhydrous hydrogen fluoride (99+% HF) is passed into the reactor through nickel pipe pressure gages were installed in the line to determine flow rates.

During regular production, the mixture of HF and H₂O which leaves the reaction chamber is condensed to a liquid, diluted with water, and disposed of by neutralization in a lime pit outside the building. When test data are to be taken, the exit gases are condensed to a liquid, as usual, and then cooled to 0°C in an ice-water cooler, as illustrated in Fig. 6. The cold liquid is then piped to a constant-level overflow cup (surrounded by an ice-water bath) in which is suspended a nickel plummet for determining specific gravities. The overflow is caught in Monel buckets, which are weighed periodically to determine the condensate flow rate. After weighing, the condensate is disposed of in the lime pit.

At the end of 7 hr the conversion to the fluoride is complete, and before the trays are removed from the furnace the reaction chamber is flushed with nitrogen to remove the remaining HF. After the trays have cooled, they are reweighed to check the conversion. Material which is less than 99% converted is re-run. From a charge con-
sisting of 180 lb of thorium oxide, 210 lb of thorium fluoride are produced. If the pilot plant is operated at full production (20 shifts per week and 1 batch per shift) and due allowance is made for casting and finishing yields, the present production capacity for the fluoride step is equivalent to 50 tons of finished virgin thorium metal a year.

The material which is satisfactorily converted is packaged in cardboard drums and transferred to the reduction plant for metal production.

Two hydrofluorination furnaces in series would increase the efficiency of HF utilization. The exit gas from the first unit would be fed to the second unit, where further reaction would take place. The process would continue only until the conversion in the first unit was complete. At this time it is estimated that the exit concentration from the second unit would be about 10% HF, which could be safely disposed of by neutralization. The next run would utilize the partially converted material in the second furnace as a reactant, and fresh thorium oxide would be placed in the first furnace for utilizing the excess HF from the reacting unit. It is estimated that two such units in series would increase the efficiency of HF utilization from the presently realized 70% to over 95%. Three such units in series would probably increase the efficiency of HF utilization to nearly 100%. Furthermore, each batch would be partially converted before it was placed in the reactor and exposed to pure HF, which would reduce the elapsed time per batch, so that the maximum production capacity would be increased.

Hydrofluorination Test Data

During routine production of thorium fluoride, the progress of the reaction may be followed by determining the concentration of hydrogen fluoride in the exit gas from the furnace. These data may be obtained titrimetrically or by specific gravity measurements with a Westphal balance, using samples taken from the exit condensate. Fig. 7 illustrates the type of curve obtained for the exit concentration vs. the weight of hydrogen fluoride feed put into the furnace. At the feed rates usually used, when less than the stoichiometric amount of hydrogen fluoride feed has been put into the furnace, the rate of reaction between the feed and the thorium oxide is the rate-determining step, which is observed to be rapid. Under the same feed conditions, when more than the stoichiometric amount of feed has been used, the exit gas increases rapidly in hydrogen-fluoride concentration because the reaction rate becomes limited by diffusion.

The second curve in Fig. 7 shows the conversion in the furnace, as calculated from the exit curve. Since the initial reaction rate is high, the conversion proceeds rapidly. However, it ap-
proaches completion slowly when the reaction rate decreases, because diffusion is the only means by which the feed gas can reach the bottom of the bed for reaction.

A rotary-type reactor, or other type of reactor which would provide more intimate contact between the solid and gaseous reactants, would give more sustained conversion rates, greater efficiency of hydrogen-fluoride utilization, and reduced process time.

Fig. 8 illustrates graphically the percentage of the feed that undergoes reaction in passing through the furnace. Both the instantaneous and the cumulative rates are given to show that, although less than 5% of the feed reacts at the end of the hydrofluorination, the overall utilization of hydrogen fluoride is above 70%. The instantaneous curve shows the effect of changes in reaction rate as the run nears completion.

**PROCESS DEVELOPMENT**

In order to obtain the necessary data for the design of large-scale plants and their operation for maximum efficiency and quality of product, an intensive study of the unit process and unit operations for producing anhydrous thorium fluoride is currently being made.

**Hydrofluorination of Thorium Oxide—Equilibrium Studies**

A detailed study has been completed of the reaction under equilibrium conditions at several temperatures between 350 and 500°C. An apparatus, illustrated in Fig. 9, was constructed of Monel metal for use in the determination of the concentration of hydrogen fluoride, in equilibrium with a mixture of granular thorium oxide and thorium fluoride, at various temperatures. The vapor phase was passed over the granular mixture by condensing the vapor to a liquid and regenerating it by boiling. The vapor was recycled for 10 to 100 hr, until successive condensate samples had identical analyses.

The equilibrium constant was calculated, at each of the several temperatures, from the equilibrium concentration of hydrogen fluoride and the barometric pressure. These results were correlated with the Clausius-Clapeyron equation, as illustrated in Fig. 10, which permitted the calculation of the enthalpy and entropy changes in reaction.

For a system of initial reactants in stoichiometric proportions, the fraction of thorium oxide which has reacted at equilibrium defines the equilibrium degree of conversion. At 350°C, this
FURNACE TEMPERATURE, 550 °C
FURNACE CHARGE, 180 LB ThO₂
FEED RATE, 12 LB HF/HR

Fig. 8. Instantaneous and cumulative per cent of feed reacted.¹⁰

Fig. 9. Hydrofluorination equilibrium apparatus.
conversion amounts to 99.96% and at 500°C to 99.29%, as calculated from the Clausius-Clapeyron equation. Fig. 11 illustrates the equilibrium degree of conversion at various temperatures, as calculated from the equation. The dashed line indicates use of the equation beyond the experimental range.

These results are in agreement with estimates of an equilibrium constant based on thermochemical calculations and equilibrium degrees of conversion estimated from pilot-plant performance.

Hydrofluorination of Thorium Oxide—Tray-type Reactor Studies

A detailed study is under way of the effect of the various operating variables on the performance of the tray type of reactor such as is illustrated in Fig. 4. A small-scale model of this reactor was made and is being used for the study. This study will permit the separate analysis of the two rate-determining steps: (1) mass transfer of the HF from the main body of the gas stream to the surface of the thorium oxide, and (2) the surface reaction of the two reactants at the solid-gas interface. The data obtained from this study will be used to determine the optimum operating conditions for similar types of reactors.

Hydrofluorination of Thorium Oxide—Rotary-type Reactor Studies

Rotary-type reactors would enable the process to be continuously operated, which is an advantage for large-scale production. This type of reactor would also produce more intimate contact between the solid thorium oxide and the gaseous feed. More intimate contact should result in more sustained conversion rates and more efficient hydrofluorination, consistent with high product quality.

A preliminary study is under way for the purpose of planning a research program for fully evaluating the performance of the rotary-type reactor in terms of the operating variables.

Conversion of Thorium Oxide to Thorium Fluoride—An Alternate Process

A preliminary study has been made of the conversion of thorium oxide to thorium fluoride by the use of ammonium bifluoride. Consistent yields of better than 98% have been obtained by reacting ammonium bifluoride and thorium oxide at 500°C for a period of 2 hr, using a molar ratio of 8:1. High yields require the pulverizing of thorium oxide and the intimate mixing of the reactants. The excess ammonium bifluoride is volatilized at this high temperature. Further studies are to be made on the process itself, and on the reduction of thorium fluoride prepared in this manner.
Calcining Thorium Oxalate

Early work on the conversion of thorium oxalate to thorium oxide, indicated that below 650°C an oxycarbonate was formed, and above 650°C the resulting oxide was less active to hydrofluorination. Several experiments are being planned that will provide quantitative answers to the questions raised by these indications.

Drying Thorium Oxalate

One drying experiment, under constant drying conditions, was made on wet thorium oxalate. The data obtained from this experiment were used in the design of the drier described in detail in this paper. The study was not complete, and experiments are being considered for determining the effect of the operating variables on the time required to dry the thorium oxalate filter cake.

SUMMARY

The Ames laboratory process for producing anhydrous thorium fluoride suitable for metal production has been described in detail. The process consists of calcining highly purified thorium oxalate at 650°C to form the oxide, which is subsequently hydrofluorinated at 550°C with anhydrous HF gas. Assuming an ample supply of thorium oxide, the present fluoride productive capacity is adequate for 50 tons of finished virgin thorium metal a year.

The experimental work leading up to the present process was described, and the elements of the process development program were discussed in detail.

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Thermal Conductivity of Uranium-bearing Material Under Irradiation at High Temperatures

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ABSTRACT

Results are given on the effects of irradiating uranium-bearing refractory materials at high temperatures. The effect of the size of the fuel particles is noted, and conclusions are drawn regarding the use of such materials in fuel elements in high-temperature piles.

INTRODUCTION

The purpose of these measurements is to determine the effects of radiation damage in uranium-bearing materials that have been irradiated under conditions similar to those which would obtain in a high-temperature reactor. In order to obtain as much data as possible from each specimen, the measurements are carried on in the pile while the irradiation is taking place. The measurement of thermal conductivity was chosen because it is reasonable to expect that the displacement of atoms in the crystal lattice of the material would most directly affect this property, and because thermal conductivity is a design parameter in calculating the thermal-rupture resistance of a pile fuel rod.

EXPERIMENTAL METHOD

The method of measuring the thermal conductivity is to measure the radial temperature differential between the center and the surface of the specimen cylinder while heat is being uniformly generated throughout its volume by the fissioning of its uranium content. The thermal conductivity may be calculated from this differential-temperature measurement as follows:

Consider an infinite cylinder of radius $R$ with a uniform heat generation of $Q$ cal/cu cm/sec throughout its volume. Within a volume of unit length and radius $r$ there are $Q\pi r^2$ cal/sec generated. This heat must flow through the cylindrical shell of radius $r$ and thickness $dr$, giving:

$$Q\pi r^2 = K2\pi r \frac{dT}{dr}.$$ 

Integrating, we have:

$$\int_0^R dt = \Delta t = \frac{Q}{2K} \int_0^R r dr = \frac{QR^3}{4K},$$

where $\Delta T$ is the differential temperature between the center of the cylinder and its surface, and $K$ is the thermal conductivity. This equation, solved for $K$, is:

$$K = \frac{QR^3}{4\Delta T}.$$ (1)
The assumption of infinite cylinder length, made in the above derivation, leads directly to the numerical factor of 4 found in the denominator. If a sphere of radius R is considered, instead of the infinite cylinder, the identical equation applies with a numerical factor of 6 in the denominator. From this it can be seen that the numerical factor for a finite cylinder must lie between 4 and 6. For the specimen cylinders used in these experiments, the factor is calculated to be 4.8. It will be convenient to express the specific heat generation, q, in watts/cu cm, so that we have \( Q = \frac{4.18}{d} \), where 4.18 is the mechanical equivalent of heat. Equation 1, adapted for our use, is then:

\[
K = \frac{q R^2}{20 \Delta T}
\]  

(2)

The assumption of uniform specific-heat generation throughout the volume of the specimen is satisfied under two conditions: (1) that the uranium fuel is uniformly distributed throughout the volume, and (2) that the attenuation of the thermal-neutron flux in the specimen is negligible.

To investigate the first condition, radiographs of cross-sectional slices of the cylindrical specimens were made at regular intervals. Figure 1 is a set of such radiographs. These radiographs show that the uranium fuel (dark areas) is quite uniformly distributed. In the case of the impregnated-graphite specimen (Fig. 1a), the individual uranium-oxide particles are too small to be seen, and the only variation in distribution is the extremely narrow dark rim, which is about 0.005 in. wide in the actual specimen. The general variation from center to edge represents, in the original radiograph, a negligible change in the fuel-material density. (See Figs. 15 and 12e in reference 2.)

In the molded-graphite uranium-oxide mixture (Fig. 1b), the larger uranium-oxide particles can be seen, but their distribution is quite uniform. In the case of the impregnated-BeO specimen (Fig. 1c), the individual uranium-oxide particles are too small to be seen, but the distribution seems to have a microscopic variation in volumes of the size of the wax-bonded granules used in the fabrication of the BeO. The macroscopic distribution is quite uniform. Tests have shown that the radiographic technique used here is capable of detecting variations of 1% of the uranium-fuel density.

To investigate the second condition, calculations of the attenuation of the thermal-neutron flux were made on a one-group model, assuming a source density of thermal neutrons in the sample equal to a fraction of the source density in the surrounding moderator of the pile. This fraction was assumed to be equal to the ratio of the graphite density in the sample to the graphite density in the pile moderator, for the case of the graphite samples. The results of this calculation show that there is a 19% thermal-flux drop from the surface to the center of the samples. Under the assumption of zero source density of thermal neutrons in the sample, a 20% thermal-flux drop was calculated. All further calculations then were made under the zero source-density assumption, since the finite source-density assumption required considerably more calculation and gave negligibly different results.

It is not immediately obvious that a 20% thermal-flux attenuation is negligible in relation to our assumption of uniform specific-heat generation. Equation 2 was accordingly recalculated using a variation of specific-heat generation in the interior of the sample equal to the variation of the thermal flux calculated above. The results of this calculation are given in Eq. 3.

\[
K = \frac{\bar{q} R^2}{21 \Delta T},
\]  

(3)

where \( \bar{q} \) is now the average specific-heat generation throughout the sample. The fact that there is only a 5% difference between the numerical factors in Eqs. 3 and 2, proves that the assumption of uniform specific-heat generation is quite good.

**EXPERIMENTAL TECHNIQUE**

The experimental method used here presents two major problems: (1) the problem of maintaining the sample temperature at a high, predetermined value, using only fission heat; and (2) the measurement of small temperature differentials at the high sample temperature. In addition to these experimental problems, there are operational conditions that must be met. The apparatus must be designed so that there is no chance for the escape of fission products, either during the irradiation period or during the discharge of the sample from the pile. The discharge of the apparatus must be carried out in such a
THERMAL CONDUCTIVITY OF URANIUM BEARING MATERIALS

Figure 1. Fuel distribution in experimental samples.

(a) Graphite impregnated with U₃O₈

(b) Molded graphite U₃O₈ mixture

(c) BeO impregnated with U₃O₈

Fig. 1. Fuel distribution in experimental samples.

way that its radioactivity is contained by a heavy shield at all times.

Figure 2 is a cross-sectional drawing of the pile apparatus. The sample, shown at (2), is a circular cylinder 5 cm long and 2 cm in diameter. It is encased in a skin tight 5-mil nickel sheath to decrease its emissivity. It is supported on six insulating lavite cones (3), which are held in two rings (4) that slide into the copper vacuum envelope (1). The sample is positioned longitudinally by the two steel points (5), which are supported from the end caps (14). In such an arrangement the fission heat generated in the sample must be carried away either by radiation
to the vacuum envelope or, if there is not a good vacuum in the system, by a combination of radiation and gaseous conduction and convection, (neglecting the conductivity of the supporting points).

The thermocouples used to measure the absolute and differential temperatures of the sample are shown at (6). These thermocouples are inserted in small holes drilled in the sample. There are three couples in each sample, one in the center, one just beneath the surface, and one on a \( \frac{1}{2} \) cm radius that is not in the plane of the first two. The thermocouples are usually made of 10 mil gold and constantan wires. There is one constantan lead that is common to all three couples, and there are three gold leads. These thermocouple leads are brought out of the vacuum chamber through a Kovar-glass seal (15). The glass of this seal also contains the pumpout lead and tipoff.

The glass seal is protected by a steel cylinder (13), which is screwed onto the vacuum envelope with a sealing cement in the threads. The end of the steel protective cylinder is capped with a steel plate (12), which contains four small tubes (11), lined with ceramic insulators, for the introduction of the thermocouple lead wires. These tubes are also sealed off with an insulating cement. The purpose of sealing the glass vacuum seal in a steel cylinder is twofold: (1) it must be protected against blows which might be received either in introducing the apparatus into the pile or in discharging it, and (2) it would prevent the escape of fission products if the glass vacuum seal should fail for any reason. The steel end plate (12) also contains a metal dog (10), which is locked into the end of a long aluminum tube that supports the apparatus in the pile. The thermocouple lead wires are conducted inside this tube to the face of the pile.

A dummy apparatus was built to determine the temperature at which a pile sample could be expected to operate under the thermal-insulation conditions of this apparatus. The sample in this dummy apparatus was an electrically heated, bare graphite cylinder, supported in a manner essentially identical to that described above for the typical pile sample. The dummy apparatus was operated with a good vacuum, with one atmosphere of argon, and with one atmosphere of helium surrounding the sample. The temperature of the sample was measured as a function of the heat dissipated in the sample.

The results of these preliminary tests are shown in Fig. 3. These results can be best understood by following a horizontal constant-temperature line and noting the powers required to maintain that temperature for each of the different atmospheres. For example, it is seen that it requires only 40 watts heat dissipation to maintain 700°K (430°C) in a vacuum, but with one atmosphere of argon present it requires 70 watts to maintain the temperature. This means that the argon is removing heat at the rate of 30 watts.

Calculations showed that a typical sample in the flux of the X-10 pile would generate heat at the rate of about 200 watts. The temperature of such a sample could be maintained at a maximum of 1050°K (780°C) in a vacuum, or 740°K (470°C) with one atmosphere of helium. Such an experimental temperature range seemed to be quite adequate to start with. Later in the investigation, it was found desirable to increase the thermal-radiation shielding of the sample. With the modified apparatus, temperatures of over 900°C were attained at the rate of 200 watts of heat dissipation.

The results of the heat-transfer experiments on the dummy apparatus made possible a check of the rate of heat evolution of the pile specimen by measuring its equilibrium temperature. Tests on the dummy apparatus, in which the emissivities of the radiating surfaces were changed and the pressure and composition of the atmosphere was varied, showed that such a measure of heat evolution was good to about 15%. This means that the dosage units, kwhr/cu cm of sample, used in this report do not depend solely on flux calculations, but that they have been checked directly to at least this accuracy (15%).

A great deal of preliminary work was done on the method of making the temperature measurements. Many thermocouples were examined with regard to materials, methods of fabrication, and methods of application. One particular requirement of this application is that the thermocouple wire used must be able to withstand a large temperature gradient without introducing significant spurious emf's. The temperature difference between the specimen and the vacuum envelope may be as high as 800°C. The length of thermocouple wire between the specimen and the Kovar tubes may be as short as 2 cm. The thermal gradient may therefore be a minimum of 400°C/cm. The differential temperature in the specimen starts...
out at about 5°C, which would give rise to about 230-microvolts emf. If the spurious emf resulting from the thermal gradient of 400°C/cm in the thermocouple lead wires amounted to as much as 80 microvolts, the initial measurement of the differential specimen temperature would be very hard to make with any accuracy. It was therefore decided to test each thermocouple wire that was to be used in the pile apparatus under a thermal gradient greater than 400°C/cm. Any wire which
developed more than 30-microvolts emf was rejected, and any combination of wires which developed more than a total of 50 microvolts were not used together.

The presence of spurious emf's in the thermocouple readings on a specimen under irradiation in the pile were detected by an examination of the variation of the differential temperature of the specimen as the pile power was changed by a small amount. According to Eq. 2, the differential temperature, \( \Delta T \), is directly proportional to the pile power (since \( q \) is directly proportional to pile power). The absolute temperature of the specimen, and therefore the temperature gradient in the thermocouple lead wires, is proportional to about the fourth root of the pile power, since most of the heat transfer from the specimen is by radiation. This then allows the differentiation of the two emf's. That part of the differential temperature can be read on the remaining two and the experiment can go on. The three differential temperatures can be compared by Eq. 2 to show up any spurious emf's not common to all three.

EXPERIMENTAL SAMPLES

To date results have been obtained on graphite impregnated with an aqueous solution of uranyl nitrate, which is dried and fired to \( \text{U}_3\text{O}_8 \); on graphite molded from a coke-pitch-\( \text{U}_3\text{O}_8 \) mixture, baked and graphitized at 2450°C; on a hot-pressed \( \text{BeO}-\text{U}_3\text{O}_8 \) mixture; and on dust-pressed low-density \( \text{BeO} \), impregnated with \( \text{U}_3\text{O}_8 \) in a manner similar to the first graphite mentioned.

There is considerable difference in these sample types from a structural point of view. In the case of both the impregnated graphite and the impregnated \( \text{BeO} \), the \( \text{U}_3\text{O}_8 \) is not an integral part of the structure but merely occupies the small pores that were initially present in the body. The crystal size of these \( \text{U}_3\text{O}_8 \) particles is very small, of the order of 2 microns. These small particles are aggregated to some extent in the high-percentage impregnations to give aggregates of about 5 microns in diameter. These structures are shown in Fig. 4. Figure 4a shows an electron photomicrograph of the individual crystals of \( \text{U}_3\text{O}_8 \), which are found in the impregnated structures. Figure 4b shows the actual aggregated structure of these crystals. This picture is a light photomicrograph of the \( \text{U}_3\text{O}_8 \) structure that remains after the graphite has been completely burned away in an impregnated-graphite sample. Figure 4c shows a magnified radiograph of one of the molded-graphite samples. Here it is noted that many of the uranium-oxide particles are quite large (50 microns), being easily visible in this radiograph. These particles are probably more intimately a part of the overall structure, since they have essentially been cemented into place by the pitch in the molding process. The \( \text{U}_3\text{O}_8 \) particles in the hot-pressed \( \text{BeO}-\text{U}_3\text{O}_8 \) mixture are shown in Fig. 4d. These particles are larger than those of the molded graphite, and they are quite an integral part of the structure of the ceramic.

These differences in structure imply two effects: (1) The particles which are an integral part of the structure of the body will have a significant effect on the thermal conductivity of the body. Damage to these particles will then be reflected as a change in the thermal conductivity of the whole body. In the case of the impregnated bodies, the effect of the presence of the \( \text{U}_3\text{O}_8 \) should be negligible, and the damage sustained by the \( \text{U}_3\text{O}_8 \) particles themselves should not affect the whole body. (2) The size of the \( \text{U}_3\text{O}_8 \) particles determines the relative number of fission recoil fragments that escape from the particles themselves and enter the matrix body structure. For a given fission flux, the change of thermal conductivity of a body containing small \( \text{U}_3\text{O}_8 \) particles should be greater than that of a similar body containing large \( \text{U}_3\text{O}_8 \) particles.

These two effects may oppose each other as in the case of the hot-pressed vs. the impregnated \( \text{BeO} \). In the hot-pressed body the \( \text{U}_3\text{O}_8 \) particles are very much larger than in the impregnated
body, and one might, therefore, expect the damage rate to be less for the hot-pressed body. However, the U₃O₈ particles in the hot-pressed body are an integral part of its structure, while those of the impregnated body are not. This might lead one to expect that the damage rate would be greater in the hot-pressed body.

All impregnated-graphite samples were prepared from National Carbon Company B-1508-A graphite, which has a specific gravity of about 1.4. This stock was chosen both for its low density and its small and uniform grain size. The low density is desirable in order that it may be impregnated to the desired concentration in a single operation. The uniformity of the stock is required to ensure the uniform impregnation necessary to the desired uniform heat generation throughout the sample. Uniformity of density throughout the sample is also necessary to ensure uniformity of thermal conductivity in the sample, since the thermal conductivity of graphite is a sensitive function of density.

The graphite was received in the form of 3-in.-diameter extruded bars. The 2 x 5 cm specimen cylinders were cut from the bars with the cylinder axis parallel to the axis of the bar. Each of these specimen cylinders was then tested for uniformity of density by placing it on the surface of a pool of mercury and noting the presence or absence of a preferred orientation. All cylinders which showed any tendency to a preferred orientation were rejected for pile experiment use.

The hot-pressed BeO-U₃O₈ mixture samples were prepared by the Norton Company. They had
a specific gravity of about 3.2. These samples were received with the central holes molded in, so that the mercury test for uniform density would be inconclusive unless the concentricities of the holes were accurately known.

The dust-pressed BeO sample cylinders were made at the Battelle Memorial Institute. This material had a specific gravity of about 1.9 and in almost every case passed the mercury test for uniform density. These samples were dust pressed from 65-mesh wax-bonded granules, fired at 1700°C, and finally ground to size. The granular structure is still apparent in the samples after impregnation as shown by Fig. 1c.

The molded-graphite samples were prepared at the Oak Ridge National Laboratory under the direction of Dr. H. G. MacPherson of the National Carbon Company. These samples were molded of a mixture of petroleum coke flour, pitch, and U₃O₈, baked 16 hr at 175°C, carbonized 1 hr at 1000°C, and graphitized for ½ hr at 2450°C. The uranium was still present after this treatment, mainly in the form of oxide. There was some evidence of a uranium-carbide skin formation over the oxide particles, but there was no large-scale carbide formation. The density of these samples was found, by the mercury check, to be quite uniform. It should be pointed out that the mercury-check method of determining the density uniformity only shows the circumferential uniformity and shows nothing of the longitudinal or radial uniformity. However, this type of uniformity ensures a symmetrical temperature distribution in the sample, which is also that is necessary. The specific gravity of these molded-graphite-U₃O₈ samples is about 1.8.

RESULTS

The results of the irradiation of these samples are given in the form of curves of relative differential sample temperature plotted against total kwhr of fission heat evolved per cubic centimeter of the sample. If the relative differential sample temperature is given by \( \Delta T/\Delta T_p \), where \( \Delta T_p \) is the initial differential sample temperature at the beginning of an experiment and \( \Delta T \) is that at a given dose, it is equal to the relative thermal resistivity \( R/R_p \), since the temperature drop in a sample is directly proportional to its thermal resistance. The relative thermal conductivity \( K/K_p \) would be the reciprocal of the temperature or resistivity ratios.

Figure 5 shows a typical radiation-damage curve plotted directly from the recorded data, temperature corrected, but without any averaging or smoothing. The lower curve shows the increase of relative thermal resistivity as the radiation-dose increases. The upper curve is a monitor of the absolute temperature of the sample as the experiment progresses. The sample represented here is an impregnated-graphite sample. The scatter of the thermal-resistivity points gives an indication of the precision of the typical sample measurement when the operation is proceeding properly.

Figure 6 shows the results obtained to date on impregnated low-density (sp gr = 1.4) graphite. The initial value of the thermal conductivity in the radial direction of these samples was about 0.1 cal/sec cm x °C. The rate of radiation dosage was about 10 watts/cu cm. There are three samples represented in these two curves, two at the 775°C temperature, and one at 630°C temperature. The crossing of the two curves is probably not significant since so few samples are represented. The marked increase in damage rate above 20 kwhr/cu cm total dose seems to be significant since it is shown by all three samples. The fact that the higher temperature curve shows a lower initial rate of damage, while reasonable, should be confirmed by more samples before being considered significant.

The minimum value of the thermal conductivity of the high-temperature sample, showing the apparent saturation effect, is about 0.0025 cal/sec cm x °C at the high temperature. This value is very nearly equal to the value of thermal conductivity found at a temperature of 775°C for an ungraphitized carbon body molded from the same materials and baked to 775°C. This fact would lead one to believe that the apparent saturation is a true saturation since the irradiated impregnated-graphite body would appear to be as disordered as can be expected at this temperature.

Figure 7 shows a comparison of the results shown in Fig. 6 with previous data on the change of thermal conductivity in irradiated graphite. The only previous experiments on irradiated graphite were made using fast-neutron irradiation, so that comparison with the fission-fragment irradiation reported here is quite difficult. The assumption is made that in the early stages of
Fig. 5. Early stages of radiation damage to impregnated-graphite sample 3.
radiation damage the effect is independent of the type of radiation.

The thermal resistivity of the pure graphite after irradiation and annealing is then compared to its initial thermal resistivity. The comparison between the relative thermal resistivities obtained in this way with those obtained by measurement on the impregnated-graphite sample while it is being irradiated at the annealing temperature, is made by adjusting the initial slopes of the relative thermal-resistivity vs. dosage curves to coincide, and plotting both sets of data to a single arbitrary-dosage scale.

The comparison shows that for the samples that were annealed simultaneously with the irradiation and the measurement, there is a considerably smaller total effect at large doses than for those samples that were irradiated cold and subsequently annealed to saturation. This may be accounted for by the assumptions (1) that there is an association of lattice imperfections (displaced atoms or lattice vacancies) which requires an unusually high activation energy for removal by annealing, (2) that the association process depends on the concentration of the lattice imperfections, and (3) that the samples damaged at a high temperature maintain a low concentration of lattice imperfections through their removal by annealing almost as soon as they are formed. The samples damaged at low temperatures cannot maintain a low concentration of lattice imperfections through annealing, therefore, the association process is greatly enhanced in these samples.

Figure 8 shows a comparison between the results obtained on impregnated graphite and molded graphite. The dosage rates of the two samples shown here were very nearly equal at about 10 watts/cu cm. The temperatures of operation of the two samples were almost identical, ranging between 630 and 650°C.

The marked difference in the observed effects may be accounted for on the basis of the difference in the size of the uranium-oxide particles present in the two cases. In the case of the molded graphite, the average size of the uranium-oxide particles is large compared to the range of
a fission fragment in uranium oxide. This would suggest that most of the damaging effects of the radiation would be sustained by the uranium oxide rather than the graphite structure. In the case of the impregnated graphite, the uranium-oxide particle size is comparable to the range of the fission fragments so that a relatively large fraction of the damaging effects of the radiation would be found in the graphite structure. If now the graphite structure is assumed to be the principal means of heat transfer through the sample, the difference in the change of thermal resistivity in the two cases is accounted for.

Figure 9 shows a comparison of data obtained on the hot-pressed BeO-\(\text{U}_2\text{O}_5\) mixture investigated here and similar mixtures investigated at the Argonne National Laboratory. The irradiation temperature of these two experiments was about 700 to 750°C. The agreement seems to be very good, considering that the operating temperature of the Argonne samples is not accurately known because it was not directly measured. The irradiation effect appears to show an early saturation in comparison to the effect in graphite. The drop in the relative thermal resistivity after about 30-kwhe/cu cm total dose may not be significant.

A comparison between BeO of specific gravity about 1.9, impregnated with uranium oxide, and the hot-pressed mixture of density about 3.2, is shown in Fig. 10. It is interesting to note here that the impregnated BeO, which has the smaller uranium-oxide particle size, shows the least damage. The reason this is true of these BeO samples, while the reverse was true of the graphite samples, may be that the large uranium-oxide particles in the hot-pressed mixture are an integral part of the structure, so that damage to them is as bad as damage to any part of the structure. In the case of the molded graphite, the uranium oxide did not seem to contribute to the thermal conductivity of the body, so that damage to it had little effect on the overall thermal conductivity. The uranium oxide in the impregnated BeO body, not being an integral part of the structure of the body, would exercise its normal effect of shielding the BeO structure to some extent from the fission-recoil fragments.

**CONCLUSIONS**

Several conclusions can be drawn from the experiments described here. First, the results as applied to the design of high-temperature pile fuel rods show that the particle size of the fuel material is quite important in determining the
total damaging effect for a given radiation dose. The method of inclusion of the fuel material in the fuel rod is also quite important in this connection. In general, it can be suggested that the fuel material be of a particle size large compared to the range of fission fragments in the fuel material, and that these fuel particles not be an integral part of the structure of the body but rather that they reside loosely in pores of the body.

The evidence would seem to indicate that the rate of radiation dosage is quite important in determining the final damaging effect. In the case of the comparison of the graphite damaged while at about 800°C with the graphite damaged at 50°C and subsequently annealed at 800°C, it was noted that the total effect at large doses was much less in the case of the samples irradiated at high temperature. The suggested explanation was based on the aggregation of lattice defects if their concentration became great enough. There are two ways of obtaining a high equilibrium concentration of lattice defects. One is to reduce the annealing rate while maintaining a constant dosage rate. (This was the case for the samples damaged at the low temperature). The other is to increase the dosage rate while maintaining a constant annealing rate. This latter experiment has not been done directly. However, the measurement of the graphite samples molded with relatively large uranium-oxide particles gives a clue to this effect. Since the large uranium-oxide particles stop most of the fission fragments within themselves, the rate of dosage of the graphite structure is considerably less than for an impregnated-graphite sample. This difference in dosage rate can be seen in the difference in the initial slopes of the two damage curves (Fig. 8). The damage curves in the latter stages, however, show a much greater difference. This last effect may be due to the greater degree of lattice defect aggregation in the case of the impregnated samples which sustain the higher actual-dosage rate. This would indicate that dosage rate is quite important in determining the final effect of radiation on graphite samples irradiated with a given total dose. Direct experiments should be done on the effect of dosage rate as soon as possible if the use of graphite is contemplated in a high-flux high-temperature pile.

From the comparison of the results obtained for impregnated graphite with those obtained for pure graphite bombarded with fast neutrons, one could make an estimate of the relative effectiveness of a fission fragment and a virgin neutron in producing a change in the thermal conductivity of graphite if there were any way of determining the relative number of fission fragments that
escape the uranium-oxide particles sufficiently to contribute to the damaging of the graphite structure. If it is assumed that they all escape effectively, the relative effectiveness may be readily calculated.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of H. E. Robertson, Jan Carpenter, and I. T. Humphreys for sample preparation; the assistance of R. Berggren for special testing; and the assistance of Jean Kincaid for data reduction.

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November 1948
A Technique for Producing Boron-Aluminum Compacts

By Harold Hirsch
Knolls Atomic Power Laboratory, General Electric Company,
Schenectady, New York
Report MEMO-HHH-1

ABSTRACT

A process is described whereby a brittle, non-reactive material like boron can be formed into simple shapes of high boron density by the use of a metal binder such as aluminum, copper, or lead using relatively low temperatures. The process in essence consists of blending the proper mixture of the two powders and hot pressing in a steel die at temperatures below the melting point of the binder. Cans prepared from boron 10 and aluminum by this technique will be used to study the neutron fission and capture cross section of reactor materials in the intermediate energy range.

INTRODUCTION

A series of experiments have been initiated by the experimental physics section of the Knolls Atomic Power Laboratory to study the effect of neutrons of intermediate energy on certain fissionable materials. The neutron spectrum is investigated by placing these materials in shields or filters composed of various substances having different energy cut-off values. The boron 10 isotope is a suitable material for such shields where neutrons of energy values 200 electron volts or higher are to be eliminated.

At the request of the physics section, the fabrication of such boron 10 shields was undertaken by the metallurgy group. The samples to be irradiated were placed in platinum capsules, which in turn were located inside boron "cans" actually consisting of three sections: (1) a top cover or cap, (2) a cylinder, and (3) a bottom cover; the two covers are identical, hence two shapes were required.

Fig. 1 shows a drawing of the cover and cylinder, both to be mounted in aluminum cans as illustrated in a later figure.

These covers and cylinders were required in three boron densities: 1.5 g/cc, 1 g/cc, and 0.5 g/cc. This report is an account of the methods developed for successful fabrication of such boron shields.

The Function of the Binder

Boron is a highly refractory material having a melting point of about 2300°C, which is much too high for any casting operation. It has been compared in brittleness to diamond and is extremely hard and abrasive even at elevated temperatures which together with its reactivity at high temperatures makes usual powder metallurgical operations with the elemental powder extremely difficult. While it forms a great many compounds with most metals, very little success has been achieved by hot pressing or cold press-sintering such mix-
Receiving little encouragement from these approaches and bearing in mind that the powder was lent to the laboratory by the Atomic Energy Commission who requested it to be returned as assembly can be handled in a reasonable time after pile exposure, and possess sufficient ductility to enable uniform density compacts to be produced. Four materials seemed to meet these requirements—aluminum, gold, copper, and lead in approximately that descending order of preference.

MATERIALS

Boron

The information supplied by the Atomic Energy Commission along with the powder stated that it was prepared by decomposition of a volatile gas of boron on a hot tantalum wire and then pulverized to what was called "200 mesh" size. An actual size analysis of the boron showed this description to be somewhat in error as indicated by the following tabulation.

<table>
<thead>
<tr>
<th>U. S. Standard Percentage of Sieve No.</th>
<th>Total Powder Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>+100</td>
<td>1.68</td>
</tr>
<tr>
<td>-100, +140</td>
<td>14.93</td>
</tr>
<tr>
<td>-140, +200</td>
<td>17.58</td>
</tr>
<tr>
<td>-200, +270</td>
<td>29.51</td>
</tr>
<tr>
<td>-270, +325</td>
<td>18.39</td>
</tr>
<tr>
<td>-325</td>
<td>17.80</td>
</tr>
</tbody>
</table>

Apparent density — 0.73 g/cc
Tapped density — 1.38 g/cc

The powder as viewed under the microscope is angular and jagged in contour which is what would be expected of a brittle, glassy material.

From the chemical standpoint, the analysis supplied with the powder states that it is composed of 96–97% boron with 94.1% boron 10, the impurities including 0.07% iron, possible traces of nickel, aluminum, and tantalum, and the balance unknown. However, when the compacts were x-rayed to detect irregularities, density differences, and possible pockets or cavities formed by bridging, a number of small dense spots were noted to be distributed throughout all the specimens; these appear as black spots in Figs. 2 and 3. The amount of these increased as the density of the boron increased, and radiographing the boron and aluminum separately definitely proved that the high density particles were incorporated in the boron. It was surmised that this impurity was probably introduced during the pulverizing operation after the chemical analysis was made. Very likely an iron mill was used since powder move-

*See The Consolidation of Boron, F. G. Stroke, Los Alamos, Report LA 127.
ment was observed when a magnet was applied to the powder. Iron particles would account for the radiographic effects mentioned. Nevertheless, the density of the powder as determined with a specific gravity bottle was 2.00 g/cc, considerably below the theoretical density of 2.3 g/cc, the difference probably due in part to blocked off pores in the powder.

Metal Binders

All of the metal binders used which include aluminum, lead, copper, and gold were powders fine enough to pass through a 325-mesh screen. The copper powder was cleaned first in dry hydrogen at 400°C before using, the other three being used as received.

Silicon

Since the boron was considered to be extremely valuable and losses had to be kept to an absolute minimum, all preliminary investigations were conducted with silicon, an ideal choice because of its similar physical characteristics to boron and, like the latter, essentially nonreactive with the binders within the temperature range of operation. The density of this powder as determined with the specific gravity bottle was also lower than the theoretical value—2.20 g/cc compared to 2.4 g/cc.

EXPERIMENTAL PROCEDURE

In the course of some previous work with boron powder, the author had succeeded in preparing compacts having a boron density of 2.1 g/cc (the theoretical density of crystalline boron is 2.3 g/cc) employing silver as the binding agent. The technique consisted of mixing an ammonium hydroxide solution containing a weighed amount of silver acetate with the boron, evaporating the solvent and decomposing the acetate leaving silver
partially coating the particles of boron. The mixture was then warm pressed at 500°C using 40 tons/in². The high density so achieved was in a large part due to proper particle size blending of the boron.

Because of the success of this earlier work, it was decided to investigate the feasibility of this technique using copper and gold salts of suitable characteristics. Three copper salts, the acetate, and the two carbonates, azurite and malachite, and one gold salt, the chloride, were selected for investigation; lead and aluminum cannot be handled in this fashion.

In addition, all four metals were added separately as pure powders to the boron, the percentage being varied to ascertain the optimum mixtures for maximum density with minimum sacrifice in strength. The temperature of pressing was varied from room temperature up to 500°C; higher temperatures presented die problems and the possibility of oxidation of the boron.

EXPERIMENTAL RESULTS

Investigation with Silicon

All of the preliminary work was conducted with a hardened steel die having a ½-in. cavity. The die was used double acting, and aquadag was adopted as the wall lubricant, being superior to stearic acid even for room temperature pressings. The type of steel limited the operation with this die to a maximum temperature of 350°C, the heating being done in a small electric muffle furnace.

As would be expected, hot pressing proved superior to cold pressing in all cases, and the optimum concentration centered around 10 vol% of the binder (obviously, the weight and the at% would be different for each binder). Lead had an advantage over the other binders for pressings could be made near its melting point whereas the limit of 350°C was considerably below the melting points of the others. The highest density was obtained with a 10 vol% lead compact (34% by weight), pressed at 300°C using a pressure of 60 tons/in²—a silicon density of 1.75 g/cc or 80% of the theoretical. The densities were somewhat lower with copper but the pellets were harder and stronger, and were better in all respects than the results with the other binders. Obtaining the copper by decomposition of one of its salts produced much better compacts than a straight powder mixture but had a distinct disadvantage in that the boron would have to be handled a great deal more which would undoubtedly increase the losses. The basic carbonate, azurite, gave the best results of the three salts tried—malachite, azurite, and the acetate.

Since the shields would be heated in the course of being irradiated, probably to a temperature ranging around 200°C, representative samples of the various pressed mixtures were heated in air at 250°C for a period of one week. None of the samples showed any change except the ones bonded with lead and here the expansion was so great (2–3%), that it was thought that there was danger of the assembly binding in the aluminum sleeves from which it must be readily removed after irradiation, and so lead was discarded as a possible bonding material.

The die for producing the final shaped pieces was prepared from a tungsten, molybdenum, chromium, vanadium high-speed tool steel so that temperatures up to 600°C could be achieved. It was hardened to Rc 60–62 and did not show any wear after some fifty pressings. Fig. 4 shows the ⅞-in. diameter die and punches, the latter fitting into the 1.175-in. cavity with a clearance of 0.0004–0.0006 in. The bottom or ejection end of the cavity was given a taper of 0.008 in./in. for a distance of one inch, an essential feature for removing such relatively fragile and nonductile pieces without laminar.

With the new die, densities comparable to those obtained with lead were achieved with aluminum and copper, and the compacts had somewhat higher strengths.

Aluminum was finally adopted as the binder for the boron for it was nearly as good as the copper and was definitely superior on the basis of its absorption and scattering cross sections.

Investigation with Boron

On substituting boron for silicon and pressing at 500°C, it was found that the aluminum content had to be increased from 10 to 15 vol% (17.1 wt%) to obtain adequate strength and resistance to density. However, the boron density was hardly decreased and so this mixture was adopted for the production of shields having the highest boron density.

In addition to the high density shields, two additional sets were required for the lower energy cut-offs, namely boron densities of 1 g/cc and 0.5 g/cc; 45.6% by volume of aluminum (49.6%...
TECHNIQUE FOR PRODUCING BORON-ALUMINUM COMPACTS

by weight) was used for the former and 72.8% by volume (75.9% by weight) for the latter, resulting in a porosity of 20% in both cases. The porosity was kept high intentionally to reduce the amount of binder. An average boron density of 1.52 g/cc was obtained for the high density compacts using a pressure of 52 tons/in². For the 1 g/cc compacts, 9.8 tons/in² was used for the caps and 10.2 tons/in² for the cylinders, while 0.5 g/cc compacts required 3.7 tons/in² and 4.2 tons/in², respectively. These pressings were all made at 500°C.

The cans and caps were radiographed to determine the density variation within each part caused by wall and internal friction. Employing an Anso-Sweet Densitometer, a series of longitudinal traverses on the cylinders showed that in most cases the maximum density change in any cylinder (comparing top to center) was less than 10% except in the case of the high density compact where some variations as large as 12-14% were found. Variations of this magnitude are certainly to be expected with such a non-yielding material as boron, and the physics group thought that they were still within tolerable limits. Examination of the films, however, revealed another unsuspected condition which apparently was a more serious fault. Studying Fig. 3, one can see a great number of light patches, some having a diameter approaching ¼ in. These represent areas of lower density than the main portion of the compacts and could be due to either cavities or pockets (formed by bridging or gassing) or lumps of some less dense material such as unmixed boron. The latter was suspected to be the actual case especially after the patches were eliminated in subsequent pressings by carefully mixing the powders on glazed paper with a spatula instead of tumbling end over end in a bottle placed in a ball mill. It

Removal of the pieces from the recessed punches required careful manipulation throughout the operation for although the compacts expanded only 0.5-1%, the abrasive nature of the material was enough to anchor the raised portions to the die and breakage often occurred. The conditions finally established and used for all the boron pressings were as follows: (1) coat the plungers first with aquadag, (2) coat with a film of aluminum flake, (3) precompact the powder at 20 tons/in² before heating (necessary only for the high density compacts), (4) heat the die and contents in a furnace for one-half hour, (5) hold at final pressure for a few seconds, and (6) remove the pieces while still warm — 200 - 300°C.

Fig. 4. High speed steel die and plungers with the compacts shown in the foreground.
was definitely proved to be the case when a few compacts were broken apart for reprocessing and the boron agglomerates were revealed. A rough calculation showed that the remaining shields with patches could be used without reprocessing which, of course, would not have been the case had these patches been due to pores, for in this condition the neutron path would have been too variable and unpredictable.

![Image](image.png)

Fig. 5. An unassembled completed capsule is shown to the left and the manner of canning is illustrated to the right. The bottom core and cylinder is canned as a unit.

Production of the Boron Shields

Three cylinders and six caps were made for each density value making a total of nine complete assemblies. A completed assembly is shown in Fig. 5, the nominal dimensions being as shown in Fig. 1. The dimensional tolerances were quite liberal but it was thought that the height of the cylinder could be maintained to ±.005 in. and the thickness of the cap to ±.002 in. if necessary. The diameter of the compacts is, of course, controlled by the actual diameter of the die, the compacting pressure, and the composition. For any given set of conditions, it does not vary more than ±.002 in.

The compacts had sufficient strength to withstand reasonable handling and did not dust unless bent over the chamfered edges. The two sections were assembled and placed in the regular aluminum cans for pile slugs in such a way that the two could later be cut apart for removal of the platinum capsule after irradiation. After cooling, the boron compacts were pulverized and the aluminum removed by dissolving in a 5% NaOH solution which has been demonstrated not to attack the boron.

ACKNOWLEDGMENT

The very competent assistance of Miss Alice Mann who performed all of the laboratory work described is gratefully acknowledged.

March 1949
Recrystallization
of Cold-Rolled Uranium

By E. E. Hayes
Metallurgical Project, Massachusetts Institute of Technology
Report MIT-1021

ABSTRACT

The first phase of this study was to determine the recrystallization range of cold-rolled, fine-grained uranium as a function of per cent reduction. With a final reduction of 25% uranium has a recrystallization range of 450-500°C (1½ hr annealing time). This range is lowered approximately 50°C for reductions over 90%. For lower reductions the recrystallization range is somewhat higher. Below 2% reduction complete recrystallization does not occur for an annealing time of 1½ hr.

After completion of the first phase of the program, additional material was annealed in the gamma range to obtain the large gamma grain size to investigate the possibility of producing suitable, fine-grained material by subjecting coarse-grained material to moderate amounts of cold rolling followed by annealing for recrystallization. Uranium given this treatment recrystallized with a resulting fine grain size at approximately the same temperatures as above (reductions of from 2% to 25% only were made). The resulting fine grains, however, appear to form clusters of grains with orientations similar or related to the original coarse-grained material.

PROCEDURES

The uranium metal used in this study had been vacuum cast and extruded with a copper jacket in the alpha region at approximately 800°C (1105°F) to a diameter of 1.3 in. and with a reduction ratio of 14:1. The composition was similar to uranium
E. E. HAYES

being cast today, having a carbon content of 0.05% and 60 ppm of iron. Fig. 1 shows the microstructure* of the as-extruded stock. The structure is uniformly fine-grained from the surface to the

center of rod with equiaxed grains. The inclusions are normal for this type of material.

To get the material into suitable form for final reduction by cold rolling, the bar was cut into short lengths and rolled into slabs at 500°C to thicknesses of ¼ in. to ¼ in. Fig. 2 shows micro-

structure of the material in this condition and indicates that some cold working took place in this preliminary rolling. The resulting slabs were cut into 2 in. lengths and machined to different thicknesses so that final thickness of each rolled piece would be approximately the same (¼ in.) for most degrees of rolling. The thickness of the final rolled pieces for the extremely high reductions was necessarily thinner.

After machining, most of the 2-in. pieces were heated at 600-610°C for 48 hr to try to get the material in as uniform condition as possible.

Fig. 1—Alpha-extruded rod as-received, transverse section, polarized light. 100×

Fig. 2—Same as Fig. 1 but hot-rolled at 500°C, transverse section, polarized light. 100×

Fig. 3 shows the microstructure after this annealing treatment. It is very similar to the as-extruded metal with somewhat more variation in the grain size. Other pieces were heated at 843°C (1550°F) for ¼ hr to obtain a large gamma grain size (Fig. 11) for the second phase of the work.

The annealed 2-in. pieces were then cold rolled with reductions varying from approximately 1% to 94.4% in the case of the alpha-annealed samples and with reductions of 2% to 25% for the gamma-annealed samples. Cold rolling was accomplished by reductions of approximately 5 to 10/1,000 of an inch or less per pass. The large grained material was more difficult to roll on account of cracking. If too large a reduction was made on any of the material, the piece would split at one end through the center with the fissure parallel to the rolling surfaces. The highest reduction made on the alpha series specimens resulted in a slight crack of similar nature through

*Specimens were electropolished by means of an ethylene glycol-phosphoric acid-ethyl alcohol solution.
RECRYSTALLIZATION OF COLD-ROLLED URANIUM

The as-rolled specimens were cut by means of a cut-off wheel and sealed off in evacuated pyrex glass tubes and annealed for a time of 1 1/2 hr at different temperatures at intervals of 25°C. Some specimens were annealed for varying lengths of time, lead being used as a heating medium for the shortest periods of heat treatment. All microstructures were examined visually and hardness values taken on most samples.

The results obtained will be presented in two parts, designated as the alpha-annealed series, which includes all the specimens that had received the 48-hr anneal at 600°C prior to cold rolling, and the gamma-annealed series, which includes the specimens that had been annealed at 843°C to obtain a large gamma grain size.

OBSERVATIONS

Alpha-Annealed Series

Fig. 4 is a graphic representation of the recrystallization range of the fine-grained uranium which had been cold rolled with from 4 to 94.4% reduction in thickness. The magnitude of the range is approximately 50°C except for the very low reductions where it is greater.

The identification of the beginning and completion of recrystallization was somewhat difficult in the microstructures of the fine-grained specimens with low reductions. A few back-reflection x-ray patterns were taken to check the interpretation of these microstructures and there was general agreement in the results.

For reductions of up to approximately 2% no evidence of recrystallization was noticed except some grain coarsening* in the 2% specimen at about 550-600°C.

Fig. 4 — Recrystallization temperature of cold-rolled uranium vs per cent reduction.

*Fine-grained uranium rolled 2% and annealed with very slowly increasing temperature up to 600°C, holding at this temperature for approximately 48 hr will result in an extremely coarse-grained structure.
The recrystallization temperature of gamma-annealed material, also indicated in Fig. 4, is discussed in the next section.

Some typical recrystallization structures as well as the as-rolled structures are as follows:

Figs. 5a-5h show the as-rolled structures for the alpha-annealed specimens with reductions of 2 to 94.4%. For the lighter reductions, the grains are distorted only slightly, the main effect of the rolling being to produce deformation bands. The grains begin to become distorted at about 10 to 15% reduction and at very heavy reductions the effect of layering is very evident.

Several series of photomicrographs illustrate the course of recrystallization for different reductions.

Figs. 6a-6e illustrate the series rolled 4% followed by annealing at temperatures of 500°C to 600°C. The first evidence of recrystallization is at 525°C where an abnormally large grain has been formed. At successively higher temperatures recrystallization has proceeded further being associated with considerable grain growth. Recrystallization is nearly complete at 600°C.

The 15% reduction series is illustrated in Figs. 7a-7e. Recrystallization appears to begin at 450-475°C and is complete at about 500-525°C.

In the 45% reduction series (Figs. 8a-8h) a few new grains are evident at 425°C when viewed at 500x; while at 100x magnification they cannot be identified. At 475°C a completely new set of grains is present although some strain bands are still present. The resulting grain size is somewhat smaller than those resulting from lighter reductions.

For the very heavy reductions, it was extremely difficult to obtain clear pictures in the cold-worked and partially annealed specimens. Examination generally had to be made at 500x for the structure to be clearly revealed. Figs. 9a-9e show the recrystallization of the 94.4% reduction for annealing temperatures of 375°C to 450°C and 600°C. At 375°C, the structure is the same as that of the “as-rolled” condition. The photomicrograph taken of the 400°C annealed specimen does not clearly define new crystallites, although it definitely indicates a breaking-up of the rolled structure and is considered the beginning of recrystallization. At 450°C, the structure has changed to a completely new set of recrystallized grains; however, evidence of the original, elongated and compressed grains is shown by the rows of alternate light and dark grains. This effect does not completely disappear even after a 1½-hr anneal at 600°C; although the grains at the latter temperature are considerably larger (approximately the same as the 45% specimen annealed at the same temperature).

For these highly reduced specimens a very pronounced preferred orientation has resulted from the rolling as evidenced by examination under polarized light.

Hardness values were taken on all specimens prior to mounting for metallographic examination. Readings were taken from two perpendicular surfaces of each specimen (1) the transverse surface (section perpendicular to the rolling surface and also to the axis of the original extruded rod) and (2) the rolling surface that corresponded to the longitudinal section of the original rod. Every hardness reading shown (Tables 1 and 2) represents the average of 3 or 4 readings which in general had a variation of from 1 to 4 points of the Rockwell G scale. This scale was used in order that a complete series of readings from the “as-rolled condition” through the annealed condition could be made on the same scale.

For the alpha-annealed series, there was a marked difference in all hardness values between the transverse and rolling surfaces. This difference was present in the original as-extruded rod, amounting to about 7 points on the Rockwell G scale, and persisted throughout all the treatments to which the specimens were subjected. The hardness values are listed in Tables 1 and 2, and the values within the recrystallization range (Fig. 4) are given between the dashed lines. For the higher reductions, the hardness of a newly recrystallized specimen is higher than for a newly recrystallized specimen that had had a lighter reduction. This is due in part, at least, to a somewhat smaller grain size. As previously mentioned, the 94.4% reduction sample had a crack through the center which probably caused the hardness values to be lower than for the 92.5% reduction. The Rockwell 30N scale was used for these last two reductions on account of the thinness of the specimens. The hardness of the 92.5% as-rolled sample corresponds to a Rockwell C hardness of 45.

From the hardness data indicated in the two preceding paragraphs, it is obvious that the material was not in a completely random condition. As alpha-extruded uranium is said to have a preferred orientation, randomly distributed about the rod axis, this difference in hardness can probably be attributed to this orientation.
RECRYSTALLIZATION OF COLD-ROLLED URANIUM

Table 1 — Transverse surface hardness — Rockwell G scale.

<table>
<thead>
<tr>
<th>% Reduction</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>55</th>
<th>65</th>
<th>75</th>
<th>85</th>
<th>92.5</th>
<th>94.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-rolled</td>
<td>73</td>
<td>75</td>
<td>80</td>
<td>84(\frac{1}{2})</td>
<td>87</td>
<td>87</td>
<td>90</td>
<td>92</td>
<td>93</td>
<td>94</td>
<td>95</td>
<td>96</td>
<td>98</td>
<td>99</td>
<td>60*</td>
<td>59*</td>
</tr>
<tr>
<td>375</td>
<td>73</td>
<td>73</td>
<td>74</td>
<td>77</td>
<td>80</td>
<td>81</td>
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<td>85</td>
<td>89</td>
<td>92</td>
<td>93</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>55*</td>
<td>33*</td>
</tr>
<tr>
<td>400</td>
<td>73</td>
<td>73</td>
<td>74</td>
<td>77</td>
<td>80</td>
<td>81</td>
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<td>89</td>
<td>92</td>
<td>91</td>
<td>91</td>
<td>51*</td>
<td>47*</td>
</tr>
<tr>
<td>425</td>
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<td>74</td>
<td>77</td>
<td>80</td>
<td>81</td>
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<td>44*</td>
</tr>
<tr>
<td>450</td>
<td>73</td>
<td>72</td>
<td>72</td>
<td>72</td>
<td>77</td>
<td>77(\frac{1}{2})</td>
<td>80</td>
<td>81</td>
<td>80</td>
<td>82</td>
<td>82</td>
<td>85</td>
<td>86</td>
<td>87</td>
<td>87</td>
<td>46*</td>
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<tr>
<td>475</td>
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<td>72</td>
<td>74</td>
<td>74</td>
<td>75</td>
<td>77</td>
<td>77(\frac{1}{2})</td>
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<td>74</td>
<td>74</td>
<td>79</td>
<td>79</td>
<td>81</td>
<td>78</td>
<td>42*</td>
<td>40*</td>
</tr>
<tr>
<td>500</td>
<td>73</td>
<td>72</td>
<td>74</td>
<td>73</td>
<td>74</td>
<td>73</td>
<td>76</td>
<td>76</td>
<td>72</td>
<td>73</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>33*</td>
<td>23*</td>
</tr>
</tbody>
</table>

*Rockwell 30N Scale.
Note: Annealing time 1\(\frac{1}{2}\) hr.
Hardness of as-received extruded rod Rockwell G 77.
Hardness of material annealed 48 hr at 600°C prior to cold rolling Rockwell G 72.

Table 2 — Rolling surface hardness — Rockwell G scale.

<table>
<thead>
<tr>
<th>% Reduction</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>55</th>
<th>65</th>
<th>75</th>
<th>85</th>
<th>92.5</th>
<th>94.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-rolled</td>
<td>82</td>
<td>84</td>
<td>86(\frac{1}{2})</td>
<td>88</td>
<td>88(\frac{1}{2})</td>
<td>92</td>
<td>93</td>
<td>94</td>
<td>96</td>
<td>97</td>
<td>98</td>
<td>100</td>
<td>102</td>
<td>104</td>
<td>64*</td>
<td>63(\frac{1}{2})*</td>
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<td>375</td>
<td>81</td>
<td>82</td>
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<td>85</td>
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<td>97</td>
<td>99(\frac{1}{2})</td>
<td>58(\frac{1}{2})*</td>
<td>60*</td>
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<td>84</td>
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<td>91</td>
<td>90</td>
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<td>95</td>
<td>95</td>
<td>96</td>
<td>56*</td>
<td>55(\frac{1}{2})*</td>
<td></td>
</tr>
<tr>
<td>425</td>
<td>82</td>
<td>81</td>
<td>83</td>
<td>82</td>
<td>85</td>
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<td>86</td>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>52*</td>
<td>52*</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>82</td>
<td>80</td>
<td>83</td>
<td>83</td>
<td>83</td>
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<td>82</td>
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<td>84</td>
<td>84</td>
<td>84</td>
<td>85</td>
<td>86</td>
<td>87</td>
<td>48(\frac{1}{2})*</td>
<td>49*</td>
</tr>
<tr>
<td>475</td>
<td>82</td>
<td>80</td>
<td>83</td>
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<td>84</td>
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<td>86</td>
<td>87</td>
<td>87</td>
<td>48(\frac{1}{2})*</td>
<td>49*</td>
</tr>
<tr>
<td>500</td>
<td>81</td>
<td>80</td>
<td>83</td>
<td>82</td>
<td>82</td>
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<td>83</td>
<td>83</td>
<td>44*</td>
<td>42*</td>
</tr>
</tbody>
</table>

*Rockwell 30N Scale.
Note: Annealing time 1\(\frac{1}{2}\) hr.
Hardness of as-received extruded rod Rockwell G 83.
Hardness of material annealed 48 hr at 600°C prior to cold rolling Rockwell G 79.
A. 2% Reduction in Thickness

B. 7% Reduction in Thickness

C. 15% Reduction in Thickness

D. 25% Reduction in Thickness

Fig. 5a–h—Microstructures as cold-rolled to various reductions, transverse section, polarised light. 100x
Fig. 5a-b — Microstructures as cold-rolled to various reductions, transverse section, polarized light. 100×
Fig. 6a–e—Microstructures of specimens with 4% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light. 100×
RECRYSTALLIZATION OF COLD-ROLLED URANIUM

Fig. 7a-e—Microstructures of specimens with 15% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light. 100×
Fig. 8a-h—Microstructures of specimens with 45% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light.
Fig. 8a-h—Microstructures of specimens with 45% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light.
Fig. 9a-e—Microstructures of specimens with 94.4% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light. 500X (except E-100X)
Several back-reflection x-ray pictures were taken of as-rolled samples to qualitatively determine the extent of line broadening as a function of reduction in thickness. Fig. 10 illustrates the patterns obtained. For a 1 to 2% reduction, there is very little broadening of the spots, but for 4% it becomes appreciable and for 7% the diffraction rings are nearly complete. At 10% reduction the density of each ring has become fairly uniform.

Effect of Annealing Time on Recrystallization Temperature.—Some specimens with 85% reduction were heated for various times at different temperatures to determine the effect of time on the recrystallization temperature. For times of 1/4 hr or more the samples were heated in evacuated pyrex glass tubes as described in the fifth paragraph under "Procedures," allowing an additional 5 to 10 minutes for the specimen to reach the furnace temperature. For 1- and 5-min treatments, the specimens were heated in lead to attain the desired temperature very quickly. The results can be summarized as follows in Table 3.

Hardness values of these specimens are listed in Table 4.
Gamma-Annealed Series

The preliminary treatment of the uranium was as described under 'Procedures.' Alpha-extruded rod was rolled at 500°C into slabs, and specimens were annealed at temperatures of from 400°C to 600°C at intervals of 25°C. The as-rolled structures are illustrated in Figs. 12a-12d. Not all the deformation or strain bands in these structures resulted from the cold

Table 3—Effect of time on recrystallization range.

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Annealing temp</th>
<th>( T_B )</th>
<th>( T_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>85%</td>
<td>350°C</td>
<td>More than 2 weeks</td>
<td></td>
</tr>
<tr>
<td></td>
<td>375</td>
<td>More than 1 week</td>
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</tr>
<tr>
<td></td>
<td>400</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td>425</td>
<td>( \frac{1}{2} ) hours</td>
<td>24 hours</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>5 minutes</td>
<td>( \frac{1}{2} ) hours</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>1 minute</td>
<td>5 minutes</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>1 minute</td>
</tr>
</tbody>
</table>

\( T_B \) — Time within which recrystallization has started.
\( T_C \) — Time within which recrystallization is complete.

Table 4—Hardness of uranium (transverse surface) rolled 85% and annealed at various temperatures with varying time—Rockwell G scale.

<table>
<thead>
<tr>
<th>Time</th>
<th>350°C</th>
<th>375°C</th>
<th>400°C</th>
<th>425°C</th>
<th>450°C</th>
<th>475°C</th>
<th>500°C</th>
<th>525°C</th>
<th>550°C</th>
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<tr>
<td>1 min</td>
<td>93</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>77</td>
<td>65</td>
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<td>5 min</td>
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<td>95</td>
<td>88</td>
<td>77</td>
<td>74</td>
<td>71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} ) hr</td>
<td></td>
<td></td>
<td>82</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} ) hr</td>
<td></td>
<td>86</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 hr</td>
<td>95</td>
<td>95</td>
<td>91</td>
<td>84</td>
<td>78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 hr</td>
<td>89</td>
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<td></td>
<td>87</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr</td>
<td>92</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1 wk</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2 wk</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Note: As-rolled hardness 99 on Rockwell G Scale.

2-in. lengths cut from these slabs were machined and annealed at 843°C for \( \frac{3}{4} \) hr (Fig. 11). After this annealing treatment to change the structure to coarse grains, the pieces were somewhat warped and the surfaces were no longer smooth necessitating some further machining to obtain flat and parallel sides. After cold rolling these pieces with from 2 to 25% reduction in thickness, individual rolling, having been prevalent in the as-annealed condition.

The recrystallization range for this material is essentially the same as for the fine-grained uranium. There is one difference, however, in that the coarse-grained material was not subjected to equal amounts of strain in all the grains. This is shown by the fact that at very low reduc-
Fig. 11—Microstructure gamma-annealed at 843°C (1550°F) for 4 hr (no subsequent reduction), transverse section, polarized light. 100x

A. 2% Reduction in Thickness
B. 7% Reduction in Thickness
C. 15% Reduction in Thickness
D. 25% Reduction in Thickness

Fig. 12a-d—Microstructures as cold-rolled to various reductions after gamma annealing, transverse sections, polarized light. 100x
Fig. 13a-c—Microstructures of gamma-annealed specimens with 2% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarised light. 100×

Fig. 14a-c—Microstructures of gamma-annealed specimens with 7% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarised light. 100×
RECRYSTALLIZATION OF COLD-ROLLED URANIUM

...itions, slight recrystallization occurred along deformation bands at a temperature lower than that at which any recrystallization took place in the fine-grained material. Also, for most of the reductions, complete recrystallization did not occur until a slightly higher temperature had been reached. An anomaly was also noted in at least one case where one specimen had perhaps several pieces of the original large grains which had not completely recrystallized at a temperature higher than that at which another specimen...
Fig. 15 — Microstructure of gamma-annealed specimen with 10% reduction and annealed at 500°C for 1½ hr, transverse section, polarized light. 100×

A. Annealed at 425°C
B. Annealed at 425°C
C. Annealed at 450°C
D. Annealed at 475°C

Fig. 16a-l — Microstructures of gamma-annealed specimens with 25% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light. 100× (except A-500×)
Fig. 16a-i—Microstructures of gamma-annealed specimens with 25% reduction and annealed at various temperatures for 1½ hr, transverse sections, polarized light. 100x (except A-500x)
exhibited in Fig. 13b, a 2% reduction sample annealed at 500°C.

2. Final resulting grain size for a completely recrystallized structure is larger for smaller reductions. (Fig. 14c shows the grain size for the 7% reduction sample at 600°C which should be compared with Fig. 16i for the 25% reduction sample also annealed at 600°C).

3. In many partially recrystallized structures some original large grains are completely recrystallized while an adjacent grain has no recrystallization. (Fig. 15, 10% reduction annealed at 500°C; also Fig. 16d, 25% reduction annealed at 475°C.)

4. Although the entire structure may be recrystallized, there may be two different resulting grain sizes, each originating from original "gamma" grains which probably received different amounts of cold working (Fig. 16f, 25% reduction annealed at 525°C).

5. In some cases there is additional evidence of the original grain structure exhibited by clusters of grains of the same size but showing a marked degree of similarity of orientation of all grains within the cluster (Fig. 16h, 25% reduction annealed at 575°C).

Most of the phenomena mentioned above can be seen in the series of pictures for specimens with 25% reduction and annealed at temperatures of 425°C to 600°C (Fig. 16). Fig. 16a merely illustrates the striking pattern of the deformation or strain bands in a specimen at higher magnification.

Hardness values were taken on the as-rolled slabs and on each specimen after heat treatment. The values obtained were too variable to give a precise indication of progressive hardening with working or progressive softening by annealing on account of the large grain size. Individual specimens varied by as much as 15 points on the Rockwell G scale. Average values are given in Tables 5a and 5b for the hardness of the transverse surfaces (surface perpendicular to the axis of the original extruded bar) and of the rolling surfaces of the slabs.

SUMMARY

The results of this study may be summarized as follows:

1. Fine-grained uranium can be cold rolled at room temperature with a final reduction of more than 90%.

2. Cold-rolled, fine-grained uranium recrystallizes over a temperature range of approximately 50°C: (a) for reductions of 4%, this range is from 525°C to 600°C; (b) for reductions of 25%, from 450°C to 500°C; (c) for reductions of 45%, from 425°C to 475°C; (d) for reductions more than 90%, from 400°C to 450°C.

3. Fine-grained uranium, cold rolled to 85% reduction will be completely recrystallized after 1 min in a lead bath at 500°C.

4. Gamma-annealed uranium (coarse grains) is more susceptible to cracking during cold rolling at room temperature than is fine-grained uranium.

5. The recrystallization range for coarse-grained uranium (annealed in the gamma phase prior to cold rolling) is approximately the same as for fine-grained uranium.

6. Recrystallization of cold-rolled uranium with large grains results in a fine-grained structure which, however, may be composed of clusters of similarly orientated fine grains; thus not eliminating all the undesired characteristics of a coarse-grained structure.

March 1949
Fabrication of $^{235}$U Discs for the General Electric Power Pile

By R. E. Eldmann and J. M. Taub
Los Alamos Scientific Laboratory

Report LA-720

ABSTRACT

The experimental critical assembly being used at the Knolls Atomic Power Laboratory of the General Electric Company utilizes thin discs of $^{235}$U metal in its construction. The discs were fabricated at the Los Alamos Scientific Laboratory through a series of casting, rolling, and blanking operations and marked and packaged for shipment. The report includes a brief description of development work which was done on the casting and rolling processes.

INTRODUCTION

The experimental critical assembly being used as a research tool at the Knolls Atomic Power Laboratory at Schenectady, New York, makes use of an assembly consisting in part of $^{235}$U discs.

The problem of preparing the $^{235}$U discs for the initial experimental work was presented to the Los Alamos Laboratory and this report describes the actual processing which was carried on in preparing the required pieces. A total of 3846 discs of two sizes was required as follows:

<table>
<thead>
<tr>
<th>Number Required</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 3450</td>
<td>1.960 - .004 + .000 in. diam by .020 ± .001 in. thick</td>
</tr>
<tr>
<td>b) 396</td>
<td>1.922 - .004 + .000 in. diam by .020 ± .001 in. thick</td>
</tr>
</tbody>
</table>

Each disc also possessed a central hole 0.194 ± .002 in. diameter to be centered within ±.002 in. Each disc was to be identified to within 0.1% as to the per cent of $^{235}$U it contained, thus involving the problem of numbering each disc and indicating the degree of enrichment. In addition, it was necessary for accountability purposes to minimize oxidation of the discs, particularly during the time the metal was being transferred from Los Alamos to Schenectady. The problem of passivating the discs was thus presented. The total weight of the discs was approximately 71 kilograms.

The actual fabricating procedures can be broken down into three major steps, namely (1) casting the rolling ingot, (2) rolling the strip to .020 in. thickness and (3) blanking the disc.

FABRICATION TECHNIQUES

Casting

All melting and casting of $^{235}$U metal was performed in vacuum furnaces operating at pres-
sures between 1 and 15 microns. The molten metal, at temperatures about 1300°C, was bottom poured from the crucible into a composite MgO-graphite mold, as shown in Fig. 1. The crucible and stopper rod material in all cases was pure, fused MgO.

The original plan for casting the rolling stock was to use investment molds and cast thin plates which would require a minimum of rolling, would possess a smooth surface for rolling, and would conserve on the amount of metal required. It was soon found that the manufacture of the investment molds was a slow and tedious process and would require a considerable amount of time of the limited number of personnel available. In addition, some of the investment mold surfaces would crack and spall during casting and make the castings unworkable or make the subsequent rolling extremely slow and complicated if the casting were to be used at all. The problem of a satisfactory investment mold could have been solved in time but the advantages of this type of mold were greatly offset by the time and personnel factors involved. Consequently, another approach was made to the mold problem and this involved the use of an all-graphite mold. The castings obtained from this mold were good dimensionally, but possessed two bad features, namely, (1) the graphite mold was never completely outgassed with the resulting castings containing blow-holes and (2) the carbon pickup in the metal was rather high. The latter problem was partially relieved by the use of a ceramic splash plate inserted into the mold.
The mold finally used for casting the rolling stock was made entirely of MgO and was inserted into a graphite sleeve to give the mold added strength. The mold proper was built up of a number of channel-like pieces of MgO, $2.375 \times 8 \times 0.250$ in. which were wired together, Figs. 1 and 2.

This assembly was then inserted into a graphite sleeve and the MgO splash plate inserted on top of the mold proper. The advantages to this type of mold were several, namely, (1) no gassing was encountered and sound castings were obtained, (2) the mold was easily assembled and disassembled, (3) no carbon pickup was encountered and (4) a smooth surface was obtained on the casting.

In the casting operation, the metal was heated to $1300^\circ$C and held at temperature until gas evolution ceased and the surface of the melt became still. The temperature was then lowered slightly and the molten metal bottom poured into the ceramic mold which was heated to temperatures between $400^\circ$C and $600^\circ$C. Five plates were cast in each mold, as is shown in Fig. 3, and pencil gates were used to feed the metal into the mold cavity. This type of gate allowed the casting to be broken from the riser instead of requiring a separate machining operation to separate the two parts.

Rolling

The cast pieces were plated with 0.003 in. thickness of silver and were given a very light pass through the rolling mill after plating in order to set the silver plate. The electroplating
was performed according to the standard practice for the plating of uranium. It was found that a plate much thicker than .003 in. would peel during the early stages of rolling. This rolling procedure has been found to make the silver plate adhere more tightly to the base metal. It had been ob-

served that flaking of the silver plate sometimes occurred during the first annealing operation if the rolling operation was not resorted to. The plates were then annealed at 600°C in vacuum, the primary purpose of the anneal being to remove hydrogen which might have been absorbed during the plating operation and would cause embrittle-
ment of the metal.

Prior to the actual working of the U^{235} material a short development program on rolling and blank-

required several months to complete all of the rolling necessary for supplying the blanking stock. Consequently, warm rolling of the material was resorted to. A Dow-Corning 550 silicone bath held at temperatures between 250°C and 300°C was used to heat the rolling stock between passes. The bath and rolling mill are shown in Fig. 4. Im-
mersion heaters were used in the tank to heat the silicone. The hood, shown in Fig. 4, was set up to draw off the fumes which are present when

Fig. 3—A uranium plate casting after removal from the mold. Note pencil gates between riser and plates.
silicone is heated to the temperatures indicated. The rolling stock rested upon a stainless steel screen situated in the silicone bath, the immersion heaters being located on the under side of the screen so that the rolling stock would not come in contact with the heating elements and possible between anneals being well over 50%. It was evident also, that the higher the rolling temperature the easier the metal rolled. Since no phase changes occur on heating pure metal to these low temperatures, the only explanation available at this time is that the metal is more

Fig. 4.—A photograph of the Standard four-high rolling mill and the silicone heating bath.

become overheated locally. The rolling mill used on this job was a Standard four-high mill with 2.5-in. diameter work rolls and 9-in. diameter backing rolls and possessing an 8-in. face.

The use of warm rolling techniques increased the speed of the process many times and eliminated most of the annealing operations. In comparison to the cold rolling techniques where anneals were necessary at each 10% reduction or less, only one intermediate anneal was necessary when warm rolling was employed, the reduction ductile and has less tendency to strain harden during the working process at temperatures indicated. A room temperature check of the specimens tested at elevated temperatures indicated that the hardness of all of the specimens returned to approximately the room temperature hardness, as indicated on the curve in Fig. 6. The effect is very definite and is shown in Fig. 5 which has two plates rolled exactly alike except for the rolling temperature. Plate B was cold rolled and possesses considerable edge cracking. Plate A was
warm rolled at 250°C to the same reduction and has very few edge cracks and none that would restrict further rolling.

At the same time that the rolling program was in progress, apparatus was being constructed and tested for hot hardness testing of metals. A Vickers hardness tester with a high speed steel indenter, employing the same angles but of somewhat larger size than the standard diamond indenter, operating at a 30-Kg load and using a ½ objective for reading the impression, was set up is the average of seven impressions. Photomicrographs which were available indicated that some grain growth occurred over this temperature range, Fig. 7. Obviously, there is a decided advantage to working uranium metal at a slightly elevated temperature.

An experiment which was carried on to show the effect of cold versus warm rolling might be described at this time. Two plates of normal uranium, cast from the same heat of metal, were subjected to the identical rolling treatment with one exception. Plate A was warm rolled at 275°C and Plate B was cold rolled. The rolling conditions of Plate A were similar to those used in rolling the UO2 metal.

From the starting thickness of 0.250 in., Plates A and B were rolled to 0.173 in. (31% reduction) and 0.193 in. (23% reduction), respectively, in the same number of passes, and, as far as could be determined, with the same roll pressure. Surface and edge cracks were observed on B at this time but A was still in good condition. Taking reduction in thickness of 0.010 in. per pass, Plate A was rolled to 0.108 in. thickness (57% reduction) and Plate B to 0.112 in. thickness (55% reduction). The cracking of Plate B had become...
so severe that it was necessary to anneal at this point. Plate A still possessed a very satisfactory surface.

Both plates were annealed in vacuum at 600°C. On the first pass after annealing, Plate B cracked completely and had to be discarded. Plate A was rolled to a thickness of 0.013 in. (88% reduction) in eleven passes without annealing. Although the rolling was stopped at this point, the plate was still in good condition and could have been rolled to thin foil if given another anneal.

It is evident that the above rolling conditions were quite drastic and Plate B, if annealed earlier and more frequently during the rolling process, could have been rolled to a thin section. This, however, makes the rolling process extremely slow and there is always the possibility of cracking if the rolling process is not done carefully. Plate A, on the other hand, rolled easily and rapidly and required the minimum time for the rolling schedule.

Fig. 6 — Effect of Temperature on the Hardness of Tuballoy.

Fig. 7 — Photomicrographs of uranium specimens used for hardness measurements.
The rolling technique which was used in rolling the U\textsuperscript{235} material was the same as the procedure followed in rolling Plate A. One anneal at 0.125-in. metal thickness (50% reduction) was used in the production rolling operations.

![Blank and pierce die](image)

Figure 8—Blank and pierce die.

At a thickness of 0.030 in. the silver plating on the sheet was chemically stripped and the sheet rolled to the final size of 0.020 in. thickness. The removal of the silver plate left the metal surface in an etched condition which was relatively rough and by stripping the silver plate at 0.030-in. thickness and then rolling bare to final size, the desired smooth surface was restored to the sheet.

Blanking

The blanking of the discs was accomplished by means of a double-action blanking and punching die which was mounted in a Niagara No. 3¾ punch press.

The blanking die was mounted in a Danly Precision die set which was fastened to the punch press. The material used in constructing the blanking die was Crocar, a high carbon, high chromium die steel produced by the Vanadium-Alloys Steel Company. Fig. 8 is a section through the blanking die. With the exception of the small diameter punch for blanking out the center hole, all cutting components of the die were hardened to Rockwell C 60-62. The small diameter punch was somewhat softer, Rockwell C 58-60.

Clearances on the blanking punches and dies were held quite small for the thickness of sheet to be blanked, a clearance of 0.0015 in. on the diameter being adhered to for all these parts.

The necessity for complete recovery of the U\textsuperscript{235} caused certain precautions to be undertaken. As shown in Fig. 9, a metal strip was fastened around the edge of the die set to form a retaining edge. Soft solder was used to form a fillet between the metal strip and the surface of the die set so that no cracks were present into which fine material could be lost and the surface of the die set was easy to clean. A slug container was securely fastened directly beneath the die set and caught all slugs punched out when the center hole was pierced. The blanking operation is actually a very clean operation and the possibility of losing material is extremely slight, particularly when the above precautions are observed.

The accuracy of the blanking die was very good and all pieces possessed dimensions well within the specifications. The efficiency of the process was not particularly good since only approximately 70% of the strip went into discs, the remainder of the material had to be reprocessed. In view of the relatively small number of pieces required, it was thought that the expense in building a more efficient, multiple unit blanking die was not warranted. The single unit die was fast enough for our demands and relatively inexpensive. Fig. 9 shows the rolled strip, a blanked disc, and the blanking punch and die.

After blanking, the edges of the discs were rounded slightly with emery cloth in order to remove the sharp edges and any loose material which might be held on the edges.

Passivating

The U\textsuperscript{235} discs were put through a passivating treatment in order to minimize the amount of oxidation which normally takes place over a period of time. The passivating treatment was not entirely satisfactory but was the only method...
available at the time and did cut down the rate of oxidation of the material.

The treatment, in brief, consisted of placing the \( ^{235}\text{U} \) discs anodically in a concentrated solution of sulphuric acid. The oxide was removed to 24 volts was applied and approximately 50 amperes flowed through the circuit at the start of the passivation treatment. The current dropped rapidly until at completion, only one ampere or less was being drawn by the bath. The rack was then

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All of the solutions used in this operation were saved and cycled through a recovery process.

The \( ^{235}\text{U} \) discs were weighed individually to the milligram and the weight, per cent \( ^{235}\text{U} \), and number of the disc was etched onto one surface of each disc by means of an electric etching pencil. The discs were then packaged in tight aluminum containers which were designed so that the amount of air remaining in the container after the discs were enclosed was extremely small.

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Extrusion of Uranium at Low Temperatures

By S. V. Arnold and R. M. Treco
Metallurgical Project, Massachusetts Institute of Technology
Report MIT-1022

ABSTRACT

A review of recent experience in the extrusion of uranium metal at temperatures below the alpha-beta phase transformation is presented. A discussion of the effects of billet temperature and reduction ratio on the properties of metal fabricated by alpha extrusion is included. It is shown that this process is quite feasible, providing a wide variety of microstructures and attendant physical properties.

INTRODUCTION

Extrusion of uranium has been practiced almost since the birth of the atomic energy industry. As early as 1943 E. C. Creutz pioneered the extrusion of uranium in both its alpha and gamma phases, evaluating the relative advantages of the two forms so that a suitable fabricating technique could be developed. Since the high-temperature gamma-phase form of the metal proved most readily extrudable, the established production procedure was to heat billets in a reducing atmosphere to the vicinity of 925°C and extrude by the direct method. Although the hot uranium was so soft as to be almost mushy, a good deal of effort had to be expended to develop a suitable refractory alloy die material to withstand service at this high temperature.

Early in 1947 interest in obtaining pile slugs with fine, equiaxed grain structure, as a possible solution to the blistering problem, directed attention toward extrusion in the alpha phase. Gamma extruded metal is invariably coarse grained. Extrusion in the beta phase is more difficult than extrusion in the upper alpha region and produces material which is normally coarse grained. Since experiments in alpha uranium extrusion had shown that, by appropriate "cold" working and annealing, the metal could be made to recrystallize into a fine-grained structure, there was reason to believe that a process for extruding could be developed which would leave the metal in a fine-grained condition or in a cold-worked condition capable of being transformed to the desired state by annealing.

HISTORY OF DEVELOPMENT

The initial alpha extrusion at M.I.T. took place in July 1947 and served to indicate (1) that alpha extrusion at 600°C presented no untoward difficulties and (2) that copper-plated billets extruded more easily and yielded sections possessing better surfaces.

Heating in a bath of lead saturated with copper proved a good method for bringing the plated metal to extrusion temperature without oxidation. The billets for this first series were only 1.25-in.
diameter × 3.00 in. long, a size which does not permit accurate determination of extrusion characteristics, but is useful in obtaining general indications of behavior. To more precisely measure the extrudability of uranium at 600°C and to study the effects of various operational techniques, additional series of 2-in. diameter × 4 in. long billets were pushed. These billets were copper plated and fitted at the leading end with introductory soft steel "cones" (see Fig. 1) which had been proved to facilitate extrusion and prevent flashing of the billet metal at the die-container interface. It was learned from these runs that the extrusion "constant"* varied between 59,000 psi for 4.1:1 reductions to 56,000 psi for 8.4:1 reduction ratios.

These findings were applied to the extrusion of alpha uranium on a commercial press when on September 18, 1947, several 4.25-in. diameter cast uranium billets clad in 16-gage copper cans and fitted with steel introductory cones were extruded to 1.20-in. diameter rounds, a reduction of 14.6:1. The billets were soaked prior to extrusion in a lead bath at 600°C for 15 min each. Graphite "cut-off" cylinders were charged into the press after each billet to assure complete expulsion of the metal. The extrusion proceeded readily at pressures which correspond to extrusion "constants" of 40,000-50,000 psi producing perfectly smooth copper-clad rounds entirely free of surface flaws. Scrap loss through cropping to remove end defect was 8.4% for an original billet length of 10 in. These rounds were found to be generally fine grained as described in a later section.

Although the copper jackets of the above-mentioned rounds possessed smooth exteriors, it developed, on peeling off the cladding, that the uranium beneath had developed a rough, bark-like texture. It required considerable machining to remove this surface irregularity which was presumably derived from the anisotropic ductility of the large cast crystals comprising the billet metal. To study factors affecting this condition a series of 2-in. diameter × 4 in. long billets were prepared for extrusion on the M.I.T. press in the following fashions: (1) possessing a copper jacket of thickness proportional to that of the larger 4.25-in. diameter × 10 in. long billets and fitted with a steel introductory cone, (2) without any

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* The extrusion constant "K" in this case is derived from the relation $P = K \ln \frac{A_0}{A_1}$, where $P$ = pressure required for extrusion, $A_0$ = original cross-sectional area of the billet and $A_1$ = final cross-sectional area of the extruded section. In this work, "K" was calculated from observed values of $P$ and includes friction effects as well as resistance to deformation.
jackets but fitted with a copper-plated steel cone, and (3) with neither jacket nor cone, i.e., machined cylindrical slugs. Data obtained from this run indicated that bare billets equipped with cones required 11% greater pressure to extrude than did the billets clad in copper and equipped with cones; the bare cylindrical billets required 16% greater pressure than did the latter. The surfaces of the rounds extruded from the bare billets were sufficiently good to indicate reasonable machining loss to clean up properly.

Despite the greater pressure required to extrude the bare cylindrical billets, greatly simplified preparation made their adoption appear attractive. Furthermore, in instances where press capacity limited the reduction obtainable, small sections could be produced by extrusion through a multi-holed die with which the use of canned and cone-equipped billets is not feasible. Scrap return on butts left within the press container by the cylindrical billets was approximately 7%, an amount comparable with that incurred by machining the forward end of billets to accommodate the introductory cones.

On the basis of the encouraging results with the bare billets on the M.I.T. press, dies were designed for use on a commercial press of 1300 tons capacity. Because two of the sections required were 1.00-in. and 0.50-in. diameter, it was necessary to use multiple-hole dies in order that the load on the press be kept within its operational limits. Accordingly, a series of dies were prepared: the first contained two 1.00-in. diameter orifices; the second, a central 1.00-in. diameter orifice about which three 0.50-in. diameter orifices were symmetrically disposed and; a third, wherein five orifices were evenly positioned about a sixth central orifice, all of 0.50-in. diameter. These dies worked successfully. However, dies with several small orifices incurred considerably more friction than would have been encountered with a single-hole die of equal cross section. As a result, the press was loaded very nearly to capacity and operation was less facile than would normally be the case. Some flashing occurred at the die-container interface, a difficulty associated with press alignment and the fit of components in the die head, and accordingly the significance of data obtained for certain extrusions was somewhat obscured. From those records which were adjudged representative of standard practice it developed that scrap loss (including the residual butt and croppage to remove "extrusion defect") was about 10% of the billet weight for the 2-hole, 1.00-in. diameter die and 7% for the 1-hole, 1.00-in. diameter plus the 3-hole, 0.50-in. diameter die.

Since flash occurred on all extrusions through the 6-hole, 0.50-in. diameter die, no estimation of normal loss could be made. Indications were, however, that the butts left from multiple-hole die extrusions were small and tended to be smaller the greater the number of orifices. Croppage to remove extrusion defect was about 4% for 1.00-in. diameter rounds and only 2% for 0.50-in. diameter rounds.

Surface of the extruded rods was moderately good for the larger sections, but rather rough for the 0.500-in. diameter rounds. The larger sections, which were well within the capacity of the press, allowed more operational freedom in setting the rate of extrusion. It was observed that slow extrusion generally promoted better surface. The roughness which did occur was associated with the formation of uranium accretions in the die orifices; the accretions would build up until they offered opposition to the metal flow greater than the shear strength of their bond to the die metal and then would be carried away with the extruding section. The dies, accordingly, were not impaired, although the rounds extruded through them were often scored in a manner seemingly inconsistent with the smooth orifice.

In December 1947 more uranium was extruded to 1.75-in. and 1.00-in. diameter rounds. The weight loss as flash and butts during the entire extrusion was 3% of the total billet weight. The end croppage return was 8.2% of the extruded weight of the 1.75-in. diameter rounds and 4.1% for the 1.00-in. diameter rounds.

In May 1948 a number of uranium billets were extruded through 2.125-in. diameter and 1.375-in. diameter dies equipped with refractory alloy inserts. These inserts appeared to alleviate accretion formation to some extent and showed excellent erosion resistance in operation. Investigation of the effect of extrusion rate on surface quality was carried out at the same time with the aid of an indicator by which the press operator could regulate the speed of ram travel as requested. As cast billets 4.25-in. diameter × 10 in. long were extruded at ram travel rates of 1.25 to 5.45 in./sec (15 to 330 in./min). It was found that the quality of the extruded surface depended primarily upon the original condition of the cast billet surface. If the cast billet surface was good, the extruded sec-
EXTRUSION OF URANIUM AT LOW TEMPERATURES

Extrusion of uranium by proper selection of extrusion rate could be produced glassy smooth and free of accretion scoring. Cast skin defects were not aggravated by extrusion and for the subject billets were not of appreciable significance. (See Fig. 2.)

The foregoing experiments over the course of a year served to develop extrusion of alpha uranium to a commercial practice capable of producing round sections of good quality with a minimum of billet preparation and scrap return.

METALLURGICAL INVESTIGATIONS

Typical Structure of Alpha-Extruded Uranium

Before any full-scale production could be done, it was necessary to examine the properties of the metal so far produced, in particular, the grain structure and working characteristics.

If the commercial scale extrusion of September 18 is considered, there were six bars having about the same extrusion conditions, and of these six, one (bar No. 3) is typical of metal extruded at 800°C with an approximate reduction in area of 14:1. After cropping this bar, the remaining length was measured and the microstructure examined at intervals along its length as shown in Table 1.

Table 1. Sectioning of extruded bars.

<table>
<thead>
<tr>
<th>Lab. No.</th>
<th>Length from lead end</th>
<th>% total length</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-6-1</td>
<td>4 in. (Transverse)</td>
<td>5</td>
</tr>
<tr>
<td>U-6-2</td>
<td>28 in. (Transverse)</td>
<td>35</td>
</tr>
<tr>
<td>U-6-3T</td>
<td>51 1/2 in. (Transverse)</td>
<td>64</td>
</tr>
<tr>
<td>U-6-3L</td>
<td>51 1/2 in. (Longitudinal)</td>
<td>64</td>
</tr>
<tr>
<td>U-6-4</td>
<td>71 1/2 in. (Transverse)</td>
<td>89</td>
</tr>
</tbody>
</table>

Fig. 3 corresponding to the 5% length, shows a typical fine-grained structure with equiaxed grains which persisted throughout the cross section. Fig. 4 for the 35% length shows the structure typical of the entire cross section, which is like that of Fig. 3. Fig. 5a taken at 64% of the bar length, shows the same structure except that the grain size is slightly larger. The longitudinal section at this point (Fig. 5b) shows a structure with definite banding of grains indicating that groups of grains recrystallized from large fibered grains retaining a difference in orientation between the original grain and the surrounding material.
A. Transverse section.

A. Longitudinal section near surface of rod.

B. Longitudinal section.

B. Longitudinal section at center of rod.

Fig. 5. Sections at the 64% length, polarized light. 100 x

Fig. 6. Sections at the 69% length, polarized light. 100 x
cause of its larger capture cross section. However, when considered on the basis of slowing down power beryllium is superior to graphite, and where space is at a premium as in naval or aircraft designs the use of beryllium permits smaller reactor dimensions for a given fuel inventory. Also when considering reactors for high temperature applications beryllium becomes a strong contender. It is comparatively unreactive in air up to 700°C, it does not appear to suffer any ill effects from radiation, and it has fairly good high temperature strength. Although no beryllium moderated reactors have as yet been built, the engineering operation of beryllium will be demonstrated by its use as a reflector in the High Flux reactor. The Intermediate Reactor to be built at Schenectady will employ partial moderation by beryllium.

The postponement of the use of beryllium has been largely the result of procurement difficulties and the relative non-existence of a technology for beryllium metal in the early days of atomic energy development. With the exception of uranium probably no other metal has received the degree of effort expended on the study of beryllium in recent years. As a result beryllium may now be obtained in fairly adequate amounts and varied forms although the cost is still high ($55/lb before extrusion or fabrication.) A new AEC sponsored plant currently under construction is expected to produce beryllium metal at one-half the present cost, however.

Beryllium is obtained from beryl ore which is unfortunately largely foreign in origin. The major source of supply is Brazil with India, Madagascar, Argentina, Australia, Portugal, and South Africa being possible additional sources. Ore prices currently run about $28/ton unit or $3.75/lb of contained beryllium. It is probable that sufficient beryllium is available for reactor uses and the prospects for lower cost supply are improving. Nevertheless, because of lack of large deposits of high-grade beryllium ores, this material will probably never be classed as cheap.

Three companies, Brush Beryllium Company, Beryllium Corporation of America, and Clifton Products Company have engaged in the production of beryllium from the ore, and slightly different methods are used in each case.

The following quoted passage gives an excellent summary of these processes:25

"All processes require an initial heat treatment with or without fluxing materials to free the beryllium for chemical attack. Brush melts the beryl in an electric arc furnace at about 1600°C and quenches the molten material in water. Clifton Products uses a potash carbonate flux, while the Beryllium Corporation uses sodium ferric fluoride at temperatures of 1200°C and 750°C, respectively. The fluoride roast converts the beryllium to a water soluble sodium beryllium fluoride and the other processes free the beryllium oxide for acid attack.

"The material from the Brush and Clifton roast is treated with sulfuric acid which dissolves the beryllium as well as all the other metals, such as aluminum, iron, and magnesium, leaving the silica as a residue. The beryllium is separated from these extraneous materials, principally aluminum, by one of two methods. Either ammonium sulfate is added to precipitate ammonium aluminum alum after which a careful evaporation of the liquors yields beryllium sulfate crystals, or if potassium is used in the initial roast, potassium alum precipitates on evaporation and a very delicate neutralization of the liquors with ammonia or soda compounds precipitates beryllium hydroxide. The crystallization of beryllium sulfate may be repeated several times or the neutralization may be carried out in steps with recycling of materials to insure pure beryllium sulfate or beryllium hydroxide.

"The fluoride process used by the Beryllium Corporation is simpler since a neutral or slightly alkaline water leach dissolves only the sodium beryllium fluoride from the roasted ore and avoids the use of acid-proof equipment. This solution which is dilute in beryllium is treated with caustic soda to give an impure beryllium hydroxide for alloy manufacture or for further purification. Since alloys, beryllium oxide, and metal are the important commercial products, the hydroxide and sulfate are usually calcined to the oxide as the next step in any process. These extraction processes recover probably 85 to 90% of the initial beryllium as beryllium oxide.

"All the processes that have been used to prepare beryllium metal involve the reduction of a halide electrolytically or with another metal. The most common method is that of Brush and the Beryllium Corporation which is the reduction of molten beryllium fluoride (produced from pure beryllium oxide and ammonium bifluoride) with chunk magnesium. The beryllium metal is separated from the magnesium fluoride slag mechanically or by water leaching.

"Clifton Products has prepared beryllium chloride on a small scale by chlorinating briquettes of carbon and beryllium oxide. This is electrolyzed in a molten solution of sodium and potassium chlorides to yield flake beryllium. Other researchers have electrolyzed molten beryllium fluoride."

The pebble beryllium produced by Brush or the Beryllium Corporation is remelted in vacuum furnaces and cast into ingots for extrusion. The extrusion operation normally takes place with a steel or copper-plated steel jacket surrounding the ingot. Fairly high pressures are required so total reductions are limited by available presses, but 5-1 to 20-1 reductions are normal practice.

High purity beryllium powder is also available and powder techniques have been developed to such an extent that fairly large sections can be made. For example, the Knolls Atomic Power Laboratory has successfully hot-pressed beryll-
B. S. OLD AND D. W. LILLIE

lium discs 12 in. in diameter by 4 in. thick and the Brush Company has hot-pressed beryllium five-finned tubes up to 72 in. long and discs 18 in. in diameter by 1½ in. thick.

There are still numerous unsolved problems in beryllium technology. The metal appears to be inherently brittle and is difficult to machine. Extruded sections exhibit a considerable degree of anisotropy due to preferred orientation and show an almost 50% reduction in strength transverse to the direction of extrusion. Corrosion characteristics in water are somewhat erratic and apparently depend on purity and prior history to a large degree. Little success has been attained to date on satisfactory welding methods. Nevertheless beryllium technology appears to have developed to the point where sufficient engineering data are available to use in design studies and where metal in a variety of forms is attainable.

Some of the considerations involved in designing about beryllium as a moderator may be shown by a brief analysis of a proposed modification of the Daniels high-temperature power pile. The original Daniels design planned to use BeO as moderator, but a secondary design placing more emphasis on breeding possibilities (i.e., the conversion of thorium to U²³₃ to produce more fuel than that consumed) envisaged using a beryllium metal moderator.

This reactor was to be a helium cooled design with the following characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas pressure</td>
<td>10 atm</td>
</tr>
<tr>
<td>Gas temperature (in)</td>
<td>500°F</td>
</tr>
<tr>
<td>Gas temperature (out)</td>
<td>1400°F</td>
</tr>
<tr>
<td>Max allowable temperature</td>
<td>1050°F</td>
</tr>
<tr>
<td>of permanent structure</td>
<td></td>
</tr>
<tr>
<td>Max allowable temperature</td>
<td>1700°F</td>
</tr>
<tr>
<td>of fuel element</td>
<td></td>
</tr>
<tr>
<td>Fuel element material</td>
<td>Be-U alloy plates</td>
</tr>
<tr>
<td>Minimum critical mass of U²³₅</td>
<td>8.0 kg</td>
</tr>
<tr>
<td>Total U²³₅ required for</td>
<td>17.5 kg</td>
</tr>
<tr>
<td>operation</td>
<td></td>
</tr>
</tbody>
</table>

The unit was to be a horizontal hexagonal prism composed of a beryllium skeleton and hexagonal fuel element units for insertion in the skeletal openings. Corrosion would not be serious in this design since helium cooling would be involved. The skeletal structure would be subject to thermal stresses as well as pressure and gravity loads; "however," so that stress considerations became the major problem.

The Intermediate Reactor to be built at Schenectady is another example of the use of beryllium. The reactor spectrum is determined mainly by the composition of the reactor core which is moderated with about 40 atoms of beryllium per atom of U²³⁵. In this core about 50% of the total fissions are due to neutrons below 700 ev while less than 10% are below the Cd cut-off (i.e., below 0.3 ev). One proposed design of the fuel element consists of a stack of hot-coined beryllium wafers into the channels of which are fitted thin U²³₅ fuel rings. A central channel provides for Na coolant flow. Fig. 12 shows the form of the wafers and fuel ring. The entire element is shown in Fig. 13. The zones indicated are as follows:

'(a). The central 18 in. of length, or core, composed of wafers of beryllium and rings of U²³₅.
'(b). Above and below the active portion of the slug, solid tubes of beryllium 3 in. in length form the reflector.
'(c). Progressing toward the end of the slug we find the 50-50 volume mixture of natural uranium and beryllium comprising part of the breeding blanket, 10 in. on top and 8 in. on the bottom.'

At an operating level of 10,000 kw the maximum temperature in the fuel element will probably be under 500°C.
Fig. 13—Assembled fuel unit for Knolls reactor (KAPL-116).
An alternate fuel element contemplates the use of sealed capsules or pins containing the U\textsuperscript{235}. The capsules themselves will be of a refractory metal such as molybdenum or columbium. In this case the core will consist of stacked 2-in. lengths of concentric beryllium tubing slotted on the outer surface to contain the fuel pins. The beryllium inner and outer cylinders and a pin are shown in Fig. 14. A third possibility is similar to the pin type, but involves spiral winding of fine fuel-containing tubes about two large concentric beryllium tubes. In both the sealed capsule or pin type and the spiral winding tube type the beryllium temperature for a given operating power would be considerably less than in the wafer-type design. It is important to note the comparative intricacy of the beryllium parts here involved. This is evidence that beryllium is reaching a state of maturity as an engineering material, at least where high stresses are not involved.

The overall reactor is described as follows:

"The central hexagonal core is 18 in. across (perpendicular distance between faces.) It is filled with a bundle of thin-walled type 347 stainless steel tubes 1.393 in. in diameter comprising a matrix into which the fuel rods are inserted. This assembly is supported on a plate at the bottom of the reactor. The next outer region consists of two additional rows of the same matrix. This accommodates the stainless steel jacketed solid beryllium rods which comprise the safety and control elements for the reactor and serve also as the side reflector. A third outer zone, also two rows of the same matrix, forms the "hot" breeding zone. The hot breeding rods ... are cooled by the primary coolant Na. The complete matrix consisting of 12 rows of tubes, 397 openings in all, is thus divided as follows: 109 fuel tubes, 102 reflector tubes, 126 breeder tubes. The interstices between tubes are filled with the Be trianguations and the whole structure is brazed together to form an integral unit. Outside of this structure is a solid Be matrix with drilled openings for insertion of solid natural uranium breeding rods. The rate of heat generation in these tubes is so low that primary coolant is not necessary. The heat is carried away by convection currents and conduction ... The fuel and breeder rods are about 51 in. long, 42 in. of this comprising the nuclear elements."

The direct incorporation of beryllium in a fuel element is also under evaluation at present. The formation of a UBe\textsubscript{3} compound generally believed to be either UBe\textsubscript{2} or UBe\textsubscript{3} and its subsequent incorporation in a beryllium matrix is being studied at the Massachusetts Institute of Technology and Sylvania Electric Corporation. The latter is concentrating on powder metallurgy methods, while the former is studying melting and casting techniques. Battelle is studying the beryllium cladding of beryllium-rich U-Be alloys for fuel complex uses.

Beryllium Oxide

The basic steps leading to the production of BeO have been outlined in the consideration of beryllium metal. Essentially three grades of powder are produced for which the producers designations are given here: 25

<table>
<thead>
<tr>
<th>Grade</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low fired (about 1200°C)</td>
<td>G.C. grade</td>
</tr>
<tr>
<td>High purity</td>
<td>Fluorescent</td>
</tr>
<tr>
<td>Low fired low purity</td>
<td>S.P. grade</td>
</tr>
<tr>
<td>High fired (fused and ground)</td>
<td>Refractory grade</td>
</tr>
</tbody>
</table>

Fig. 14—Beryllium cylinder and pin type fuel element for Knolls reactor (KAPL-116).

Modifications of conventional ceramic methods can be used to produce simple BeO forms such as bricks, but considerably refined techniques are required for any intricate shapes, since machining by conventional methods used for metals is not possible. Factors such as grain size control, purity, pressing conditions, and firing temperature influence the final product. It is desirable to obtain as high a density as possible since moderating characteristics are thus improved. Theoretical density for BeO is 3.025 g/cc and hot-pressed densities of up to 2.8 or 2.9 g/cc have been reported. Densities for cold-pressed and ceramic-fired materials are considerably lower, however, normally in the range 1.9 to 2.2 g/cc. The limiting factors are available firing tem-
peratures and grain sizes (finer grain generally results in higher final density.) Schofield Long, and Waldschmidt at Battelle have developed techniques for imbuenent of BeO bodies with Be salts from aqueous solutions. This involves repeated imbuenements followed by refirings, and densities up to 2.4 to 2.6 g/cc may thus be obtained.

The high melting point (2570°C) of BeO and its comparatively good thermal conductivity (e.g., estimated 17.0 Btu/hr ft °F at 1000°F for 2.0 g/cc density material) make it very attractive for use in high temperature reactors. Strength properties vary over wide ranges depending on fabrication techniques, but are generally high. Crushing strengths at high temperatures, for instance, are much higher than those for graphite. BeO has a high modulus of elasticity (e.g., 45.8 x 10^6 psi for 2.85 g/cc density) and this coupled with almost complete absence of plasticity makes it somewhat susceptible to thermal shock and very sensitive to impact. The degree to which these latter factors may affect its use as a reactor material has not been adequately evaluated as yet.

The major instance of design with BeO moderation is that of the proposed Daniels high-temperature gas-cooled reactor. This reactor was designed primarily to produce power. The heat exchange medium selected was helium to operate at an inlet temperature of 500°F and outlet temperature of 1400°F and a pressure of 10 atm. The fuel was to be enriched uranium incorporated directly into a portion of the moderating material of the pile. Graphite, beryllium, and beryllium oxide were all considered as possible moderators, with BeO being the preferred choice. The main structural units of the reactor were to consist of hexagonal BeO bricks 6 in. long x 3 in. across the flat with a 2-in. diameter central hole (cf Fig. 15 for typical assembly). The combined fuel and moderator units fitted within the openings of the structural units, and various lattice work designs were considered. Helium flowed directly through the fuel element lattice, out at the top of the reactor and into a secondary heat exchanger.

The selection of moderating material in the fuel element was based on the following considerations:

1. Ease of fabrication.
2. Possibilities for easy incorporation of fuel (by impregnation or alloying.)
3. Thermal conductivity.
4. Thermal stresses.
5. Deformation under stress.
6. Thermal rupture tests.
7. Neutron economy.
8. Probability of radiation damage.

Graphite was largely eliminated at the time on the basis of radiation damage considerations. While unirradiated graphite has extremely high resistance to thermal rupture, it was thought that the known effects occurring under irradiation at low temperatures indicated that serious lowering of thermal rupture resistance might occur. This is somewhat alleviated by knowledge that there is a "self-annealing" effect at high temperatures and also that plastic flow may take place in graphite at these temperatures. More detailed knowledge of the effects of irradiation on graphite are needed if questions such as these are to be answered accurately.

A second objection to graphite was apparent difficulty in obtaining a stable uranium carbide in graphite. There appeared to be a tendency for some uranium to remain as U3O8 and then convert to UC or UC2 at a later time, possibly after incorporation in the reactor. Current work at Battelle is attempting to improve knowledge of this system. Objections to beryllium metal were based on the possibility of loss by volatilization if operating temperatures should go above 1700°F. It was also thought that there might be fabrication difficulties with beryllium as well as possible
troubles with warping of thin sections at high temperatures. Preliminary radiation damage experiments in the Hanford reactor indicated that pure BeO was not seriously affected, but that BeO containing fissile material suffered a five-fold thermal conductivity loss. Even with this knowledge and the dearth of information on fabrication and such properties as thermal rupture resistance, the designers thought that BeO was the most promising of the moderators considered.

The above discussion serves to point out that there is no clear-cut choice of material for high temperature moderation. A great deal more study, particularly on radiation effects at high temperatures, is needed before the engineers can make soundly based choices on the best moderator for any basic design.

The following excerpt from one of the Lexington Project reports is an excellent summary of the present status of BeO.32

"The first question is whether it will be possible to fabricate beryllium in the densities required, i.e., 2.9 to 3.0. Secondly, will the resulting material be capable of withstanding the thermal stresses resulting from moderation? Thirdly, will it be possible to alleviate the thermal shock problem by proper section design or by incorporating a glass flux into the beryllium oxide? "The function of the glassy phase would be to lower the plastic range to lower temperatures where stresses arising from thermal gradients could be absorbed by the creep of the beryllia body.

"A further unanswered problem is the degree of attack of beryllia by water vapor at temperatures from 1800°F (980°C) up to 2500°F (1370°C). Even at 1840°F (1000°C) the reaction rate between beryllia and water vapor may be rapid enough to cause serious damage to the moderator. This would call for a coating problem for beryllia in that event. There is some evidence that although this reaction is serious at 2500°F (1370°C) it may not be serious at 1840°F (1000°C)."

One further moderating material should probably be mentioned here, namely, mixtures of Be and BeO. The Massachusetts Institute of Technology has developed a method of mixing Be and BeO powders in various proportions, compacting cold in a steel can, sealing, and extruding the canned compact. Sound bodies have been extruded in the range of 0 to 75% BeO. Optimum creep properties have been observed in 25% BeO bodies.

It is possible that further work on this system will develop a material of better high temperature strength than beryllium metal and better thermal shock resistance and thermal conductivity than BeO.

Beryllium Carbide

Referring again to Table 3 it may be seen that Be$_2$C has excellent moderating properties. In addition it has good high temperature properties, as is shown by the following tabulation comparing a few selected properties of BeO and Be$_2$C.33

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of thermal exp. (per °C)</th>
<th>Compressive stress (psi)</th>
<th>Thermal conductivity (cgs units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be$_2$C</td>
<td>2.100 (d)</td>
<td>12.4 x 10$^{-7}$ (20-800°C)</td>
<td>40,000 (approx.)</td>
</tr>
<tr>
<td>BeO</td>
<td>2.570</td>
<td>6.9 x 10$^{-6}$ (18-1000°C)</td>
<td>40,000/100,000</td>
</tr>
</tbody>
</table>

(d) decomposes

It must be remembered that the values for compressive stress and thermal conductivity listed here are those at room temperature, and that all properties are sensitive to fabrication variables.

Norse value much is known about the reactivity of Be$_2$C in air, but it seems probable that protective coatings will be required at very high temperatures. Some preliminary work at Battelle gave conflicting results on loss in weight of Be$_2$C samples heated in air up to 2700°F.34 The Battelle group have successfully prepared Be$_2$C by heating BeO powder with powder graphite, and also by heating Be flake with graphite. Carbide bodies have been fabricated by both hot and cold pressing.

A large amount of data is yet to be collected before this material can be evaluated adequately.

Lithium

In Table 1 it may be observed that lithium compares rather poorly with moderators previously mentioned. The value of 0.0083 for the "moderating ratio" would indicate that this material would be definitely unsatisfactory. It should be noted, however, that this is largely because of the high thermal absorption cross section (~70 barns) of the naturally occurring isotopic mixture, and that when separate isotopes are considered the picture is somewhat different. Lithium occurs in two isotopes Li$^6$ and Li$^7$. Of these Li$^7$ comprises 92.5% of the natural mixture and has a low cross section, the latest and presumably best value being that of Hughes and Goldfarb35,36 of .033 barns. Even lower values of .0017 and < .004 barns38 have been reported. If .033 barns is used for the absorption cross section and 1.6 barns for the absorption cross section and 1.6 barns for the
Bands of inclusions also follow the deformation texture. A section taken at 89% of the length showed a fine-grained structure, except that areas were found of mixed coarse and fine grains. Fig. 6a is a longitudinal section near the surface of the bar, while Fig. 6b shows the mixed structure in the central part of the rod.

With this and other similar metallurgical analyses it becomes apparent that:

1. Uranium extruded at 600°C with a heavy reduction (e.g., greater than 10:1) possesses a recrystallized, fine-grained structure over most of the bar length, although the end of the bar may require cropping to maintain uniformity of structure in the bar length.

2. Higher reductions (i.e., 14:1) are more beneficial since they always produce more homogeneous structures. In this connection, it is noteworthy that a minimum reduction in area is required before uniform structures are obtained from center to surface in the useful part of the bar.

3. Fibered, worked structures similar to those obtained by cold rolling are produced in uranium with lower reduction ratios and temperatures, since recrystallization does not occur under these conditions. Such structures may be recrystallized by proper heat treatment.

Effect of Billet Temperature on Extrusion Behavior

Up to this point attention has been given only to the possibility of producing fine-grained metal in rod form for pile exposure. Further requirements are that the metal be uniform in structure and have a reasonably random crystal arrangement in order that anisotropic growth effects from this source be minimized.

In order to investigate the factors affecting the properties mentioned and to provide metal for recrystallization studies, a program of extrusion was planned in which both temperature and reduction in area were varied independently. The temperatures chosen were 600°, 500°, 400°, 300°, and 200°C, the latter depending on extrudability at these lower temperatures. For each temperature nominal reductions in area of 2:1, 4:1, 8:1, and 14:1 were scheduled.

Billets 1 1/2-in. diameter x 4 in. long were prepared from previously extruded rod and annealed at 816°C (1500°F) for one hr. This treatment produced a coarse-grained structure typical of metal annealed in the gamma phase which approaches the characteristics of as-cast metal (See Fig. 7). The billets were extruded without cladding, introductory cones, or lubricant other than a mixture of graphite and oil applied to the die orifice and container bore. Die and container were heated to 427°C (800°F) or the extrusion temperature, whichever was lower. Billets were heated to extrusion temperature in a lead bath or within a graphite container if the temperature was too low for lead. All extrusions were performed at a ram travel speed of about 45 in./min.

The running pressures required to extrude the billets at various reductions and temperatures are presented in Table 2. Extrusion "constant" values calculated from these data are also tabulated and plotted against reduction ratio in Fig. 8. The "constant" values are not equal at a given temperature as the relation \( P = K n R \) predicts. If the sharp drop between 1.97:1 and 4.03:1 reduction ratios is ignored on the basis that the mechanism of metal flow is abnormal below the latter ratio, then variation at 500°C and 600°C is moderate; but at lower temperatures the "constant" falls

Fig. 7. Microstructure typical of metal annealed in the gamma phase, polarized light. 100x
off rapidly with increasing reduction. This behavior is also reflected in the relation of extrusion pressure to billet temperature as shown in Fig. 9. It will be noted that the data for the lower reductions hold fairly well to the formula* 

\[ P = A e^{-\lambda T} \]

and those for higher reductions at 500° and 600°C appear to do likewise; but high reductions at lower temperatures require less pressure than adherence to the formula would predict. It was observed that the exit metal was considerably hotter (at a visible red heat) than the initial billet temperature. This heating was a result of the severe working of the metal in the conical approach leading to the die orifice. The metal passing through the die was thus at a higher temperature than the billet and this led to a lower extrusion pressure than would otherwise be required. The initial deformation called for high pressures which dropped immediately, as extrusion commenced, to the values listed.

Hardness and Microstructures of Alpha-Extruded Uranium

If we now consider the properties of the rods extruded in the manner already indicated, we find that the anomalous extrusion behavior at the lower temperatures is reflected in both hardness and structure. Fig. 10 shows a plot of as-extruded hardness vs billet temperature for each reduction ratio. Increasing the amount of reduction produced softening of the metal rather than hardening, since the more severe work combined with its heating effect caused the metal to recrystallize. In general, the lower reductions (2:1 and 4:1) provided sufficient cold working of the metal to harden it increasingly as the extrusion temperature was lowered. The hardness of the 8 and 14 times reduced metal changed very little as the extrusion temperature was lowered. The original billet metal had a Rockwell G hardness of only 68, showing that hardening was achieved under all extrusion conditions described here.

The appearance of the hardness curves suggests that below 400°C the properties of the extruded bar were critically determined by the amount of reduction.

In order to determine the structure of the extruded metal, microspecimens of each bar were taken at a position equivalent to two-thirds of the billet diameter.
EXTRUSION OF URANIUM AT LOW TEMPERATURES

Fig. 8. Relation of extrusion "constant" of uranium to reduction ratios at various temperatures.
IN RELATION \( P = A e^{-\lambda T} \):
- \( P \) = EXTRUSION PRESSURE FOR A GIVEN REDUCTION RATIO
- \( A \) = CONSTANT FOR SAME REDUCTION RATIO
- \( e \) = BASE OF NATURAL LOGARITHMS, 2.7183
- \( \lambda \) = CONSTANT COEFFICIENT
- \( T \) = EXTRUSION TEMPERATURE

VALUE OF \( \lambda \) FROM ABOVE DATA IS 0.0020

STRAIGHT LINES SHOW EXTENT OF ADHERENCE TO FORMULA \( P = A e^{-\lambda T} \) AT VARIOUS REDUCTION RATIOS, \( R \).

EACH POINT INDICATES SINGLE BILLET

**Fig. 9.** Relation of extrusion pressure of uranium to billet temperature.
EXTRUSION OF URANIUM AT LOW TEMPERATURES

extruded length perpendicular to the extrusion axis. Rods extruded under the same conditions appeared to have identical physical properties. Fig. 11 shows these microsections (original magnification 100x), while Table 3 gives the accompanying grain size. These clearly illustrate the structures developed during working. Considering the 2:1 reduction, a cold-worked structure was obtained for all temperatures, although partial recrystallization was evident at 600°C. This amount of reduction is insufficient to produce a homogeneous material. However, this series did show a progressive increase in the amount of cold-working with decreasing temperature which is in agreement with the hardness data.

By doubling the reduction ratio to 4:1, entirely different structures were obtained. At 600°C the recrystallization was not only complete, but a scattered grain size was visible. The cold-worked structure previously found at 500°C was changed to a fine-grained aggregate and, interestingly, showed no sign of a duplex structure at the surface. In other words, the cross section of the rod was extremely uniform. This was also true at 400°C, although the grain size was much smaller. At 300°C we again found a cold-worked structure and a correspondingly large increase in hardness. A partially recrystallized structure was found at 200°C with a consequent softening. For this reduction it is apparent that the temperature was quite critical in determining the as-extruded metal properties.

Again doubling the reduction (to 8:1) we found that the increased working led to recrystallization at all temperatures. The photomicrographs for the 600°C, 500°C, and 400°C extrusion temperatures showed a coarse grain size at the surface. This is believed to be related to the greater working and heating at the surface. Such a layer must be removed from the extruded rod by machining if the properties of the interior structure are to be realized in use. Lowering the extrusion temperature at first decreased the interior grain size, but did not eliminate the coarse surface layer until
Fig. 11. Extruded uranium microstructures.
Fig. 11. Extruded uranium microstructures.

REDUCTION RATIO

8:1

14:1

BILLET TEMP. °C

600

500

400

300

200
300°C was reached. At this temperature there was a reversal in the trend toward finer grain size with an increase to A.S.T.M. No. 7 and no surface effect visible. Since the hardness dropped for these conditions, it is evident that the metal was heated well above the initial temperature by the heat generated by the extrusion operation. At 200°C a thin surface layer persisted and the interior had been completely recrystallized.

On deforming the material with a reduction as high as 14:1, the previously mentioned surface effects were greatly exaggerated and the structure showed tremendous crystals which had grown radially toward the center merging rather abruptly with the fine-grained interior. At both 500°C and 600°C the grain size was mixed where grain growth had started selectively. At 200°C the radial and center grains were much smaller because of the shorter time at grain growth temperature. At 200° the extrusion pressure required was so great that the container split open.

Since one of the major objectives of alpha-phase extrusion was to produce uniformly fine-grained material, it is of interest to see what can be done with the extruded metal. In general, as-extruded microstructures consisting of fine, equiaxed, completely recrystallized grains were very stable up to 600°-650°C. Some grain growth may occur if the annealing temperature exceeds the maximum temperature reached by the rod during extrusion. Grain growth also increased with time at temperature, but the growth was negligible for times as short as the present canning cycle.

The cold-worked structures obtained by low reduction or low temperature extrusion can be easily recrystallized with consequent control of grain size. Such a fine-grained structure obtained by heat treatment is shown in Fig. 12. The effect of time and temperature on the recrystallization of extruded uranium will be the subject of a subsequent paper.

**SUMMARY**

It is apparent from this work that a variety of structures and properties may be obtained in uranium by varying the extrusion conditions. The optimum conditions depend upon the individual equipment and the type of material desired, either as-extruded or extruded and heat-treated. Alpha-phase extrusion within the scope of the conditions defined is a practical form of fabrication capable of producing homogeneous fine-grained metal on a commercial scale.

**REFERENCES**


March 1949
Problems in the Use of Molten Sodium as a Heat Transfer Fluid

By Clifford E. Weber and Leo F. Epstein

Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York

Report KAPL-139

PART I

PREFACE. As a result of the recent interest in the use of liquid metals as heat-transfer fluids, sodium and sodium-potassium alloys in particular, rather extensive literature has accumulated, mostly in project reports. For some time, it has been apparent that there is need for a critical study of this scattered information and correlation and evaluation of the results to date. This presentation is the first of a two-part paper which will attempt to evaluate the data on the use of sodium as a heat-transfer fluid. The emphasis in the title on "problems" is deliberate for, as will appear, there are many gaps which will have to be filled before sodium can be used in a nuclear reactor with any degree of assurance. Part I gives the reasons for the current interest in sodium and the best data available to date on its physical properties and chemical reactions of importance in heat-transfer applications. Part II will deal with corrosion of metals by liquid sodium, mass-transfer phenomena (carburization and decarburization, etc.), diffusion bonding, the effect of oxygen, the purification of sodium, and similar topics.

This paper is in the nature of an interim report, a review of the current status of the development of methods for using molten sodium, and the problems which have arisen in this study. Many laboratories have contributed to this field and are continuing intensive work. While general principles are constantly evolving from these researches, an objective evaluation of the subject to date must lead to the conclusion that the numerical data available are of low precision, and in most cases are only qualitative rather than quantitative. Sodium technology at the present time is in a highly mobile state, with new information and new interpretations of data arising continually. It should not be surprising if many older concepts of these problems change radically in the future.

ABSTRACT

The basis for the current interest in liquid metals as coolants for nuclear reactors is discussed, and the favorable characteristics of liquid sodium as a heat transfer medium are pointed out. This is followed by a critical analysis of the available data on the physical properties of Na of importance in this application, i.e., density, heat capacity, viscosity, surface tension, thermal conductivity, electrical resistivity, heat transfer coefficients, and nuclear characteristics. The chemical properties of sodium are discussed, including its reactions with oxygen, water, hydrogen, nitrogen, carbon, metallic oxides, and other metals.

I. INTRODUCTION

The current research on power-producing, high-temperature nuclear reactors has stimulated interest in sodium and sodium-potassium alloys for use as coolants and has accelerated work in this field. Nuclear power sources release energy in a much more concentrated form than almost any type of system previously encountered in engineering practice. This fact is illustrated by Table 1, in which the power generated per unit volume is given for various heat sources.
As presently conceived, to use this energy for power production it is necessary to remove it from the reactor and use it to produce steam or some similar material, which will then be used to drive a conventional turbine and generator. For practical use, such installations must produce around 10,000 to 100,000 kw, that is, they must generate heat at a rate equivalent to the burning of several tons of coal per hour. Removal of these large quantities of heat, generated in a small volume, requires the use of an extremely efficient heat-transfer fluid. "Limitations on the pile output are determined mainly by the method used to remove the heat, that is, on the design of the cooling system. The source of energy is for all practical purposes unlimited." 74 The need for an efficient coolant can thus be established on this basis.

Credit for the following analysis of the physical and chemical properties which a coolant for a power-producing nuclear reactor should possess is due to Martinelli. 1 Assuming that gases, liquids, or low melting solids can be used, Martinelli 74 has stated the following requirements for coolant material.

1. The coolant material should introduce a minimum of interference with the nuclear reaction itself. This requires that:
   a. The coolant should have a minimum possible volume.
   b. The coolant material should have good nuclear properties, especially with respect to absorption of neutrons.

2. There should be low power consumption in pumping. This requirement essentially eliminates the use of gases since with gaseous coolants in reactors of small dimensions the power required for pumping may be greater than the power output of the reactor itself. Increasing the pressure of the gaseous coolant alleviates this situation.

This remark by Martinelli on the limitations of gas cooling applied in particular to power-producing reactors such as the KAPL system. For maximum thermodynamic efficiency in a turbine-generator installation it is desirable to operate at rather high temperatures, say in the range 300 to 600°C. A simple analysis of the use of gases as coolants shows that because of their relatively small heat capacity, extremely large volumes of gas must be circulated to effect the amount of heat transfer required; this in turn means high gas velocities and operating pressures, perhaps of the order of 10 atm or greater. However, gases certainly are possible coolants under some conditions.

The Brookhaven reactor also is to be air cooled, 81 but in this case the operating temperatures are relatively low, 200 to 350°C, and the heat produced will not be utilized. An air flow rate of about 270,000 cu ft/min is contemplated, and to keep this mass of gas moving will require 5,600 kw of the expected 28,000 kw output of the reactor, i.e., the equivalent of 20% of the heat generated will have to be supplied to operate the system. Such a high pumping-power requirement, while possible for an experimental reactor, would perhaps be prohibitive for a unit designed primarily to produce useful power. A comparison of the relative power required for the pumping of various proposed coolant materials has been made by Martinelli 75 and is given in Table 2. This comparison has been made for a system similar to the KAPL reactor with respect to heat flux at about 320°C; the effect of different operating levels is shown in Fig. 1.

3. High heat-transfer coefficients within the reactor and high thermal conductivities, if possible, are required. These requirements are particularly important to take care of dead flow spots or stagnant points within the reactor. In this connection water, which is satisfactory from the heat transfer standpoint when flowing at high velocities but which does not have a high thermal conductivity, would not be satisfactory. Sodium, however, is satisfactory from both standpoints.

4. A high reactor output temperature is necessary. The critical temperature of water is about 374°C. This means that in order to obtain reasonably high reactor tempera-

---

Table 1 — Power Generated by Various Heat Sources

<table>
<thead>
<tr>
<th>Heat source</th>
<th>Power generated, watts/cu cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam boiler (natural circulation)</td>
<td>0.5</td>
</tr>
<tr>
<td>Forced-circulation steam boiler</td>
<td>10</td>
</tr>
<tr>
<td>Gas turbine</td>
<td>25</td>
</tr>
<tr>
<td>KAPL reactor (10,000 kw rating)</td>
<td>120</td>
</tr>
<tr>
<td>Argonne fast-neutron reactor</td>
<td>459</td>
</tr>
<tr>
<td>V-2 rocket</td>
<td>20,000</td>
</tr>
</tbody>
</table>

*Dr. Raymond C. Martinelli, whose many contributions to the field of heat transfer will be referred to in this report, was born in Lucca, Italy, April 27, 1914, and died at Oakland, California, January 9, 1949. He was an associate professor of Mechanical Engineering at the University of California, and was on loan to the Knolls Atomic Power Laboratory of the General Electric Company from October 1946 to September 1948, at which time he returned to California to resume his academic duties.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

In addition to these general criteria for a reactor coolant, Martinelli [76] has also listed the following three heat-transfer limitations on the reactor output which must be taken into account in the choice of a coolant:

1. The maximum temperature of the reactor parts. In this respect a gas cooled reactor is less satisfactory than a liquid cooled reactor since for the same output temperature a gas cooled reactor will require the fuel slugs to be at about 1000°C, for example, while a liquid cooled reactor will permit them to be at 550°C."

In Fig. 2 the difference between the temperature of the fuel element and that of the coolant stream is shown for a number of different possible reactor coolants; again on this basis gas cooling is much less satisfactory than liquid cooling.

2. The capacity of the coolant flow system.
   a. The pumping power.
   b. The coolant velocity.
   c. Size of the inlet and discharge headers."
be used to compare the relative heat-transfer characteristics of liquids. Thus, for streamline flow the function is:

\[ x = \frac{\mu}{C_p \rho^2 k} \]  

(1)

and for turbulent flow:

\[ y = x/(C_p \mu/k)^{0.4} \]  

(2)

These parameters essentially measure the pumping power required for the various liquids under conditions from those computed on this basis. Such a comparison has been made by Gilliland from whose work Table 3 is taken. In each case, the ratios \( x/x_{H_2O} \) and \( y/y_{H_2O} \) are listed.

The superiority of sodium for streamline flow, and its excellence under turbulent flow conditions, are clearly apparent from this tabulation. Water which appears to be better for turbulent flow conditions is limited by the low boiling point, but for low-temperature systems (such as the Hanford reactors) it is a satisfactory coolant. Most of the other substances in this table can be dismissed as impracticable for use in nuclear reactors on the basis of radiation and temperature instability. This essentially eliminates polyatomic molecules as coolants for high-flux, high-temperature systems. Metals, on the other hand, are stable. Those which are liquid at room temperature would be preferred, other factors being equal, for example: mercury (mp, \(-38.9^\circ C\)), gallium (mp, 29.8^\circ C),

![Fig. 1. Pumping-power requirement for various coolant fluids.](image-url)
and sodium-potassium alloy (eutectic, \(-12.5^\circ C\)).

Mercury, unfortunately, has a high density (which means a high pumping-power requirement, cf. Table 2), and a boiling point (357°C) somewhat too low for maximum efficiency in currently available turbo-generators. Mercury cooling is, nevertheless, to be used in the Los Alamos plutonium fast reactor. Gallium is rare and expensive and, judging from the available data, extremely corrosive in its action on other metals. Sodium-potassium alloys are being intensively studied for use in the Argonne fast-neutron reactor. Sodium-potassium alloy, however, has the same disadvantages as sodium from the point of view of chemical reactivity (if anything, sodium-potassium alloy is probably worse in this respect), and the introduction of potassium has a significantly deleterious effect on the nuclear, thermal, and hydrodynamic properties of the coolant.

It may be observed from Table 3 that all of the other conceivably practical heat-transfer fluids are much less efficient than sodium because of their thermal and hydrodynamic characteristics, and further that they have much higher melting points. Low-melting alloys of some of these elements might be of value, and some of these are currently being studied. Unfortunately, many of the common low-melting alloys, such as Wood's metal (mp 68°C), contain cadmium, which cannot be tolerated in a coolant from a nuclear point of view for low energies and probably not for intermediate energies. Other low-melting alloys contain bismuth, which yields the relatively long-lived (140-day half-life) alpha-emitting polonium with its attendant radioactivity problems. This difficulty with bismuth has, however, never been completely evaluated. Lead-bismuth alloys (eutectic, mp 124°C), and similar systems with lower melting points, have been extensively studied.

![Fig. 2. Temperature drop for various coolant fluids.](image-url)
CLIFFORD E. WEBER AND LEO E. EPSTEIN

melting points are of interest, and studies on such materials are now in progress.\(^{25,49}\)

From the currently available information, sodium would appear to have some outstandingly superior characteristics, with only sodium-potassium alloy a close competitor. The high thermal conductivity of sodium and its consequent advantages as a heat-transfer fluid have been realized almost from the isolation of sodium by Sir Humphrey Davy\(^{15,10,54}\) in 1807. The extreme chemical reactivity of the molten metal has, however, until comparatively recent times defeated any attempts to take advantage of its excellent physical properties. Because of its relatively high electrical conductivity, sodium has been used to replace copper and aluminum in large bus bars,\(^8\) but the utilization of the corresponding thermal properties has lagged somewhat behind. The first practical use of liquid sodium as a heat-transfer medium appears to have been in the valves of internal-combustion engines, where large temperature differences between the head and the stem of the valve are undesirable. Such sodium-filled valves are used in all modern airplane engines and in many engines for heavy duty trucks and buses.\(^{36}\)

On the basis of the arguments developed above, the General Electric Power Pile (KAPL reactor) is being designed to use liquid sodium as a coolant. The characteristics of this system are given in Table 4.\(^{34}\) Sodium is favored over sodium-potassium alloy in this system, in spite of its higher melting point, because of its higher heat capacity, higher thermal conductivity, lower atomic volume, and lower neutron absorption.

While the principal emphasis in this report is on the use of sodium as a heat-transfer medium in nuclear reactors, it may be pointed out that sodium (and sodium-potassium alloy) would also appear to have a promising future in other fields. One such application has already been made: "During World War II the Dow Chemical Company operated a process which necessitated the removal of large quantities of heat at high temperature levels. After spending considerable effort on other unsatisfactory media, we found that metallic sodium was the ideal fluid. Centrifugal pumps were used to circulate the metal through steel pipes to the hot zone (400 to 650°C) and then to an air-cooled coil where the heat was given up before the sodium returned to the source. The largest such installation had a capacity of 1,500,000 Btu/hr."\(^{44}\) This system, which operated at about 400 kw, has unfortunately been shut down "because of economic reasons not in any way connected with the sodium coolant."\(^{44}\) The Sun Oil

<table>
<thead>
<tr>
<th>Table 3. Comparison of possible liquid coolants.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>H\text{2}O</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Sn</td>
</tr>
<tr>
<td>Hg</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>Na\text{NO}_3,Na\text{NO}_3,K\text{NO}_3</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
<tr>
<td>Glycol</td>
</tr>
<tr>
<td>Freon-12</td>
</tr>
<tr>
<td>Aniline</td>
</tr>
<tr>
<td>Diphenyl</td>
</tr>
<tr>
<td>Naphthalene</td>
</tr>
<tr>
<td>Glycerin</td>
</tr>
</tbody>
</table>
Company has for some years been using liquid mercury as a heat-transfer medium in the preparation of lubricating oils where close temperature control is essential (the widely publicized "Mercury Made Oil"). For this and similar applications, sodium would appear to have a number of advantages. The development of sodium technology, therefore, has important implications beyond the sphere of nucleonics, and promises to be of considerable importance in the future.

Table 4. Characteristics of sodium-cooled KAPL reactor.

<table>
<thead>
<tr>
<th>Operating</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power output (heat)</td>
<td>10,000 kw</td>
</tr>
<tr>
<td>Na flow rate</td>
<td>1250 gal/min</td>
</tr>
<tr>
<td>Temperature rise</td>
<td>100°C</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>400°C</td>
</tr>
</tbody>
</table>

Sodium, as has been established, readily fulfills most of Martinelli's criteria for an ideal coolant. The available data, which will be discussed later, indicate that its nuclear properties are quite satisfactory, and that in the absence of contaminating oxygen, extremely low corrosion rates on other reactor materials can be achieved with sodium. Its melting point (97.8°C), on the other hand, is somewhat higher than might be desired. This fact is in part the reason for the current interest in sodium-potassium alloys rather than sodium. But the alkali metals are decidedly difficult to handle because of their extremely high reactivity with oxygen, metallic oxides, hydrogen, water, and similar substances (see Section II B). It is this factor, perhaps more than any other, which has proved to be the stumbling block in the development of a technique for handling liquid sodium, and the future of this art is highly dependent on the establishment of methods for avoiding or minimizing the effects of this high chemical reactivity. Experience to date has shown no reason to doubt that this can be successfully done, although a relatively long program of study and development may be required. It appears that sodium will always remain a rather delicate material, in the sense that techniques other than those of the highest degree of refinement may vitiate the advantages to be gained by its use.

II. THE PROPERTIES OF SODIUM

A. The Physical Properties of Sodium

1. Density

The density of liquid sodium is given by:

\[ \rho = 0.9514 - 2.392 \times 10^{-4}T \]  

where \( \rho \) is in g/cu cm and T is in °C. This equation is good to 0.5% or better over the range from the melting point (97.8°C) to 700°C, and is based on the data of Hagen, Rinck, Griffiths and Griffiths, Hackspill, Chiong, Bernini and Cantoni, and the Naval Research Laboratory. From Eq. 3, the coefficient of cubical expansion of liquid sodium is:

\[ \beta = \frac{2.392 \times 10^{-4}}{(0.9514 - 2.392 \times 10^{-4}T)^{1/3}} \]  

From these equations, the values of the physical constants given in Table 5 are obtained.

Table 5. Density and thermal expansion of liquid sodium.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>( \rho, \text{g/cu cm} )</th>
<th>( \beta, \text{C}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.928</td>
<td>2.58 \times 10^{-4}</td>
</tr>
<tr>
<td>500</td>
<td>0.832</td>
<td>2.88 \times 10^{-4}</td>
</tr>
</tbody>
</table>

The coefficient of thermal expansion is comparable with that of other liquids (\( \beta \) at 20°C is 2.07 \times 10^{-4} for \( H_2O \) and 1.82 \times 10^{-4} for mercury). According to Bridgman, the volume change on melting, \( \Delta v \), is +2.71% at about 1 atm, which is again quite normal behavior.

2. Heat Capacity

Older data on this property of sodium are not in particularly good agreement. Data have been reported by Renegade, Griffiths, Dixon and Rodebush, Jitaka, and at the Naval Research Laboratory. Recently, however, a definitive study of this property of sodium has been com-

*Much of the material of this section is abstracted from a study by Betty O. Newman. In some cases, reference is made to preliminary experimental data from the classified project literature, which may be subject to correction as further information is obtained.
pleted by Dr. T. B. Douglas and his associates at the National Bureau of Standards. The preliminary data fit the equation:

\[ C_p = 0.34339 - 1.3874 \times 10^{-4}T + 1.1049 \times 10^{-7}T^2 \]  

(4A)

where \( C_p \) is in cal/g°C and \( T \) is in °C, over the range from the melting point to 900°C. The resulting data are believed to be good to better than ±0.5%. From this equation the values in Table 6 are obtained.

Table 6. Heat capacity of liquid sodium.

<table>
<thead>
<tr>
<th>( T ), °C</th>
<th>( C_p ), cal/g°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.331</td>
</tr>
<tr>
<td>200</td>
<td>0.320</td>
</tr>
<tr>
<td>300</td>
<td>0.312</td>
</tr>
<tr>
<td>400</td>
<td>0.306</td>
</tr>
<tr>
<td>500</td>
<td>0.302</td>
</tr>
<tr>
<td>600</td>
<td>0.300</td>
</tr>
<tr>
<td>700</td>
<td>0.300</td>
</tr>
<tr>
<td>800</td>
<td>0.303</td>
</tr>
<tr>
<td>900</td>
<td>0.308</td>
</tr>
</tbody>
</table>

\( C_p \) initially has a negative temperature coefficient. The curve of \( C_p \) vs. \( T \) passes through a minimum at about 628°C. This behavior is similar to that reported for mercury by Barnes, where a minimum in \( C_p \) occurs at about 140°C.

In the course of this study, the heat of fusion of sodium at the melting point (97.81 ± 0.03°C) was found to be 622 cal/mole, only slightly less than the value obtained by earlier workers.

3. Viscosity

The data of Chiong on the viscosity of liquid sodium have been substantially confirmed by Ewing, Atkinson, and Rice at the Naval Research Laboratory. Chiong's data are smoothed by the equation:

\[ \mu = \rho^{0.5} K \exp \left( \frac{C_p}{T} \right) \]  

(5)

where \( \mu \) is the viscosity in poises, \( \rho \) is the density, \( T \) the Kelvin temperature, and the constants \( K \) and \( C \) have the values:

\[ K = 0.001183, \quad C = 716.5 \]

for the range 98 to 355°C. Ewing, et al, used the same equation form, with the constants:

\[ K = 0.001074, \quad C = 764.6 \]

These two equations yield the results given in Table 7 at 100 and 500°C.

Table 7. Viscosity of liquid sodium.

<table>
<thead>
<tr>
<th>( T ), °C</th>
<th>( \mu ), centipoises</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiong</td>
<td>NRL</td>
</tr>
<tr>
<td>100</td>
<td>0.685</td>
</tr>
<tr>
<td>500</td>
<td>0.241</td>
</tr>
</tbody>
</table>

The differences between the values calculated from these two equations are less than 5%, and thus the equations are essentially equivalent for practical engineering computations.

4. Vapor Pressure

The pressure of the vapor containing the equilibrium ratio of sodium to \( \text{Na}_2 \) molecules over liquid sodium is given by Kellely as:

\[ \log p \text{ (atm)} = \frac{-5775}{T} - 1.274 \log T + 8.863 \]  

(6)

From this equation, the normal boiling point of sodium is 892°C, and the vapor pressure as a function of temperature is as given in Table 8.

Table 8. The vapor pressure of liquid sodium.

<table>
<thead>
<tr>
<th>( T ), °C</th>
<th>p, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.82 \times 10^{-4}</td>
</tr>
<tr>
<td>200</td>
<td>1.35 \times 10^{-4}</td>
</tr>
<tr>
<td>300</td>
<td>0.0143</td>
</tr>
<tr>
<td>400</td>
<td>0.365</td>
</tr>
<tr>
<td>500</td>
<td>3.33</td>
</tr>
<tr>
<td>600</td>
<td>24.1</td>
</tr>
<tr>
<td>700</td>
<td>101</td>
</tr>
<tr>
<td>800</td>
<td>318</td>
</tr>
</tbody>
</table>

It should be noted that an appreciable proportion of sodium vapor exists as \( \text{Na}_2 \) dimeric molecules, probably about 1% at 500°C, and 8% at 800°C.
5. Surface Tension

The surface tension of liquid sodium was measured by Quinckes in the presence of dry carbon dioxide by the drop-weight method; by Poindexter and Kernaghan who used the modified flat-drop (sessile drop) method in high vacuum; and recently at the Naval Research Laboratory by capillary-rise measurements in high vacuum. The data of the first two methods are in surprisingly good agreement if the required corrections are made. The more recent measurements of Poindexter and Kernaghan were obtained over the temperature range from the melting point to about 250°C, with the surface tension, \( \sigma \), expressed by:

\[
\sigma = 211.5 - 0.04848 T \text{ dynes/cm} \quad (7)
\]

and a standard deviation of \( \pm 0.6 \) dyne/cm. From this equation, at 100°C, \( \sigma = 206.7 \) dynes/cm. A contact angle greater than 90 degrees was observed in these measurements.

The data reported from the Naval Research Laboratory are preliminary in nature and cover the temperature range from the melting point to 193°C. The sodium was observed to wet the glass, and the surface tension was obtained using the standard capillary-rise technique, assuming zero contact angle under the wetted conditions. As a result of experimental deviations, an average of the values was reported as 92 \( \pm 10 \) dynes/cm over the temperature range, 98 to 193°C.

In addition, Mellor reports a value of \( \sigma \) near the melting point, of 27.23 mg/mm, equivalent to 267 dynes/cm. This measurement is supposed to have been made by Hagen, but the reference to the original work given by both Mellor and Friend is incorrect and it has not been possible to locate the paper from which this figure is taken.

The disagreement between the two series of measurements of \( \sigma \) cannot be resolved at present. Accurate determination of the surface tension of sodium may be very difficult since this property is probably quite sensitive to traces of impurities such as oxygen. Dissolved impurities generally tend to reduce the surface tension of liquids, and the most common impurity in sodium, \( \text{Na}_2\text{O} \), might be expected to behave in this way. It is difficult, however, to believe that the large differences noted here can be attributed entirely to this effect. Of the three techniques used to date, only the capillary-rise method is directly dependent on the contact angle. This parameter is very sensitive to the surface condition, and at present the higher values of surface tension are to be preferred.

6. Thermal Conductivity

Considering the data on all the physical properties of sodium required for its evaluation as a heat-transfer medium, those available for thermal conductivity are perhaps the worst (cf. Fig. 3). The measurements of \( k \) are difficult to make, because of the convection currents which arise due to the high coefficient of thermal expansion of liquid sodium. The measurements of Hall appear to be very good (the author claims an error of \( \pm 0.4\% \)), but only cover the range from the melting point, where \( k = 0.206 \text{ cal/(sq cm sec } ^\circ\text{C/cm)} \), to 200°C, where \( k = 0.193 \). A recent series of measurements at the Naval Research Laboratory give much lower values of \( k \) (0.091 at 100°C, 0.118 at 500°C). A new investigation of this property of sodium has recently been made by Robinson and Droms of the General Electric Company in an attempt to resolve the discrepancies between Hall's measurements and the Naval Research Laboratory results. From a series of twelve points lying between 100 and 325°C obtained in their work, the equation

\[
k = 0.216 - 1.29 \times 10^{-4}T \quad (8)
\]

can be derived, with a standard deviation of \( \pm 0.005 \text{ cal/(sq cm sec } ^\circ\text{C/cm)} \). Values of the thermal conductivity computed from this equation at rounded temperatures are tabulated in Table 9. These data are in excellent agreement with Hall's results, with respect to the magnitude of \( k \) and the sign of the temperature coefficient.

| Table 9. Measured thermal conductivity of liquid sodium. |
|---------------|---------------|
| \( T \), \(^\circ\text{C} \) | \( k \), \text{cal/(sq cm sec } ^\circ\text{C/cm)} \) |
| 100 | 0.203 |
| 150 | 0.197 |
| 200 | 0.190 |
| 250 | 0.184 |
| 300 | 0.177 |
| 350 | 0.171 |
Values of \( k \) can be estimated theoretically from the Wiedemann-Franz\(^{108,984} \) ratio between electrical resistivity \( r \) and thermal conductivity \( k \). This relation should be particularly good for sodium and is given by the equation (derived from the electron theory of metals):

\[
k = T\left(\pi \frac{k}{e}\right)^2/(3r)
\]

where \( T \) is the absolute temperature, \( k \) is Boltzmann's constant, and \( e \) is the electronic charge. Expressing \( k \) in cal/(sq cm sec °C/cm), and \( r \) in ohm-cm, Eq. 9 reduces to:

\[
k = 5.33 \times 10^{-9} \left(\frac{T}{r}\right)
\]

Using the data of Hackspill\(^{65} \) and others for \( r \), extrapolating when necessary, the resulting \( k \) values are given in Table 10.

<table>
<thead>
<tr>
<th>( T ), °C</th>
<th>( k ), cal/(sq cm sec °C/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.206</td>
</tr>
<tr>
<td>200</td>
<td>0.188</td>
</tr>
<tr>
<td>300</td>
<td>0.179</td>
</tr>
<tr>
<td>400</td>
<td>0.172</td>
</tr>
<tr>
<td>500</td>
<td>0.168</td>
</tr>
</tbody>
</table>

The data of Hall, and those of Robinson and Droms,\(^{55} \) are in extremely good agreement with these theoretical values.

8. Heat-transfer Characteristics

To evaluate the use of sodium as a heat-transfer fluid, it is necessary to determine the so-called "film temperature drop," \( \Delta T \), that is, the difference in temperature between the surface and the fluid. This is given by the relation:

\[
\Delta T = \frac{Q}{Ah}
\]

where \( Q \) is the total amount of heat flowing across a surface of area \( A \) per unit time, and \( h \) is the so-called "heat-transfer coefficient." The value of \( h \) is determined from the physical properties of the coolant fluid and the geometry and hydrodynamics of the system. It has been customary to express the results in terms of various dimensionless parameters, for example:

\[
\text{Nu} = \text{Nusselt's Modulus} = \frac{hD}{\kappa}
\]

\[
\text{Re} = \text{Reynolds' Number} = \frac{vD\rho}{\mu}
\]

\[
\text{Gr} = \text{Grashof's Modulus} = \frac{H^3\rho g\Delta T}{\nu^2}
\]

\[
\text{Pr} = \text{Prandtl's Modulus} = \frac{C_p}{\mu/k}
\]

In these relations all the symbols have the significance previously assigned and the only new ones are \( D \), the hydraulic diameter of the pipe through which the liquid is flowing, \( g \), the acceleration of gravity, \( H \), a characteristic length of the heated solid, and \( v \), the linear flow velocity of the fluid in the closed conduit.

For natural convection, the value of \( h \) can be obtained from the relation:

\[
\text{Nu} = C(\text{Gr} \cdot \text{Pr})^n
\]
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Fig. 3. The thermal conductivity of liquid sodium. The experimental points of Robinson and Droms are shown scattering around the curve derived from the Wiedemann-Franz Ratio.

where \( n \) lies between \( \frac{1}{4} \) and \( \frac{1}{3} \) for normal shapes and temperatures. Therefore, the dimensionless constant \( C \) is of the order of 0.45 to 0.55.

For forced convection at low velocities, where the flow is essentially streamline (Re < 2,100), McAdams recommends the relation:

\[
Nu = 1.86 (Re \cdot Pr (D/L))^{\frac{1}{3}}
\]  

(17)

where \( L \) is the length of the flow channel. For the turbulent flow region, the corresponding relation is:

\[
Nu = 0.023 \ Re^{0.8} \ Pr^{0.4}
\]  

(18)

The exponent of Pr is also often taken as 0.33. Since reactor systems will be operated under conditions of turbulent forced convection (for the
KAPL reactor, Re lies substantially in the region 5,000 to 50,000), Eq. 18 is the most important of this series. This equation has been obtained empirically from studies of fluids with Prandtl numbers between about 0.5 and 200. Liquid metals, however, are characterized by extremely low Prandtl numbers, of the order of 0.005 to 0.05, so that the applicability of this relation is open to doubt. Furthermore, for low flow velocities where conduction rather than convection is the more important process, Nu should be nearly independent of Re instead of varying as the 0.8 power as shown by McAdams' formula. Because of these questions on the validity of Eq. 18, Martinelli's analysis is restricted to the case of symmetrical heat transfer from a fluid flowing between two surfaces to the walls; Harrison and Menke have extended this theory to the asymmetric case.

Fig. 4. Older heat-transfer data for liquid metals.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

against the Peclet Modulus, Pe,

$$\text{Pe} = \frac{\text{Re}}{\text{Pr}}$$

(19)

a single curve is obtained, independent of Pr. Lyon has fitted an empirical equation to this curve, and he initially recommended the use of three equations:

$$\text{Nu} = 8$$

$$\text{Pe} = 100$$

(20)

$$\text{Nu} = 8 + 0.02(\text{Pe} - 100)^{0.44}$$

$$\text{Pe} = 100,$$

$$\text{Pr} = 0.5$$

(21)

$$\text{Nu} = 0.023 \text{Pe}^{0.8}/\text{Pr}^{0.4}$$

$$\text{Pe} = 100,$$

$$0.5 < \text{Pr} < 200$$

(22)

This last equation is completely equivalent to McAdams' (Eq. 18). Later, Lyon suggested the equation:

$$\text{Nu} = 7 + 0.05 \text{Pe}^{0.5} + 0.023 \text{Pe}^{0.8}$$

(22A)

instead of Eq. 21, and in a still more recent publication:

$$\text{Nu} = 7 + 0.025 \text{Pe}^{0.8}$$

for circular tubes (22B)

$$\text{Nu} = 4.9 + 0.0175 \text{Pe}^{0.8}$$

for annuli (22C)

The differences between these various forms are quite negligible however.

The experimental data for liquid metals, on which a check of the validity of these results might be based, are quite meager. Furthermore, as has been suggested in previous paragraphs, the physical constants of sodium and sodium-potassium alloy are not well enough known to make a completely unequivocal comparison of theory and experiment. In Fig. 4, the best data available until comparatively recently are plotted from work at the Argonne National Laboratory on mercury and sodium-potassium alloy,80 from the Naval Research Laboratory on sodium-potassium alloy81 (the experimental work here was done at the Mine Safety Appliances Company), from work of Musser and Page on mercury,78 and from work of Styrikovich and Semenovker on mercury.106 There are in addition some experimental data on sodium by Bennett,8 but the interpretation of the results is in doubt. The values of Nu computed by Martinelli's theory (the solid curved line labelled Pr < 0.5), and those computed from McAdams' equation (solid straight lines) are also plotted in this figure. It is obvious that no clear cut choice between these two theories can be made from these older data.

Recently, however, a new and extensive, series of measurements (134 points) on sodium-potassium alloy has been reported by Werner and King100 of the Mine Safety Appliances Company, which cover a wide range of Pe (75 < Pe < 2250) and Pr (0.0045 < Pr < 0.021). These data were presented in sufficient detail so that using the values of the Prandtl moduli as a function of temperature recommended by Newman,79 the points given on Fig. 5 were obtained. The theoretical curves are also shown, computed as before from Eqs. 20, 21, and 22. It seems evident from these data that Martinelli's theory gives the correct answer and should be used for liquid metals, rather than the extrapolated McAdams' equation.8 More extensive measurements on sodium and other materials are needed, however, to confirm this beyond any doubt, and experimental work of this nature is in progress at Mine Safety Appliances Company, KAPL, and other laboratories.

There are two further points to be noted before concluding this section. For Re > 106, Martinelli's theory tends to give somewhat low values, compared with the McAdams' equation; for small values of Re, the Martinelli formulation predicts that the values of h should be only slightly larger than those calculated for a static system where conductivity, rather than convection, is the main process for heat transfer. It is also fortunate that, due to the high thermal conductivity of liquid metals, the calculated film drops are quite small. Thus an error of 100% in h is not nearly as serious for these coolants as it would be for a fluid with a smaller value of k, as for example, water and gases.

3. Neutron Physics of Sodium as a Reactor Constituent

The nuclear properties of sodium which affect its usefulness as a heat-transfer fluid in a nuclear reactor are its tendencies to moderate, scatter, and absorb neutrons, and to become radioactive under neutron bombardment. These properties will be taken up in the order given.

*At the "Symposium on Basic Properties of Liquid Metals," held at the Argonne National Laboratories, Chicago, Illinois, April 5-6, 1949, further work supporting the Martinelli theory was presented by Lyon and Kittes of Oak Ridge, on NaK alloys, and Untermyer of Argonne on Pb-Bi-Sn eutectic. The recent work of Elser on mercury is also in reasonably good agreement with Martinelli's theory.
a. Neutron Moderation

Sodium has a low atomic weight, so that neutrons colliding with sodium atoms lose, on the average, 8.5% of their energy in each collision. This moderation can be fairly important in a fast or intermediate energy reactor, where other moderators are present in comparatively low proportions.

b. Nuclear Scattering

The scattering cross section, $\sigma_s$, of sodium has been found to be 4 barns for thermal neutrons, a value intermediate among the scattering cross sections of the elements. For neutrons of other than thermal energies, the only measurements available give the total cross section, $\sigma_t$, which is the sum of $\sigma_s$ and $\sigma_c$, the capture cross section. However, $\sigma_c$ is negligible compared to $\sigma_s$ for neutron energies above a few electron volts, so that for practical purposes, $\sigma_t \approx \sigma_s$ to an accuracy of 1%.

The older total cross section data on sodium cover a range of neutron energies from 0.023 MeV to 2.8 MeV, and these have been summarized by Goldsmith, et al., in a curve showing $\sigma_t$ ranging smoothly between the limits 2.5 and 5.8 barns. More recent work of Barschall, however, done with a nearly monochromatic neutron beam, shows that in the neutron energy range 0.03 MeV to 1.0 MeV, $\sigma_t$ for sodium varies between 2 and 8 barns, with several peaks indicating resonances. It is almost certain that these are predominantly scattering resonances, with comparatively little capture being involved.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Its extremely low atomic density, combined with its fairly low scattering cross section per atom, makes sodium more nearly transparent to neutrons than most reactor constituents. This has been verified in preliminary reactor assemblies at KAPL where, for equal volumes, sodium was found to have only 30% of the effectiveness of beryllium as a reflector for intermediate reactors. It should be emphasized that this transparency is primarily due to the atoms in metallic sodium being so far apart; typical atomic volumes are (in units of $10^{-24} \text{ cu cm}$) 8 for beryllium, 17 for aluminum, and 39 for sodium. Atom for atom, sodium has a slightly larger average scattering cross section than beryllium in the intermediate energy region, as will be shown in the next paragraph.

Relative danger coefficients for these three elements are given in Table 11 for the intermediate energy spectrum of one of the KAPL preliminary reactor assemblies. The "danger coefficient" of a material is the increase in reactivity produced by filling an empty space in the reactor with a specified amount of the material. A central danger coefficient is found when the material is placed in the center of the reactor where its transport cross section plays no part in affecting the concentration of neutrons. A central danger coefficient measures the negative effect of neutron losses caused by absorption in the material, plus the positive effect of neutron moderation in the material. When absorption in the material is small (as in the three elements below), the central danger coefficient essentially measures the moderating effect, $\xi \sigma_s$. (Here $\xi$ is the mean logarithmic energy loss per collision.) A reflector danger coefficient is found when the material is placed in the reflector of the reactor, just outside the core. Here the transport cross section $\sigma_t$ is the principal property measured (when the absorption can be neglected as before), and this is proportional to the scattering cross section.

c. Neutron Absorption

Among those elements which might be used as liquid heat-transfer media in reactors, sodium has the lowest fast-neutron capture cross section; a value of 1.4 millibarns for fission neutrons can be deduced (see the next-to-last paragraph of this section). Its thermal neutron capture cross section is also quite low (but is not the lowest among possible heat-transfer media). Way and Haines give $\sigma_c = 0.45 \text{ barn (±10%)}$ as a best value in their survey of the literature. This is based primarily upon the careful reactor oscillator work of Hoover and his co-workers at Oak Ridge.

No measurements of the absorption cross section of sodium for intermediate energy neutrons are reported in the literature, but Dearnley has recently studied the mean activation cross section over three ranges of neutron energy: roughly 0.5 ev to 0.4 Mev, 30 ev to 0.4 Mev, and 200 ev to 0.4 Mev. (The energy spectrum of the neutrons in this experiment is not well known but has been estimated by Brooks of KAPL to follow a rough $1/E^{0.8}$ law.) In each experiment a sample of $^{235}\text{U}$ was also subjected to the same neutron irradiation, and it was the ratio of the activation cross section of sodium to the fission cross section of $^{235}\text{U}$ that was actually measured. These ratios, as given in Table 12, include the thermal neutron and fission neutron data from the literature. These ratios furnish some evidence for the existence of one or more resonance absorptions in the intermediate range of neutron energies.

---

Table 11. Relative danger coefficients per atom of material.

<table>
<thead>
<tr>
<th>Element</th>
<th>Central Coeff. $\xi$</th>
<th>Coeff./$\xi$</th>
<th>Reflector Coeff.</th>
<th>Coeff./Coeff. of Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.208</td>
<td>0.207</td>
<td>1.00</td>
<td>0.236</td>
</tr>
<tr>
<td>Na</td>
<td>0.086</td>
<td>0.085</td>
<td>1.01</td>
<td>0.266</td>
</tr>
<tr>
<td>Al</td>
<td>0.051</td>
<td>0.072</td>
<td>0.71</td>
<td>0.130</td>
</tr>
<tr>
<td>Quantity compared</td>
<td>$\sigma_s$</td>
<td>$\sigma_t$</td>
<td>$\sigma_t/\sigma_t$ (Be)</td>
<td></td>
</tr>
</tbody>
</table>

---
Studies of the sodium absorption of neutrons filtered through varying thicknesses of boron carried out by Dancoff, et al.,\textsuperscript{14,13} led them to assign the lowest absorption resonance at 1,710 ev. Their value for the activation integral $\int \sigma_a \, dE/E$ is 0.30 barn for the epicaladium range of energies, the resonance integral contributing 0.06 barn of the total. (Their values for the activation integrals have been increased by a factor 0.45/0.40 to make them consistent with the 0.45-barn thermal used above, since they had used 0.40 barn). The combined integral is $0.9 \times 10^{-4}$ times the similar integral for $^{235}$U fission. This value appears in Table 12 and is consistent with the other values. Langsdoft, et al.,\textsuperscript{58} used a reactor oscillator method and estimated this same integral to be 0.27 barn, which is a further check upon its value.

Practically all of the data quoted so far are for absorption in the reaction $^{23}$Na(n,$\gamma$)$^{24}$Na. However, fission neutrons can produce other reactions, for which the cross sections are given in Table 13.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cross section, millibarn</th>
<th>Threshold, Mev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}$Na(n,$\gamma$)$^{24}$Na</td>
<td>0.29</td>
<td>0 (ref. 57)</td>
</tr>
<tr>
<td>$^{23}$Na(n,p)$^{23}$Na</td>
<td>0.7</td>
<td>4.2 (ref. 55)</td>
</tr>
<tr>
<td>$^{23}$Na(n,$\alpha$)F$^{20}$</td>
<td>0.4</td>
<td>2.9 (ref. 55)</td>
</tr>
<tr>
<td>$^{23}$Na(n,2n)$^{22}$Na</td>
<td>0.006</td>
<td>11.7 (ref. 56)</td>
</tr>
</tbody>
</table>

The total of these four cross sections is the 1.4 millibarns quoted at the beginning of this section. Because of their high threshold energies, the contribution of the last three of these reactions should be fairly unimportant in most reactors.

The work with the preliminary reactor assemblies at KAPL has shown the capture section of sodium to be low over yet another spectrum. Not only have these assemblies not been poisoned by the inclusion of as much as 30\% (by volume) sodium, but they show that sodium has a positive central danger coefficient. Thus, the moderating effect of the sodium nuclei overrides their absorbing effect, at least in an intermediate neutron energy spectrum.

d. Induced Radioactivity

The $^{24}$Na activity is the principal one produced in sodium by neutrons of energies obtained in nuclear reactors. This has a 14.8-hr half-life, corresponding to 2.05 days for reduction in activity by a factor of 10. The radiations consist of a 1.39-Mev beta particle followed at once by two successive gamma rays of 2.76 Mev and 1.38 Mev coming from the excited Mg$^{24}$ nucleus that is formed. This makes sodium, in so far as it absorbs neutrons, an emitter of a more penetrating delayed gamma ray than any known fission product.

In a power reactor the gamma radiation from a sodium coolant can be expected to be initially a few per cent of that emitted by the fission products. For example, in a reactor whose core contains 5 times as many atoms of sodium as of $^{235}$U, the sodium system as a whole should contribute about 3\% as many hard gamma photons (1.3 Mev or harder) as do the fission products, 2 hours after shutdown. Two days after shutdown, the sodium contributes only 1\% as many hard gamma photons as do the fission products and proportionately less at times thereafter. The sodium

Table 12. Measurements of the ratio of the activation cross section of sodium to the fission cross section of $^{235}$U.

<table>
<thead>
<tr>
<th>Neutron energy range</th>
<th>Spectrum</th>
<th>Reaction</th>
<th>$\sigma_a/N\sigma_f^{(235)} \times 10^{-4}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal $\sim 0.025$ ev</td>
<td>--</td>
<td>(n,$\gamma$)</td>
<td>0.8</td>
<td>--</td>
</tr>
<tr>
<td>Epicaladium $\sim 0.5$ ev</td>
<td>de/E/E</td>
<td>&quot;</td>
<td>0.9</td>
<td>Dancoff\textsuperscript{13,14}</td>
</tr>
<tr>
<td>0.5 $-$ 400,000 ev</td>
<td>de/E/E$^{6,8}$</td>
<td>&quot;</td>
<td>1.4</td>
<td>Dearnley\textsuperscript{15}</td>
</tr>
<tr>
<td>30 $-$ 400,000 ev</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>200 $-$ 400,000 ev</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.4</td>
<td>&quot;</td>
</tr>
<tr>
<td>Fission $\sim 1$ Mev</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.22</td>
<td>Hughes\textsuperscript{57}</td>
</tr>
<tr>
<td>Fission $\sim 1$ Mev</td>
<td>&quot;</td>
<td>all captures</td>
<td>1.1</td>
<td>Hughes, et al.\textsuperscript{56,58}</td>
</tr>
</tbody>
</table>

Table 13. Absorption cross sections of sodium.
activity dies down much more rapidly than that of the fission products, but it is more difficult to shield against because the activated atoms are circulated outside the reactor structure through pumps and heat exchangers.

It is worth noting that the total sodium activity in the primary circulating system depends only on the quantity of sodium in the reactor itself, chiefly the core, and not upon the quantity in the whole system.

The (n,α) and (n,p) capture processes are of no importance because the resulting activities have half-lives of less than a minute. The Na\textsuperscript{23}(n,2n)Na\textsuperscript{22} reaction, however, gives a product with a 3-yr half-life, and the cross section for formation from fresh fission neutrons is only 50 times smaller than that for the (n,γ) process leading to the Na\textsuperscript{24} activity discussed above. The amount of Na\textsuperscript{22} activity that might be generated in a reactor containing a large percentage of sodium (about 1 Na atom to 10 atoms of other constituents) is estimated to be of the order of 1 curie per megawatt of reactor power. This is not negligible compared with an initial Na\textsuperscript{24} activity of about 5,000 curies per megawatt (estimated for one particular intermediate reactor), since this Na\textsuperscript{24} activity would be less than 1 curie a week after shut-down of the reactor.

Proper shielding around the entire primary coolant system, of course, will take care of the gamma radiations from the coolant in ordinary operation, and this activity does add materially to the total shielding requirement. It is only when the coolant system has to be serviced or repaired that the coolant radioactivities again have to be considered.

B. THE CHEMICAL PROPERTIES OF SODIUM

The outstanding property of sodium, chemically, is its extreme reactivity. A detailed description of the many compounds which sodium forms can be found in the standard textbooks and reference manuals on inorganic chemistry.\textsuperscript{18,35,74} This section will, therefore, be restricted to the interactions of sodium and those substances which are important in the use of this material in heat-transfer work; namely, oxygen, water, the rare gases, nitrogen, and oxides of various elements.

1. Sodium and Oxygen

At room temperature, sodium combines with oxygen to form Na\textsubscript{2}O in accordance with the reaction:

\[2\text{Na}(s) + \frac{1}{2}\text{O}_2(g) = \text{Na}_2\text{O}(s)\] (23)

The heat and free energy of these reactions are given by Thompson\textsuperscript{102} as

\[\Delta H = -94,736 + 20.04 T - 6.32 \times 10^{-3} T^2 - 586.6 T^{1/2}\] (24)

\[\Delta F^\circ = -94,736 - 20.04 T \ln T + 6.32 \times 10^{-3} T^2 - 1173.2 T^{1/2} + 197.89 T\] (25)

(Energies will be expressed in gram-calories, and temperatures in degrees Kelvin, with \(T_0 = -273.16°C\), unless otherwise noted.)

For the reaction:

\[2\text{Na}(1) + \frac{1}{2}\text{O}_2(g) = \text{Na}_2\text{O}(s)\] (26)

in the range from the melting point to the boiling point (892°C), the corresponding equations are:

\[\Delta H = -93,143 + 15.06 T - 0.78 \times 10^{-3} T^2 - 586.6 T^{1/2}\] (27)

\[\Delta F^\circ = -93,143 - 15.06 T \ln T + 0.78 \times 10^{-3} T^2 - 1173.2 T^{1/2} + 165.26 T\] (28)

The free energy of formation of Na\textsubscript{2}O from the elements, as determined by these equations, is \(-90\text{ kcal/mole at 25°C, -75 kcal/mole at 500°C, and -54 kcal/mole at 1000°C.}\)

Na\textsubscript{2}O is a crystalline white hygroscopic powder, with a density\textsuperscript{3,38} of 2.27 to 2.31 g/cu cm. Its crystal structure has been determined by Zint\textsuperscript{113,114} and his associates: Na\textsubscript{2}O is an anti-fluorite (face-centered cubic) crystal with an \(a_o\) of 5.55 Å. It is commonly obtained in industry as an intermediate in the manufacture of the commercially important sodium peroxide, Na\textsubscript{2}O\textsubscript{2}, and pure Na\textsubscript{2}O has been prepared\textsuperscript{113} by the reaction of Na\textsubscript{2}S and Na\textsubscript{2}CO\textsubscript{3} at about 275°C. At elevated temperatures Na\textsubscript{2}O is one of the most corrosive materials known\textsuperscript{37} it reacts with all the common metals (including the platinum metals), graphite, and ceramic materials. This fact has made it impossible to date to measure many physical properties of this material. It has been estimated that the melting point is about 1100°C ± 300°C, and the heat of fusion is about 3.6 ± 1.4 kcal/mole.\textsuperscript{21}
The vapor pressure\(^2\) of \(\text{Na}_2\text{O}\) has been estimated as:

\[
\log p_{\text{mm}} = 7.755 - \frac{7704}{T} \quad (29)
\]

From this equation the normal boiling point of \(\text{Na}_2\text{O}\) is \((1310 \pm 200)\text{°C}\), and the heat of vaporization is \(35.2 \pm 4.0\) kcal/mole. Vapor pressures computed from this equation are given in Table 14. Direct experimental confirmation of these values is lacking, however.

Table 14. Estimated vapor pressure of \(\text{Na}_2\text{O}\).

<table>
<thead>
<tr>
<th>T, °C</th>
<th>(p, \text{mm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>(3.0 \times 10^{-8})</td>
</tr>
<tr>
<td>300</td>
<td>(2.1 \times 10^{-8})</td>
</tr>
<tr>
<td>400</td>
<td>(2.0 \times 10^{-8})</td>
</tr>
<tr>
<td>500</td>
<td>(6.2 \times 10^{-9})</td>
</tr>
<tr>
<td>600</td>
<td>(8.5 \times 10^{-9})</td>
</tr>
<tr>
<td>700</td>
<td>0.69</td>
</tr>
<tr>
<td>800</td>
<td>3.8</td>
</tr>
<tr>
<td>900</td>
<td>15</td>
</tr>
</tbody>
</table>

The most detailed recent study of the properties and reactions of \(\text{Na}_2\text{O}\) is that of Bunzel and Kohlmeyer.\(^8\) Using a crucible of MgO (which seems to be one of the few materials not drastically attacked by \(\text{Na}_2\text{O}\)) they found a melting point of \(920\text{°C}\), in reasonable agreement with the estimated value above. From their work, the vapor pressure of \(\text{Na}_2\text{O}\) becomes "appreciable" at \(1350\text{°C}\), and they estimate the normal boiling point to be over \(1600\text{°C}\), which is considerably higher than the value computed from Eq. 29. \(\text{Na}_2\text{O}\) and \(\text{Na}_3\text{O}\) form a continuous series of solid solutions, with a minimum melting point of about \(575\text{°C}\). The system \(\text{Na}_2\text{O}-\text{Al}_2\text{O}_3\) is sketched as having a simple eutectic at \(720\text{°C}\), 10 mol\% \(\text{Al}_2\text{O}_3\), and from this the heat of fusion of \(\text{Na}_2\text{O}\) can be estimated, assuming the ideal solution laws to hold (a somewhat doubtful hypothesis), to be about \(1.24\) kcal/mole, which is significantly less than the value estimated above. There is, however, rather good evidence that the solute is \(\text{Na}_3\text{AlO}_4\) rather than simply \(\text{Al}_2\text{O}_3\), and if this compound and ideal behavior are assumed, the heat of fusion of \(\text{Na}_2\text{O}\) is \(4.77\) kcal/mole, in better agreement with the estimates above. Crucibles of \(\text{BeO}, \text{ZrO}_2, \text{ThO}_2, \text{MgO}, \text{Al}_2\text{O}_3\), and \(\text{NiO}\) are all rapidly attacked by molten \(\text{Na}_2\text{O}\) at \(1000\text{°C}\). Evidence is presented for the formation of the compounds \(\text{Na}_2\text{O}-\text{MoO}_3\), \(\text{Na}_2\text{O}-\text{WO}_4\), and \(2\text{Na}_2\text{O}-\text{FeO}\), by reaction of the metals and \(\text{Na}_2\text{O}\), the reaction with \(\text{Fe}\) occurring at about \(900\text{°C}\). Mo, W, Fe, Co, and Ni are all attacked by \(\text{Na}_2\text{O}\), Mo to a great extent, Ni to a much lesser degree, and the other materials falling in between, in the relative order given. This paper\(^9\) contains a wealth of detail on the behavior of \(\text{Na}_2\text{O}\) and is a valuable contribution to the study of the properties of this extremely intractable material.

The solubility of \(\text{Na}_2\text{O}\) in sodium has recently been measured by Weber and Pepkowitz.\(^{10}\) Preliminary results indicate that the solubility is \(0.3\) wt\%, independent of temperature over the range \(125\) to \(425\)°C, but later studies have suggested that this value may be too high by factor of 5 or 10. \(\text{Na}_2\text{O}\), while denser than sodium, tends to float on the surface of the molten metal because of the high surface tension of the latter. Above about \(125\)°C, the \(\text{Na}_2\text{O}\) is wetted by the sodium and tends to sink into the bulk phase of the liquid in the form of a coarse sludge which can be filtered out. There is some indication that solid \(\text{Na}_2\text{O}\) may also be strongly adsorbed on glass or metal surfaces. These factors make the sampling and control of sodium for oxygen contamination extremely difficult, in that solid \(\text{Na}_2\text{O}\) may be present in the system and not show up on analysis.

Much of the work at KAPL on the determination of oxygen in sodium has depended on the analytical technique developed by Pepkowitz and Judd.\(^{11}\) Essentially, this method consists in the extraction of the sodium in the sample (under an inert atmosphere) with mercury, and the titration of the residual \(\text{Na}_2\text{O}\), which is insoluble in mercury. Repeated analyses by this method of sodium triple-distilled in Pyrex glass at about \(1\) mm pressure have yielded a value of \(0.02\) wt\% oxygen. This technique, which fulfills a long standing need in the field of sodium technology, is good to about \(0.01\)%. Salmon\(^{12}\) has recently developed another method of analysis in which the bulk of the sample is reacted with chlorine gas in the presence of carbon, and the oxygen determined gasometrically as CO. This technique has given \(0.031\)% as the oxygen content of triple-distilled sodium, which is in good agreement with the other method. It is of interest to be able to determine oxygen in sodium in the range \(0.001\)% or less, and lower limits of the amalgamation and chlorination techniques are currently being explored along with other possible methods for determining \(\text{Na}_2\text{O}\) in sodium.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Some reference sources\(^{35}\) indicate that Na\(_2\)O is thermally unstable, decomposing according to the reaction:

\[
2\text{Na}_2\text{O} = 2\text{Na} + \text{Na}_2\text{O}_2 \quad (30)
\]

Controlled experiments in an inert atmosphere, as well as thermodynamic calculations, indicate that this reaction does not occur to any appreciable extent.\(^{20}\) The partial pressure of sodium over Na\(_2\)O is no more than 0.1 mm at temperatures as high as 1300°C. It is believed that the erroneous conclusion on the stability of Na\(_2\)O may have been drawn from experiments in which oxygen was not excluded, where the well-known reaction

\[
\text{Na}_2\text{O} + \frac{1}{2}\text{O}_2 = \text{Na}_2\text{O}_2 \quad (31)
\]

occurred.

Na\(_2\)O\(_2\) is a common article of commerce, and is important as an oxidizing agent, as a source of free oxygen according to the reaction

\[
\text{Na}_2\text{O}_2 + \text{H}_2\text{O} = 2\text{NaOH} + \frac{1}{2}\text{O}_2 \quad (32)
\]

and as an intermediate in the preparation of other materials (high purity H\(_2\)O\(_2\), organic peroxides, etc.). The direct reaction of sodium and excess oxygen at elevated temperatures always yields nearly pure Na\(_2\)O\(_2\). In work with sodium, Na\(_2\)O\(_2\) is not often encountered since the reaction

\[
\text{Na}_2\text{O}_2 + 2\text{Na} = 2\text{Na}_2\text{O} \quad (33)
\]

occurs readily at temperatures of 300 to 400°C. This is a convenient way of preparing sodium containing known amounts of oxygen, since Na\(_2\)O\(_2\) of high purity is readily available. The reaction must be carried out slowly and carefully however, because too rapid heating of a Na-Na\(_2\)O\(_2\) mixture has been observed to result in an explosion.

A third product of the reaction between sodium and oxygen should be mentioned here. When sodium containing an excess of sodium oxide is melted in an inert atmosphere, the white oxide which floats on top initially is observed to turn darker as the temperature is raised, finally yielding a completely black powdery material. This is extremely pyrophoric, and bursts into flame on exposure to air at temperatures near the melting point of sodium. If it is first cooled, then brought out into the air, it slowly transforms into the white oxide. The black powder is completely soluble in alcohol without residue, and is believed to be a mechanical mixture of Na\(_2\)O and finely divided sodium. This is probably the material which has occasionally been called a suboxide of sodium in the literature, but there appears to be no basis for assuming the existence of the Na\(_2\)O and sodium in this material in the fixed stoichiometric ratio which would be required if it were, for example, Na\(_2\)O or Na\(_2\)O\(_2\). Friend\(^{35}\) states that "The so-called 'sodium suboxide' obtained by combustion of sodium in a limited supply of oxygen seems to be either a mixture or solid solution of sodium and sodium oxide," and the observations at the Knolls Atomic Power Laboratory are in complete agreement with this statement.

Very recently, a fourth oxide of sodium, NaO\(_2\), has been reported by a group working at the University of Kansas.\(^{51,52,53}\) This superoxide is prepared either by the rapid oxidation of sodium dissolved in liquid ammonia, or by the high temperature-high pressure reaction of Na\(_2\)O\(_2\) and gaseous oxygen. From its physical and chemical properties, NaO\(_2\) would be expected to be rapidly reduced to the monoxide in the presence of liquid sodium, and its formation in a sodium-filled heat-transfer system is quite unlikely.

2. Sodium and Water (Alcohols)

The reaction of sodium and water

\[
\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \frac{1}{2}\text{H}_2 \quad (34)
\]

is important because it "fixes" hydrogen and introduces it into the heat transfer fluid. The presence of hydrogen in a nuclear reactor in any form may be undesirable (particularly for an intermediate or fast neutron spectrum) because of the strong neutron slowing-down and scattering properties of this material. In the KAPL Intermediate-energy reactor, for example, it has been estimated that no more than 0.5% of hydrogen can be tolerated in the coolant sodium.

It has been suggested that the presence of NaOH may accelerate attack by liquid sodium,\(^4\) but the evidence for this is by no means conclusive, and it is believed that the principal effects may be due to Na\(_2\)O produced by the reaction

\[
\text{NaOH} + 2\text{Na} = \text{Na}_2\text{O} + \text{NaH} \quad (35)
\]

and subsequent thermal dissociation of the sodium hydride according to:

\[
\text{NaH} = \text{Na} + \frac{1}{2}\text{H}_2 \quad (36)
\]

so that the overall reaction is:

\[
\text{NaOH} + \text{Na} = \text{Na}_2\text{O} + \frac{1}{2}\text{H}_2 \quad (37)
\]
This reaction, at 25°C, is known to proceed with a free energy change of -9 kcal. It is not possible however to compute the extent of the reaction at higher temperatures (which are of greater interest) because of lack of data on the heat capacity of NaOH. This quantity was last measured in 1885, in the range 0 to 98°C, by Blümcke, who obtained a mean value of 0.78 cal/g·°C. This corresponds to a molal heat capacity of 31 cal/mole·°C, which is much greater than 9R or 18 cal/mole·°C computed from the Dulong and Petit rule. If Kopp's Law and his empirical "atomic heat capacities" are used, the result is 13 cal/mole·°C. It would thus appear that Blümcke's value may be much too high and new measurements on Cₚ for solid NaOH are badly needed.

NaOH exists in a solid alpha form up to a temperature of 299.6°±0.5°C, where it transforms to a beta form with a heat of transition of 990 cal/mole, according to von Hevesy. The beta form melts at 318.4°±0.2°C, with a heat of fusion of 1,602 cal/mole. Nothing is known of the structure of the two solid forms and this topic warrants investigation. Above the melting point, the heat capacity of liquid NaOH has been measured by Terashkevich and Visnevskii over the range 350 to 650°C. Their data yield a mean value of 0.482±0.006 cal/g·°C. This value is in much better agreement with theory than Blümcke's data on the solid. By extrapolating the data on concentrated aqueous solutions of NaOH, as reported by Wilson and McCabe for the range 25 to 150°C, to zero water content the heat capacity of (hypothetical) supercooled liquid NaOH is obtained. This yields the equation:

Cₚ = 0.4611 - 1.918 × 10⁻⁵ T + 7.047 T⁻¹ cal/g·°C (38)

At 466°C (the mean temperature of Terashkevich and Visnevskii's measurements), this equation gives Cₚ = 0.459 cal/g·°C, and the two results check to within 5%.

It is quite surprising to find that so little has been published about NaOH in view of its importance in industry. An exact evaluation of the role of NaOH in corrosion of metals by liquid sodium must await a more careful study of the thermodynamic properties of this material.

The reactions of sodium and liquid water are of further interest because the problem of cleaning equipment which has contained sodium often arises in practice. As is well known, sodium and water frequently react with explosive violence. In an inert atmosphere, this may occur because of the rapid evolution of H₂ and steam. When air is present, there is, in addition, the possibility of explosive combination of hydrogen and oxygen. The kinetics of this reaction are being studied at the Naval Research Laboratory, and the Mine Safety Appliances Company.

In cleaning up equipment which has contained sodium, it is common practice to use ethyl alcohol rather than water since the reaction is much slower and more easily controlled. Furthermore, the boiling point of the liquid (78.5°C) is less than the melting point of the metal, which reduces the likelihood of explosion, although there is an additional hazard due to the low flash point of alcohol. Experiments at KAPL on the relative rates of reaction of sodium with alcohols have led to the following conclusions: in general, the speed of the reaction becomes less as the number of carbon atoms in increased, and it is less for secondary and tertiary alcohols than it is for primary alcohols. Thus an extremely slow reaction is obtained with t-butyl alcohol, and by using mixtures of this material and water a wide range of reaction velocities can be attained.

3. Sodium and Hydrogen

The reaction of sodium and hydrogen is also of interest. Sodium hydride is a strong reducing agent, and is now commercially produced. The dissociation pressure of NaH has been measured by Keyes, Sollers and Crenshaw, and by Troost and Hautefeuille. The data are all in substantial agreement, and for the reaction,

NaH(s) = Na(l) + ½H₂(g) (39)

the partial pressure of hydrogen may be represented by Keyes' equation:

log pH₂ (mm) = -5700/T + 2.5 log T + 3.956 (40)

From this equation, the dissociation pressure of NaH is 1 atm at 423.4°C. Other thermodynamic properties are summarized in Table 15.

Hydrogen, present as sodium hydride can be removed from liquid sodium by heating it above
about 425°C, or at a much lower temperature if vacuum or an inert gas sweep is used. If the conversion of NaOH to NaH occurs (Eq. 35) below this temperature at an appreciable rate, all of the contaminant hydrogen can be effectively eliminated by this procedure. Most of the hydrogen in sodium is apparently formed by a surface reaction between the metal and atmospheric moisture: a sample taken from the interior of a brick of sodium was found to contain a total of 0.006 ± 0.001 wt% hydrogen.\textsuperscript{83}

Table 15. Thermodynamics of the reaction—

\[
\text{NaH} (s) = \text{Na} (l) + \frac{1}{2}\text{H}_2 (g)
\]

<table>
<thead>
<tr>
<th>T, °C</th>
<th>(\Delta F^\circ)</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta S^\circ)</th>
<th>(P_{H_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6635</td>
<td>13,980</td>
<td>19.7</td>
<td>1.3 \times 10^{-3}</td>
</tr>
<tr>
<td>200</td>
<td>4859</td>
<td>14,220</td>
<td>20.3</td>
<td>0.40</td>
</tr>
<tr>
<td>300</td>
<td>2589</td>
<td>14,480</td>
<td>20.7</td>
<td>6.07</td>
</tr>
<tr>
<td>400</td>
<td>187</td>
<td>14,720</td>
<td>21.1</td>
<td>362</td>
</tr>
<tr>
<td>500</td>
<td>-1633</td>
<td>14,980</td>
<td>21.5</td>
<td>6370</td>
</tr>
</tbody>
</table>

In the KAPL reactor, the system is to be surrounded by a helium blanket, and since hydrogen is a common contaminant in helium it is important to be able to determine the tolerable limits of this impurity in the gas and still remain below the limits of fixed hydrogen established by nuclear considerations. To do this, further information on the solubility of solid NaH in sodium, and the rates of reaction of gaseous hydrogen and liquid sodium, over a range of temperatures and partial pressures, is desirable.

4. Sodium and Nitrogen (Inert Atmospheres)

Nitrogen gas has frequently been used as an inert atmosphere in experiments with sodium and sodium-potassium alloy. The question of possible reaction of these elements with the production of explosive compounds has often been raised. It should, therefore, be emphasized at once that there is no evidence whatsoever for this reaction.

Two compounds of sodium and nitrogen are known. The first, the nitride NaN\textsubscript{3}, does not form by direct interaction of the elements under normal conditions.\textsuperscript{84,85} Its preparation by the action of the silent electric discharge on sodium in a nitrogen atmosphere has been reported.\textsuperscript{113,33} The nitride reacts with water with vigorous evolution of \(\text{NH}_3\), and it is to be expected that it will react readily with oxygen to form \(\text{Na}_2\text{O}\) and free nitrogen. It is apparently very unstable, and its formation in sodium at elevated temperatures is extremely unlikely.

The mistaken fear of explosive reaction products may originate from the fact that the second known compound of sodium and nitrogen is the azide NaN\textsubscript{3}. While the heavy metal azides are extremely explosive and sensitive to shock, the alkali azides "do not explode even on percussion, and may almost be melted without decomposition, as they explode only at high temperature."\textsuperscript{114} This material has furthermore never been prepared by direct combination of the elements: the only well known methods of synthesis involve such comparatively indirect procedures as the action of sodamide, NaNH\textsubscript{2}, and N\textsubscript{2}O; the decomposition of hydrazoyl chloride, N\textsubscript{2}C\textsubscript{1}Cl, with NaOH; or the neutralization of the difficultly obtained hydrazoic acid with NaOH. It does not appear likely that sodium azide could ever be formed by direct interaction of the elements under proposed reactor operating conditions.

While in some cases it is convenient to use \(\text{N}_2\) gas, at KAPL one of the rare gases, argon or helium, is preferred for small-scale experiments with sodium because of the relative ease of removing trace oxygen and water vapor (e.g., using heated metallic calcium). It is of interest to note that Langmuir\textsuperscript{87} has estimated the solubility of xenon in sodium at 500°C to be about 3 \times 10^{-4} cu cm of gas (measured at one atmosphere and 25°C) per cu cm of sodium, and that the solubility decreases as the temperature goes down. Other rare gases would be expected to behave in somewhat the same way.

5. Sodium and Carbon

The observed action of sodium in the carburization and decarburization of steels and other metals, which will be discussed at length in Part II, makes it worth while to examine the compounds of these two elements. Again, as in the case of nitrogen, there seems to be no evidence for formation of sodium carbide by direct combination of the elements.\textsuperscript{88} In fact, the only known carbide is sodium acetylide Na\textsubscript{2}C\textsubscript{2} prepared by the direct reaction of sodium and acetylene gas C\textsubscript{2}H\textsubscript{2}. This
reaction is most conveniently carried out in solutions of sodium in liquid NH₃. Na₂C₉ is of doubtful thermodynamical stability. Kelley reviewed its properties and concluded that the data are quite undependable: different methods of measurement give +5300 cal/mole or −9660 cal/mole for the heat of formation at 25°C. The free energy of formation at room temperature is given as −6.57 kcal/mole, but this is as uncertain as the heat data, with regard to both magnitude and sign.

It would be extremely interesting to determine whether carbon has an appreciable solubility in liquid sodium, since this would be an important factor in carburization phenomena. To date this has not been possible, mostly because no satisfactory method for the analytical determination of carbon in sodium at low concentrations has been developed. Studies on this subject are in progress at KAPL.

It should be noted here that brick sodium as normally obtained also contains significant amounts of Na₂CO₃, formed by a surface reaction between Na₂O and CO₂. No effects on the properties of liquid sodium that can be attributed to this material have been observed. Its solubility in sodium may be so low as to be inconsequential, and it is probable that Na₂CO₃ in small concentrations is quite harmless. Moreover, it is rapidly attacked by sodium at elevated temperatures, and yields Na₂O and carbon.

Since metallic sodium will reduce CO and CO₂ to free carbon, CO₂ extinguishers may be ineffectual.

### Table 16. Variation of free energy of formation of oxides with temperature.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxide</th>
<th>ΔF° at 25°C</th>
<th>ΔF° at 500°C</th>
<th>ΔF° at 1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al₂O₃</td>
<td>−366</td>
<td>−330</td>
<td>−288</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb₂O₃</td>
<td>−149</td>
<td>−120*</td>
<td>−92</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As₂O₃</td>
<td>−135</td>
<td>−104</td>
<td>−72</td>
</tr>
<tr>
<td>Barium</td>
<td>BaO</td>
<td>−126</td>
<td>−115</td>
<td>−104</td>
</tr>
<tr>
<td>Beryllium</td>
<td>BeO</td>
<td>−132</td>
<td>−121</td>
<td>−109</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi₂O₃</td>
<td>−117</td>
<td>−83</td>
<td>−40</td>
</tr>
<tr>
<td>Cadmium</td>
<td>CdO</td>
<td>−60</td>
<td>43</td>
<td>23</td>
</tr>
<tr>
<td>Calcium</td>
<td>CaO</td>
<td>−144</td>
<td>−133</td>
<td>−121</td>
</tr>
<tr>
<td>Carbon</td>
<td>CO</td>
<td>−33</td>
<td>43</td>
<td>54</td>
</tr>
<tr>
<td>Cerium</td>
<td>CeO₂</td>
<td>−220</td>
<td>−198</td>
<td>−176</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs₂O</td>
<td>−79</td>
<td>−74</td>
<td>−69</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr₂O₃</td>
<td>−249</td>
<td>−215</td>
<td>−180</td>
</tr>
<tr>
<td>Cobalt</td>
<td>CoO</td>
<td>−51</td>
<td>43</td>
<td>34</td>
</tr>
<tr>
<td>Columbium</td>
<td>CuO₂</td>
<td>−426</td>
<td>−400</td>
<td>−373</td>
</tr>
<tr>
<td>Copper</td>
<td>CuO</td>
<td>−35</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga₂O</td>
<td>−75</td>
<td>−64</td>
<td>−53</td>
</tr>
<tr>
<td>Germanium</td>
<td>GeO₂</td>
<td>−142</td>
<td>−210</td>
<td>−197</td>
</tr>
<tr>
<td>Gold</td>
<td>Au₂O₃</td>
<td>19</td>
<td>31</td>
<td>44</td>
</tr>
<tr>
<td>Hafnium</td>
<td>HfO₂</td>
<td>−256</td>
<td>−237</td>
<td>−215</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂O</td>
<td>55</td>
<td>49</td>
<td>42</td>
</tr>
<tr>
<td>Indium</td>
<td>In₂O₃</td>
<td>−218</td>
<td>−184</td>
<td>−147</td>
</tr>
<tr>
<td>Iridium</td>
<td>IrO₂</td>
<td>28</td>
<td>9</td>
<td>51</td>
</tr>
<tr>
<td>Iron</td>
<td>FeO</td>
<td>59</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>La₂O₃</td>
<td>−436</td>
<td>−403</td>
<td>−368</td>
</tr>
<tr>
<td>Lead</td>
<td>PbO</td>
<td>45</td>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li₂O</td>
<td>−138</td>
<td>−130</td>
<td>−123</td>
</tr>
<tr>
<td>Magnesium</td>
<td>MgO</td>
<td>−138</td>
<td>−127</td>
<td>−114</td>
</tr>
<tr>
<td>Manganese</td>
<td>MnO</td>
<td>−69</td>
<td>82</td>
<td>−75</td>
</tr>
<tr>
<td>Mercury</td>
<td>HgO</td>
<td>−14</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>MoO₃</td>
<td>−122</td>
<td>−100</td>
<td>−80</td>
</tr>
</tbody>
</table>

*Orthorhombic. †White.
effective and should not be used on sodium fires. (CCl, and similar materials are even more dangerous: sodium often reacts with organic halides with explosive violence.) For smothering sodium fires, dry soda ash, anhydrous Na₂CO₃ or rock dust, and powdered limestone, appear to be best.

6. Sodium and Metallic Oxides

In subsequent sections, where the corrosion of materials by liquid sodium will be considered, the reactions of sodium and metallic oxides will be shown to be of considerable importance. These can all be represented by the equation:

\[ M_\text{O} + 2b \text{Na} = aM + b \text{Na}_2\text{O} \]  \hspace{1cm} (41)

Among the metals, there are many whose oxides are completely reduced by sodium, and others which can reduce Na₂O to free sodium. The direction in which the reaction proceeds depends on whether the free energy of formation of the metallic oxide per atom of oxygen, i.e., \( \Delta F^\circ/b \), is greater or less than the free energy of formation of Na₂O. The \( \Delta F^\circ \)'s of formation of a large number of oxides are listed in Table 16. In each case, only the lowest stable oxide has been tabulated, and for many elements the data are little more than crude approximations. Generally speaking, the accuracy of the data is such that a difference of less than 5 to 10 kcal between \( \Delta F^\circ/b \) and \( \Delta F^\circ_{\text{Na}_2\text{O}} \) is not significant.

7. Intermetallic Compounds of Sodium

In the KAPL reactor, and some other systems which have been considered, the heat generated in the reactor core is carried away by sodium as the primary heat-transfer fluid and eventually used to heat steam for a normal turbo-generator installation. The danger of explosion from a sodium leak into the steam part of the system is obviously very great, and a number of schemes have been devised using a third fluid to reduce this hazard. For example, the heat-transfer units might be designed in the form of three concentric tubes: the outer one to contain the water to be heated, the central tube the flowing sodium (or sodium-potassium alloy), and the middle tube might contain a stagnant pool of mercury or some other appropriately low melting alloy. Presumably a break in the sodium line could be detected by suitable instrumentation before it resulted in reaction of the sodium and H₂O. (A simultaneous break in the sodium-mercury wall and the mercury to H₂O wall would be quite dangerous, but such concurrent accidents are not considered very probable.)

As is well known, considerable heat is evolved when sodium reacts with mercury as a result of the formation of intermetallic compounds. Possible deleterious effects of the heat evolved have been considered, and in Table 17 the available data on the heats of formation of intermetallic compounds with sodium have been tabulated. The heats were taken from Bichowsky and Rossini unless otherwise noted, and the melting points were read from phase diagrams given by Hansen. The notation (U) after a melting point means that the compound is unstable, i.e., decomposes before melting.

The reaction of sodium with the metals listed in Table 17 has been observed to take place with explosive violence. The magnitude of the effect will depend on the relative amounts of the reactants and the nature of the system. If 1 gram mole of mercury and sodium are reacted adiabatically, assuming the intermetallic compounds to be unstable at the ultimate temperature and no volatilization, the temperature rise can be calculated to be nearly 1000°C. Careful design that
provides for rapid heat transfer, and a system of relatively high heat capacity, should minimize the hazard involved.

ACKNOWLEDGMENTS

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April 1949 (Revised June 1949)
Dimensional Changes in Uranium Under Thermal Cycling

By L. R. Kelman
Argonne National Laboratory
Report ANL-FF-54 (Del.)

ABSTRACT

Uranium undergoes permanent dimensional changes when thermal cycled in the alpha-temperature range without passing through any phase transformations. This deformation is attributed to the anisotropy of thermal expansion inherent in noncubic metals. Alpha uranium, which is orthorhombic, is especially susceptible because of its high anisotropy of thermal expansion. Uranium rods prepared by a wide variety of fabrication and heat-treat methods were thermal cycled between 100°C and 550°C. Observations were made on the effects of fabrication technique, heat treatment, and thermal cycling on the dimensions, surface roughening, microstructure, and preferred orientation of these rods.

INTRODUCTION

This investigation was started about 1½ years ago as a study of the effects of thermal cycling upon the warp of 8-in. long, 0.364-in. diameter rolled uranium rods then under consideration for use in reactor rod assemblies for the CP-4 pile.1 It soon became evident that permanent dimensional changes other than warp resulted from thermal cycling. It was found that heating and cooling of rolled uranium rods in the alpha temperature range (without passing through any phase transformations) resulted in a permanent increase in length with a corresponding decrease in diameter, and that continued thermal cycling of these rods resulted in continued elongation with no indication of an appreciable change in rate of elongation.2

Previous investigators have noted very small dimensional changes as a result of heating and cooling in the alpha temperature range. Battelle Memorial Institute was the first to note anomalous dilatometric behavior of uranium which they attributed to the anisotropy of the metal.3,4 They were actually heating through the alpha-beta transformation, but obtained some indications that uranium undergoes permanent deformation in the high alpha region. Further experiments were made to check this point, but dimensional changes on heating and cooling through the transformation plus surface roughening of the specimens confused the results.5,6,7,8 They also studied causes of surface roughening9 but in no case did they attribute dimensional instability or surface roughening to plastic deformation during heating and cooling in the alpha range.

In a study of the dimensional changes during annealing of 8-in. long slugs, Foote and Van Echo9 found that annealing alpha-rolled slugs in the alpha region resulted in an increase in length.
and a decrease in diameter and that on one or two subsequent anneals these dimensional changes continued in the same direction at approximately the same rate. Although they claimed that the changes in dimensions increase with increasing time and temperature of annealing, their data show a definite temperature effect but no appreciable time effect. One of their 8-in. long slugs elongated 12.9 mils on annealing four hours at 585°C and 7.6 mils on a subsequent anneal of 24 hr at 465°C. Several slugs were given three successive anneals at 465°C for times of 6, 6, and 16 hr, and on each anneal the specimens elongated approximately 5 mils. They found that, on the average, diameter changes were such as to just compensate for the elongation, giving a constant density. Annealing gamma-extruded slugs at 465°C resulted in small but erratic dimensional changes. They offered no mechanism explaining elongation of alpha-rolled slugs on annealing in the alpha region.

In a recent series of papers Boas and Honeycombe have shown that plastic deformation occurs when certain noncubic metals are repeatedly heated and cooled. They attribute this deformation to the anisotropy of thermal expansion inherent in these metals. They first noted that the surface of tin-base bearings roughened on heating and cooling whereas lead-base bearings showed no signs of surface roughening. They then thermal cycled the noncubic metals, tin, zinc, and cadmium along with a cubic metal, lead, and found that only lead was unaffected by this cyclic treatment of 30°C-150°C. In the noncubic metals they observed deformation marks, a roughening of the smooth surfaces of the specimens with accentuation of grain boundaries, and migration of grain boundaries as a result of thermal cycling.

From their test results they proposed the mechanism diagrammatically shown in Fig. 1 in which the stress between adjacent grains of different orientations is plotted against temperature of a thermal cycle. On heating, thermal expansion results in a stress between adjacent grains which is proportional to the increase in temperature until plastic deformation begins. Further heating results in plastic deformation which relieves any further stress except for the slight increase in stress due to work hardening. On cooling, elastic deformation in the reverse direction occurs until zero stress is reached at some elevated temperature. Further cooling results in stresses in the opposite direction which may exceed the yield point at this lower temperature resulting in plastic deformation in the opposite direction. Repeating this cycle results in stress reversals similar to those occurring when alternate external tensile and compressive stresses are applied. Because of this analogy, Boas and Honeycombe named the phenomenon "thermal fatigue." This mechanism assumes a definite yield point and is very much simplified because it does not consider the effect of time on the creep of metals such as uranium.

An interesting consequence of this phenomenon is that, no matter how stress-free an anisotropic metal may be at an elevated temperature, cooling after annealing will result in new stresses. Therefore, polycrystalline aggregates of anisotropic metals cannot be obtained in a stress-free condition at room temperature by casting or annealing. This was first suggested by C.H. Desch.
in 1923 during a controversy over the possibilities of grain growth on annealing noncubic cast metals without prior plastic deformation. He pointed out that anisotropy of thermal expansion gave rise to plastic deformation during cooling of the casting and on heating to the annealing temperature.

Boas and Honeycombe studied factors influencing plastic deformation of noncubic metals on thermal cycling. They found that rate of cycling had a negligible effect and also that no plastic deformation occurred in lead from which they concluded that it is unlikely that nonuniform expansion due to temperature gradients was responsible for the observed deformation. They also found that the number and intensity of deformation lines as well as the extent of surface roughening increased with increasing number of thermal cycles, and also with the temperature range of cycling. Deformation of individual grains in a polycrystalline aggregate occurred regardless of grain size, but a single crystal of cadmium showed no evidence of deformation. They also found some indication that less plastic deformation occurred in individual grains of a specimen possessing a preferred orientation than in a specimen of randomly oriented grains. However, they made no measurements of the overall dimensions of the specimen.

Estimates of the magnitude of stresses produced during the heating of a noncubic metal have been made by Boas and Honeycombe and Laszlo. These calculations indicate that plastic deformation on thermal cycling is more dependent on the anisotropy of thermal expansion than on the anisotropy of Young's modulus or the critical shear stress.

Boas and Honeycombe have also shown that the presence of hard second phases such as CuSn and SnSb in tin-base bearing alloys considerably reduces the deformation on thermal cycling, whereas deformation in tin-base alloys consisting only of a solid solution was almost as severe as in pure tin.

The phenomenon investigated by Boas and Honeycombe and the mechanism they propose to explain their findings appear to be related to the dimensional instability of uranium when thermal cycled. Alpha uranium is orthorhombic and highly anisotropic in thermal expansion. High temperature x-ray diffraction measurements at Battelle Memorial Institute gave the following mean coefficients of expansion:

<table>
<thead>
<tr>
<th>Crystallographic direction</th>
<th>25° to 300°C</th>
<th>25° to 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>[010]</td>
<td>-3.5</td>
<td>-1.4</td>
</tr>
<tr>
<td>[001]</td>
<td>17</td>
<td>22</td>
</tr>
</tbody>
</table>

Two of the coefficients are fairly large and positive whereas one is actually negative.

PROCEDURE

Since it was desired to apply the results of this investigation toward the design of the CP-4 fuel rods, the specimen dimensions and the thermal cycling setup were designed to simulate CP-4 conditions.

Fabrication and Heat Treatment of Specimens

Uranium rods were prepared by a wide variety of fabrication and heat treat methods resulting in a considerable variation in preferred orientation and grain size. In most cases alpha-rolled ¼-in. metal was used for starting material. The methods of fabrication included casting, swaging, and extruding in the alpha and in the gamma temperature ranges, and rolling in the high alpha region and at 300°C (below the recrystallization temperature range). The heat treatments used included annealing at 575°C to recrystallize slightly above the maximum cycling temperature; beta annealing for 2 hr at 725°C to eliminate preferred orientation but with extreme grain coarsening; and fast-beta treating by dipping in a lead pot at 725°C, holding for a short time, and then water quenching in an attempt to obtain a fine-grained, randomly oriented structure. Also studied were some coarse-grained, highly oriented uranium rods prepared by the strain-anneal method and a highly oriented plate rolled at 300°C.

Preparation of Specimens for Cycling

The same procedure was used to prepare all rods for cycling. The rods were fabricated to approximately ½ in. diameter at which size some of them were given a desired heat treatment. They were then machined to 0.384 in. diameter and either 4-in. or 2-in. lengths. At this stage they were electropolished and deep etched and their macro grain structures were noted.
The rods were then annealed in a stainless steel container filled with NaK as a heat transfer medium for 2 hr at 575°C and furnace cooled. NaK has been used throughout these experiments as a heat transfer medium because it does not alloy with the bare uranium rods, it is liquid in the range of temperatures used for this study, it is a fairly good thermal conductor, and its high coefficient of thermal expansion produces convection currents that help to eliminate thermal gradients. The annealing temperature was arbitrarily chosen as 575°C, which is 25°C higher than the maximum cycling temperature. Thus dimensional changes which might be caused by recrystallization, grain growth, and possibly by transformation of unstable phases in the fabricated rods were eliminated prior to cycling.

Following the anneal, the rods were centerless ground to 0.364 in. diameter and the ends were ground square to eliminate warp due to annealing.

Thermal Cycling of Specimens

The rods were thermal cycled under conditions which roughly simulate pile conditions. They were supported freely in a vertical position with 20 mils clearance in retaining rings at each end of the rods. Hence, the rods stand on end and are free to elongate and warp without restraint other than that produced by their own weight. This assembly was held in a stainless steel container filled with NaK as a heat transfer medium as shown in Fig. 2. The container was heated by induction using a 20 kva Ecco converter. By locating thermocouples in the center of a rod and at several points along the length of a 10-in. column of NaK, it was found that heating from 100°C to 550°C in 5 min gave no appreciable thermal gradients. Cooling from 550°C to 100°C by means of several fans took from 20 to 25 minutes. The upper temperature of 550°C was arbitrarily chosen. It is somewhat higher than the maximum temperature initially contemplated in the center of the CP-4 pile fuel rods. The lower temperature was fixed at 100°C as a temperature which could be reached in a reasonable time by air cooling.

To determine the effect of small temperature fluctuations at elevated temperatures, a few rods were cycled between 500°C and 550°C. Heating and cooling each took about 2½ min for this test.

Inspection and Measurement of Rods

In most cases, three duplicate rods were cycled for each type of fabrication and heat treatment. Specimens for metallographic study of microstructure and x-ray diffraction study of preferred orientation were cut from one rod after various numbers of cycles. The other two rods were used as duplicate specimens for length, diameter, surface roughening, and warp studies. Lengths and diameters were measured with a hand micrometer after 50, 100, 300, 700, and in some cases 1500 cycles. Measurements at the beginning of the tests were fairly accurate, but warp and surface roughening precluded accurate measurements of some rods as cycling progressed. Surface roughening was noted visually, and recorded by
means of full size photographs, but no attempts were made to quantitatively measure the size, shape, or number of bumps. Warp measurements were made with the rod supported on V-blocks using a Federal dial gage graduated in 0.0001-in. divisions and eccentricity was taken to be half the total run-out.

Specimens were prepared for preferred orientation determination by machining to true cylinders and then electroetching a 0.005-in. layer from the surface. X-ray photograms were taken using copper K-alpha radiation, with 0.025-in. pinhole, 5-cm specimen to film distance, 3-cm pinhole to specimen distance, and one hour exposure. The settings used were: (1) the beam perpendicular to the rolling direction; (2) the beam at 18 degrees to the rolling direction. The specimens were rotated about their own axes at 1 rpm to get an integrated picture. The sharpness of the texture was measured by the length of the Debye arc of the (002) plane which indicates the degree of scatter of the "C" axis from the mean orientation. For further details see references 24 and 25.

DISCUSSION OF RESULTS

No attempt is made in this report to thoroughly discuss every specimen that has been cycled in the course of this investigation. However, the elongation data of most of the specimens are tabulated and discussed briefly to show how they fit into the general cycling program. Representative specimens are discussed in detail to illustrate the effects of fabrication technique, heat treatment, and thermal cycling on elongation, surface roughening, microstructure, and preferred orientation of the specimens. Within the accuracy of a hand micrometer in measuring rods which did not warp and whose surfaces did not bump or oxidize during cycling, diameter changes were such as to just compensate for the length changes. Diameter measurements included large errors due to surface roughening of many rods and due to surface oxidation of some rods and are, therefore, not given. Some density determinations were made which will be discussed later. Warp determinations are not reported because it is thought that the amount of warp was strongly influenced by the way the specimens were supported during the test. This is especially true in the case of rods which elongated so much that their upper ends were well above the retaining ring. Also, the 4-in. long specimens warped considerably more than the 2-in. long specimens. Photographs of some of the rods after cycling (see Figs. 5 and 6a) give an idea of the extent of warp.

Rolled Rods — Alpha Annealed

Uniformity and Reproducibility

Uranium rods that have been rolled in the alpha temperature range by a variety of methods have been thermal cycled up to 1500 times between 100°C and 550°C. The length changes of these rods are tabulated in Tables 1, 2, and 3 where the results are arranged according to the type of rolling. The only heat treatment these rods were given before cycling was a 575°C anneal which is slightly above the maximum cycling temperature.

Hot-Rolled Rods.—When this investigation was started, the standard method for alpha rolling uranium was to heat to 600°C and then roll to finished size without returning the rods to the furnace. The rods tend to become hotter as rolling proceeds, so they are held in air between passes until they appear to be about 600°C. Non-uniformity in rolling texture and grain size along the length of standard alpha-rolled rods results from this poor temperature control, and there are indications that the rods are sometimes heated through the alpha-beta transformation.

The erratic structure of these rods was reflected in their behavior when thermal cycled (Table 1). Three sets of specimens consisting of 3 supposedly duplicate specimens in each set—(5, 8, and 9), (40, 41, and 42), and (15, 16, and 17)—showed large variations in elongation. In general it was found that the rods which elongated the least (8, 41, and 15) had the roughest surfaces after cycling and had the largest grain size. One set of the standard alpha-rolled rods, (15, 16, and 17), were submerged in liquid nitrogen (-195.8°C) for 5 days in an effort to transform any retained beta phase. The cold treatment resulted in no perceptible changes in dimensions and the cycling results were erratic.

A 4-in. length of a standard alpha-rolled W-size slug received from Hanford (No. 997 from G material of billet No. 1735) was found to elongate 12.0% in 700 cycles which is about the same elongation as the similarly fabricated small diameter rods 5, 8, and 9.
Table 1—Elongation of standard alpha-rolled uranium rods due to thermal cycling between 100°C and 550°C

<table>
<thead>
<tr>
<th>Fabrication and heat treatment</th>
<th>Rod length (in.)</th>
<th>Per cent elongation $\frac{L-L_0}{L_0} \times 100$</th>
<th>Elongation coefficient $\frac{1}{L_0} - 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rod No.</td>
<td>Due to anneal</td>
<td>Number of cycles (N) 100</td>
<td>300</td>
</tr>
<tr>
<td>575°C annealed</td>
<td>5 4</td>
<td>0.01</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>8 4</td>
<td>-0.03</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>9 4</td>
<td>-0.05</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>40 4</td>
<td>-0.03</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>41 4</td>
<td>0.15</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>42 4</td>
<td>0.01</td>
<td>3.60</td>
</tr>
<tr>
<td>Hanford slug—575°C annealed</td>
<td>997 4</td>
<td>0.00</td>
<td>2.13</td>
</tr>
<tr>
<td>575°C annealed—5 days in liquid nitrogen</td>
<td>15 4</td>
<td>-0.08</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>16 4</td>
<td>-0.04</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>17 4</td>
<td>-0.07</td>
<td>2.33</td>
</tr>
<tr>
<td>725°C annealed</td>
<td>4 4</td>
<td>-0.34</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>6 4</td>
<td>-0.28</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>10 4</td>
<td>-0.28</td>
<td>-0.02</td>
</tr>
<tr>
<td>600°C rolled, 15 min at 725°C between passes, 75% reduction from std alpha-rolled rod, 575°C annealed</td>
<td>82 4</td>
<td>0.03</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>83 4</td>
<td>0.02</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>84 4</td>
<td>-0.01</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*Rod cut up for samples at various stages of cycling.
†Rod cycled 2200 times between 500°C and 550°C before further cycling between 100°C and 550°C, but recorded elongations are corrected for the elongation that occurred on 500°C-550°C cycling.
‡Coefficients too small to be measured accurately.

Table 2—Elongation of 600°C-soak-rolled uranium rods due to thermal cycling between 100°C and 550°C

<table>
<thead>
<tr>
<th>Fabrication and heat treatment*</th>
<th>Rod length (in.)</th>
<th>Per cent elongation $\frac{L-L_0}{L_0} \times 100$</th>
<th>Elongation coefficient $\frac{1}{L_0} - 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rod No.</td>
<td>Due to anneal</td>
<td>Number of cycles (N) 100</td>
<td>300</td>
</tr>
<tr>
<td>30 min at 600°C after every pass, 575°C annealed</td>
<td>53 4</td>
<td>0.00</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>55 4</td>
<td>0.00</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>57 4</td>
<td>-0.03</td>
<td>1.75</td>
</tr>
<tr>
<td>30 min at 600°C after every pass, not annealed</td>
<td>54 4</td>
<td>1.71</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>56 4</td>
<td>1.71</td>
<td>4.53</td>
</tr>
<tr>
<td></td>
<td>58 4</td>
<td>1.72</td>
<td>4.18</td>
</tr>
<tr>
<td>15 min at 600°C after every 2 passes, 575°C annealed</td>
<td>69 4</td>
<td>0.00</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>70 4</td>
<td>0.02</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>71 4</td>
<td>0.04</td>
<td>1.45</td>
</tr>
<tr>
<td>15 min at 600°C after every 2 passes, 2 min at 717°C, water quenched, 575°C annealed</td>
<td>88 4</td>
<td>-0.05</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>89 4</td>
<td>-0.03</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>90 4</td>
<td>-0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>15 min at 600°C after every 2 passes, 2 min at 687°C, water quenched, 575°C annealed</td>
<td>91 4</td>
<td>-0.04</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>92 4</td>
<td>-0.04</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>93 4</td>
<td>-0.03</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*All rods reduced 75% by 600°C soak rolling from standard alpha-rolled rod.
†Rod cut up for samples at various stages of cycling.
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

In an effort to obtain reproducibility of structure in rolled uranium rods, several rods were rolled at 600°C and soaked in a furnace at that temperature between passes. Better reproducibility in structure and in growth on cycling was achieved by this method (Table 2), but the method is cumbersome, time consuming, and not always successful. The use of a liquid-metal bath to keep the rods at constant temperature during rolling might make this a feasible production technique.

The effect of the anneal before cycling was examined by annealing one set of 600°C-soak-rolled rods (53, 55, and 57) and not annealing an identical set of rods (54, 56, and 58). These rods all elongated between 8.8% and 10% in 700 cycles regardless of whether or not they were annealed prior to cycling.

Table 3 — Elongation of cold-rolled uranium rods due to thermal cycling between 100°C and 550°C

<table>
<thead>
<tr>
<th>Fabrication and heat treatment</th>
<th>Rod length (in.)</th>
<th>Due to</th>
<th>Number of cycles (N)</th>
<th>Per cent elongation $\frac{L_0 - L}{L_0} \times 100$</th>
<th>Elongation coefficient $1 \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temp rolled — 18% reduction</td>
<td>1</td>
<td>4</td>
<td>-0.01</td>
<td>2.22, 7.19, 19.70</td>
<td>250</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>2</td>
<td>4</td>
<td>0.05</td>
<td>2.34, 8.10, 21.80</td>
<td>260</td>
</tr>
<tr>
<td>300°C Soak-rolled — 75% reduction</td>
<td>3</td>
<td>4</td>
<td>-0.06</td>
<td>2.08, 7.20, 21.05</td>
<td>260</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>47</td>
<td>4</td>
<td>0.25</td>
<td>3.11, 9.48, 21.85</td>
<td>60.25</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>48</td>
<td>4</td>
<td>0.22</td>
<td>3.20, (*)</td>
<td>320</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>49</td>
<td>4</td>
<td>0.21</td>
<td>3.18, 9.86, 25.20</td>
<td>64.0</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>94</td>
<td>4</td>
<td>0.52</td>
<td>11.27, 29.5</td>
<td>360</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>95</td>
<td>4</td>
<td>0.54</td>
<td>10.45, 30</td>
<td>360</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>1 - 4</td>
<td>2</td>
<td>1.35</td>
<td>2.83, (*)</td>
<td>280</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>5 - 8</td>
<td>2</td>
<td>1.27</td>
<td>2.64, 9.02, 26.47</td>
<td>290</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>11 - 14</td>
<td>2</td>
<td>1.61</td>
<td>3.31, 11.28, 31.41</td>
<td>360</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 575°C annealed</td>
<td>15 - 18</td>
<td>2</td>
<td>1.65</td>
<td>3.41, 11.48, 31.83</td>
<td>370</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>21 - 24</td>
<td>2</td>
<td>0.10</td>
<td>0.31, 0.72, 1.68</td>
<td>24</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 725°C annealed</td>
<td>25 - 28</td>
<td>2</td>
<td>0.19</td>
<td>0.41, 1.09, 2.42</td>
<td>32</td>
</tr>
<tr>
<td>725°C annealed</td>
<td>31 - 34</td>
<td>2</td>
<td>0.28</td>
<td>0.47, (*)</td>
<td>50</td>
</tr>
<tr>
<td>575°C annealed</td>
<td>35 - 38</td>
<td>2</td>
<td>0.13</td>
<td>0.20, 1.25, 1.45</td>
<td>21</td>
</tr>
<tr>
<td>300°C Soak-rolled — 89% reduction</td>
<td>41 - 44</td>
<td>2</td>
<td>0.00</td>
<td>0.01, (*)</td>
<td>(?)</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 725°C annealed</td>
<td>45 - 48</td>
<td>2</td>
<td>0.00</td>
<td>0.03, 0.25, 0.99</td>
<td>14</td>
</tr>
<tr>
<td>½ min at 725°C, water quenched, 575°C annealed</td>
<td>51 - 54</td>
<td>2</td>
<td>0.15</td>
<td>0.08, 0.25, 1.24</td>
<td>18</td>
</tr>
<tr>
<td>300°C Soak-rolled — 75% reduction</td>
<td>55 - 58</td>
<td>2</td>
<td>0.02</td>
<td>0.08, 0.35, 1.24</td>
<td>18</td>
</tr>
<tr>
<td>from std alpha-rolled rod, 2 min at 723°C, water quenched, 575°C annealed</td>
<td>50</td>
<td>4</td>
<td>-0.02</td>
<td>0.04, 0.49, 1.23</td>
<td>2.58</td>
</tr>
<tr>
<td>51</td>
<td>4</td>
<td>0.00</td>
<td>0.02, 0.25, 0.80, 2.71</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>4</td>
<td>0.19</td>
<td>(*)</td>
<td>(*)</td>
<td></td>
</tr>
</tbody>
</table>

*Rods cut up for samples at various stages of cycling.
*Coefficients too small to be measured accurately.

Cold-Rolled Rods. — Rolling below the uranium recrystallization temperature was another possible method of obtaining reproducible rolling results. One attempt was made to roll at room temperature, but only 18% reduction was attained before fracture occurred. However, cycling of 3 of these rods (1, 2, and 3) resulted in almost identical elongations in 700 cycles (Table 3).

Rolling at 300°C with a 5-min soak at 300°C between every other pass to insure maintaining the proper temperature during rolling resulted in rods of very uniform grain structure and strong preferred orientation which reacted similarly to thermal cycling. Also, this method of rolling results in considerably less oxidation of the uranium than does 600°C rolling which is an important consideration in the rolling of U235. It was,
therefore, decided to use 300°C-soak-rolled rods for the major part of this investigation.

Elongation

The amount of longitudinal growth on thermal cycling was found to increase directly as the number of cycles. In Figs. 3 and 4 are plotted elongation data for at least one rod of every type that was cycled. A plot of per cent elongation based on the original length against number of cycles, as shown in Fig. 3, shows an apparent acceleration of elongation as cycling proceeds. This type of plot does not represent the instantaneous growth of the rods and, therefore, gives a false rate of growth. If the instantaneous change in length, \( \Delta L/L \), is integrated between the original length, \( L_0 \), and the instantaneous length, \( L \),

\[
\int_{L_0}^{L} \frac{\Delta L}{L} = \ln \frac{L}{L_0}
\]

and the resulting expression, \( \ln L/L_0 \), is plotted against the number of cycles, a true rate of growth is obtained.\(^{26}\) The slope of the curve gives a coefficient of elongation on cycling representing the increase in length per unit length in one cycle. Coefficients of elongation, henceforth referred to as kappa (K), were obtained in this manner for all rods cycled and are included in all tables showing growth on cycling. Warp and surface roughening were not appreciable near the beginning of the cycling tests, but, as can be seen from the cycled rods shown in Figs. 5 and 6, they introduced large errors in length measurements in the latter stages of the cycling tests. Therefore, in drawing the curves, more weight was given to the earlier points. In all tests, length measurements after 50 or 100 cycles were sufficient to predict fairly accurately the rate of elongation on further cycling.

Study of the data in Tables 1, 2, and 3 and of Figs. 3 and 4 shows that, in general, the greater the reduction in area during rolling, the greater the rate of growth. Further, rods rolled at lower temperatures seem to grow at higher rates. A rod (15-18) that had been rolled at 300°C to an 89% reduction in area showed the greatest rate of elongation on cycling — \( K = 370 \times 10^{-9} \) or approximately 30% elongation in 700 cycles (Table 3). Continued cycling to 1500 cycles of rods (47, 49) that had been 300°C rolled to 75% reduction resulted in as much as 64% elongation (\( K = 320 \times 10^{-8} \)). These rods are shown in Fig. 5 after cycling. Specimens approximately \( \frac{1}{2} \) in. diameter \( \times \) 1 in. long were machined from these cycled rods and were recycled 700 times. The recycled rods elongated at about the same rate as did the original rods (Figs. 3 and 4).

To examine the possible effect of the dimensions of the rods on elongation due to cycling, 0.364-in. diameter rods of lengths of \( \frac{1}{4} \) in., \( \frac{1}{4} \) in., \( \frac{1}{2} \) in., 1 in., and 2 in., shown in Fig. 7, were machined from the same highly oriented 300°C-rolled rods and thermal cycled together. The test results (Table 4) show that varying the length of these rods had no appreciable effect on the amount of growth after 300 cycles.

Within the accuracy of the measurements of length and diameter, density appeared to be unaffected by thermal cycling. Density determinations made before and after 1500 cycles of rod 4, which elongated 64% (\( K = 320 \times 10^{-8} \)) indicated a slight decrease in density. The method consisted of accurately weighing and measuring \( \frac{1}{2} \)-in. diameter \( \times \) \( \frac{1}{2} \)-in. long polished cylinders. Checks of duplicate specimens showed a decrease in density of 0.17 g/cc due to thermal cycling. Making liberal allowances for possible errors in each step of the density measurement procedure, the calculated maximum and probable errors were 0.039 and 0.038 g/cc.

Surface Roughening

In general, uranium rods rolled in the alpha temperature range and then annealed at 575°C remained smooth on cycling. As was previously pointed out, the nonuniformity in rolling texture and grain size of hot rolled uranium rods was reflected in the erratic elongation results on cycling. The rolled rods with the least preferred orientation elongated the least. At the same time, these rods had the largest grain size of all the rolled rods, and their surfaces were roughened slightly on cycling. Typical surface appearance of rolled and annealed rods after cycling is shown in Fig. 5 (47, 49 and 55, 57) and in Fig. 6a (Group I).

Preferred Orientation

It is well known that plastic deformation of metals produces texture in which the individual
Fig. 3—Per cent elongation of uranium rods due to cycling between 100°C and 550°C.
Fig. 4—True elongation of uranium rods due to cycling between 100 °C and 500 °C.
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

"Cast
600°C rolled
725°C anneal
for 2 hr
600°C
soak-
rolled
300°C
soak-
rolled
300°C soaked
rolled Pb
pot dipped
at 723°C

*Cast slugs were cycled 1700 times.

Fig. 5—Uranium rods fabricated by various methods after 1500 cycles between 100°C and 550°C. Approx. 1 x
Fig. 6a — 300°C-rolled rods of various thermal histories after 700 cycles between 100°C and 550°C (from M-4315). 1×

- **Group I** — Annealed 2 hr at 575°C
- **Group II** — Annealed 2 hr at 725°C, then 2 hr at 575°C. (slow-beta treatment).
- **Group III** — 3⁄4 min dip in lead pot at 725°C and water quenched, then annealed 2 hr at 575°C. (fast-beta treatment).

Fig. 6b — Macrostructures of the rods shown in Fig. 6a before cycling (from M-4383). 1×
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

grains take up preferred orientations with respect to the direction of working. Three general types of preferred orientation have been found in rolled uranium rods depending upon the temperature of rolling and the amount of reduction. The mean orientation textures are as shown in Table 5.

![Image](image.png)

**Fig. 7**—Specimens used to study the effect of rod dimensions on growth due to cycling. Rods were 0.364 in. diameter and 2 in., 1 in., ¼ in., ½ in. and ¾ in. long (from M-4267). 1×

<table>
<thead>
<tr>
<th>Rod dimensions (in.)</th>
<th>Elongation coefficient (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>Diameter</td>
</tr>
<tr>
<td>¼</td>
<td>0.364</td>
</tr>
<tr>
<td>½</td>
<td>0.364</td>
</tr>
<tr>
<td>⅔</td>
<td>0.364</td>
</tr>
<tr>
<td>1</td>
<td>0.364</td>
</tr>
<tr>
<td>2</td>
<td>0.364</td>
</tr>
</tbody>
</table>

From Table 5 it may be seen that the c-axis is radial to the rod axis while the b-axis orientation varies with amount and temperature of cold work. Room temperature rolling is characterized by a b-axis orientation parallel to the rolling direction. The least amount of working occurs with 600°C-soak rolling where the (110) pole tends to line up with the rolling direction, placing the (010) (b-axis) as much as 45 degrees from the rolling direction in the most oriented condition. The texture produced by 300°C rolling is characterized by a duplex orientation of the axis which orients in the rolling direction and also at an angle to the rolling direction. This texture may be described by a major and minor mean orientation with a scatter as may be seen from the pole figures (Fig. 8).

**Table 4**—Effect of rod dimensions on growth of 300°C rolled uranium rods when cycled 300 times between 100°C and 550°C

---

Major texture: c-axis radial with a scatter of 15 degrees toward the rod axis and b-axis at 31 degrees from the rolling direction with a scatter of 15 degrees to and away from the rolling direction.

Minor texture: c-axis same as above, and b-axis parallel to the rolling direction with a scatter of about 10 degrees away from the rolling direction.

Thermal cycling was found to sharpen the preferred orientation texture as may be seen from the x-ray data in Table 6. The scatter of the (001) pole decreases from 15 degrees dark and 19 degrees light to 10 degrees dark and 15 degrees light after 700 cycles. The decrease may be due to better ordering of the lattice upon cycling inasmuch as the width of the lines decreases as well as the length of arc. A similar decrease in scatter was noted on other rods and, in some cases, indication of preferred orientations of the b-axis occurred where none could be detected previous to cycling.

**Microstructure**

The effect of thermal cycling on the microstructure of a 300°C-rolled and 575°C-annealed rod (1-4) is shown in Fig. 9. The fine grain structure resulting from the recrystallizing anneal was not appreciably changed after 100 cycles, was slightly coarsened after 300 cycles, and was appreciably coarsened to a mixed grain size after 700 cycles as shown in Fig. 9d. Cycling 1500 times of rods 47 and 49, which were similar to those shown in Fig. 9, resulted in a somewhat larger grain size. However, 700 more cycles of specimens machined from these 1500-cycled rods resulted in no further change in the microstructure.

There was some evidence that grain size or some other unknown factor contributes to the rate of growth on cycling. For example, standard alpha-rolled rod 41 grew 9.00% (K = 160 × 10⁻⁵) and rod 42 grew 20.25% (K = 270 × 10⁻⁵) in 700...
cycles, as shown in Table 1. These were supposed to have been duplicate specimens from the same rolled rod, and x-ray diffraction studies showed no appreciable difference in preferred orientation. However, rod 41 was found to have about twice thermal expansion of these specimens, as measured by Schwwope and coworkers at Battelle Memorial Institute, are given in Table 7 along with the elongation on cycling.

The coarse grains were larger than that of any

Table 5 — Preferred orientations in rolled uranium rods

<table>
<thead>
<tr>
<th>Rod No.</th>
<th>X-ray No.</th>
<th>Fabrication</th>
<th>Radial Pole</th>
<th>Rolling direction Pole Scatter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scatter</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(001) 20</td>
<td>(010) 48</td>
</tr>
<tr>
<td>1</td>
<td>453</td>
<td>18% Reduction — room temp</td>
<td>(001) 42</td>
<td>(010)* 35</td>
</tr>
<tr>
<td>53</td>
<td>475</td>
<td>Soak-rolled — 800°C</td>
<td>(001) 15</td>
<td>(010)† 30</td>
</tr>
<tr>
<td>1-4</td>
<td>633</td>
<td>89% Reduction — 300°C, duplex</td>
<td>(001) 15</td>
<td>(010) 10</td>
</tr>
</tbody>
</table>

* (010) pole 35 degrees from rolling direction.
† (010) pole 31 degrees from rolling direction.

Table 6 — The effect of 700 thermal cycles on the preferred orientations of 300°C-rolled uranium rods

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Rod No.</th>
<th>X-ray No.</th>
<th>Degree of scatter (poles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>575°C anneal</td>
<td>1-4</td>
<td>633</td>
<td>001 15 D 35 L</td>
</tr>
<tr>
<td>Before cycling</td>
<td>5-8</td>
<td>634</td>
<td>010 19 L 45</td>
</tr>
<tr>
<td>After cycling</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


the grain size of rod 42. This same apparent grain size effect was found in another set of rods, and numerous tests by Schwwope, et al.\textsuperscript{27} have been interpreted by them to show the same effect. To divorce the grain size effect from the effect of preferred orientation, very coarse-grained, highly oriented specimens were cycled along with specimens having similar preferred orientations but comparatively finer grains. The coarse-grained specimens were obtained from the gage length and the finer grained specimens from the ends of the tensile bars shown in Fig. 10 prepared by the strain-anneal method.\textsuperscript{21,22} The coefficients of the rods cycled during this investigation as shown in Fig. 11a. Nevertheless, they elongated 15.2% (K = 200 × 10\textsuperscript{-6}) and 13.8% (K = 180 × 10\textsuperscript{-6}) in 700 cycles. The finer grained rods were slightly less anisotropic than the coarse-grained rods and grew 21.0% (K = 270 × 10\textsuperscript{-6}) and 22.0% (K = 280 × 10\textsuperscript{-6}) in 700 cycles. This greater elongation may reflect a grain size effect, however, the results of this test confirm previous indications that the degree of preferred orientation is the major factor influencing the rate of elongation on thermal cycling. The extreme surface roughening of the coarse-grained specimens may ac-
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

Fig. 8—Pole figures of 300°C-rolled and 575°C-annealed rod No. 1-4 showing a duplex preferred orientation. (X-ray specimen No. 633)

count for the lower rate of elongation of the coarse than the fine-grained specimens. The grain size in the coarse-grained specimens was large compared to the diameter of the specimens.

The microstructures of the coarse and fine-grained specimens before and after 700 cycles are shown in Fig. 11. Cycling of the coarse-grained specimen resulted in the development of small similarly oriented grains clustered in areas approximately the same size as the original large grains (Fig. 11b). Further discussion of this grain structure which was developed on cycling will be reserved for a later section concerned with the thermal cycling of other coarse-grained specimens. The finer-grained specimen actually had a mixed grain structure before cycling (Fig. 11c) which reacted to cycling in much the same manner as the 300°C-rolled, 575°C-annealed rod (1-4) shown in Fig. 9.

Rolled Rods—Beta Heat Treated

Elongation

Early test results indicated that the elongation of rolled uranium rods on thermal cycling was a function of the degree of preferred orientation and that any treatment which produced a random orientation would minimize the tendency to elongate. To examine this possibility, several standard alpha-rolled rods (4, 6, and 10) and 300°C-rolled rods (21-24, 25-28, 31-34, and 35-38) were annealed for 2 hours at 725°C and slow cooled. As shown in Tables 1 and 3, their tendency to grow on cycling was practically eliminated by the beta anneal. However, the anneal produced extremely large grains as shown in Fig. 15a and the rods were badly warped and twisted and had rough gnarled surfaces after cycling as shown in Figures 5 and 6a.
Fig. 9a-d. — The effect of thermal cycling between 100°C and 550°C on the microstructure of a 300°C-rolled rod (1-4). Polarized light at 150x.
Another possible method of obtaining a random structure in rolled uranium rods consisted of heating into the beta temperature range between passes while rolling at 600°C. Pods 82, 83, and 84 were rolled at 600°C with a 15-min soak at 725°C after every two passes. A more random structure was obtained, and the elongation on cycling was about half that found in standard alpha-rolled rods as shown in Table 1.

It was apparent from the above tests that a fine-grained random structure was desirable to minimize both growth and surface roughening on cycling of uranium rods. Therefore, a method was sought whereby the grain growth could be minimized during a beta heat treatment. An approach to the desired results was obtained by heating rapidly into the beta temperature range by dipping into a lead pot at 725°C, holding for a short time (3 min and ½ min were tried) and water quenching.

Several highly oriented rods were given this fast beta heat treatment, and in all cases, the growth on cycling was drastically reduced. A 2-min fast beta treatment of a rod (51) similar to the ones that grew as much as 64% in 1500 cycles ($K = 320 \times 10^{-6}$) resulted in only 2.7% elongation in the same number of cycles ($K = 13 \times 10^{-6}$) as shown in Figs. 3, 4, and 5. In another case, a ½-min fast beta treatment decreased the tendency of the highly oriented rods shown in Fig. 6a to grow from 31.8% ($K = 370 \times 10^{-6}$) to 1.24% ($K = 18 \times 10^{-6}$) in 700 cycles.

Since highly oriented rods that had been fast beta treated still showed a slight tendency to grow on cycling, a study was made to determine the effects of successive fast beta treatments. Highly oriented 300°C-rolled rods (75% reduction) were given 1, 2, 4, and 8 fast beta treatments to approximately 720°C for 2 min. Also, one of these rods was given one fast-beta treatment to 744°C. Growth results are given in Table 8. It is apparent that more than one fast beta treatment did not decrease the tendency for rods to elongate on cycling. The higher temperature fast beta treatment resulted in slight if any improvement in tendency to grow.

Table 7 — Thermal expansion coefficients and elongation on cycling of coarse and fine-grained specimens of similar orientation

<table>
<thead>
<tr>
<th>Tensile bar No.</th>
<th>Thermal expansion coef $\times 10^6/\degree C$</th>
<th>Elongation (per cent) No. of 100 to 550°C cycles</th>
<th>Elongation coefficient $1 , dL/L , 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse</td>
<td>4.8 4.05</td>
<td>0.97 1.69</td>
<td>0.97 1.69</td>
</tr>
<tr>
<td>Fine</td>
<td>17.3-20.3</td>
<td>2.03 2.52</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse</td>
<td>4.05 5.8</td>
<td>0.97 1.59</td>
<td>0.97 1.59</td>
</tr>
<tr>
<td>Fine</td>
<td>19.1-19.8</td>
<td>2.21 2.92</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse</td>
<td>5.8 6.05</td>
<td>0.97 1.65</td>
<td>0.97 1.65</td>
</tr>
<tr>
<td>Fine</td>
<td>18.0-18.3</td>
<td>2.52 3.12</td>
<td>134</td>
</tr>
</tbody>
</table>

Fig. 10 — Strain-anneal tensile bars used to compare the effect of cycling on coarse and fine-grained uranium of similar preferred orientation (from M-4944). 1×
Fig. 11a-d—Microstructures of coarse and comparatively fine-grained specimens of similar orientation before and after cycling. Polarized light at 150x.
Surface Roughening

Comparison of Fig. 6a with Fig. 6b shows the general relationship between the amount of surface roughening on cycling and the grain structure of all rods examined during this investigation. The coarser the grain structure, the greater the surface roughening. This criterion can be used to predict whether or not a rod will roughen on cycling. Metallographic sections through surface bumps show that large clustered areas of small grains are directly associated with the bumps. Although inspection under low magnification gives a general idea of the size of clusters, it is often difficult to relate one cluster to a surface bump.

Rotation of the stage under polarized light causes groups of grains within a cluster to shift to adjacent clusters resulting in new apparent cluster boundaries. The cluster behaves mechanically like a large grain. This was found to be the case even after rods had been cycled many times. For example, cycling coarse-grained castings 1700 times resulted in the extremely fine-grained clustered structure shown in Fig. 18b. However, specimens that were machined from the cycled cast rods and then recycled 700 times surface roughened as badly as the original rods.

The surfaces of all fast beta treated rods showed a slight tendency to roughen after a large number of cycles which can be attributed to the coarsening of the grain structure as shown in Figs. 6b and 16a.

Preferred Orientation

The effect of heating alpha-rolled uranium rods dom around the ring (Fig. 14e). The slow-beta heat treatment resulted in a much coarser grain structure as shown in Fig. 14c.

The effect of thermal cycling was to increase the degree of scatter within each individual cluster as shown by the greater uniformity of the Debye rings (Figs. 14d and 14f).

As an average measure of preferred orientation, dilatometric measurements of the anisotropy in the coefficients of thermal expansion of specimens representing the 300°C-rolled and heat-treated rods, shown in Fig. 6, were made by Schwope and co-workers at Battelle Memorial Institute. The expansion coefficients along the length of the rods (the rolling direction) and across two diameters (perpendicular to the rolling direction) are given in Table 9 along with average elongation coefficients on thermal cycling. These results indicate that the high anisotropy of the annealed rolled rods as well as their tendency to grow on cycling was greatly reduced by the slow and fast beta treatments.

Microstructure

The effect of thermal cycling on the micro-
structures of the slow beta treated and fast beta treated 300°C-rolled uranium rods of Fig. 6a are shown in Figs. 15 and 16. A 300°C-rolled rod that had been annealed at 725°C (31-34) had a coarse grain structure before cycling. Rotation of the stage under polarized light revealed a macro-mosaic pattern of subgrains within the large grains which were so closely oriented that they were hardly distinguishable. After 100 cycles it was much easier to distinguish between the small subgrains in some of the original large grains, but most of the structure was not changed as shown in Fig. 15b. After 300 cycles the new large areas were extremely jagged, and rotation under polarized light revealed numerous subgrains of various sizes and orientations clustered within these areas. There was no appreciable change in this structure after 100 cycles, but small equixed subgrains were easily distinguished across entire areas after 300 cycles. Further cycling accentuated this new structure to give the fine-grained clustered structure shown in Fig. 16d.

Further cycling of uranium rods similar to the slow beta treated and fast beta treated rods discussed above did not cause any further change in their microstructures. This was evident from the microexamination after 700 cycles of specimens which had been machined from rods that had already undergone 1500 cycles.

The above-described subgrain structure was also found after cycling coarse-grained uranium formed by the strain-anneal method as shown in Fig. 11b. The maximum temperature during the strain-anneal process was 650°C and the microstructure of the specimen before cycling as well as x-ray diffraction studies showed no indications of a subgrain structure. The formation of the substructure seen in cycled rods is, therefore, not dependent upon prior heating of the uranium into the beta region. Fig. 11b also shows the formation of similarly oriented parallel rows of subgrains within the large clustered areas. These rows are not parallel to rows of inclusions, but

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Rod No.</th>
<th>Thermal expansion coefficient $\times 10^6/°C$</th>
<th>Elongation coefficient $\frac{\Delta L}{L \Delta D}$</th>
<th>10$^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed 2 hrs at 575°C</td>
<td>1-4</td>
<td>4.9</td>
<td>16.5</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>11-14</td>
<td>5.4</td>
<td>16.1</td>
<td>16.4</td>
</tr>
<tr>
<td>Annealed 2 hrs at 725°C, then annealed 2 hrs at 575°C</td>
<td>21-24</td>
<td>12.9</td>
<td>16.0</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>31-34</td>
<td>14.3</td>
<td>11.9</td>
<td>13.4</td>
</tr>
<tr>
<td>1½ min at 725°C, water quenched, then annealed 2 hrs at 575°C</td>
<td>41-44</td>
<td>13.2</td>
<td>15.4</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>51-54</td>
<td>12.6</td>
<td>14.6</td>
<td>12.6</td>
</tr>
</tbody>
</table>

*Coefficients too small to be measured accurately.

grains were apparent throughout the structure, Fig. 15c, and after 700 cycles they were so prominent that it was difficult to determine the original large grains. However, at low magnification, it was apparent that the new grains were still clustered in areas of about the same size as the original grains. Study of these new grains formed by cycling indicates that, even though they became more randomly oriented within patches as cycling progressed, their size was not much affected by cycling and they appeared simultaneously across entire areas rather than at grain boundaries. This suggests that they were not formed by nucleation and growth.

Water quenching a 300°C-rolled rod (41-44) after a 30-sec dip in a lead pot at 725°C and then 575°C annealing resulted in the confused looking structure shown in Fig. 16a. The boundaries of
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

(a) 675°C anneal — before cycling

(b) 675°C anneal — after 700 cycles

(c) Slow beta treated — before cycling

Fig. 14a-c — Comparison of x-ray diffraction structures and microstructures before and after cycling of rods shown in Fig. 8a. Photomicrographs under polarized light at 150×. X-ray photograms 2×.
they are lined up parallel to deformation lines.

The subgrain structure described has been shown to form on cooling from the beta temperature region. Slow cooling from 725°C resulted in fairly large subgrains so closely oriented that careful metallographic technique was required to bring them out under polarized light (Fig. 15a). Water quenching from 725°C resulted in smaller subgrains which were easily observed under polarized light because of the greater scatter between adjacent subgrains (Fig. 15a). A test was made to determine whether or not the substructure could be formed by a single cooling from the high alpha region without cooling through the beta-alpha transformation. A uranium specimen containing both the coarse and fine-grained parts of a strain-annealed tensile bar similar to those shown in Figs. 10 and 11 and known to be free of the subgrain structure, was dipped in a lead pot at 633°C for ½ min and then quenched in water. The quenched specimen showed no signs of a substructure, and the only change in the microstructure was a slight increase in the number of straight deformation lines.

There is a marked similarity between the conditions which form subgrains in uranium and the conditions necessary to produce veining in alpha iron. Veining is the subboundary pattern often
DIMENSIONAL CHANGES IN URANIUM UNDER THERMAL CYCLING

Fig. 15a-d — The effect of thermal cycling between 100°C and 550°C on the microstructure of a 300°C-rolled rod (31-34) that had been slow-beta treated. Polarized light at 150x.
Fig. 18a-d — The effect of thermal cycling between 100°C and 550°C on the microstructure of a 300°C-rolled rod (41-44) that had been fast-beta treated. Polarized light at 150X.
found in ferrite if very careful metallographic technique is used. Greninger has described the macromosaic structure in alpha iron and has pointed out that it is composed of many mosaic lattices which show a scatter in orientation from 1 to 10 degrees. The veining is attributed to the boundary lines of these closely oriented areas which can be considered as subgrains. Hultgren and Herrlander have shown that veining can be induced by external loading or by cooling through the gamma-alpha transformation. However, anisotropy of thermal expansion is a possible source of these stresses on thermal cycling of uranium at elevated temperatures. Hundreds of fairly slow cycles to 550°C produced a substructure in uranium which became more prominent with continued cycling. One rapid cycle to 633°C did not result in any perceptible substructure. It remains to be seen whether the formation of subgrains in uranium is a function of the rate of heating and cooling on cycling and whether it can be induced by external loading at elevated temperatures as in the case of ferrite.

An interesting effect of thermal cycling was the distortion of deformation lines in most of the cycled rods. Before cycling, these were straight lines crossing entire grains as shown in Figs. 11a and 15a. Cycling caused them to become peculiarly curved as they crossed clustered areas of subgrains. This is especially clear in Fig. 17 which represents a 600°C-soak-rolled rod (54) after 700 cycles. Closer inspection shows these curved lines to be made up of several short fairly straight lines each related to one of the subgrains formed on cycling.

**Cast, Swaged, and Extruded Rods and Rolled Plate**

Cast, Swaged, and Extruded Rods

Other methods of fabrication used to produce rods for cycling included casting, swaging, and extruding. Elongation data showing the effect of cycling on these rods are given in Table 10. The cast rods (18 through 23) had a very coarse-grained structure as did a set of rods (59 through 66) which were supposed to have been alpha extruded but had apparently overheated during extrusion. Where a very large grain size occurred, no preferred orientation was assumed because the arcs occurred in random positions on the x-ray photograms. The accuracy of measuring the small dimensional changes noted for these rods was greatly influenced by extreme surface bumping and warping as shown in Fig. 5.
Fig. 1a-b — The effect of cycling between 100°C and 550°C on the microstructure of a cast rod (22). Polarized light at 150x.

Fig. 1a-b — The effect of cycling between 100°C and 550°C on the microstructure of a coarse-grained extruded rod (52). Polarized light at 150x.
A cast rod (22) had a coarse-grained structure with a secondary structure of fairly large sub-grains which were easily distinguished as shown in Fig. 18a. In this case the structure was not appreciably changed after 300 cycles, but the extremely fine-grained structure shown in Fig. 18b was formed after 1700 cycles. These fine grains were clustered in areas about the size of the original large grains as could be seen by rotating the stage under polarized light. Continued cycling to 700 more cycles of rods machined from these 1500 cycled cast rods resulted in no further change in microstructure.

A coarse-grained extruded rod (59) (Fig. 19a) also contained small grains clustered in large areas after 700 cycles as shown in Fig. 19b. In this specimen some areas showed none of the small grains. The curved deformation lines described in connection with Fig. 17 were also apparent in this specimen.

Another set of alpha-extruded rods (740-1, 2, and 3) that were cycled were extremely fine grained and highly oriented. They elongated considerably (Table 10 and Figs. 3 and 4) and their surfaces remained smooth on cycling. The mean orientation and pole figures of these rods are shown in Fig. 20.

Several swaged rods (97, 98, 99, LA-3, and LA-4) were also cycled. These rods also had considerable preferred orientation as shown by the mean orientation and pole figures in Fig. 21. They elongated considerably on cycling (Table 10), and, here again a fast beta treatment reduced the elongation in 700 cycles to a small amount, (LA-1, and LA-2).

Cycling of 300°C-Rolled Plate

To study the effect of thermal cycling on rolled uranium plate, two square specimens 3/4 in. x 3/4 in. x 3/4 in., which had been machined from a 300°C rolled plate (61.7% reduction—rolled in one direction), were cycled 700 times between 100°C and 550°C. The square specimens were cycled by the same procedure as that used for cycling rods except that they rested flat on a square face.

The specimens are shown in Fig. 22 after 700 cycles and dimensional changes during cycling are summarized along with coefficients of thermal expansion in Table 11. Flaring at the edges, which had been noted in cycling of rods, was very prominent in these specimens. In 700 cycles, the specimens elongated as much as 44.1% ($K = 500 \times 10^{-6}$) in the direction of rolling and contracted 14.6% ($K = -230 \times 10^{-6}$) perpendicular to the direction of rolling and 16% ($K = -210 \times 10^{-6}$) perpendicular to the plane of rolling.

The mean orientation of the rolled plate differs from that of the rolled rods in that the c-axis is at an angle of approximately 17 degrees to the normal to the plate with a small scatter in the rolling direction and complete scatter in the cross direction. The b-axis is at an angle to the rolling direction corresponding to 90 degrees from the c-axis with a scatter in both directions.

Effect of Cycling Variables

Temperature Interval

Most of the cycling tests for this investigation were made between 100°C and 550°C. However, to determine the effect of small thermal fluctuations at elevated temperatures, several rods were cycled 2200 times between 500°C and 550°C. These rods included the standard alpha-rolled and 575°C-annealed rods 40, 41, and 42, the standard alpha-rolled and 725°C rods 4 and 10 shown in Table 1 and the cast and 575°C-annealed rods 18, 19, and 20 shown in Table 10. Most of the rods had been previously cycled 100 times between 100°C and 550°C and growth due to this cycling is included in Table 12 for comparison with the results of cycling between 500°C and 550°C. It is apparent that rods which tend to grow on thermal cycling between 100°C and 550°C will also grow when cycled between 500°C and 550°C and that rods which tend to grow the most when cycled over a large temperature range will also grow the most when subjected to small thermal fluctuations at elevated temperatures. The rate of elongation on cycling over the large range was approximately 30 to 70 times as great as the rate on cycling over the small range.
time allowed at temperature and essentially the same rate of heating and cooling for each test. Equipment has been designed for the purpose of studying time-temperature relationships during cycling. The role creep plays in deformation during cycling is being studied in this equipment.

Table 10 — Elongation of cast, swaged, and extruded uranium rods due to thermal cycling between 100°C and 550°C

<table>
<thead>
<tr>
<th>Fabrication and heat treatment</th>
<th>Rod length (in.)</th>
<th>Due to anneal</th>
<th>Number of cycles (N)</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>EL</th>
<th>10⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast — 575°C-annealed</td>
<td>21</td>
<td>-0.02</td>
<td>0.03</td>
<td>-0.03</td>
<td>0.03</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>-0.01</td>
<td>0.00</td>
<td>-0.01</td>
<td>0.00</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>Cast — 2 min at 723°C, 575°C annealed</td>
<td>18</td>
<td>-0.03</td>
<td>(2)</td>
<td>-0.26</td>
<td>0.58</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>(2)</td>
<td>0.01</td>
<td>(2)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.08</td>
<td>(2)</td>
<td>-0.26</td>
<td>-0.56</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>Swaged tapered castings, 30% to 50% reduction — 575°C annealed</td>
<td>97</td>
<td>0.92</td>
<td>1.63</td>
<td>4.70</td>
<td>11.80</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>0.91</td>
<td>1.67</td>
<td>4.78</td>
<td>12.03</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>99</td>
<td>(2)</td>
<td>(2)</td>
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<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>Swaged castings, 50% reduction (by LA) — 575°C annealed</td>
<td>LA-3</td>
<td>2</td>
<td>1.01</td>
<td>1.37</td>
<td>16.7</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LA-4</td>
<td>2</td>
<td>0.95</td>
<td>1.63</td>
<td>5.09</td>
<td>16.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swaged castings, 50% reduction (by LA), 2 min at 723°C, water quenched — 575°C annealed</td>
<td>LA-1</td>
<td>2</td>
<td>-0.08</td>
<td>0.31</td>
<td>1.37</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>LA-2</td>
<td>2</td>
<td>0.00</td>
<td>0.59</td>
<td>1.80</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha extruded (by MIT), fine-grained — 575°C annealed</td>
<td>740-1</td>
<td>2</td>
<td>0.34</td>
<td>2.44</td>
<td>5.23</td>
<td>9.72</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>740-2</td>
<td>2</td>
<td>0.18</td>
<td>2.19</td>
<td>4.83</td>
<td>8.58</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>740-3</td>
<td>2</td>
<td>0.12</td>
<td>2.12</td>
<td>4.75</td>
<td>9.16</td>
<td>210</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha-extruded (by MIT), coarse-grained — 575°C annealed</td>
<td>59</td>
<td>4</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.37</td>
<td>1.07</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4</td>
<td>0.02</td>
<td>-0.12</td>
<td>0.30</td>
<td>0.99</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>4</td>
<td>0.03</td>
<td>0.17</td>
<td>0.29</td>
<td>0.86</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha-extruded (by MIT), coarse-grained — 2 min at 723°C, water quenched, 575°C annealed</td>
<td>64</td>
<td>4</td>
<td>0.01</td>
<td>0.16</td>
<td>0.66</td>
<td>1.64</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>4</td>
<td>0.01</td>
<td>0.12</td>
<td>0.57</td>
<td>1.41</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>4</td>
<td>0.01</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
</tbody>
</table>

* Rod No. cycles
† Cycled 100 times between 100°C and 550°C and then 2200 times between 500°C and 550°C before fast beta treatment.
‡ Rod cut up for samples at various stages of cycling.
§ Coefficients too small to be measured accurately.

Also, very high thermal gradients can be induced by fast heating and cooling in this equipment, and their effects are under investigation.

SUMMARY

The similarity in dimensional changes of uranium due to thermal cycling and that due to pile exposure suggests a common cause. This, together with the practical and fundamental interest

Time-Temperature Relationships

For all previously described thermal cycling tests a saw-tooth type of cycle was used with no
in the problem of obtaining stress-free, dimensionally stable uranium and other anisotropic metals has motivated this investigation of thermal cycling effects.

Uranium rods prepared by a wide variety of fabrication and heat treat methods were thermal cycled between 100°C and 550°C in a vertical position under conditions roughly simulating "P-4 pile conditions. Rolled uranium rods elongated when thermal cycled, and their diameter changes were such as to just compensate for the length changes. In general, the greater the reduction in area during rolling and the lower the rolling temperature, the greater the rate of growth. The amount of longitudinal growth increased directly as the number of thermal cycles with no indication in rate of growth after 1500 cycles. Rolled at 300°C elongated as much as 64% in normal cycles between 100°C and 550°C.

The degree of preferred orientation was the major factor influencing the rate of elongation of rolled uranium rods on cycling. There were some indications that grain size or some other unknown factor influenced the rate of growth, but these had minor effects. Fast heating into the beta temperature range followed by water quenching almost completely removed preferred orientation in rolled uranium rods and greatly decreased the tendency for growth on cycling. However, a moderate to coarse-grained structure resulted from this treatment, and the rods roughened slightly on cycling. Highly oriented rods that were given a fast beta heat treatment still had a slight tendency to elongate on cycling, and as many as eight such treatments on the same rod did not remove this tendency to elongate.

Thermal cycling of coarse-grained uranium rods resulted in rumpled and sometimes badly

Fig. 20—Pole figures of alpha-extruded and 575°C-annealed uranium rod No. 740. (X-ray specimen No. 622)
bumped surfaces whereas fine-grained rods remained smooth on cycling.

A substructure of similarly oriented grains clustered within larger grains was noted in uranium that had been heated into the beta region and also in uranium that had been thermal cycled in the alpha region. Slow cooling after annealing in and were directly associated with surface bumps. The conditions which cause the formation of a substructure in uranium are very similar to the conditions necessary to produce veining in alpha iron.

Specimens prepared by other fabrication methods which caused preferred orientation also elongated on thermal cycling. These included alpha-extruded rods, swaged rods, and rolled plate.

Small thermal fluctuations at elevated temperatures caused elongation of oriented uranium rods. The rate of elongation on cycling between 500°C and 550°C was considerably less than that due to cycling between 100°C and 550°C. Thermal cycling between 20°C and 300°C also caused these rods to elongate but at a slower rate than when cycled between 100°C and 550°C.
## Dimensional Changes in Uranium Under Thermal Cycling

Table 11 — Dimensional changes of 300°C-rolled uranium plate due to thermal cycling between 100°C and 550°C

<table>
<thead>
<tr>
<th>Direction</th>
<th>Sample No.</th>
<th>Exp coeff ( \times 10^6/\degree\text{C} )</th>
<th>Elongation (per cent)</th>
<th>Number of cycles</th>
<th>Elongation coefficient ( 1 \text{dL} \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel rolling direction</td>
<td>2</td>
<td>6.6</td>
<td>2.44</td>
<td>5.03</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.50</td>
<td>4.93</td>
<td>15.4</td>
<td>43.0</td>
</tr>
<tr>
<td>Perpendicular rolling direction</td>
<td>2</td>
<td>15.7</td>
<td>-1.38</td>
<td>-2.49</td>
<td>-6.99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-1.30</td>
<td>-2.62</td>
<td>-7.04</td>
<td>-14.0</td>
</tr>
<tr>
<td>Perpendicular rolling plane</td>
<td>2</td>
<td>18.6</td>
<td>-0.72</td>
<td>-2.10</td>
<td>-8.16</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.79</td>
<td>-1.93</td>
<td>-5.86</td>
<td>-15.0</td>
</tr>
</tbody>
</table>

Table 12 — Growth of uranium rods due to small thermal cycles at elevated temperatures

<table>
<thead>
<tr>
<th>Fabrication and heat treatment</th>
<th>Rod No.</th>
<th>Elongation (per cent)</th>
<th>Elongation coefficient ( 1 \text{dL} \cdot \text{L dN} )</th>
<th>Elongation (per cent)</th>
<th>Elongation coefficient ( 1 \text{dL} \cdot \text{L dN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard alpha-rolled</td>
<td>43</td>
<td>0.69</td>
<td>0.69</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>0.58</td>
<td>0.56</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.36</td>
<td>0.36</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>575°C-annealed</td>
<td>40</td>
<td>2.45</td>
<td>200</td>
<td>0.66</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>1.95</td>
<td>180</td>
<td>0.74</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>3.60</td>
<td>270</td>
<td>1.89</td>
<td>8.5</td>
</tr>
<tr>
<td>Standard alpha rolled and 725°C-annealed</td>
<td>4</td>
<td>-0.04 (†)</td>
<td>0.05 (†)</td>
<td>0.05 (†)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.02 (†)</td>
<td>0.05 (†)</td>
<td>0.05 (†)</td>
<td></td>
</tr>
<tr>
<td>Cast and 575°C-annealed</td>
<td>18</td>
<td>-0.04 (†)</td>
<td>0.00 (†)</td>
<td>0.00 (†)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.00 (†)</td>
<td>0.00 (†)</td>
<td>0.00 (†)</td>
<td></td>
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<tr>
<td></td>
<td>20</td>
<td>0.00 (†)</td>
<td>0.00 (†)</td>
<td>0.00 (†)</td>
<td></td>
</tr>
</tbody>
</table>

*Coefficient too small to be measured accurately.*
ACKNOWLEDGMENTS

This paper summarizes the results of a program in which a large number of Argonne National Laboratory Metallurgy Division personnel participated. Most of the data were the results of the efforts of S. T. Zegler with significant contributions by R. M. Mayfield and laboratory assistance of G. J. Pokorny and P. G. Drugas. The x-ray diffraction work was done by A. D. Fischer, and most of the metallographic work was done by M. D. Odle. The author also wishes to acknowledge the contributions of R. E. Macherey who fabricated the specimens, E. S. Fisher who prepared the strain-anneal specimens, R. A. Noland who developed a technique for macroetching uranium, L. K. Arthur for photographic assistance, J. M. Barnes for stereographic assistance, and other members of the Argonne National Laboratory Metallurgy Division for their cooperation. A. D. Schwope and co-workers at Battelle Memorial Institute made the measurements of thermal expansion coefficients. F. G. Foote and J. W. Halley assisted in the direction of the program and the interpretation of results.

REFERENCES

Some Considerations Involved in the Design of a Laboratory for Work with Alpha Active Materials

By F. M. Walters
Los Alamos Scientific Laboratory

ABSTRACT

Factors requiring consideration in designing laboratories for chemical and metallurgical research on alpha-active materials are discussed, and plans for a proposed building at Los Alamos designed to meet the special requirements are presented with explanations, including the first floor plan for the building.

INTRODUCTION

The design of laboratories for the work of the Atomic Energy Commission presents many problems more or less peculiar to the type of work to be carried on, and it is believed that the manner in which we propose to solve them at Los Alamos may be of interest. Some of the considerations involved in chemical and metallurgical research on alpha-active materials are the conditions imposed by health hazards, by the regulations arising out of security and accountability for source and fissionable materials, by the need for unusual flexibility, and by special safety requirements. Complying with these special considerations results in an unusually expensive building with a large amount of space not directly useful for laboratory purposes.

HEALTH HAZARDS

The health hazards involve not only those who work in the building but also those who live in the immediate and neighboring communities. Equipment and apparatus should be so engineered that the laboratory space is uncontaminated even though large quantities of "worse than toxic" material may be handled. At the same time, adequate provision must be made for the limitation of contamination in case of accidents and for rapid and complete decontamination. To protect the community, gaseous and liquid wastes must be specially treated to bring them below human tolerance before they are released upon a more or less unsuspecting world.

The type of work to be done at Los Alamos requires that all air entering the laboratory be freed from dust and that the temperature and humidity be controlled. The exhaust air must be decontaminated either as it leaves a laboratory room or as it leaves the building. We shall probably try to do both. Each inlet to the exhaust ducts should be provided with a filter which will collect the larger particles at least. It is probable that the final purification of the exhaust air will be by sprays or condensing steam. Since a chemical hood, 8 ft long and 3 ft front opening, must be pro-
vided with 2400 cu ft of air a minute, the ventilation system is so important a part of the building that it should be designed first and the structure fitted to it.

The decision to remove contaminated air from the laboratories at or below floor level was based on our experience in the buildings now occupied. In these, the attempt is made to exhaust air through the roof. It is necessary to keep the blowers going constantly. If the power goes off or if there is a strong wind from the wrong direction, the working space in the hood to which the blower is attached will show high contamination. High air counts in the room also result. The oxide and other particles involved have high densities so that they lodge in the ducts and seldom get as far as the roof, which is usually free from contamination. The room used for melting and alloying had over-tolerance air counts so often that work in it was impossible more than half the time until provision was made for taking the air out through the floor.

Not only is it planned to exhaust the air through the floor, but all other services which may become contaminated, such as circulating water for cooling, will be carried below floor level. In one of our present buildings, the service space over some of the laboratories is so “hot” that workmen enter it only in diving suits. Recently a careless workman stepped part-way through a ceiling, and the resulting contamination stopped work in that room for three weeks.

The large amount of space required for the ventilating system and the desirability of completely separating contaminated and uncontaminated services make a “one-story” design mandatory for the laboratory wings.

SECURITY REQUIREMENTS

Security control implies a minimum number of entrances to a building and affects the design in a number of other ways; e.g., it makes a “sealed building” with permanently closed windows desirable. At Los Alamos, SF accountability requirements are likely to add at least two million dollars to the cost of the Chemistry-Metallurgy Research Laboratory. Analytical work on plutonium, enriched uranium, and normal uranium must be carried on in separate rooms; chemical analysis is required at more stages of recovery processes than is necessary for process control, and some sort of isotopic analysis is usually requested by the AEC as an accounting control. All of these require added facilities.

SAFETY REQUIREMENTS

Special safety requirements demand that the doors of individual laboratories open out but do not project into the hall, that there are at least two doors for each laboratory. Exits from the building must be placed at minimum distances (at one stage in our planning, there were 85 outside exit doors and one entrance). There are rules about the frequency of stairways.

It will be necessary to have a central indicating system for the fire detection devices and for determining the failure of ventilation equipment, water and electrical supplies throughout the building; an indicating system to keep track of the maintenance men, security guards, and fire guards as they tour the building out of working hours.

FLEXIBILITY PROVISIONS

Nuclear energy is so new a field that it is impossible to predict with confidence the trend in chemical and metallurgical research, so that in designing a building for this purpose, a large degree of flexibility is essential. To achieve this, the modular system has been adopted. It will be possible to supply each laboratory unit with all of the services going to any other unit, and the use of metal partitions will permit rearranging the space to suit the programs undertaken at a particular time.

PLAN LAYOUT

The general plan of the proposed Chemistry-Metallurgy Research Laboratory is shown in the accompanying sketch as planned at present. There are seven laboratory wings, an office wing, and a service wing containing small maintenance shops and other facilities necessary for the operation of the laboratory. These nine wings are connected by a central corridor. Each laboratory wing has its own locker and change rooms, as well as separate ventilating systems. The degree of hazard will vary from wing to wing, from none to that requiring a complete change of clothing. The wing-wise distribution of change rooms is expected to make easier the enforcement of health regulations.
PROPOSED LABORATORY FOR WORK WITH \( \alpha \) ACTIVE MATERIALS

The module or unit of laboratory space is 12 by 24 ft. The two rows of fourteen modules are separated by a utility corridor which can serve as an escape route in case of accident and through which contaminated material may be moved. The personnel corridors permit circulation throughout the wing. The small rooms, 12 by 12 ft, will serve as offices, stock rooms, cold laboratories, small shops, and the like.

All operations involving more than microgram amounts of active material will be carried out in dryboxes or other enclosed space. However, the problem of what to do about airlocks on the dryboxes has not been completely solved. If the operations in a drybox involve any amount of contaminated dust, part of this will enter the airlock when the door between the drybox and the airlock is opened, and then some of it gets out into the

ESSENTIAL FEATURES

If a laboratory is to be readily decontaminated in the event of an accident, then certain policies must be followed: the walls and floors must be
smooth and free from cracks in which dust can lodge; there must be no exposed pipes which are hard to clean; laboratory furniture should be removable so that it can be decontaminated elsewhere. Metal partitions appear to be the best solution for smooth and crack-free walls, while asphalt tile can be laid with smaller cracks than any other floor material of which we know. Usually contamination by alpha active material can be trapped by a coat of paint, but it would be desirable to be able to remove one side of a partition without disturbing that in the next room. At Los Alamos, there will be no drains in the floor into which valuable fissionable material can be washed. If considerable material is spilled, there is a problem of recovery as well as decontamination.

SPECIAL CONSIDERATIONS

The special considerations involved in the design of a laboratory for chemical and metallurgical research on alpha-active materials give rise to certain consequences: the ratio of useful laboratory space to gross space will be much smaller than for a laboratory designed for work with less hazardous materials. There will be more working space per man because: drybox set-ups require more space than the same operations on un-enclosed benches; equipment set up and used with active materials becomes contaminated and will not be taken down if it is likely to be needed again; and there must be sufficient working space so that there is little possibility of one worker endangering another.

June 1949
INTRODUCTION

The Brookhaven pile is an air-cooled, graphite-moderated, natural uranium pile. In this respect it is identical with the Clinton pile which served as a model for it. It differs in that the power level will probably be seven to ten times the present rating for the Clinton pile. To accomplish this purpose and still use air cooling, the fuel channels have been changed from the diamond shape used at Clinton to a circular one which measures 2.670 in. ID. The fuel element differs from the Clinton 4 in. by 1.1 in. slug in that it makes use of an extended surface and although it consists of 4 in. segments, it is 11 ft long.

The problem of making the fuel elements resolves into: (1) the development, with the aid of a commercial company, of a six-finned aluminum tube, the length of the fins to be 0.8 in., and the overall volume ratio relationship of aluminum to uranium to be 0.2; (2) the machining of the uranium fuel under a subcontract; and (3) the canning of the uranium. Much emphasis by the heat transfer people was laid on the desirability of keeping the void space between the uranium and the aluminum at a minimum. Their calculations were based on a one mil gap between the uranium and the aluminum. Since this one mil gap becomes 2½ mils as a result of the differential coefficient of expansion of aluminum and uranium, it is seen that the starting gap should be as small as possible for the most effective heat transfer.

DEVELOPMENT OF THE ALUMINUM FINNED TUBE

Although several concerns were approached, only the Aluminum Company of America was willing to attempt fabrication of finned tubing. Credit is due F. R. Marshall of that company for acceptance and guidance of a difficult job, and to R. Couchman for the successful completion of the contract. The complete history of this development is given in a report by F. R. Kemmer and P. Miller of the H. K. Ferguson Company, report number HKF-5. A resume is included in this report for continuity.

Although the Aluminum Company of America was contacted in March, 1947, they were not able to show any progress until August, 1947. By the end of September, it was apparent that the uniformity of the tubing was below that desired. The finned tubing is formed from a solid aluminum billet by extruding it through a web-type port-hole die. The metal is forced through six openings beyond which there is a mixing chamber and a stationary mandril. After passing through the mixing chamber, the metal sees a continuation of the mandril which faces the female portion of the die where the fins and walls of the tube are formed. The gland of the mandril facing the fins is of the order of ¼ in. in bearing surface. The requisite, so essential to the success of this extrusion, lies in the dressing of the glands of the fin and the mandril to the proper degree such that the surface frictions for the formation of the fins
and tube are equal. On many attempts, the extrusion resulted in fins sans tubes or tubes sans fins. The tolerances and the shape of the required section are given in Fig. 1.

Fig. 1. Drawing showing transverse section of finned tube, design detail and fabrication tolerances for Brookhaven fuel elements.

The extruded shape could not be made in the tolerances required; therefore, the tube was extruded oversize and one drawing operation was included. See Fig. 2. In this operation the tube wall is drawn and since the fins are attached to the tube proper, they are thus worked. The total amount of cold work is of the order of 15%; i.e., the ID extruded section was 0.012 in. greater than the finished drawn ID. By making up a total of four dies, the Aluminum Company of America was able to finally produce the 4,000 tubes requested.

It should be noted that the tolerances on this section are not as liberal as those considered normal production for tubing. This was necessitated by the need for holding the volume ratio. Also, these tolerances were required to attain the uniformity required.

MACHINING OF URANIUM

The uranium which was selected for the Brookhaven pile is the gamma-extruded material. The reason for its selection was two-fold: (1) the cost of rolled material was much higher than that for extruded metal, and (2) gamma-extruded material was known not to elongate as much on cycling as the rolled metal, although the latter had a greater tendency to warp.

The uranium was extruded and was shipped to the Chapman Valve Company. A detailed description of this machining is given in a report by F. R. Kemmer and T. P. Musgrave of the H. K. Ferguson Company and G. E. Fox of the Chapman Valve Company, report number HKF-4.

The general procedures for machining and for the heat treatments were laid out by Brookhaven National Laboratory; however, the details of the set-up of the machines and the inspection and general production details were entirely handled by the H. K. Ferguson and Chapman Valve companies. In the opinion of the writer, the machining was done in a very workmanlike fashion and demonstrates that even uranium can be set up on a truly production basis. The dimensions and tolerances of the finished slugs are given in Fig. 3. After the bars were straightened, they were machined in a six-spindled Conromatic lathe. Average time per 4 in. slug was 30 sec. It came out of this machine approximately 0.010 in. oversize in diameter and about 0.020 in. oversize in length. It was then heat treated for 12 hr. at 600°C. in an argon atmosphere. The next step was to grind it to final diameter in a centerless grinder using four plunge cuts. Next a button was machined on the end of the slug after which it was finished to length on a hand operated turret lathe. This operation was followed by the milling of a slot for the full length of the slug. Finally, the slugs were again heat treated at 400°C. for 3 hr. in an argon atmosphere to remove the last traces of oil and water from the exterior surfaces. They were then packaged in hermetically sealed cans and shipped to the Brookhaven National Laboratory. The dimensions of the slot and of the button were calculated so that their volume, when added to the void volume resulting from the difference in the final ID of the finished aluminum tube and the OD of the slug, was such as to give essentially zero surging of the gas on raising the temperature of the assembly from room temperature to pile operating temperature.

It can readily be shown that, if the assembly is considered to be at a uniform temperature, this volume is equal to:

\[ V_g \left( \frac{273 + t_2}{273 + t_1} \right) = V_g + V_{\text{void}} - 3\alpha' \left( t_2 - t_1 \right) \]
where

\[ t_u = \text{upper operating temperature} \]
\[ t_i = \text{canning temperature} \]
\[ V_g = \text{gas volume built into assembly (i.e., slot + button + peripheral void)} \]
\[ V_a = \text{volume of uranium} \]
\[ 3\alpha' = \text{difference in volume coefficients of aluminum and uranium} \]

This reduces to

\[ V_g = V_a \times 3\alpha' (273 + t_i) \]

Actually, the volume selected was somewhat greater than the ideal volume so that on cooling the pile down, the surging would be toward the assembly, thus resulting in sucking volatile fission products into the cartridge.

To clarify this point further, some detail is required with respect to the helium leak detection system. What was desired was a system which allowed for constant checking of the tightness of the fuel assembly. At Hanford and at Oak Ridge a break in the slug announces itself by the presence of fission product activity in the cooling streams. Due to the high background in the pile, true particularly at Clinton, much of the slug is oxidized and much of the activity is distributed throughout the pile prior to the cognizance of a break. Because of the proximity of large centers of population at Brookhaven, it was decided to use a helium detection system. The fuel rod assembly (cartridge) is under constant helium pressure.
The adjacent rows of cartridges end up on headers which are bucked against each other through a differential recording manometer. The presence of a leak results in a change of pressure in one of the headers; something of the order of 10 cc of helium gas should be readily detectable. The location of the leaking cartridge is accomplished by a switching arrangement where horizontal headers can be made to buck each other.

One other detail should be presented prior to a description of the actual canning operation. In order to run at the power levels mentioned earlier in this report, it will be necessary to attain a 350°C interface temperature between aluminum and uranium. The maximum interface temperature now in use is 225°C., the operating temperature of the Clinton pile. When canning of uranium in aluminum was first considered, work at the Metallurgical Laboratory in late 1942 demonstrated that uranium reacts with aluminum to form uranium-aluminum compounds. Since this may result in a complete deterioration of the can, this is an undesirable condition. Work at that time performed at Battelle Memorial Institute and Chicago indicated that the reaction proceeded moderately fast at temperatures as low as 300°C. Recent work at Massachusetts Institute of Technology, in cooperation with Brookhaven National Laboratory indicates that this reaction proceeds at much lower temperatures. It should be pointed out that the compound formed, primarily UAl3, is thermodynamically stable and that the amount formed, therefore, is purely a matter of rate or kinetics of this reaction.

Also, it was tentatively demonstrated that an anodic coating on aluminum slowed down the interdiffusion. Work performed at Massachusetts Institute of Technology confirmed this and, therefore, all of the finned tubes used in canning operations were anodically coated in a sulfuric acid medium by a sub-contractor. Obtaining a uniform and continuous coating on the internal diameter of an 11 ft tube is rather tricky. An internal cathode was used and it was found that a slight tilt of the tube was better than a forced circulation, since the latter resulted in areas completely void of oxide film. All tubes were checked for continuity of oxide film prior to leaving the plater's plant by drawing a mandril through the ID of the tube. In addition, since it was known that this surface would be abraded in the insertion step of the canning operation, a tentative standard of 200 abrasion strokes was set. The material was constantly checked on an abrasion apparatus. Based on these requirements, i.e., continuity and abrasion resistance, the sulfuric acid bath was selected and the temperature and time of anodization was determined. To thoroughly remove the sulfuric acid, a boiling water wash was selected. This is identical to the sealing of anodic coatings which, it should be pointed out, gave rise to some difficulties later in the canning operation because of the incorporation of water in the anodic film.
CANNING OF URANIUM

The total operation can be broken down into thirteen individual steps. These are:

1. Chemical stripping of one end of the finned tubing.
2. Trimming of fins on this end and trimming of tube so as to allow less than a 0.1 in. stripped portion.

These two operations were performed so that this end of the tube could be argon arc welded, as the development work indicated that, unless a chemical cleaning was employed, the welds were porous and unsound.
3. Welding of butt cap, accomplished in a specially designed welding machine (Figures 4 and 5).
4. Removing the water of hydration of the anodic film in a 15 ft furnace at 300°C.

It was at first thought that this step would be unnecessary and several hundred tubes were made without undergoing this treatment. It was hoped that on heating the assembly up to pile operating temperatures, the water of hydration would react with uranium to give a uniform hydride and oxide coating; however, experiments performed to confirm this showed that the water seemed to attack locally with the result that small but well defined bumps developed on the uranium which could be shown to be uranium hydride and oxide.
5. Testing the cooled tubes for vacuum tightness using the helium mass spectrograph with a shroud of helium around the exterior of the tube.

Many tubes had to be rejected for porosity even though they had passed a 90 psi bubble test by the manufacturer.
6. Loading. The finned tube was first encased in a handling tube, after which it was loaded with 33 slugs.
7. Trimming the assembly to length, using the last slug against which to gage.
8. Brazing. Prior to the induction brazing the OD of the aluminum tube was scraped to remove the anodic film. This was a hand operation and was extremely successful. A brazing cap was inserted and a braze effected using highfrequency induction heating and an aluminum-5% silicon alloy and No. 33 flux. See Figs. 6 and 7. A completed cartridge is shown in Fig. 8.
9. Testing for tightness both at the brazed joint as well as at the welded joint and the full length of the tube, using a helium mass spectrograph.
10. Compressing. It should be noted that at this stage, the OD of the slug and ID of the tube differ by 5 mils. In order to bring down this gap to the value set by heat transfer requirements, the whole assembly was subjected to a hydrostatic pressure of 2500 psi. This was accomplished by putting a rubber stopper on the open end of the tube and immersing the whole unit in a pressure vessel which was filled with water. Ten strokes on a hand operated pump gave the desired pressure and excellent compression; however, there was some spring-back. Metallographic examination indicates that, on the average, a 0.6-mil gap exists around the slug. This is well within the limits set.
11. Hand brazing of an anchor 20 in. from the welded end of the cartridge. This anchor drops into a slot in the graphite so that the cartridge remains fixed relative to the slot in the pile. In the absence of this anchor it is conceivable that, due to the ¾ to 1 in. elongation, at operating temperatures, the tube might walk into the slot or away from the slot on heating and cooling of the pile.
12. Hand brazing the 40 ft length of ¼ in. aluminum tubing into the brazing cap using an aluminum-12% silicon alloy.*

After these operations, the three brazed joints were chemically and mechanically cleaned using a mixture of nitric acid and sodium dichromate and a wire brush.
13. Final leak testing. The whole assembly was inserted in a 12 ft long by 3 in. ID vacuum chamber (Fig. 9). One end of the ¼ in. tubing was pulled through a vacuum gland. This end was attached to pressure gages and a source of helium. A dead volume was placed in series with the cartridge, and by bringing up the pressure in the dead volume to a predetermined value, and then opening the valve between the dead volume and the assembly and noting the pressure change on the gage in the system, it was possible to check the void volume of each of the tubes. These were remarkably uniform; the variation was of the order of 2 cc maximum, which is the accuracy of measurement. Following this measurement, the helium pressure on the inside of the cartridge was raised to 100 psig. A vacuum pulled around the cartridge terminated in a heli-

*This alloy could not be obtained from the Aluminum Company of America and since it is to be preferred to copper containing alloys, arrangements were made with Mr. J. A. Kyger of the Oak Ridge National Laboratory to cast and fabricate sheet for this operation.
Fig. 4. Machine for welding butt cap on the flanged tubes.
Fig. 5. Fixtures used in argon arc welding of bolt ends on the finned tubing.
Fig. 6. Machine for brazing helium end cap.
Fig. 7. Fixture used in brazing helium end cap.
Fig. 8. Drawing showing complete cartridge details.
Fig. 9. Schematic showing helium, continuity and leak test equipment.
um mass spectrograph. Although there is considerable degassing which tends to cut down the sensitivity of this leak test, it was demonstrated that the sensitivity attainable was approximately 0.02 μ cu ft/hr.

ENGINEERING TESTS OF FINISHED ASSEMBLIES

Tests are still in progress to determine the creep of fins, the effect of cycling of the assembly, the maximum temperature to which the cartridge can be raised before excessive interdiffusion takes place, and the extent of breathing or surging. The complete details of the canning process, a cost analysis, and recommendations as to improvements in the process will be forthcoming shortly in an extensive report.

ACKNOWLEDGMENTS

Much of the planning and development for the canning operations described above was due to the energetic efforts of the Brookhaven National Laboratory Metallurgy Division. The men most responsible are J. Atherton, C. Binge, H. Cook, R. Teitel, B. Turovlin, and W. Warner.

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Some Aspects of the Recrystallization of Thorium

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ABSTRACT

This paper is an account of experimental work on the recrystallization of thorium as affected by cold work.

It is found that, for thorium cold reduced from 30 to 60%, the recrystallization temperature is in the range 550° to 650°C, and the heat of activation for recrystallization is in the order of 44,000 cal/mole.

INTRODUCTION

In view of the interest in thorium as a breeder material, it was thought desirable to obtain information on certain aspects of the physical metallurgy of the element.

This report contains an account of an investigation of the recrystallization of thorium after plastic deformation.

An attempt was made to systematize the experimental work by obtaining information in a form suitable for presentation by methods suggested by Johnson and Mehl and other investigators who have studied recrystallization in metals.

Impurities in the thorium produced some lack in precision in results and introduced difficulties in interpretation. These problems are discussed in detail in this report.

MATERIAL

Four lots of thorium representing different levels of purity were available for use in the investigation.

The high-purity thorium was produced by the calcium reduction of thorium fluoride at Iowa State College at Ames. This metal was cast into a square ingot 4 x 4 in. This ingot was forged to a 2-in. square and hot rolled to 1/2-in. round bar at Ames. The Ames billet number for this heat was A-93.

At Battelle the bar was skinned by machining and pickled in nitric-hydrofluorosilicic acid. After pickling, the bar was heated for 2 hr at 800°C and hot rolled to 0.50-in. flat at about 0.05 in. per pass. The 0.05-in. strip was cut into four bars labeled 1, 2, 3, and 4 for purpose of identification. These four strips were cold rolled to 0.25-in. thickness and in this form were used as starting material for the test program.

Three additional lots of thorium were available. These lots had much higher impurity content than the one described above. Nothing is known of their origin except that they were made prior to 1947.

The analyses of the various bars are given in Table 1.

From Table 1 it will be noted that all bars contained substantial amounts of oxygen and that 5 and 6 also had high carbon. While the material available had substantial amounts of impurities it was thought that bars 1, 2, 3, and 4, at least, would be suitable for use in a pile.

*Now with Brush Beryllium Corporation.
Iron baths were found unsatisfactory for vacuum-fusion analysis of thorium giving low-oxygen results. When the analyses were carried out in a tin bath at 1650°C, the results were considered more valid and are reported above. One hour was required to extract the gas from each sample. Evidence of thorium carbide formation was found in the vacuum-fusion residue.

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†Ames material.

Studies Preliminary to the Work on Recrystallization

It would be expected that the impurities present would affect the course of recrystallization; accordingly, prior to starting recrystallization experiments, some information was gathered on the effect of impurities.

As it developed, the two most influential impurities were carbon and oxygen.

The solubility of carbon in thorium was studied by Grennel and Saller by means of x-rays and metallographic examination. Their work indicated that about 0.5% C is soluble in thorium at 1050°C and 0.1% at 900°C. An eutectic is formed at 1.23% C, having a melting point of 900°C. Two compounds of thorium and carbon are formed, ThC and ThC2.

The solubility of oxygen in thorium is apparently less than 0.1% and the only known oxide is ThO2. There appears to be little information on the solubility of nitrogen. It has been suggested that oxygen, nitrogen, and carbon may form a face-centered-cubic compound with thorium, substituting freely for each other in an NaCl-type structure.

To supplement the above information from the literature, the following experimental work was done.

Hardness Exploration and Microstructure

Small test pieces cut from the various bars of thorium were annealed by heating for 2 hr at 800°C and furnace cooling. These test pieces were then heated to various temperatures for 2 hr and water quenched. After grinding and polishing one face, Brinell hardness measurements (1-mm ball, 10-kg load, 15 sec) were made. Fig. 1 summarizes these measurements.

From this figure it will be noted that the "as annealed" hardness of the high-carbon material is higher than that for the low-carbon material. The increase in hardness of low-carbon material for heating temperatures above 650°C probably indicates that constituents precipitated from solution during annealing are redissolved.

This effect is also evident in the microstructure* as is shown in Figs. 2 and 3. Both of these figures show the extent of impurities present. They also indicate that more of the impurities are in solution in the water-quenched material than in the slowly cooled material. On comparing Figs. 2 and 3, it will be noted that excess impurities have more of a tendency to precipitate at grain boundaries in high-carbon material than in low-carbon thorium.

Thermal Analysis

The hardness curves shown in Fig. 1 indicate that impurities appear to dissolve in the low-carbon thorium at about 650°C and at a somewhat higher temperature in the high-carbon thorium.

In order to check this interpretation of the hardness data, a few thermal analyses curves were made.

*See Appendix A for description of polishing and etching technique.
The thermal analysis used the differential method of plotting cooling curves in which the temperature of a sample of thorium was plotted against the difference between the temperature of a sample of nickel and the one of thorium at equal time intervals. These curves showed a small but definite change in the cooling rate for the low-carbon thorium in the temperature range 650 to 750°C and one about 50°C higher for the high-carbon thorium. These changes in cooling rate could be interpreted as indications of extensive precipitation from solution in the temperature ranges indicated.

While the exploratory analyses described above were not complete enough to separate the effects of the various impurities present, they indicate the temperature ranges in which metallurgical changes such as solution and precipitation are most pronounced.
THE EFFECT OF COLD WORK ON RECRYSTALLIZATION OF THORIUM

Background

The conventional methods of exploring the effect of cold work on the recrystallization of a metal may be summarized as follows:

1. Samples of the metal are cold worked to some selected reduction in area.

2. Samples are then either heated to a given temperature for successively longer times, or are heated for a constant length of time at successively higher temperatures. In either case a different sample is used for each time or temperature.

3. The extent of recrystallization in the various samples is then estimated by metallographic or x-ray methods or by measuring the change in some physical property such as hardness, tensile strength, yield strength, etc.

4. Attempts are then made to evaluate and coordinate estimates of recrystallization with conditions producing recrystallization through the use of one or more of the current rate process theories as described in references 1 through 6. In the course of this evaluation procedure, attempts may be made to separate nucleations of crystals from their subsequent growth.

While the process outlined above occasionally yields straightforward results, in most cases there are factors peculiar to the metal or alloy being studied which complicate the interpretation of results and must be taken into consideration.

In this case the complications were introduced by the impurities in the thorium. As a result of these, considerable investigation was required before reasonably reliable methods of studying recrystallization were devised.

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Fig. 2. Effect of heat treatment on low-carbon thorium (Bar No. 3).
Fig. 3. Effect of heat treatment on high-carbon thorium (Bar No. 5).
The methods and reasons for their adoption can be summarized as follows:

1. Most samples of thorium were heated to 720°C and cooled slowly before any cold work was introduced. The purpose of this slow cooling was to precipitate as many impurities as possible, so that recrystallization would be influenced as little as possible by simultaneous precipitation.

2. After exploration of other methods, hardness measurements were chosen as the means of determining the extent of recrystallization. While metallographic and x-ray methods were effective to some extent in determining when recrystallization is complete, it is difficult to use these methods in determining intermediate amounts of recrystallization.

3. Most experiments were made on thorium that had substantial amounts of cold work. The idea here is that the rate of recrystallization is governed by two factors—the rate of formation of nuclei for recrystallization and the rate of growth of nuclei. When only a few nuclei are present to start, as is the case for small amounts of cold work, the rate of formation of new nuclei is an important part of the process. On the other hand, when there are so many nuclei present to start that new ones formed are a small percentage, then only the rate of growth need be considered and the analysis is greatly simplified. In
view of this, rather large amounts of cold work were used.

4. In the experiments, both the effect of time on recrystallization at constant temperature, and
tory (Bars 1-4, Table 1). As mentioned earlier, this material was in the form of bars about 0.25 in. thick which had been cold rolled. Test pieces cut from these bars were heated to 720°C for

![Graph showing Brinell hardness vs. temperature.](image)

Fig. 5. Effect of temperature on the Brinell hardness of thorium from bars, Nos. 1-4, cold rolled 30% reduction in thickness. Time at temperature—1 hr.

the effect of temperature at constant time were used.

Both methods lead to essentially the same conclusions regarding the activation energy for recrystallization.

Experimental Results

Preparation of Material

All recrystallization experiments were conducted with the material from the Ames Laboratory (Bars 1-4, Table 1). As mentioned earlier, this material was in the form of bars about 0.25 in. thick which had been cold rolled. Test pieces cut from these bars were heated to 720°C for several hours and slowly cooled. In this condition they were completely recrystallized and had an average Brinell hardness of 74. The test pieces were then cold rolled so that their thickness was reduced by the various percentages noted later. The rolling was done with polished rolls using kerosene as a lubricant. The cold reduction per pass was 0.025 in. or less. All heating for recrystallization tests was carried out in a vacuum. The test pieces were sealed in evacuated glass or silica tubes.
The heating temperature was controlled to ±2°C and after heating for the prescribed length of time, the test pieces were cooled, removed from the tubes, and hardness measurements were made. It was considered that this initial change was not associated with recrystallization. Figs. 8 and 9 show the percentage recrystallization curves at various temperatures derived from the hardness curves.

Experiments with Constant Time — Variable Temperature

Figs. 4 to 7 show the changes in hardness produced by heating. It will be noted that in all cases the hardness curve shows a rapid drop in the temperature range from 450° to 520°C. Micro-examination showed no evidence of any recrystallization in this range on any of the samples so it is considered that this initial drop is associated with "recovery" or possibly with some additional precipitation. Whatever the cause, it was considered that this initial change was not associated with recrystallization. Figs. 8 and 9 show the percentage recrystallization curves at various temperatures derived from the hardness curves.

The percentage recrystallization was computed by means of the equation

\[ x = \frac{H_c - H_T}{H_c - H_a} \]  

where \( H_c \) is the hardness after the initial "recovery" change, \( H_T \) is the hardness after one hour at temperature, and \( H_a \) is the hardness after complete recrystallization. It should be recognized that the use of hardness changes as a means of estimating extent of recrystallization assumes...
SOME ASPECTS OF THE RECRYSTALLIZATION OF THORIUM

that there is a one-to-one correspondence between hardness changes and amount recrystallized. This is almost certainly not correct; however, the proportionality is good enough to warrant its use. Experience with other metals has indicated that the use of physical properties other than hardness usually result in changing the position of the recrystallization curve without changing the slope from which the heat of activation is computed.

The data in Figs. 8 and 9 were then used to compute a heat of activation for recrystallization by means of the equation

\[ \ln t = \ln \ln \frac{1}{1 - x} + A + \frac{Q}{RT} \]  \hspace{1cm} (2)

in which \( t \) is the time at temperature \( T \) in hours, \( x \) is the fraction recrystallized in time \( t \) computed from (1), \( A \) is a constant, and \( R \) is the gas constant per molecule (1.986 cal/°C/mole).

As mentioned earlier, Eq. 2 assumes that the number of nuclei being formed during recrystallization is small compared with the number already present, and the process of recrystallization is essentially one of growth from nuclei already available.

The method of computing \( Q \) from Figs. 8 and 9 and Eq. 2 was as follows:

1. Temperatures required to produce 30% and 70% recrystallization were obtained from the curves. The value of \( Q \) was then computed from the equation

\[ Q = R \left( \ln \ln \frac{1}{1 - x_2} - \ln \ln \frac{1}{1 - x_1} \right) \left( \frac{T_2 - T_1}{T_2 - T_1} \right) \]  \hspace{1cm} (3)

Values computed are given in Table 2.

In order to demonstrate the effect of averaging values of \( Q \) from Table 2 to arrive at a figure for the heat of activation it is instructive to use an
Fig. 8. Per cent thorium recrystallized after 1 hr at temperature. Computed from hardness measurements.

Fig. 9. Per cent thorium recrystallized after 1 hr at temperature. Computed from hardness measurements.
Table 2. Heat of Activation for Recrystallization of Thorium.

<table>
<thead>
<tr>
<th>Material, cold rolled, %</th>
<th>Q cal/mole</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>31,900</td>
<td>-24.59</td>
</tr>
<tr>
<td>30</td>
<td>40,500</td>
<td>-24.59</td>
</tr>
<tr>
<td>45</td>
<td>46,000</td>
<td>-25.24</td>
</tr>
<tr>
<td>60</td>
<td>46,000</td>
<td>-25.39</td>
</tr>
</tbody>
</table>

average value of 44,000 cal/mole, and reconstruct recrystallization curves by means of Eq. 2. This has been done and computed values are shown as triangular points in Figs. 8 and 9. Note that agreement is quite satisfactory.

Experiments at Constant Temperature—Variable Time

Using the same heating methods as were used for the tests described above, a series of test pieces cold rolled various amounts were heated at 525°C, 575°C, and 600°C, respectively, for lengths of time ranging from $\frac{1}{2}$ to 50 hr. This treatment resulted in a series of samples for each temperature which had been recrystallized to varying degrees. These were brought to a common basis through the use of Eq. 2 arranged in the following manner.

\[
\ln t - \ln \ln \frac{1}{1-x} = A + \frac{Q}{RT} = \ln t_e, \quad (4)
\]
where \( t_e \) is an "effective time" defined by the relation
\[
\ln t_e = \ln t - \ln \frac{1}{1 - x}.
\]

In Fig. 10 the reciprocal of the temperature is plotted against \( t_e \). A value of \( Q \) can be computed from the slope of the curve of \( \ln t_e \) vs \( 1/T \) and the value obtained from the curve drawn in Fig. 10 is
\[ Q = 43,500 \text{ cal/mole}. \]

Miscellaneous Experimental Results

After cold rolling, the grains in the thorium used in these experiments were elongated. Typical grain dimensions were 0.02 mm wide by 0.2 mm long. There is rapid recrystallization in the temperature range 600° to 660°C. The recrystallized grains obtained are more nearly equiaxed than the ones in the rolled material with a typical diameter of about 0.02 mm. These recrystallized grains are quite stable and do not begin to grow further until a temperature of 1100°C is reached. Heating for an hour at 1100°C increased the typical grain size to about 0.026 mm, and for an hour at 1200°C the size increased to 0.103 mm.

**DISCUSSION AND CONCLUSIONS**

As pointed out earlier, the thorium available for this investigation was not as free from impurities as would be desired for a fundamental investigation of recrystallization. Nevertheless, it was pure enough to be considered for application in a pile, and it was thought that a practical knowledge of the recrystallization habits of this type of thorium was desirable, even though greater precision might be obtained with more highly purified material.

With the above limitations in mind, the effect of cold work on recrystallization of this grade of thorium can be summarized as follows:

1. Cold-worked thorium recrystallizes in the temperature range from 500° to 660°C. The region of most rapid recrystallization is 620°C or higher.
2. Above about 700°C solution of impurities present in the thorium becomes quite substantial.
3. The heat of activation for recrystallization of thorium is in the vicinity of 44,000 cal/mole.

**APPENDIX**

The problem of metallographic examination of relatively pure thorium metal is rather difficult because of the ease of formation of oxide films on the prepared surface. This obscures and disguises the true microstructure. If an oil-immersion objective is used the oxide films become invisible and the structure is revealed. However, for low magnifications, this method is not very practical.

The thorium metal was wet ground and polished with a carborundum-soap solution. A chemical polish consisting of an aqueous solution of HNO\(_3\) (10-50%) with 1% H\(_2\)SiF\(_6\) was also found useful. The sample was then etched electrolytically in a solution of glacial acetic acid (75%) and 96% phosphoric acid (25%). To obtain a clean etch it was found that the bath had to be used for some time and become polluted with thorium oxide. The etching conditions used under agitation with a stainless steel anode were as follows: 2 to 3 min, 60 to 75°F, 0.75 to 1.25 amp/sq. in.

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August 1949
The Production of the Light Rare Earths in the Massive Metallic State


Iowa State College

Report ISC-75

ABSTRACT

Cerium, lanthanum, praseodymium, and neodymium metals have been prepared in high purity in the massive state by reducing the appropriate rare earth chloride with calcium metal, using iodine as an auxiliary oxidant. Vacuum remelting of the product metal is employed to eliminate small amounts of calcium and magnesium. Attempted reductions of samarium and yttrium halides have not been successful.

INTRODUCTION

The rare earths, because of their unique similarity, have been the source of much fruitful work on the electronic structures of the elements. For the same reason, this group of elements should offer an excellent opportunity to evaluate existing theories of metals and to establish a more precise explanation for the relations between the properties of metals and their electronic structures. With the advent of atomic piles, interest in the rare earths has been heightened since these elements make up an appreciable fraction of the fission products from such piles. The study of the rare earths being carried out in this laboratory has as its aim the preparation and study of pure rare earth salts and metals to shed light on the above problems.

The preparation of the rare earth metals was accomplished as early as 1827 by the reduction of cerous chloride with sodium or potassium by Mosander who obtained powdered metal in poor yields, contaminated with excess reductant and reaction products. Wohler, de Marignac, and others subsequently used similar procedures with the same results. Klemm and Bommer prepared the powdered metals of all the rare earths by reducing the chlorides with alkali metals and used these powders for x-ray and magnetic studies.

Cerium fluoride was reduced by calcium or aluminum by Moldenhauer who obtained alloys of the metal. More recently, Trombe and Mahn reduced the chlorides of cerium, neodymium, and gadolinium by molten magnesium to obtain alloys of the rare earths in 50 per cent yields; from these, they distilled the magnesium to prepare metal of 99 per cent purity. Most of the rare earth metals produced prior to their production at this laboratory were prepared by electrolysis of the chloride or fluoride by Hillebrand and Norton; subsequently by Muthmann and associates, Trombe, Kremers, and Hopkins and associates.

Work in this laboratory has shown the metalthermic reduction of rare earth halides to be a very effective method of obtaining several of the rare earth metals in the massive state in a high degree of purity. The present paper is the first of a series on the preparation and properties of the rare earth metals, and it establishes that cerium, lanthanum, neodymium, and praseodymium metals can be produced in a very pure state with high yields by the reduction of the rare earth chloride with calcium, using iodine as an auxiliary oxidant.

The preparation of samarium and yttrium metals has been effected, although the yields and quality of the metal obtained were poor.
MATERIALS, APPARATUS, AND GENERAL PROCEDURE

Materials

The pure rare earth salts used for the preparation of the metal were obtained from several sources. The commercial grade of "pure" cerium (95 to 98 per cent cerium), as the oxalate and the chloride, and spectroscopically pure lanthanum, as the oxalate, were purchased from the Lindsay Light & Chemical Co. Spectroscopically pure cerium was supplied as the hydrated chloride or as cerium ammonium nitrate by the G. Frederick Smith Chemical Company.

The commercial grade of cerium salts was used to determine the conditions for optimum yields of cerium metal, and the pure grade was used to produce pure metal in high yields. Some of the commercial grade cerium chloride was purified by dissolving it in water and precipitating the thorium as the insoluble Th(IO₃)₄. Ceric ion present in the solution to the extent of several grams per liter served as a carrier for the thorium by precipitating as Ce(IO₃)₄.

The other rare earths studied were obtained in the pure state by elution through Amberlite columns as the citrates.15-18 The various rare earth salts were analyzed for other rare earths and other impurities by spectroscopic methods developed in this laboratory.19,20

The anhydrous rare earth chlorides were prepared by a method similar to that of Kleinheksel and Kremers.21 This consisted in dissolving the rare earth oxide in hydrochloric acid and evaporating this solution to a syrup which boiled at 128°C. This solution was poured into a large porcelain dish and stirred while it cooled, forming the hydrated chloride crystals. The hydrated chlorides were heated slowly to 400°C in a stream of HCl gas at about 5 cm pressure to give the anhydrous chlorides.

Anhydrous samarium trichloride was obtained by drying an intimate mixture of hydrated samarium iodide and ammonium iodide under an atmosphere of hydrogen iodide by the procedure of Jantsch and Skalla.22 Samarium trifluoride was prepared from samarium oxalate by passing dry hydrogen fluoride over the oxalate at 300 to 325°C for 6 hr.

Samarium dichloride was prepared by the method of Jantsch, Ruping, and Kunze23 which consisted in reducing the trichloride with a mixture of hydrogen and ammonia at elevated temperatures.

Analysis of these halides showed them to contain the theoretical amounts of the two components, and consequently they were certain to be free from the oxyhalides which are notoriously difficult to reduce.

The calcium metal used in this work was obtained from Metal Hydrides, Inc., and the Electrometallurgical Co. in the form of high purity aggregates which contained less than the indicated amounts of the following impurities: Mn, 5 ppm; Fe, 5 ppm; Al, 10 ppm; and Mg, 0.5 per cent. These aggregates were first broken up by a punch press and then cut to -10 mesh particles in a rotary knife mill. This material was sieved, and only particles larger than 50 mesh were used. It was found that by this sieving essentially all of the small amount of loose calcium oxide coating passed into the "fines," leaving behind a relatively stable but reactive reductant.

The oxidants used were resublimed iodine, potassium chlorate, and sulfur, which were supplied as reagent grade chemicals by the J. T. Baker Chemical Company. Zinc chloride, which was used as a co-reductant, was also obtained from this company.

Apparatus

The reduction was carried out in bombs constructed from standard black steel pipe by welding a bottom of ¾-in. steel plate on one end. The top of the bomb was threaded to receive a standard steel or cast iron pipe cap. Four sizes of the bombs were used. The largest, 4 in. in diameter and 24 in. long, was utilized for large scale production; other sizes were 2½ by 12 in., 1½ by 8 in., and 1 by 5 in.

Contact of the reaction mixture with the steel wall of the bomb was prevented by containing the reactants in a smooth-surfaced refractory oxide liner ¼ to ⅛ in. thick, depending on the size of the bomb. The liners usually consisted of a sintered crucible inserted into the bomb and held in place by filling the narrow annular space between the crucible and the bomb walls with loose lime (Fig. 1). The loose lime prevented leaks in case the crucible cracked during reaction. Loose packed liners were also used; these were prepared by placing a mandrel inside the bomb and jolting loose calcium oxide into the annular space between the bomb wall and mandrel by means of a pneumatic jolter. After thoroughly packing the liner by this means, the mandrel was carefully removed, leaving a firm, smooth-surfaced liner. This jolt packed liner was relatively porous and was used only in the largest scale reductions (1600 g of CeCl₃), but even on this scale the yields were reduced by several percent by this practice.

The sintered crucibles were made by jolting the lime or dolomitic oxide in a graphite crucible in a manner similar to that employed in preparing the loose packed liners, and then sintering by heating in an induction furnace to 1750°C. Crucibles, so prepared, are dense, smooth-surfaced, mechanically strong, and fairly resistant to thermal shock. They absorb moisture from the atmosphere and hence must be stored in closed containers.

To provide insulation on the top of the bomb, a ⅛- to ⅛-in. layer of lime was tamped into the pipe-cap...
PRODUCTION OF LIGHT RARE EARTHS IN THE MASSIVE METALLIC STATE

lid of the bomb, and to prevent any of this lime from falling into the charge, the liner was covered with a sintered lime or graphite lid. Plumbers seal applied to the threads of the bomb effectively sealed it, preventing loss of volatile components, and reducing losses by air oxidation.

An alternative method of raising the final temperature of the bomb was to add materials to the bomb which would undergo an exothermic or booster reaction at the same time the principal reaction took place. Several important requirements of such a booster reaction are:

1. It should be highly exothermic.
2. It should not introduce impurities into the product.
3. It should be easily controlled, i.e., it should not fire prematurely.

Since calcium was already a component in the bomb as the reductant, one obvious choice for a series of boosters was oxidants which would react exothermically with calcium, such as iodine, sulfur, and potassium chlorate. Iodine was found to be particularly successful as a booster since its reaction with calcium was very exothermic and gave as a product calcium iodide which added to the calcium chloride from the primary reaction to give a low melting slag which greatly promoted the collection of the metal. Although iodine vapor tended to diffuse through the packed bomb and slowly react with the calcium at room temperature, the major portion of the booster reacted at the ignition temperature along with the primary reaction.

An example of a second type of booster which was used is anhydrous zinc chloride. This material, which has been used in cerium and samarium reductions, provides an exothermic reaction with calcium, forming zinc and calcium chloride, and in this case the zinc reacts with the product metal to give an alloy more easily agglomerated by virtue of its larger mass and possibly its lower melting point, although this last point has not been confirmed. In cerium reductions the zinc is not a serious contaminant, for in vacuum casting the zinc distills out of the product metal completely. This is not the case for the several reductions that have been carried out with samarium salts. Other boosters in this same class would be salts of cadmium, antimony, etc.

In preparation for the reduction, a bomb was lined and then filled with a thoroughly mixed charge of rare earth halide, calcium, and oxidant. The charge was tampered into the bomb and then covered by a refractory lid, after which the lined cap was screwed on. These operations were usually carried out in a dry atmosphere; however, this precaution was found to be unnecessary for production runs in the large 4-in. bomb provided that the anhydrous chloride to the moisture of the atmosphere was limited.

To initiate reaction the loaded and sealed bomb was placed in a furnace held at 650 to 750°C. When the bomb reached a temperature of about 400°C the reaction suddenly went to completion in a matter of seconds as evidenced by the sudden rise of the bomb temperature. The heat of reaction was sufficient to melt both the slag and the metal allowing the metal
to collect in the form of a massive cylinder in the bottom of the bomb. As soon as the bomb fired, it was removed from the furnace and allowed to cool before being opened.

EXPERIMENTAL

Reduction of Cerium

The first small scale reductions of cerium were made by heating in a bomb a mixture of cerous chloride and 10 per cent more calcium than the stoichiometric amount required for the reaction

\[ 3\text{Ca} + 2\text{CeCl}_3 \rightarrow 3\text{CaCl}_2 + 2\text{Ce} \]

After the reaction subsided, heating was continued until the bomb reached a temperature above the melting point of cerium, on the assumption that such heating would melt the metal and slag, and assure separation and collection of the metal. It was found, however, that the prolonged heating produced a boiling action which resulted in the continued mixing of slag and metal as well as in greater wetting and penetration of the liner by the metal. These conditions resulted in poor ingots which were highly contaminated with slag, poorly formed, and covered with a tightly adhering crust of slag.

To eliminate this prolonged post-reaction heating period with its resulting poor yields, a flux of potassium chloride was added to the reaction mixture so that the final slag contained 20 mole % potassium chloride and 80 mole % calcium chloride. This permitted separation of the slag and metal at lower temperatures by lowering the melting point of the slag, and by this means, cleaner metal was obtained in yields of from 50 to 80 per cent.

While this procedure was moderately successful, it appeared that, for large scale production, the high temperature of the post reaction heat was both tedious to maintain and difficult to control. It was decided to attempt to obtain the heat necessary for melting the components of the system by adding materials to the bomb which would undergo a highly exothermic reaction simultaneously with the principal reaction.

Iodine was first investigated as a booster, and, for the initial set of reductions, charges of anhydrous cerous chloride and iodine in the ratio of 1 mole of iodine to 1 mole of the chloride were reduced by calcium in a 5 per cent excess over the stoichiometric amount. Approximately 300 g of cerous chloride with corresponding amounts of iodine and calcium were reacted in each charge in 2½- by 8-in. bombs with sintered lime crucibles as liners by heating the bombs to 700°F in a resistance furnace or a gas-heated soaking pit. Yields of 58 to 78 per cent of fairly clean castable metal were obtained with an average yield of 65 per cent for seven runs.

A study of the effect of varying the ratio of iodine and calcium to cerous chloride was made, using a 312-g charge of cerous chloride. Varying the iodine and calcium ratios independently, it was found that optimum yields of cerium metal were obtained with an iodine to cerous chloride ratio of 0.625 to 1, with 15 per cent excess calcium. Using this ratio, more than 5 kg of cerium were prepared with an average yield of over 93 per cent. Some work carried out on 1600-g charges of cerous chloride showed that an iodine to cerous chloride ratio of only 0.5 to 1, with 10 per cent excess calcium was required to obtain yields of over 94 per cent on this scale; the higher thermal efficiency of the larger scale reaction requiring less booster heat to permit separation of metal from slag.

In an effort to find a substitute for the iodine, which is expensive and was relatively unavailable at the beginning of this investigation, other boosters were investigated. Sulfur was tried in the range of 0.5 to 2 moles of sulfur per mole of cerous chloride. Although considerable heat was generated, as evidenced by the outside temperature of the bomb, no separation of the metal and slag occurred.

Potassium chlorate was next tested as an auxiliary oxidant with more satisfactory results. The range from 0.10 to 0.16 moles of potassium chlorate per mole of cerous chloride was investigated. An optimum yield of 83 per cent was obtained with 0.11 mole of potassium chlorate per mole of cerous chloride. Even under the best conditions the use of potassium chlorate did not produce cerium metal in yields comparable to those produced by use of iodine, either externally with respect to adhering slag, or internally, with respect to inclusions.

Since the small scale (30 g) reductions of cerium chloride with iodine booster gave yields of only about 70 per cent, ZnCl₂ was tried as a booster on this scale reduction, still employing as the reductant calcium, present to the extent of 10 per cent above the stoichiometric quantity. ZnCl₂ was added in such proportions as to make the final product contain 2.8 and 5.5 per cent zinc, respectively, assuming a 100 per cent yield. These two runs gave yields of better than 98 per cent, and on recasting in a vacuum, an over-all yield of better than 90 per cent was obtained in both cases, with the amount of residual zinc being below 20 ppm, the limit of detection by spectroscopic analysis. The ratio of reactants described above was used in the preparation of over 1,000 lb of 95 to 99 per cent cerium metal, containing other rare earths and calcium as the impurities. For reductions in the 2½-in. bomb, as used for the preparation of 4 kg of pure cerium, the re-
actants were mixed in the ratio of 0.63 mole of iodine per mole of cerous chloride with a 15 per cent excess of calcium. With this ratio the metal was obtained as well-formed ingots weighing 150 to 175 g with an average yield of 93.5 per cent. The ingots obtained were almost invariably very clean with smooth sides and top, as illustrated in Fig. 2. The cerium metal thus produced contained from 1 to 5 per cent calcium and 0.1 to 1 per cent magnesium.

Preparation of Lanthanum, Neodymium, and Praseodymium Metals

The ratio of reactants used with optimum yields for the preparation of cerium was successfully applied for the reduction of lanthanum chloride, neodymium chloride, and praseodymium chloride to metal. Several kilograms of lanthanum and 500 g of neodymium were prepared with better than 90 per cent yields. The praseodymium metal was produced on a smaller scale in the 1½-in. bomb with a 76 per cent yield for the 33-g ingot produced in the only reduction attempted. The results of the praseodymium reduction compare with the 75 to 85 per cent yields obtained for cerium reductions carried out on this scale and indicate that, when larger charges are reduced, yields equal to those obtained for cerium will be obtained. With respect to yields, contamination by calcium and magnesium, and quality of ingots, the results of the above reductions duplicated those obtained for cerium metal.

Preparation of Samarium and Yttrium Metals

Extension of the reduction method using iodine or potassium chlorate as oxidants for the preparation of samarium metal was not successful. Attempted reductions of samarium trifluoride, samarium trichloride, and samarium triiodide by calcium with an iodine booster in the ratio of 0.63 mole per mole of halide were failures, the dihalide being formed in each case. The reaction between the calcium and iodine and the trihalide proceeded quite vigorously as evidenced by the heat generated in the bomb at the time of the reaction and the complete collection of reaction products in the bottom of the liner, but in no case was metal obtained. This result is in agreement with previous findings that the rare earths having a stable divalent state are extremely difficult to reduce to metal.7

Use of potassium chlorate as a booster was also tested in the attempted reduction of samarium trichloride to metal. In two runs in a 1-in. bomb using 25 g of samarium trichloride with 0.1 and 0.167 mole of potassium chlorate per mole of chloride, the bombs were heated to a bright red heat by the reaction. The reaction products were completely fused, but only the dichloride was formed. A small amount of metal was prepared as a calcium alloy by the reduction of samarium dichloride by calcium; however, it could not be recovered for recasting. A zinc alloy of samarium was produced and separated in low yields by the co-reduction of samarium trichloride or trifluoride and zinc chloride by calcium. A small amount of this alloy was recast to give 2 g of metal containing greater than 80 per cent samarium.

The first experimental reduction of yttrium chloride was carried out on a 70 per cent yttrium chloride (70 per cent Y, 18 per cent Nd, 10 per cent Sm, and 2 per cent Gd). Using a ratio of 0.63 mole of iodine to 1 mole yttrium chloride with 10 per cent excess of calcium, 58 g of this salt was reduced to give 29 g of metal for a 79 per cent yield. However, on 90 per cent yttrium chloride (90 per cent Y, 6 per cent Dy, 2 per cent Gd, and 2 per cent other rare earths) no ingot was obtained by two attempted reductions on the same scale. In these latter reductions, the metallic yttrium produced by the reduction was intimately mixed with the slag, but there apparently was not enough heat generated to fuse the metal although the reaction proceeded vigorously enough to permit complete slag collection. The high melting point which has been reported for this metal8 may conceivably be a factor in this unsuccessful attempt to obtain fused massive metal.

Experimental work is continuing on the preparation of these metals.

Purification of the Ingot Metal

As mentioned previously, the ingot metal contains as its major impurities 1 to 5 per cent calcium and...
0.1 to 1 per cent magnesium. Evidence has been gathered which indicates that the calcium is present in the ingots as pure calcium metal, while the magnesium is probably present as an intermetallic compound with the rare earth metal. It has been found that, in melting the ingot metal in a vacuum, the calcium and magnesium may both be distilled from the rare earth metal, leaving less than 200 ppm of either of these metals in the product. The vacuum induction furnace assembly used for this purification consists of a silica tube closed at one end and fitted at the other with a water-cooled brass vacuum head equipped with a window to permit reading the temperature of the furnace by means of an optical pyrometer. The ingot metal is placed in a suitable crucible, usually made of MgO, CaO, BeO, or Ta metal, and this is set in a larger graphite crucible which serves as the inductor-heater. This graphite crucible is equipped with a lid and a chimney through which the volatile material escapes from the inner crucible and condenses in a cool portion of the furnace. The 1 1/2- to 3-in. space between the graphite crucible and the wall of the silica vacuum jacket is packed with insulation such as granular electrically fused dolomitic oxide or graphite powder. A Hypervac 20 vacuum pump serves to maintain a vacuum of less than 50 μ during a melting operation, once a preliminary degassing has been effected. The high frequency source used for heating the furnace was a 20 kva Ajax-Northrup unit.

In a typical melting run for lanthanum, the loaded furnace is heated slowly to 1250°C, the ingot melting at approximately the melting point of pure lanthanum, 780°C. At 1000°C the calcium and magnesium begin to distill at an observable rate, and during the 1/2 hr required to raise the temperature from 1000 to 1250°C the distillation of the major portion of the calcium and magnesium is completed. The melt is held at 1250°C until the bubbling ceases, usually in about 10 to 15 min, and the furnace is then shut off and allowed to cool before opening. The purified metal from such a melt invariably represents a yield of better than 95 per cent and can easily be cleaned of any adhering crucible material, leaving a smooth walled casting. The pick-up of any crucible material by the molten metal is quite small, for example, a sample of lanthanum metal melted in a beryllium oxide crucible was found to contain 140 ppm of beryllium and less than 150 ppm of calcium.

Typical analyses of metals purified in this manner are shown in Table 1.

**SUMMARY**

The reduction of cerium, lanthanum, praseodymium, and neodymium chlorides with calcium using iodine as an auxiliary oxidant provides an extremely effective method of preparing these rare earth metals. Except for a very small amount of calcium and magnesium (less than 200 ppm), the purity of the metal is limited only by the purity of the original rare earth compound. The yield increases with increasing size of charge, 70 per cent yield on 30-g charge and 93 per cent yield on 312-g charge. Reductions of samarous and samaric halides gave only small amounts of highly contaminated metal, while reductions of yttrium chloride gave only an impure powdered product.

**REFERENCES**


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Where Are We Going in Reactor Development?

By E. P. Wigner
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At the General Information Meeting held in Oak Ridge in October 1949, Dr. Wigner gave the introductory talk at Session II on the subject "Where Are We Going in Reactor Development?" The interest shown in this talk was such that we thought it appropriate to reproduce it verbatim in the Journal of Metallurgy and Ceramics.

Dr. Weinberg has asked me to participate in a round-table discussion on nuclear reactors. I told him that I had been out of the business for such a long time that my opinion would be of but little value. He said that he just wanted to hear someone who was farther from the works than he was. I then told him how far my views usually were from the accepted ones and how often I already had made myself unpopular by voicing them. He said that it would be understood that I would speak only for myself.

I shall group my remarks under three headings:
(1) What are the brakes on the reactor program which should be eliminated,
(2) what may be some of the immediate goals of the reactor program, and
(3) how has recent theoretical and experimental progress influenced our thinking on breeders. My comments to the last point will be, of course, very scanty.

I do not think that anyone will disagree with me when I say that the reactor program has not developed as rapidly and successfully as we hoped in 1944 that it would. Up to this point, I believe, I have presented the official view, however, I will be expressing my own opinions throughout the rest of the discussion.

REACTOR DEVELOPMENT IN THE PAST

Until recently, it could have been said that our 1944 hopes did not come true because we underestimated the difficulties. What actually happened is, I believe, that we overestimated the effort which, for various reasons, was available for reactor work. Actually, the effort directed toward reactor development was smaller than had been expected, and I wish to analyze the most important causes of this. There are, I believe, three of them.

There is the obvious one, that the reactor work could, in the general scheme of things, take only second priority to the weapon work. It does not seem to me, however, that this was a decisive reason. More important, in my mind, was the circumstance that with German competition eliminated, we lost our primary incentive toward rapid progress. As a result, we who performed reasonably well under the misapprehension of menacing foreign competition performed much less well under the misapprehension of the absence of it. The lack of a sense of urgency pervaded the whole effort—it included scientists, administrators, and industrialists. Added to this was the difficulty of defining adequate aims for our reactor program, and as a result the reactor effort was seriously disoriented.

It is to be hoped that now, after the September 23 news of developments in the U.S.S.R., the sense of disorientation will soon be replaced by an objective and well-founded appraisal of the situation based on an adequate knowledge of the conditions and on common agreement among all.

The announcement of September 23 will also make clear to us that we are in competition, that we must
work hard if we are not to be outpaced hopelessly. We will stop glorifying our past, forget about the unique abilities and accomplishments of ourselves and our industrial organizations, and get back to work. Our self-confidence will return as soon as we have done these things. It seems that we find it very hard to work vigorously and effectively in the absence of competition. We might just as well acknowledge this, and, since we cannot always count on the stimulating influence from abroad, we should try not to eliminate competition completely within our own country. In fact, nobody can judge whether an installation really does as well as possible if there is no other installation with which its performance can be compared. All this should warn us against the dangers of overcentralization.

The second aspect of our having become large-scale operators, the absence of real experimentation, is equally noteworthy. It is my judgment of the extent of our knowledge of physical phenomena that we cannot foresee with certainty the behavior of any physical system the likeness of which we have no direct experience with. Our science does teach us principles which can be utilized for given purposes, but the human mind is not powerful enough to foresee all complications which may be encountered with proposed equipment, even if those complications are consequences of well-known principles. The fact that no unforeseen complications have turned up with the Richland reactors is not so much a triumph of our thinking, though an enormous amount of thinking was done on the plans of that reactor, but rather the result of the fact that all parts of that reactor are of conventional nature. However, novel features may promise great advantages, and it would be a great loss to confine ourselves permanently to reactors with only conventional parts. If we are to do better, we must be able to make small-scale experimental reactors that are not sure to succeed, even such that are likely to fail. In other words we must recover the faculty of making small, cheap reactors on the basis of only a moderate area of blueprints. Our wealth and financial resources could be used to much better advantage in this connection by trying out many different cheap, experimental types, rather than by making a single piece of final equipment which is perfect.

It has often been said that no pilot plants are possible for reactors, because the reactor will not react below the critical size. Actually, I believe that this is a fallacy. Most of the expense of a high-output reactor is not in the reactor itself but in the auxiliary equipment; hence the full-scale reactor can well be its own pilot plant if the auxiliary equipment is properly scaled down. The mock-up of the MTR, which is in Oak Ridge, cost about 3 per cent of the lowest price estimate of the full-scale reactor and can well demonstrate the workings and feasibility of the most important parts thereof.

If our big reactors are to become less expensive, as they have to become, the interplay between design and engineering groups must be intensified, and all unexpectedly large expenditures must be scrutinized as to their necessity. I feel convinced that if properly handled this can lead to a contraction rather than an expansion of the time schedules. It should abbreviate the time needed to obtain a decision.

The third and last cause to adversely affect reactor development is the belief, the widely advertised belief, of so many of our colleagues that reactor work and even nuclear physics are not physics any more. The folly of this opinion has since been amply demonstrated, but the harm these statements caused has not entirely been undone. They have caused a frame of mind among physicists in which, for a time, few of us were willing to devote full attention to reactor work, the way full attention is being devoted to the engineering of cyclotrons. We certainly should have learned by now that this much of the myth of the difficulty of reactor work is true: that the word cannot be done with the left hand while the right hand and the mind are engaged in another pursuit. It is too difficult for that.
If we are to restore the reputation of reactor work, those of us who are interested in it must stand up and be counted whether we are participating in active work or not. We must point out that the work has its particular charms and interest and that its results will be useful for both science and industry, not to forget the standing of the country.

There are, of course, many other problems in the reactor program, some of which were solved recently but independently of the Russian announcement. I am referring in particular to the problem of the cooperation between scientists and engineers, in which mutual confidence and appreciation of the functions of the other group is replacing the old rivalry. Here is a problem that was adjusted without outside help.

PROBLEMS OF IMMEDIATE URGENCY

Unfortunately, the effect of recent events was not so favorable in every respect as it was in teaching us a bit of humility. There is little question that attention will be diverted from the ultimate goals of reactors, such as may play a permanent role in our economy, and will be refocused on more immediate objectives.

There are two such objectives: the old one of producing plutonium and the production of power from nuclear energy. This last will have to be undertaken with a certain disregard—we hope only with temporary disregard—of the expense of power in terms of fissionable material.

Progress in the field is good so far but not yet spectacular. One of the important accomplishments is the isolation of a number of auxiliary problems, the solution of which is relatively independent of the decisions to be taken concerning the other parts of the machine. Chief among these auxiliary problems is the problem of a light, thin, and effective shield.

I do not wish to go deeper into the question of power reactors, since many of the problems are still controversial. It often seems to me that too thorough an engineering exploration of isolated proposals may prove more time consuming than the increased reliability of the insulting judgment can warrant. A quicker, less thorough, but perhaps more encyclopedic review of the whole field may have the added advantage that it would be less dependent on long-time changes in the reviewers' standards, optimism, and maturity.

The second problem of immediate urgency, or should I have called it the first one, is the standard one of producing plutonium at the expense of $^{238}$U. The reason for the revival of interest in this problem is, of course, the revival in interest in increased plutonium production, coupled with the fact that the ratio of plutonium to heat production is at least three times higher in an old-fashioned unit than it would be in a breeder. Hence the same production rate of fissionable material necessitates a much smaller investment if it occurs at the expense of the $^{235}$U in the natural uranium than if it is done in a breeder.

It may be expected that all the already proposed methods of plutonium manufacture will be reviewed in the near future. I am thinking of the heavy-water moderated units, both heterogeneous and homogeneous, and of the circulating and stationary hex systems with all the different heat-transfer media that have been proposed, some of which are already under investigation. Proposals will emerge from this review which will take into account our increased state of knowledge, the aims to be set, and the availability of raw and semifinished materials. Some new ideas and methods will probably be uncovered, but the principal glamour of the work will derive from its usefulness. Engineers and physicists will have to collaborate with chemists on the job, since it is unlikely that it will be possible to maintain the traditional independence of the chemical plant from the reactor. An outsider would think that it will be of great importance to limit the group or the groups, which are to undertake the review, to very small numbers. This, I would think, is desirable from the point of view of speed and in order to avoid undue specialization.

STATUS OF BREEDERS

In the meantime I hope that the work on breeders will not be altogether forgotten. I have done some work lately on the theory of the nuclear physics of the breeder and wish to tell about this now.

The first question that I was wondering about is whether or not the fission-product poisoning is really as dangerous for a reactor working in the resonance region as we feared. It now seems to me that our fears in this regard were somewhat exaggerated.

On the basis of older work of Bethe and of more recent work of Feshbach, Pease, and Weisskopf, it is possible to arrive at a definite expression for the absorption cross section of a nucleus in the nonthermal region. If we measure the energy $E$, the radiation width $P_r$ and the level distance $D$ in electron volts, the capture cross section in barns becomes

$$\sigma = \frac{1800f}{\sqrt{E}} \frac{P_r}{P_r + 4.4 \times 10^{-19}D \sqrt{E}}$$

The value of $f$ should be about $\frac{1}{2}$ theoretically, but it actually decreases from about 2 for very light elements to about 0.2 for heavy ones. The radiation width is about 0.15 volt for the light fission fragment and about 0.10 volt for the heavy one. The same formula should hold for the fission cross section with the fission width $P_f$ replacing $P_r$.

According to the above formula the average absorption cross section is first proportional to $1/\sqrt{E}$ and
should have the same value for every element. At a higher energy, when the second term in the denominator becomes larger than the first, the cross section should drop as 1/E. The dividing point between the two regions is at about 200 volts for the light fraction and at about 5 to 6,000 ev for the heavy fraction. I should remark that, for the really light elements (lighter than any of the fission fragments), there is no first region and that there is no second region for fission. The 1/\(\sqrt{E}\) region covers in this case the whole energy region of interest.

It follows, then, that the absorption of the light fission fragment can be more or less forgotten as long as the reactor operates well over 200 ev. The absorption of the heavy fragment does not exceed the fission cross section and drops below it above about 6,000 ev. As long as one operates well above 200 ev, leaving the fissionable material in the reactor until a fraction \(p\) of it is used up, it causes a breeding loss of only \(\frac{1}{2} vp\), the \(\frac{1}{2}\) coming from the circumstance that on the average only \(\frac{1}{2}\) fission fragments are in the reactor. Thus if one depletes the original fissionable material by 10 per cent, the average breeding loss caused by fission fragments will be about 12 per cent. This is probably too much to tolerate. However, at a 5 per cent maximum depletion the fission fragment causing breeding loss is probably tolerable.

The above observation does not apply, of course, to thermal breeders for which the xenon accounts for most of the breeding loss and which hardly could support a loss of about 6 per cent.

Nothing in the above observations is really new. It is reassuring to know just the same that the fission-product losses in breeding efficiency do not necessarily force one to operation at very high energies, by which I mean the 100,000-ev region. On the other hand, at energies around 200 ev, the losses will increase not only because the light fragment will also begin to absorb but also because self-protection, caused by the line structure, will diminish, by self-protection, the effective value of the fission cross section.

The above facts reemphasize the question of the feasibility of breeding in the 1,000-ev range and the importance of the value of \(\eta\) in that region. Recent experiments at the Knolls Atomic Power Laboratory indicate that the situation is not rosy from the point of view of \(\eta\) at a few hundred volts. The question then is whether \(\eta\) may improve in the 1,000-ev region. One would be inclined at first to answer this question in the negative: neither the fission width nor the radiative absorption width can be expected to change appreciably below 100,000 ev or so. Hence one would conclude, the ratio of the two \(\alpha's\), and hence also \(\eta = \sqrt{v/(1 + \alpha)}\) should remain constant.

However, the following effect may cause a change in \(\alpha\). Let us assume that the fission width is not the same for every absorption line but undergoes fluctuations from one line to the next. We know that this is true for the neutron width but not true for the radiation width. In my opinion, it is not possible now to tell whether or not it is true for the fission width.

If the fission width fluctuates from level to level, most of the radiative absorption will be caused by the levels in which the fission width is abnormally low. However, the effect of these levels will be greatly reduced at higher energies, where the neutron width overshadows both and thus renders them scattering levels. Thus, even though the ratio of the probabilities of radiative capture and of fission may not change with increasing neutron energy for the arbitrary level, the bad levels, in which the ratio is large, may be reduced to insignificance at a few thousand electron volts.

The reason that I make so much of this possibility is not only because technical difficulties increase so much as one goes in a breeder to higher and higher neutron energies, I do it also because the question of whether or not the fission width fluctuates from level to level can already be answered in the low-energy region, where velocity selector measurements can provide the answer. Dr. Brooks and I convinced ourselves that the present data are not yet sufficient to evaluate the magnitude of the fluctuations. However, we both felt that it would not be impossible to refine the experiments sufficiently to provide at least an approximate answer.

Repeating then the old comparison between thermal, resonance, and fast breeders, one is struck, first of all, by the difficulty of maintaining a high-power breeder at high average neutron energy. The point is, of course, that very efficient cooling is needed in order to reduce the "burn-up time," i.e., the time which the average plutonium atom spends in the breeder before it fissions and thus earns the "breeding gain." Assuming sodium to be the heat-transfer agent and allowing it to increase its temperature 400°C during the transit through the reactor, in order to obtain a two-year burn-up time, so much sodium has to be pumped through the breeder that it will always contain eight sodium atoms per plutonium atom even if the time of transit of the sodium atoms is as short as 0.2 sec. The conversion time will be a good deal longer than the burn-up time because of the need for repeated reprocessing of the fuel elements, with the accompanying large times of sojourn of the plutonium in the chemical and fabricating plants.

The moderating power of 8 moles of sodium is just about equal to the absorbing power of 1 mole of plutonium. It may be expected, however, that there will be enough coating and piping material in the reactor so that the total moderating power, including the moderating power of the plutonium, will equal two or three times the absorbing power of the plutonium. As a result it seems hard to believe that it could be possible
to operate a high-power breeder much above 100,000 ev. This is in essential agreement with considerations at Argonne.

Whether one wants to operate at this high energy, which will aggravate many engineering and metallurgical problems, or whether one will wish to take it somewhat easier and operate in the region of a few thousand volts, will depend on the ratio of the $\eta$ at these energies. If the ratio is close to 1, operation at 100,000 ev will offer little advantage. On the other hand the experiments at the Knolls Atomic Power Laboratory already show that it will hardly be possible to breed below about 2,000 volts but substantially above the thermal region.

The safest bets remain, as they were, first in the thermal breeders. These require very close attention toward minimizing all sorts of losses, and any small error may convert them into losers rather than breeders. The $\eta$ for $^{233}U$ is now well established for the thermal neutrons. Quite safe bets are, second, very high energy breeders which do not require equally close watching of all possible sources for losses. On the other hand it may be very difficult to design high specific power units on their principle.

Whether it would be possible to operate a plutonium breeder in the 5,000 to 10,000-ev region remains the principal problem. This energy region may conceivably avoid the pitfalls of both the very low energy and of the very high energy region. It may be, on the other hand, that they will be sure losers. Investigation of the structure of the absorption lines in the low-energy region may give, however, an indication for the chances for a winning game.

As Dr. Borst mentioned in an earlier paper, the Knolls Atomic Power Laboratory experiments relate only to plutonium breeders. The $\eta$ for $^{234}U$ is not known in the 100-volt region, so that this may be a possible breeding region for $^{234}U$ although it is not for $^{235}Pu$. The question remains, then, whether it offers advantages to operate $^{234}U$ in the resonance rather than in the thermal region.

October 1949
The Recovery of Uranium from Low-grade Ores*


Mineral Engineering Laboratory, Massachusetts Institute of Technology

Report MITG-243

INTRODUCTION

Prior to the recent demand for uranium, this metal was rather a drug on the market. Its extraction from ores was a necessary evil in connection with the recovery of radium or vanadium. As a result, industrial practice was by no means advanced, analytical methods were rudimentary, and rich ores only were treated.

In 1944 the decision was reached by the Manhattan District that it would be wise to consider the treatment of low-grade ores in order to develop a personnel familiar with uranium, the analysis and processing of its ores and, if possible, to devise new methods for extracting the newly precious metal. It is a pleasure to record here the important part taken by Lt. Col. John E. Vance and Maj. Phillip L. Merritt, working under the direction of Col. W. E. Kelley, in making the initial moves to get this work under way.

The so-called "low-grade ores" turned out to be fabulously rich by present standards, although they were low grade indeed by standards of the 1930's. The various ores received, all of which came from the Congo, assayed from 2 to 4 per cent \( \text{U}_3\text{O}_8 \). Since that time study has been extended: in 1946 to ores assaying from 0.1 to 0.2 per cent, in 1947 to ores assaying 0.015 to 0.03 per cent, and now to ores assaying less than 0.010 per cent.

Concomitant with the consideration of low-grade ores is the treatment of larger tonnages by simpler and cheaper processes. Otherwise, the cost of the metal will vary inversely with grade. We have found that under favorable engineering circumstances uranium can be obtained from ores assaying 0.02 per cent \( \text{U}_3\text{O}_8 \) at a cost of the same order of magnitude as that for treating ores containing 2 per cent \( \text{U}_3\text{O}_8 \).

To make progress in the treatment of increasingly poorer and poorer ores, it is obvious that the methods of analysis must be capable of giving the desired information as to material balances with substantially the same precision on successively leaner and leaner samples. Thus an error in uranium assay of 0.02 per cent is tolerable in dealing with any product made from a 2 per cent ore, very annoying in dealing with a 0.2 per cent ore, but intolerable in dealing with a 0.02 per cent ore. A major activity has therefore been the development of a succession of analytical methods to deal with the various problems presented by the succession of ores that were studied.

Because of its radioactivity uranium presents certain opportunities for analysis by nuclear methods. In addition various titrimetric, colorimetric, and fluorimetric procedures are useful. The various analytical methods used at our laboratories are presented in the second section of this paper.

A second major activity has had to do with ascertaining the mineralogical anatomy of the ores under study. Although a chemical analysis is sufficient to show the quantities of the various constituents of an ore, it fails to show in what form, what texture, and what structure these constituents occur. Identification of the minerals in an ore and determination of the

*This article is included in the Journal through the kind permission of Jesse Johnson and Evan Wilson of the Raw Materials Operations Office. The work described was done under the auspices of the Raw Materials Operations Office of the Atomic Energy Commission.
**Table 1 — Classification of Mineral-separation Processes**

<table>
<thead>
<tr>
<th>Type of separation</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without substantial change of phase</td>
<td>Hand sorting</td>
</tr>
<tr>
<td>According to appearance and heft</td>
<td>Mechanical pickers</td>
</tr>
<tr>
<td>According to nuclear properties</td>
<td>Screening, classification</td>
</tr>
<tr>
<td>According to size</td>
<td>Jigging, tabling, ransing, heavy-medium separation</td>
</tr>
<tr>
<td>According to specific gravity</td>
<td>Magnetic separation</td>
</tr>
<tr>
<td>According to magnetic susceptibility</td>
<td>Electrostatic separation</td>
</tr>
<tr>
<td>According to electrical properties</td>
<td>Flotation, agglomeration</td>
</tr>
<tr>
<td>According to surface chemistry</td>
<td></td>
</tr>
<tr>
<td>With partial change of phase</td>
<td></td>
</tr>
<tr>
<td>Processing in contact with gases only</td>
<td>Roasting</td>
</tr>
<tr>
<td>Processing in contact with liquids only</td>
<td>Leaching</td>
</tr>
<tr>
<td>With complete change of phase</td>
<td>Smelting</td>
</tr>
</tbody>
</table>

In the particular case of uranium ores, prewar practice in the Canadian and Congo deposits of pitchblende had centered on the use of gravity-concentrating processes, particularly jigging and tabling. The rich concentrate was then leached in small batches of a ton or so with hot, concentrated acid. The carnotites of the Colorado plateau were not concentrated, but the entire material was roasted and leached with strong, hot solutions.

The fourth section of this paper reviews typical applications of the various unit processes for physical separations, without substantial change of phase, to the ores that came to our attention.

The fifth section describes our work with chemical separations, with partial change of phase. This study led to the development of a leaching process using a cold, dilute, aqueous solution of sulfuric acid and ferric sulfate. At the time of writing it seems as though such a process would be suited for the extraction of uranium from any siliceous ore with uranium present as oxide, complex phosphate, silicate, or vanadate. The fifth section deals also with the application of this leaching process to what are currently describable as low-grade ores, that is, ores assaying under 0.03 per cent $UO_2$.

**ANALYTICAL METHODS FOR THE DETERMINATION OF URANIUM IN LOW-GRADE ORES AND ORE-TESTING PRODUCTS**

Radioassay Methods

Usually, when suitable precautions are taken, the natural radioactivity of uranium can be used for quantitative determination of the element in ore-testing products. Uranium analyses made by measuring radioactivities of low-grade ores usually require from 15 to 30 min. One person operating two counters can make 50 determinations per day. This rate is higher than the rate at which one mineral engineer ordinarily produces samples.

Uranium is the parent of one family of radioactive elements formed by successive disintegrations accompanied by the emission of either $\alpha$ or $\beta$ particles. Because of their range and the high efficiency with which they may be counted, $\beta$ particles were chosen for use as an index of radioactivity. Although uranium itself is not $\beta$-active, there are seven $\beta$-active nuclides among its daughter elements, four of which give radiation strong enough to be measured by the Geiger-Mueller detector tube. In order to keep the $\beta$ activity of an ore proportional to its uranium content, however, the conditions of radioactive equilibrium must be maintained and the thorium and potassium concentrations must not exceed their interference levels.

Radioassaying was begun toward the end of work on the ores containing several per cent uranium, but it did not make a significant contribution to that program. It was first used to advantage on samples from the South African Witwatersrand, containing between 0.1 and 0.3 per cent $UO_2$. The technique employed was standard at that time and consisted in placing a shallow tray of ore beneath a cylindrical Eek and Krebs Geiger detector tube, the whole unit being shielded with lead. The maximum sensitivity obtained with that system was about 4,000 counts per minute (c/min) for each per cent $UO_2$. As the background remained fairly steady at about 30 c/min, no difficulty was encountered in obtaining a probable error not exceeding 2 per cent on products assaying as low as 0.03 per cent $UO_2$. To avoid errors from segregation, however, samples were pulverized to pass 100 mesh and then thoroughly mixed.

In order to increase the capacity for analyzing ore samples, an automatic sample changer was constructed after the design of Peacock and Good. This instrument automatically recorded the time required to count a predetermined number of events from each of 24 samples. A Victoreen end-window counter tube was used, and an Eagle reset counter on the output
THE RECOVERY OF URANIUM FROM LOW-GRADE ORES

Nearly all uranium assays performed on ores and products of flotation and other physical processes were carried out by one of the above methods. A few chemical checks were obtained, especially if a disturbance of equilibrium was suspected, but accurate material balances were obtained consistently.

Some hesitation was felt in extending radioassays to leach solutions because of the extent to which chemical action might disrupt equilibrium in the uranium disintegration series. A few preliminary experiments justified a limited extension, however, because they indicated that $\text{UX}_4$ (thorium) and $\text{UX}_5$ (protactinium) followed the uranium in the sulfuric acid–ferric sulfate leaching process, while other $\beta$ emitters remained almost entirely in the residue; consequently a proportionality remained between $\beta$ activity and uranium content in the leach solution. A small amount of decay with a short half-life was found to occur, but it did not introduce any errors into the standard laboratory practice. The technique of counting solutions was, again, to surround the detector tube with a concentric container or to use a jacketed counter tube.

If, however, an acid leach solution is neutralized to pH 3.5 in order to precipitate ferric iron, the thorium and protactinium isotopes responsible for the $\beta$ activity precipitate and the proportionality does not exist, the strong uranium solution being almost devoid of activity.

The low-grade ores with which we have dealt do not lose an appreciable amount of radon in grinding, or else the amount lost by different samples is in strict proportion. However, when the ground ore is suspended in water as in the flotation process, some radium migrates from the uranium and is adsorbed on the barren material, in proportion to its surface. The barren material is subsequently found to have several per cent of the total activity which is no longer associated with uranium. Furthermore, because fine particles have high surfaces per unit weight, if the finest fraction of barren material is separated, it will be found to have most of the migrated activity and may give a counter analysis several times as high as that due to its own uranium content.

Even with this error, it will be desirable to use continuous radioassays of pulps, mill feed, and products in order to give operators an immediate indication of changes in assay. The mill counter can easily be placed in a large tank. The more rugged $\gamma$ counter is preferred for use with this large sample.

Radioassaying has its limitations. Its success in the work of this project does not mean that identical techniques could be applied to other ores and products of other processes.

Chemical Methods

The Congo ores which contained 2 to 4 per cent $\text{U}_4\text{O}_6$ represent a relatively simple analytical problem by
present standards. However, these were the first uranium-bearing ores to be encountered in the Mineral Engineering Laboratory. At first we tried some of the prewar methods described in the literature, but these methods were designed for higher grade materials, and the results were not satisfactory.

Early in 1945 methods developed by Furman and his group\textsuperscript{8} at Princeton were made available to us. Two of these methods, both volumetric, were particularly useful. In the first method, a cupferron precipitation step removed interfering elements, and the uranium was reduced in a Jones reductor, aerated, and oxidized with ceric sulfate, using o-phenanthroline-ferrous complex as an indicator. The second method removed interfering elements by utilizing the fact that uranyl nitrate in a saturated aqueous nitrate solution can be quantitatively extracted into diethyl ether. Some development work had to be done to modify the Princeton methods so that they could be applied to the M.I.T. problems, but with slight modifications they provided adequate sensitivity and precision for the analysis of Congo ores and their products.

The first of the low-grade Rand ores appeared in our chemistry laboratory in March 1946. These ores contained one-tenth (later one-hundredth) as much uranium as the lowest Congo ores. It was thought at first that by simply increasing the size of the sample the methods previously used could be applied to the new ores. However, the decrease in the uranium concentration was accompanied by a higher ratio of interfering elements (particularly iron) to uranium. The cupferron separation alone required a prohibitive consumption of cupferron on some samples. The ether extraction method could not be applied directly because the minute fraction of certain elements, particularly iron and vanadium, that accompany the uranium into the ether layer became appreciable compared to the small quantity of uranium present. A temporary answer to this problem was the use of both purification steps in sequence.

It was then found that, if most of the iron had been removed by electrolysis with a mercury cathode, the remainder of the interfering elements could be precipitated from solution by cupferron. Furthermore, a complicated procedure to ensure the removal of all organic matter was required. Even at its best the volumetric method required 3 days to produce a result.\textsuperscript{9}

The basic volumetric method required at least 3 mg of \( \text{U}_3\text{O}_8 \) to give reliable results. More than 50 g of sample was needed on leach residues analyzing 0.005 per cent \( \text{U}_3\text{O}_8 \) or less. Such large samples were difficult to handle in conventional analytical apparatus.

To meet the requirements for increased speed and sensitivity, a colorimetric method\textsuperscript{10} first developed by Rodden and his group at the National Bureau of Standards was adapted to the analysis of residues from Rand ores. Hydrogen peroxide in alkaline solution develops a bright-yellow color, the intensity of which is proportional to the concentration of uranium. This color is relatively specific, although chromium, manganese, and cerium do interfere. To ensure adequate removal of interferences, a preliminary ether extraction step was used to separate the uranium. The peroxide colorimetric method required only 0.5 mg of \( \text{U}_3\text{O}_8 \), so that 10 g of sample was adequate for residues analyzing 0.005 per cent \( \text{U}_3\text{O}_8 \). It is faster than the volumetric method because not over a day and a half was required to complete an analysis.\textsuperscript{9} Until June 1948 this method was used for the analysis of all solid samples containing less than 0.05 per cent \( \text{U}_3\text{O}_8 \).

Recent developments have changed the analytical picture for low-uranium materials. A new application of an old principle has made possible the analysis of uranium in very low concentrations without chemical separations.\textsuperscript{11} The very strong fluorescence of uranium fluoride has been the basis of several very sensitive methods for uranium analysis reported in the unclassified literature and other fluorescent methods developed under the Manhattan Project. However, these methods have had little application because the presence of small quantities of other elements markedly decreases (quenches) uranium fluorescence.

Because of the quenching phenomenon most fluorescent methods required the complete separation of uranium from other elements. However, a very high sensitivity made it possible to dilute solution samples to a point where elements other than uranium were in such low concentration that they no longer caused quenching. For analysis of solids a small sample is taken. This sample can easily be dissolved. Most of the ore products encountered so far at M.I.T. have been analyzed by the fluorimeter without chemical separation. In a few instances chemical separations are necessary, but simple procedures suffice because quantitative removal of interferences is not required.\textsuperscript{12}

Fluorescent analysis is very rapid. A result can be obtained on a solution within 15 min. By making four to six measurements per sample by the fluorimetric method, the average answer is sufficiently accurate for most purposes (2 to 7 per cent).

Another new procedure which provides high precision of analysis is the microvolumetric method. This method is not nearly so rapid as the fluorimetric but is more precise. It is used mainly to check the fluorimetric method. The chemical steps in the microvolumetric method are the same as those employed in the basic volumetric method, but all the operations are carried out on a 1/10 scale. This means that a 5-g sample can be used where previously a 50-g sample was needed. A decrease in sample size makes possible a decrease in solution volume so that evaporation is faster and reagent consumption is greatly
Mineralogical Identification Methods

The identification of the various minerals and the study of their grain size, structure, and intimacy of association are accomplished chiefly by means of the microscope, supplemented by x-ray diffraction studies and microchemical tests. The transparent minerals are identified by the petrographic microscope on the basis of their refractive indices as determined from grains mounted in liquids of known refractive index and from a study of their other optical characteristics, such as orientation, pleochroism, color, and dispersion. The opaque minerals, after mounting in plastic and polishing, are identified by the metallurgical microscope on the basis of their color, anisotropy, hardness, and reaction to various etching and staining reagents. The structure of the minerals and intimacy of association are determined from microscopic studies of thin sections and polished sections of pieces of ore and sized mineral fractions.

Besides mineral identification and structural studies, quantitative mineral studies are generally undertaken. These include determination of the abundance not only of the various minerals in the ores received and in various treatment products but also of particular types of mineral associations. The quantitative studies are based on grain counts, area and volume measurements, and analysis of specially prepared fractions produced by fractionating a quantity of material by a combination of sizing, heavy-liquid separation, and magnetic fractionation.

The fractionating procedure consists in screening or otherwise sizing the material to be studied into various size ranges. The fractions coarser than 400 mesh (37 μ) are then separated in various heavy liquids, such as methylene iodide, tetrabromomethane, or aqueous thallium formate-malonate, in a centrifuge or separatory funnel. The various specific-gravity fractions may then be further fractionated by means of a powerful electromagnet. By means of these procedures the various minerals in an ore are pigeonholed.

Results

The low-grade ores from the Belgian Congo, containing from 2 to 4 per cent U₃O₈, consist largely of various magnesium-aluminum silicates of the chlorite group and magnesium and calcium-magnesium carbonates. The uranium occurs as uraninite and in the great variety of yellow, orange, and green, simple and complex, hydrated uranium oxides, phosphates, and silicates derived from the alteration of the uraninite. The uranium minerals in Table 2 were all identified in the Congo ores. Other minerals in the ore include various cobalt and nickel sulfides and oxides, hydrated iron and manganese oxides, copper, molybdenum, and iron sulfides.
These minerals are intimately associated. Fractionation studies showed that, in general, for those ores in which uraninite accounts for the greater part of the uranium,¹³ liberation of the uraninite takes place at a relatively coarse size (65 mesh), whereas for ores in which the bulk of the uranium is present as uranophane, torbernite,¹⁶ and related minerals only uraninite, and (3) ores that showed higher acid consumptions contained increased proportions of magesite.¹⁷

The Rand ores consist of pebbles which have been cemented into a hard indurated mass, the matrix of which is composed of quartz, pyrite, sericite, pyrophyllite, chlorite, and chloritoid. In addition, small amounts of a hydrocarbon occur as thin seams and as disseminated grains throughout the softer portions of the ore. The uranium content of typical samples varies from 0.005 to about 0.20 per cent U₂O₅, although mine-run material rarely exceeds 0.020 per cent U₂O₅. Mineralogical study showed that uranium is present as uraninite, partly as grains attached to quartz, pyrite, and silicate minerals and partly completely enclosed in the hydrocarbon. The grain size of the uraninite is less than 50 μ, and many of the grains are less than 1 μ in diameter. Despite the fine size of the uraninite,

<table>
<thead>
<tr>
<th>Table 2 — Uranium and Common Gangue Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td><strong>Uraninite</strong></td>
</tr>
<tr>
<td><strong>Hydrated Oxides</strong></td>
</tr>
<tr>
<td>Gummite</td>
</tr>
<tr>
<td>Curite</td>
</tr>
<tr>
<td>Scheelite</td>
</tr>
<tr>
<td>Ianthinite</td>
</tr>
<tr>
<td>Fourmarierite</td>
</tr>
<tr>
<td>Becquerelite</td>
</tr>
<tr>
<td><strong>Phosphates</strong></td>
</tr>
<tr>
<td>Autunite</td>
</tr>
<tr>
<td>Torbernite</td>
</tr>
<tr>
<td>Metatorbernite</td>
</tr>
<tr>
<td>Parsonite</td>
</tr>
<tr>
<td>Dumontite</td>
</tr>
<tr>
<td>Dewindite</td>
</tr>
<tr>
<td><strong>Silicates</strong></td>
</tr>
<tr>
<td>Uranophane</td>
</tr>
<tr>
<td>Sklodowskite</td>
</tr>
<tr>
<td>Soddyite</td>
</tr>
<tr>
<td>Kasolite</td>
</tr>
<tr>
<td><strong>Vanadates</strong></td>
</tr>
<tr>
<td>Carnotite</td>
</tr>
<tr>
<td>Tyuyamunite</td>
</tr>
</tbody>
</table>

*Composition variable depending on age.

 partial liberation can be effected by grinding. However, these secondary uranium minerals are soft and even after gentle grinding become very fine. This suggested the use of a sizing procedure for the concentration of uranium. Mineralogical studies often give the explanation for unexpected results obtained in testing. For example, among the Congo samples (1) ores that gave poor extraction in leaching were found to contain metatorbernite,¹⁷ (2) ores that required higher ferric sulfate concentrations in the leaching liquor had the uranium present mainly as uraninite, and (3) ores that showed higher acid consumptions contained increased proportions of magesite.¹⁷
the grinding treatment normally given to the ore during the processing to recover the gold is adequate to detach almost all the uraninite and gold from the quartz, which is the major mineral present, but not from the other gangues. Various samples of these ores were fractionated in heavy liquids at specific gravities of 2.60 and 2.70. The quartz fraction (between 2.60 and 2.70) accounted for 80 to 90 per cent of the weight. Table 3 shows the assay of this quartz fraction from various samples. The assays of quartz products, separated by flotation in subsequent testing, are given for comparison.

The results of mineralogical fractionation showed that a physical separation of almost barren quartz on a feed belt. Dr. Christian LaPointe of the Canadian Department of Mines and Resources developed such a machine for uranium ores. A Geiger counter, placed over the belt, feeds pulses to a rate meter which, when the high rate indicates a rich piece, triggers a kicker which in turn, removes this piece from the belt.

Although radioactive ores are the simplest to treat by this method, the principle has been used for concentrating beryl by an induced nuclear reaction.24

Separation According to Size or Hardness

The carnotite ores of the Colorado plateau are essentially sandstones in which the uranium-bearing mineral carnotite is soft and finely disseminated. If the ore is violently agitated in air or water, the soft material, such as clay and carnotite, will be rubbed off the sand grains. The cleaned sand grains can then be settled out, and the dust or slimes recovered separately. This fine material accounts for only one-third the weight but contains about 80 per cent of the uranium.25

In early test work a sample of dump material from the Congo operations was found to respond to a similar treatment.26 This material assayed 2.7 per cent U3O8. Prolonged agitation, followed by a size separation, gave a fine product containing 75 per cent of the uranium and assaying 8.7 per cent U3O8. However, a subsequent sample of the same material did not respond well to this treatment.27 The fines assayed only 5 per cent and accounted for only one-half the uranium. When this method is applicable, it offers a relatively inexpensive way of rejecting the major part of the ore so that only a minor portion of the feed must be treated by more expensive and selective methods.

Separation According to Specific Gravity

Uranium minerals are heavy, and, when they occur as discrete grains that can be liberated from the lighter barren minerals by grinding, they can be sep-

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**Table 3 — Results from Mineralogical Fractionation vs. Results Obtained in Ore Testing**

<table>
<thead>
<tr>
<th>Ore</th>
<th>U3O8 %</th>
<th>Au, oz/ton Wt. %</th>
<th>U3O8 %</th>
<th>Au, oz/ton Wt. %</th>
<th>U3O8 %</th>
<th>Au, oz/ton Wt. %</th>
<th>Qass from flotation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>3.40</td>
<td>91</td>
<td>0.021</td>
<td>0.11</td>
<td>80</td>
<td>0.039</td>
<td>0.059</td>
</tr>
<tr>
<td>2</td>
<td>0.17</td>
<td>3.20</td>
<td>80</td>
<td>0.017</td>
<td>0.16</td>
<td>79</td>
<td>0.017</td>
<td>0.033</td>
</tr>
<tr>
<td>3</td>
<td>0.003</td>
<td>0.72</td>
<td>82</td>
<td>0.009</td>
<td>0.03</td>
<td>80</td>
<td>0.012</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>0.029</td>
<td>0.71</td>
<td>93</td>
<td>0.008</td>
<td>0.04</td>
<td>93</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>5</td>
<td>0.024</td>
<td>0.78</td>
<td>90</td>
<td>0.005</td>
<td>0.04</td>
<td>90</td>
<td>0.014</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*This product contained 0.04 per cent U3O8 and 0.16 oz of gold per ton before cleaning and 0.017 per cent U3O8 after cleaning by sink and float in the centrifuge. The sample was not assayed for gold after cleaning but was undoubtedly of lower grade.
Separation of fine mineral particles. The separation is accomplished by making the desired mineral or minerals water-repellent and by passing bubbles through a suspension of the mineral particles in water containing a froth-producing agent. The water-repellent particles adhere to the air bubbles and are lifted to the surface where they form a froth which may be skimmed off. Meanwhile the water-wetted particles remain in suspension and are carried through the machine. The air bubbles can be blown into the pulp, as in a pneumatic machine, or beaten in by an impeller in a mechanical machine.

Frequently, as with ores containing different metals, the reagents added will cause the mineral containing one metal to become water-repellent so that it can be removed by flotation, after which other reagents are added to make another mineral water-repellent. This step by step flotation of two or more different concentrates is known as selective flotation.

Some minerals such as the hydrocarbon and pyrophyllite in the Rand ores are naturally water-repellent. To float these minerals only a frother such as pine oil is required. Sulfide minerals, such as pyrite in the Rand ores, and native metals, such as gold, are easily rendered water-repellent and floatable with small additions in solution of substances such as potassium ethyl xanthate.

Uraninite and other oxide minerals may be made water-repellent by addition of oleic acid. Therefore the addition of pine oil, xanthate, and oleic acid to the Rand ores will float all the minerals but the quartz. As 80 per cent of the rock is quartz, over 88 per cent of the uranium from these ores can be recovered in a concentrate containing about 20 per cent of the total weight. Recoveries which are almost as high can be obtained at a moderate reagent cost by using smaller quantities of impure fatty acids and supplemental reagents. Under either set of conditions, between 98 and 99 per cent of the gold is floated from most of the samples tested. Typical tests with high and low reagent costs are summarized in Table 4.

Flotation of the Rand ores does not yield a final product, but it can serve as a cheap method of rejecting the bulk of the weight of the original ore as a waste product. After about 80 per cent of the original ore is discarded, the nearly fivefold-enriched concentrate can be treated by more expensive processes such as leaching. Thus, on this type of ore preconcentration by flotation becomes more and more important as the grade of ore drops. The resulting concentrate, containing 85 per cent of the uranium and over 98 per cent of the gold, can be leached and cyanided to recover these metals.

It was suggested, for the Rand mines which have existing cyanide mills, that uranium be floated from the cyanide residue so as not to interfere with the present gold metallurgy. However, lime is added in cyanidation, and the lime in the cyanided residues...
THE RECOVERY OF URANIUM FROM LOW-GRADE ORES

prevents the oleic acid from selectively filming the uranium minerals so that they will float. Lime also floculates the pulp so that fine particles of uraninite cannot be selectively filmed and floated; also it removes collector by the formation of insoluble calcium oleate. In order to obtain a substantial recovery of uranium from cyanided residues by flotation, it may be necessary to remove the lime by washing the ore with 5 lb of acid per ton. Because of these complications, it is not planned to use the flotation process on material being cyanided in existing mills. A leaching process has been developed which is economically more desirable. However, the flotation process may still be applied to ore from new mines in this district where no mill has yet been erected.

Table 4—Typical Flotation Tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Reagents of ore</th>
<th>Product</th>
<th>Wt. %</th>
<th>UO₂ %</th>
<th>Gold per ton, oz</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>5R-38</td>
<td>Oleic acid 4.5</td>
<td>Concentrate</td>
<td>19.5</td>
<td>0.118</td>
<td>4.45</td>
<td>88.8</td>
</tr>
<tr>
<td>Xanthate</td>
<td>0.075</td>
<td>Tailing</td>
<td>80.5</td>
<td>0.0026</td>
<td>0.013</td>
<td>11.2</td>
</tr>
<tr>
<td>Pine oil</td>
<td>0.03</td>
<td>Total</td>
<td>100.0</td>
<td>0.0259</td>
<td>0.078</td>
<td>100.0</td>
</tr>
<tr>
<td>5D-19</td>
<td>Indusol 1.4</td>
<td>Concentrate</td>
<td>23.4</td>
<td>0.052</td>
<td>3.59</td>
<td>82.4</td>
</tr>
<tr>
<td>No. 637</td>
<td>No. 242 0.5</td>
<td>Tailing</td>
<td>76.6</td>
<td>0.0060</td>
<td>0.012</td>
<td>17.4</td>
</tr>
<tr>
<td>No. 242</td>
<td>0.15</td>
<td>Total</td>
<td>100.0</td>
<td>0.0261</td>
<td>0.049</td>
<td>100.0</td>
</tr>
</tbody>
</table>

*American Cyanamid reagents: No. 637 is an organic dispersant and No. 242 is a sulfide collector.

As predicted by the mineralogical study of the Congo ores, flotation of these materials did not concentrate the uranium satisfactorily. However, another use for flotation was found on these ores. The current material, as compared with the material mined earlier, contains an increased proportion of magnesite. The presence of magnesite increases the acid required in leaching, and the leach solution requires magnesia for precipitation. It was shown that magnesite could be floated from these ores with oleic acid and sodium silicate at pH 10. The magnesite concentrate contained some of the uranium, and it could be calcined, ground, and used for precipitation of the solution obtained by leaching the rest of the ore.

The Randores contain pyrite. After leaching the ore or concentrate with sulfuric acid, the pyrite can be floated from the residue and roasted to convert its sulfur into enough sulfuric acid for the leaching.

In the treatment of other ores it may also be found desirable to use flotation (or other physical separation methods) to remove minerals which would interfere with the subsequent recovery of uranium by leaching, or minerals which can be used to produce the leaching reagents.

The various flotation separations which have been made on uranium ores have represented, for the most part, the application of well-established reagent combinations and techniques which are not specific to uranium. The potential uses of flotation for low-grade ores clearly justify a broader and more fundamental attack on the surface chemistry of uranium minerals and the flotation of uranium ores.

LEACHING

Acid leaching has been an important step in uranium extraction for decades, but the leaching is carried out on batches of ore, using hot, strong solutions of nitric, sulfuric, or hydrochloric acids. Such a procedure is far too expensive to be considered for low-grade ores; even for ores containing as much as 1 per cent UO₂, it is not as attractive as might be wished. Accordingly, the leaching studies to be described have been directed toward development of leaching processes which can be carried out on a scale of thousands of tons of low-grade ore per day, in continuous rather than batch equipment, in the cold, and with small consumption of acids, generally well under 100 lb per ton of ore, and low concentrations of cheap reagents. These requirements must be met if leaching is to prove economically attractive in processing ores in the range of 1.0 to 0.01 per cent UO₂.

The mechanical techniques, equipment, and even flow sheets for large-scale low-cost leaching of ores fortunately have been developed to a high degree in the treatment of ores of other metals, particularly gold ores. Figures 2a and 2b are flow sheets which show the main steps of typical large-scale leaching plants. In both, the essential features are a crusher and a mill to crush the ore, usually to particles less than 0.1 or 0.2 mm in size, a series of leaching agitators, and a liquor-ore separation system. In the countercurrent decantation system (CCD) shown in Fig. 2a, the separation of liquid from solids is accomplished in thickeners which are tanks where the solids can settle and be raked to the center and pumped out.
while the clear solution overflows around the top rim. The overflow solution is treated to precipitate the valuable metal, and the barren solution plus water is mixed with the thickened solids from the first thickener and resettled in another thickener. The wash liquor which overflows from this thickener is returned to the leaching step.

In the filtration system (Fig. 2b) the ore is crushed and leached in Pachuca agitators. The liquor is continuously separated from the ore by a rotary filter. Wash water is applied to the filter cake at the top of the drum. The filtrate is precipitated, and the barren solution may be reused.

Extra steps of filtration or thickening are often justified to improve washing and to reduce losses. The equipment for these flow sheets is standard all over the world, and generally requires only acid-proofing to adapt it for uranium leaching. As will be seen later, the flow sheets are subject to various modifications to meet the specific requirements of a given ore.

Figure 3 is a photograph of thickeners and agitators used for gold extraction from Rand ores.

Dissolution of Uranium

A wide variety of leaching agents has been tested in the laboratory, including acids, alkali carbonates, oxidizing agents, complexing agents, and organic solutions. For the ores tested in this laboratory a di-
THE RECOVERY OF URANIUM FROM LOW-GRADE ORES

A sulphuric acid and ferric sulphate solution containing sulfuric acid and ferric sulphate has clearly emerged as the cheapest and also the most effective lixiviant (see references 34 and 36 to 41). The chief limitation of this combination is that the ore should not contain large proportions of barren reagent-consuming materials, such as limestone, dolomite, or metallic iron (from iron grinding equipment). Where such materials are present in the ore, their removal, before leaching, by a physical separation process or other means is sometimes feasible.

Metatorbernite requires strong leaching solutions and elevated leaching temperatures, but, if heated to about 250°C to obtain partial dehydration, the resulting copper uranyl phosphates are leachable with cold, dilute sulfuric acid-ferric sulfate solutions. Dissolution data show that the ferric iron is essential, not as an oxidizing agent for this mineral but as a phosphate-complexing agent. \(^{47,48}\)

The chemical requirements for effective leaching on the Congo ores (calcined if torbernite is present) and

---

**Fig. 3 — Thickeners and Pachuca agitators as used at Rand cyanide plant.**

The leaching behavior of the uranium minerals listed in Table 2 has been studied both by small-scale leaching tests on separated portions of the pure minerals and by larger scale ore-leaching tests. All the uranium minerals listed can be made to dissolve in cold, dilute sulfuric acid and ferric sulfate. The yellow and orange hydrated minerals (all but uraninite and the torbermites) dissolve readily in cold dilute acid alone at pH 3.0 or less. Uraninite, which at present is the uranium mineral of greatest economic importance, has an appreciable part of the uranium in uranous form and does not dissolve in dilute acid alone. However, uraninite is leached by dilute ferric sulfate solutions at pH 2.0 or less, ferric iron serving as an oxidizing agent. Other oxidizing agents may be used, but stronger agents like nitric acid attack pyrite and are consumed. Manganese dioxide can be used to oxidize ferrous iron to ferric. \(^{45,46}\)

for the Rand ores or cyanide residues are that sufficient acid and oxidizing agent be added to give a pH of 2.0 or less and excess ferric iron of at least 0.3 g per liter at the end of the leaching period. Since these figures represent dilute solutions, it is apparent that the consumptions of acid and oxidizing agent may be little more than stoichiometrically equivalent to the quantities of acid-consuming constituents and of reducing constituents of the ore, respectively. High percentages of the uranium have been extracted from some of the clean siliceous ores with the use of as little as 20 lb of sulfuric acid and 10 lb of ferric sulfate per ton of ore. The Congo ores require more reagents because of the higher percentage of uranium minerals and also because of their content of acid-soluble carbonates. Some Congo samples contain so much carbonate that direct leaching is unattractive; for these materials it was found that the carbonates
could be effectively removed by flotation leaving a product leachable with moderate reagent quantities. Another reagent-consuming substance, which caused much trouble before it was discovered, is metallic iron which entered some ore samples tested through abrasion of the crushing and grinding equipment. A simple stoichiometric calculation shows that 1 lb of metallic iron per ton of ore (0.05 per cent of the weight of the ore) will reduce 7 lb of ferric sulfate per ton of ore.

The pregnant leach liquor from leaching with acid ferric sulfate is still an impure and relatively low-grade product. It contains ferric and ferrous iron, aluminum, calcium, and silica in concentrations comparable to or greater than the uranium concentration. Cobalt, nickel, and manganese are additional major constituents of leach liquors from the Congo ores. In the solutions obtained from Canadian ores, arsenic, cobalt, and copper are found. Analytical data for a typical leach liquor obtained from a Rand gold ore assaying 0.02 per cent UO₂ are given in Table 5.

### Table 5—Typical Leach Liquor Analyses

<table>
<thead>
<tr>
<th>Component</th>
<th>Assay, g/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe⁺⁺⁺⁺</td>
<td>2.20</td>
</tr>
<tr>
<td>Fe⁺⁺⁺</td>
<td>1.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.50</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Precipitation of Uranium from Leach Liquor by Simple Neutralization

One method of treating the leach liquor has been to neutralize it with alkali to obtain a crude precipitate, carrying the bulk of the solution impurities along with the uranium. To obtain reasonably complete precipitation of uranium, the solution must be neutralized to approximately pH 8.0.

The low uranium concentration in the leach liquor and the colloidal properties of the precipitates obtained with alkalis have made necessary extensive testing of the precipitation step. These studies have consisted of both batch and continuous precipitation, followed by settling tests to determine settling velocity and ultimate solids content of the sediment, filtration-rate tests, and, of course, chemical analyses of precipitate and decanted solution. An indication of some of the technical and analytical difficulties is given by the realization that a barren solution containing only 1 ppm of UO₂ represents a loss of 2 per cent of the uranium from a pregnant solution which assays 50 ppm before precipitation. Important variables affecting the properties of the precipitate include pH, choice of alkali, time of treatment, form and procedure of adding alkali, temperature, agita-
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tion, and some variables not yet recognized or understood. Although a practical procedure has been developed, the work has clearly demonstrated the need for fundamental work on hydroxide precipitation of uranium and the associated metals to elucidate the complex chemical and surface-chemical phenomena involved.

Different alkalis produce precipitates having different properties. Sodium hydroxide and ammonium hydroxide give voluminous precipitate which, after thorough settling and decantation of barren solution, contain only 1 per cent solids. Lime and magnesia precipitates on the other hand are reasonably compact, settling to 10 per cent or more solids without difficulty. Lime neutralization of sulfate solutions dilutes the product with much calcium sulfate, a troublesome substance in the further treatment of the precipitate. Thus caustic-calcined magnesia has been found the most satisfactory of the cheap alkalis for the Congo leach solutions. For most efficient utilization and minimum dilution of the product, a highly reactive magnesia should be chosen, ground finely, and added as a slurry. Calcined dolomite is only half as objectionable as lime. Dolomite overlies the Rand ores and outcrops nearby. Calcined dolomite slakes to a reactive slurry and does not need to be ground. For the Rand solutions, calcined dolomite appears peculiarly useful.

The precipitate obtained as a product from leaching the Congo ores of 2 to 3 per cent U₂O₉ assays in the range 30 to 40 per cent U₂O₉ (dry basis). This product is of shipping grade and is satisfactory input material for the refinery making pure oxide by other extraction and other steps.

On the other hand, the precipitate obtained in treating Rand ores contains only 2 to 4 per cent U₂O₉ (dry basis). Although this represents a concentration ratio of better than 100/1, or less than 20 lb of precipitate per ton of ore, the grade is too low to be satisfactory for shipping, and no refining plant is operating at

Present on such intake material. Accordingly, a further step of precipitate retreatment at the site of the ore-leaching plant is desirable. The precipitate retreatment can be relatively extensive and can utilize more expensive reagents or higher reagent concentrations than the primary leaching and precipitation steps without seriously adding to over-all costs since the feed to the retreatment section will amount to only 8 to 16 lb of solids per ton of original ore.66

Precipitate Retreatment, Selective Precipitation

Intensive research has been carried out on the problem of producing high-grade uranium products suitable for refinery feed by retreatment of the low-grade precipitate or by selective removal of uranium from leach liquors. The development of these processes will be described in a future article, but three methods of precipitate retreatment and two methods of selective recovery of uranium from the leach solution are outlined briefly below:

![Flow sheets for simple and countercurrent leaching.](image-url)
Acid digestion—peroxide retreatment process. Leaching of the low-grade precipitate with acid will dissolve the uranium at pH 3.0 to 3.5, but it also produces a gel from the silica in the precipitate. This makes the resulting slurry unfilterable. Heating the slurry near boiling for several hours results in the formation of a more granular solid which can be filtered easily to give a relatively concentrated uranium solution in which the amounts of other impurities are less than the amount of uranium present. It is best to precipitate uranium from this solution as peroxide, although other reagents may be used.

Carbonate leaching of precipitates. The specific reaction of uranyl with carbonate to form the soluble uranyl-tricarbonate complex has been the basis of well-established procedures of purifying uranium solutions. Precipitates made by adding alkalis to crude uranium solutions are treated with soda ash to dissolve the uranium, leaving the bulk of the impurities behind in the hydroxide precipitate. Although the extraction in a single carbonate leach is inadequate and somewhat erratic, use of a second and third carbonate leach results in a high uranium extraction. The uranium can be precipitated from the carbonate solution by standard methods, such as acidification and neutralization, or by sodium hydroxide. Another method which promises reuse of the carbonate solution involves precipitation of the uranium with lime.

Ether leaching of precipitates. Attempts to dissolve the precipitate in nitric acid and to extract uranium from the resulting aqueous solution with ether fail owing to emulsions produced by the silica and to interference from sulfate. It was found, however, that the uranium could be dissolved by leaching the dry precipitate with ether containing nitric acid. Uranium is then precipitated from the ether solution with ammonia or lime.

Selective precipitation with pyrophosphate. Reduction of the leach solution with metallic iron converts the uranium to the uranous ion which can be precipitated more selectively than the uranyl ion. This procedure by-passes the production of a low-grade precipitate. Although encouraging results were obtained by precipitation of uranium from reduced solutions with hydroxide, fluoride, or phosphate, the most satisfactory results were obtained with pyrophosphate. The green pyrophosphate precipitate is hydrous and flocculated. After it is recovered by thickening, the slurry is centrifuged, treated with sodium hydroxide to remove phosphate, washed, and roasted to give a high-grade oxide product.

Recovery with anion-exchange resins. Though uranyl is normally considered a cation, it does form anionic complexes to some extent in almost all acids. It has been found that uranium can be removed with strong-base anion-exchange resins such as Amberlite IRA-400 from the dilute sulfate leach solutions. This removal is selective so that when the column is eluted with acidified brine or a stronger sulfate solution and neutralized to precipitate uranium the product obtained is high-grade.

Manufacture of Leaching Reagents

As the grade of ore tested has decreased, the consumption of reagents has decreased also, but not in proportion. Accordingly, the cost for leaching reagents per pound of uranium extracted, while relatively trifling for the 1 to 3 per cent Congo ores, has become a substantial item for the 0.02 per cent Rand ores. Therefore, for these ores it has been necessary to investigate means of reducing reagent costs below purchase and delivery costs for commercial sulfuric acid and ferric sulfate at the plant site. Dilute sulfuric acid containing ferric sulfate can be manufactured by passing sulfur dioxide and air through solutions containing a few grams of iron per liter. This so-called "auto-oxidation" process has been known for many years but has not received widespread attention because it yields only a dilute acid, relatively high in iron. Also, the engineering problems in obtaining sufficiently intimate gas-solution contact have not previously been solved to the satisfaction of everyone. The process may be regarded as two simultaneous reactions (1) and (2) proceeding at the same rate:

\[
2\text{H}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \quad (1)
\]

\[
2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \quad (2)
\]

The sum of the two reactions, or the net result, is the production of acid

\[
2\text{H}_2\text{O} + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{SO}_4 \quad (3)
\]

The \( \text{SO}_2 \)-air process outlined above is attractive for manufacture of leaching agents for the 0.02 per cent Rand ores because they contain both pyrite (FeS\(_2\)) as a source of sulfur dioxide and some acid-soluble iron minerals as a source of iron. A pyrite concentrate can be separated cheaply by flotation and then roasted by conventional methods to furnish sulfur dioxide.

Various techniques of carrying out the gas-solution reactions were tested to avoid having to compress dust-laden hot roaster gases before introduction into the leach solution. It was found that \( \text{SO}_2 \) could be absorbed from roaster gases by leach solutions in a packed tower. Passing fine air bubbles through the tower effluent in a separate tank completes the reaction.\(^{48}\) Optimum results are obtained if the retention time for the air-oxidation step is enough so that solution returning to the packed tower is free of sulfate. The ferrous iron dissolved from the ore and left
THE RECOVERY OF URANIUM FROM LOW-GRADE ORES

unprecipitated in the barren solution not only provides the iron needed for the acid-making reaction, but also is oxidized in the process to obtain the ferric iron needed for leaching the ore.

Manganese is even more effective than iron in promoting the acid-making reaction, and if the amount of iron present in the barren solution is inadequate, small amounts of manganese dioxide can be added. If the amount of acid needed to leach the ore is less than 10 g per liter the oxidation tank can be omitted and the barren solution containing dissolved SO₂ can be fed directly to a Pachuca agitator where the air used to suspend the pulp will accomplish the oxidation of the sulfite and the ferrous iron. Where this procedure can be used, the cost of obtaining leaching reagents is very small. Even on ores requiring stronger solutions, where a separate oxidation tank is needed, the cost of producing sulfuric acid will probably be less than the cost of conventional contact or chamber methods. Another advantage is that this process also produces the oxidant needed for leaching at no additional cost.

If the SO₂-air process is not used, pyrolusite ore may be added in lieu of ferric sulfate. Pyrolusite oxidizes the ferrous iron dissolved from the ore or from the metallic iron abraded from the grinding equipment to provide the ferric iron needed for leaching. Except for oxygen as provided by air, manganese dioxide usually is about as cheap a source of oxidizing power as may be found.

Table 6—Leaching Results

<table>
<thead>
<tr>
<th>Ore</th>
<th>Type of Leach</th>
<th>Ferric Sulfate</th>
<th>MgO</th>
<th>Precipitate Recovery, %</th>
<th>Uranium Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congo ores</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dump</td>
<td>Simple</td>
<td>80</td>
<td>35</td>
<td>42</td>
<td>0.07</td>
</tr>
<tr>
<td>Fresh</td>
<td>Simple</td>
<td>150</td>
<td>40</td>
<td>42.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Nonfloat</td>
<td>Simple</td>
<td>80</td>
<td>0</td>
<td>27.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Rand mill feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whole ore</td>
<td>Simple</td>
<td>20</td>
<td>10</td>
<td>7.2</td>
<td>0.0043</td>
</tr>
<tr>
<td>Flotation concentrate</td>
<td>Simple</td>
<td>30</td>
<td>15</td>
<td>4.5</td>
<td>0.0033</td>
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<tr>
<td>Whole ore</td>
<td>Cyclic CC</td>
<td>10</td>
<td>5</td>
<td>4.0</td>
<td>0.0041</td>
</tr>
<tr>
<td>Whole ore</td>
<td>Cyclic CC</td>
<td>20</td>
<td>10</td>
<td>6.0</td>
<td>0.0057</td>
</tr>
<tr>
<td>Cyanide residue</td>
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<tr>
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<td>Simple</td>
<td>80</td>
<td>50</td>
<td>8.0</td>
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<tr>
<td>Nonmagnetic</td>
<td>Simple</td>
<td>30</td>
<td>15</td>
<td>3.5</td>
<td>0.0056</td>
</tr>
<tr>
<td>Whole residue</td>
<td>Cyclic CC</td>
<td>30</td>
<td>5</td>
<td>3.5</td>
<td>0.0056</td>
</tr>
<tr>
<td>Carnotite, Colorado</td>
<td>Simple</td>
<td>125</td>
<td>0</td>
<td>3.0</td>
<td>0.014</td>
</tr>
<tr>
<td>Roscoelite, Colorado</td>
<td>Simple</td>
<td>80</td>
<td>40</td>
<td>4.0</td>
<td>0.0060</td>
</tr>
<tr>
<td>Marysvale aurinite</td>
<td>Simple</td>
<td>60</td>
<td>0</td>
<td>6.0</td>
<td>0.017</td>
</tr>
<tr>
<td>Sunshine uraninite</td>
<td>Simple</td>
<td>500</td>
<td>100</td>
<td>96.0</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Note: All tests at room temperature for 24 hours. The simple leach tests use the flow sheet of Figure 4a and the cyclic countercurrent tests use the flow sheet of Figure 4c.

Manganese floated to reduce acid required.
Precipitated with calcined magnesite floated from ore, 100 lb/ton.
This concentrate 13.3% MnO₂ and contained about 95% of the uranium in the flotation feed, so the over-all uranium recovery was 56.0% per cent. Only 4 lb of H₂SO₄ and 2 lb of Fe₂(SO₄)₃ per ton of ore used.
10 lb of SO₂ per ton.
Ore cyanided in laboratory for gold extraction before leaching.
Abraded iron removed with alnico magnet before leaching.
Pounds of MgO per ton added as oxidizing agent, equivalent to 4.6 times as much Fe₂(SO₄)₃.
Ore cyanided for partial neutralization to precipitate ferric iron. Only 12 lb of MgO per ton, additional, needed to precipitate uranium. The high-grade precipitate is the result of removing a large ferric iron precipitate after partial neutralization.

Reagent Requirements and Metallurgical Results

Table 6 gives condensed data for a number of typical laboratory leaching tests on the various types of ores. The tests on the Congo ores show that the fresh ore requires more acid than the dump ore because of the increased proportion of magnesite and more oxidant because the uraninite has not been weathered, and that flotation of magnesite from fresh ore results in a saving of both acid and alkali. The tests on the Rand mill-feed sample show that little more reagents are needed to leach the flotation.
concentrate than to leach an equal weight of whole ore, although the concentrate is six times richer in uranium, and that the flotation concentrate uses only one-fifth the quantity of leaching reagents per pound of uranium; however because not all the uranium mineral floats, the over-all recovery is less. The tests show that countercurrent leaching halves the reagents required for simple leaching and results in an improved grade of precipitate, that the reagents can be made from the ore by the SO₂-air process, and that cyanidation before acid-leaching does not greatly affect the quantities of reagents required to get good uranium extraction.

The tests run on the Rand cyanide plant residue show that the quantities of reagents required for leaching are much higher than those for the mill-feed sample, owing, largely, to the presence of iron abraded in grinding, that manganese dioxide can be used in place of ferric sulfate, and that, as with the Rand mill-feed sample, countercurrent leaching halves the reagents required.

The carnotite ore needs no oxidizing agent, although oxidant was helpful for the roscoelite ore. A similar difference is shown for the Marysvale, Utah, autunite, and the Sunshine, Idaho, uraninite ore.

Summary

Uranium minerals can be dissolved from low-grade ores or concentrates by dilute, unheated solutions of sulfuric acid and ferric sulfate. The dissolved uranium may then be recovered by neutralization of the leach solution with lime, magnesia, or mixtures of them. The major impurities in the precipitate are iron oxides, alumina, and silica. The proportion of these impurities can be decreased by partial neutralization of the pregnant solution before precipitation of the uranium. If the precipitate is still low-grade, it can be purified by one of several methods alternatively. A selective method of recovering uranium from the leach solution can be used instead of neutralization. Manganese dioxide or air plus sulfur dioxide (from the pyrite in the ore) can be used for economical production of leaching reagents.

ECONOMICS

Uranium can be extracted from ores by a leaching process, or the uranium can first be physically concentrated and then leached from the concentrate. In order for a physical separation to be justified, it must be able to reject a major part of the ore at a low cost without the loss of any substantial proportion of the uranium.

Generally speaking, physical methods are less expensive than leaching, but the over-all recovery is usually less. The choice of method depends on an economic balance in which a higher value for uranium would favor leaching and a lower grade of ore would favor physical separation.

A more accurate evaluation of test work could be made if uranium had a market price like other metals and if schedules of payments for concentrates could be obtained.

Fig. 5—Relative cost vs. grade of ore.

Economic treatment of low-grade ores can be accomplished only by using simple processes on a large scale. As already shown, much of our effort has been concerned with applying leaching, normally a relatively expensive process, to low-grade ores at an economical cost.

Too many uncertainties in the local situation at the mine site have prevented reliable cost forecasts. Nevertheless, tentative, and sometimes very rough, cost estimates have been made from time to time. The results of one such cost forecast for leaching the Rand ores are summarized in Fig. 5. This is a graph of relative leaching and precipitation costs per pound of uranium extracted vs. grade of ore.

CONCLUSION

The subject presented in this paper is now in an era of rapid growth. Future requirements point to the necessity of devising modifications of the sulfuric acid–ferric sulfate process to adapt it to more complex ores of a grade possibly lower still than ores tested to date. The necessity exists for expanding work on certain phases of the process, notably in connection with the recovery of uranium from leach solutions. Much of the fundamental inorganic chemistry is yet to be worked out, especially for dilute aqueous solutions in which uranium occurs with other metals. Still another line of study requiring development is the devising of automatic analyzing and controlling equipment to make the operation of large plants foolproof and simple.
In spite of these needs for further developments, it is clear that uranium-bearing materials which four years ago could not have been considered seriously as ores may now be counted on to provide a major source of uranium in the near future.

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April 1950
Feasibility of Plutonium Breeding*

By H. Brooks
Knolls Atomic Power Laboratory, General Electric Company,
Schenectady, New York

Report Memo HB-32

THE NEED FOR BREEDING

The achievement of all but the most restricted uses of nuclear energy appears to hinge on the development of nuclear reactors which simultaneously generate heat at a thermodynamically efficient temperature and produce nuclear fuel more rapidly than they consume it. Such reactors are called “power converters” or “breeders.” A converter is a reactor which consumes one type of fuel and produces another, for example, consumes U\textsuperscript{235} to produce Pu\textsuperscript{239}. It is called a breeder if it produces the same type of fuel that it consumes and if its net production exceeds its net consumption. The importance of breeders arises from the fact that only 0.7 percent of normal uranium is the fissionable isotope U\textsuperscript{235}, while the more abundant element thorium is not fissionable. Both the abundant isotope of uranium, U\textsuperscript{238}, and the isotope Th\textsuperscript{232} can be transformed, by a (n,\gamma) reaction followed by two successive spontaneous beta disintegrations, into the fissionable isotopes Pu\textsuperscript{239} and U\textsuperscript{233}, respectively, neither of which occurs naturally in measurable quantities. Breeders containing Pu\textsuperscript{239} as fuel in combination with U\textsuperscript{233} as fertile material can be used to convert all the U\textsuperscript{238} to Pu\textsuperscript{239} and hence ultimately to useful energy. Similarly, breeders employing U\textsuperscript{233} as fuel in combination with thorium can be used to convert the entire supply of thorium into a source of energy. This is only possible if the reactors are true breeders, i.e., produce more than they consume, otherwise the supply of fuel will run out long before all the inert isotope has been converted to active material. A converter, even when it produces more of the new fuel than it consumes of the old, still can be used to convert only a small fraction of the inert isotope to a useful source of energy.

Although the total abundance of uranium in the earth's crust is fairly large, it occurs for the most part in concentrations of less than 100 ppm. The cost of concentrating such dilute ores is, at present, probably prohibitive in relation to the energy content of the contained nuclear fuel. The total U\textsuperscript{238} content of the few rich deposits now known is of minor significance in relation to the total energy requirements of the world. This supply might be increased by a factor between 2 and 3 by the use of converters. On the other hand, by means of breeding with Pu\textsuperscript{239} and U\textsuperscript{233} the total fuel may be increased by a factor of 140, and, if breeding with U\textsuperscript{233} and thorium is also feasible, the original U\textsuperscript{233} content of the rich ores might be multiplied by a factor as large as 500, in terms of the energy content of the fuel produced. Furthermore, the possibility of breeding increases the ultimate energy potential of the more dilute ores and thus makes recovery of uranium from them more profitable.

As can be seen from the above discussion, most reactors will have to be breeders, supplying enough fuel to keep themselves going, with enough left over to start new breeders and to supply reactors for special applications which, of necessity, are not breeders. Conversely, most breeders will have to be power generators. Otherwise, a substantial fraction of the total energy potential of the thorium and U\textsuperscript{233} will be wasted in the breeding process itself. This becomes less significant as the breeding gain increases.

DEFINITIONS

In order to avoid confusion in the discussion it is desirable to fix a few definitions of terms. The follow-

*This article is concerned mostly with factors affecting neutron economy and is based on Chap. 3 of the Feasibility Report (KAPL-238, pp. 45 to 72) submitted in connection with the proposed WMA reactor developed by the Knolls Atomic Power Laboratory.
ing definitions are not universally accepted but are convenient, and the terms will be used throughout this article in the sense given here.

For a converter, the number of atoms of the new type of fuel produced per atom of the old type of fuel destroyed is known as the "conversion ratio." For breeders, the number of atoms of new fuel produced per atom of fuel destroyed is known as the "breeding ratio." The breeding ratio minus one is called the "breeding gain" and represents, essentially, the interest rate on the turnover of fuel in the breeder, that is to say, it is the amount of new fuel produced over and above that required to replace the fuel which was destroyed in the breeding process.

There are a number of ambiguities in these definitions as they stand. In the first place, the breeding or conversion ratio of an actual reactor can be spoken of when only the nuclear parts of the problem are being considered. It is then the number of neutrons captured in fertile material divided by the total number of neutrons absorbed by the fissionable material. For many practical purposes, however, it is more legitimate to speak of an "effective" breeding or conversion ratio, which takes into account chemical and metallurgical losses in the complete cycle, carrying both the bred and depleted fuel back to a condition in which they may be loaded into a reactor.

In the second place, fuel which is initially pure isotopically will, after a number of cycles of the breeding process, contain a great many isotopes which are not necessarily fissionable but cannot be separated from the fuel by any chemical means. Under these circumstances no simple definition of breeding gain is possible. Nevertheless, it is possible to set up a system of simultaneous differential equations for the growth and decay of each isotope in the over-all fuel supply. It is easily shown that, as new fuel and isotopes are produced and fed back into the system, the isotopic constitution of the fuel inventory becomes constant, and thereafter the inventory builds up exponentially with a simple period in terms of which an effective breeding gain can be defined.

GENERAL ATTRIBUTES OF A POWER-BREEDER SYSTEM

The complete breeder system involves not only the reactor itself but also the associated heat-transfer systems and chemical and metallurgical reprocessing facilities. All these must be integrated into a single system, the over-all performance of which defines the actual merit of the system.

The essential attributes of a power-breeder system may be summarized generally as follows:

1. Favorable neutron economy
2. High specific power
3. High temperature for efficient power utilization
4. Favorable reprocessing economy
   a. Low over-all loss per cycle
   b. High burn-up
   c. Low hold-up in inventory

Most of the items in this list are self-evident. It is worthwhile, however, to point out how the items under "4" tie in with the items more specifically related to neutron economy. In this connection the following elementary formula is of some value. This formula (given in this form originally by T. M. Snyder) defines a quantity known as the effective doubling time of a reactor and is given by

\[
\text{Effective doubling time} = \frac{(10^9 \times \frac{M}{P}) \times T}{b - \beta} \tag{1}
\]

where \( T \) = the time required for complete reprocessing of the fuel
\( f \) = the fractional burn-up of fuel allowed before it is removed from the reactor
\( b \) = the breeding gain computed on the basis of neutron economy alone
\( M \) = the total mass of fissionable material invested in the reactor in kilograms
\( P \) = the total power of the reactor measured in kilowatts
\( \beta \) = the fractional reprocessing loss per cycle

The effective doubling time is the time required for the power-breeder system, operating under steady-state conditions of operating inventory and reprocessing, to double the total inventory of fuel by breeding. The effect of inventory and reprocessing losses in the blanket is much less important than in the case of the core, for, so far as the valuable fuel isotopes are concerned, the losses are nonrepetitive. Equation 1 shows clearly the importance of a large \( f \) in maximizing the effective breeding rate. Equation 1 neglects the influence of fission-product poisoning, which also depends upon burn-up but is in general not important unless \( f \) becomes much larger than is now considered attainable for other reasons.

FACTORS IN NEUTRON ECONOMY

The neutron economy of a breeder or converter depends upon a number of factors in the design and composition of the reactor. For an intermediate or fast reactor, such as is discussed in this article, the most important factors are

1. The value of the capture-to-fission ratio (alpha) of the fuel as used in the particular neutron spectrum and fuel geometry of the reactor.
2. Absorption by structural materials and coolant used in the reactor not only in the core but also in the reflector and breeding regions.
3. The poisoning effect of fission products under the average conditions of fuel burn-up present in the reactor.

4. The poisoning effect of heavy isotopes of the fuel under the conditions of isotopic-fuel composition resulting from multiple recycling of the fuel through the reactor.

5. The poisoning effect of the \((n,\alpha)\) reaction and the multiplication effect of the \((n,2n)\) reaction in beryllium when it is used as a moderator and reflector.

6. The enhanced neutron production arising from fast fissions produced in the natural uranium of the breeder region.

In this article the six effects listed above will be discussed in detail not only as applied to the present reactor as designed but also as they bear on the design of a future power breeder employing plutonium as the fuel. It must be borne in mind that one of the prime objectives of the reactor is to investigate the factors listed, both in greater detail and with substantially better precision than is possible with present available facilities, and to evaluate the breeding capabilities of future reactors following the same general principles of design. Consequently, the picture developed at this stage is necessarily tentative.

**CAPTURE-TO-FISSION RATIO**

A true breeder must employ plutonium or \(^{233}\text{U}\) as fuel. Thus for the choice of spectrum which is optimum for breeding, it is the value of the capture-to-fission ratio (alpha) for plutonium rather than for \(^{233}\text{U}\) which must be considered in the design. Even now, some five years after the operation of the first nuclear reactor at high power, knowledge of the nuclear constants of plutonium is rather sketchy. The main effort at KAPL on this problem has followed two different lines.

The first effort has been to measure the average value of the capture-to-fission ratio in a number of intermediate-energy-neutron spectra. Milligram samples of plutonium especially prepared to have low \(^{239}\text{Pu}\) content have been exposed in a Hanford reactor in special shields designed to produce epithermal-neutron spectra. After exposure, foils are prepared from the samples, and the change in \(^{239}\text{Pu}\) content is determined by measuring the change in spontaneous-fission rate resulting from the exposure. At the same time the number of fissions occurring during exposure is determined by fission-product analysis, and the mean value of alpha for the given shield follows directly from the ratio of \(^{239}\text{Pu}\) production to fissions. The techniques and theory have been described in detail by Kanne et al.

The combination of a neutron-absorbing shield (resonance absorbers and boron) with the neutron spectrum of the Hanford reactors leads to a fission distribution in the sample as a function of neutron energy, which has a broad maximum at a certain energy depending on the amount of boron used in the shield. An experiment is designated by its median energy such that in the given shield 50 per cent of the fissions are above and 50 per cent below this energy. So far experiments have been completed for three spectra: (1) thermal neutrons, (2) median energy, 30 ev, and (3) median energy, 100 ev. In cases 1 and 3 resonance absorbers were used to suppress to less than 1 per cent the contribution of fissions below 5 ev, therefore the strongly capturing 0.3-ev resonance in plutonium did not influence the measurements.

The results for the three energies are summarized in Table 1.

Best values of alpha and estimated probable error are shown in Table 1. The values are slightly smaller than those reported in KAPL-64, KAPL-116, and KAPL-136. The change arises entirely from better determinations of the number of fissions in the samples during exposure. This determination has now been made by the so-called "K-factor technique" in which the chemical and counting procedures are calibrated directly against a fission counter in a thermal column. The fission-product determination was performed at KAPL by R. P. Schumann and checked independently at Los Alamos by R. D. Spence, and the values of alpha resulting from both determinations are shown in Table 1. The discrepancy between the KAPL and Los Alamos determinations is rather large and has not been fully explained.

The value of alpha is surprisingly large and is higher with increasing average energy, contrary to early speculations regarding the probable behavior which indicated that the capture probability would become negligibly small above 1 ev. In the highest energy shield only 75 per cent of the fissions are due to neutrons below 1000 ev in energy. Thus, if alpha becomes small above 1000 ev, its average value in the low energy region must be nearly 1. Experiments are in progress with shields having roughly 1200 and over 5000 volts median energy. Results of these experiments will be available late in 1950.

In the second type of experiment the value of alpha is deduced from reactivity changes accompanying the

<table>
<thead>
<tr>
<th>Median fission</th>
<th>At 0.025 ev</th>
<th>At 30 ev</th>
<th>At 100 ev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plutonium alpha (KAPL chemistry)</td>
<td>0.42 ± 0.04</td>
<td>0.60 ± 0.06</td>
<td>0.72 ± 0.06</td>
</tr>
<tr>
<td>Plutonium alpha (Los Alamos chemistry)</td>
<td>0.52</td>
<td>0.64</td>
<td></td>
</tr>
</tbody>
</table>
addition of fuel at various positions in a critical assembly. The interpretation of this measurement requires auxiliary measurements of the effectiveness of fast and slow neutrons in the reactor. Furthermore, the value of alpha is quite sensitive to small inaccuracies in these auxiliary measurements.

The value of the capture-to-fission ratio is calculated from the formula

\[ 1 + \alpha = \frac{1}{F_L} (\nu F_H - D.C.) \]  

(2)

where \( \nu \) = the number of neutrons per fission for the fuel added

\( F_H \) = the net probability that an average fast, i.e., fission spectrum, neutron released in the reactor at the position of the sample will result in a fission

\( D.C. \) = the danger coefficient of the fuel added expressed as cents of reactivity change divided by fractional change of the total number of fissions in the reactor

\( F_L \) = the average probability that a slow neutron absorbed in the new fissile material would have otherwise produced a fission in the remainder of the reactor.

For the theory on which this analysis is based see references 6, 7, and 8.

The terms \( F_H \) and \( F_L \) must be expressed in reactivity units consistent with D.C. It is the measurement of these quantities which presents the greatest experimental problems. The quantity \( \nu F_H \) is obtained from reactivity measurements on fuel inside a neutron trap which traps all slow neutrons reaching it but allows fission neutrons to escape freely into the reactor. The quantity \( F_L \) is obtained from comparison of activation with reactivity effect for various resonance absorbers. The most accurate quantity which can be inferred from the measurements is the ratio of \( 1 + \alpha \) for plutonium to \( 1 + \alpha \) for U\textsuperscript{235}. So far the measurement has been performed only in an intermediate spectrum assembly having a composition of about 32 atoms of beryllium to 1 atom of U\textsuperscript{235}. At the center of this assembly the median fission energy is approximately 3000 ev. In this spectrum it is found that

\[ \frac{1 + \alpha_{\text{pl}}}{1 + \alpha_{\text{Pu}}} = 1.07 \pm 0.008 \quad \text{or} \quad \alpha_{\text{pl}} = 0.07 \pm 1.07 \alpha_{\text{Pu}} \]  

(3)

At the outside of the reactor, next to the beryllium reflector, the spectrum is much slower, having a median energy between 100 and 200 ev. The calculated neutron spectra of the critical assembly at various positions are shown in Fig. 1. Here the result is

\[ \frac{1 + \alpha_{\text{pl}}}{1 + \alpha_{\text{Pu}}} = 1.10 \pm 0.01 \quad \text{or} \quad \alpha_{\text{pl}} = 0.14 \pm 1.14 \alpha_{\text{Pu}} \]  

(4)

At the center of the reactor the best value of alpha is 0.3 for U\textsuperscript{235} and 0.4 for plutonium. At the edge of the reactor the best value for U\textsuperscript{235} is 0.3 and for plutonium 0.45.

The maximum error in \( \nu F_H \) is 6 per cent, leading to an uncertainty of \pm 0.1 in alpha. The maximum error in \( F_L \) is about \pm 3 per cent, leading to a \pm 0.035 uncertainty in alpha, while the quantity D.C. is also accurate to \pm 3 per cent producing an uncertainty of \pm 0.015 in alpha. The sum of these uncertainties is \pm 0.15. However, such an extreme range is highly improbable in the light of the excellent internal consistency of the experimental results and theoretical calculations. A few of these checks, which are the work of H. B. Stewart and R. Ehrlich, are listed below.

1. The quantity \( \nu F_H / F_L \) has been calculated theoretically by the multigroup method. The chief uncertainty in the calculation arises from the assumed value of alpha for the assembly as a function of energy. For this a curve was used which started from 0.05 at high energies and rose to a plateau in the intermediate region such as to give an average, over the whole spectrum, of 0.3, in agreement with the best measurements. The theoretical and experimental values of \( \nu F_H / F_L \) agree to better than 3 per cent for thin gold foil.

2. A theoretical multigroup calculation of \( \nu \text{po} \) for a reactor having the composition and geometry of the critical assembly predicts that the assembly should be critical to an accuracy of 3 per cent. The same assumptions as used in 1, above, in regard to alpha were used.

3. With the same assumed cross sections as in 1 and 2, the predicted neutron spectrum of the critical assembly is in excellent agreement with experimental measurements on the self-absorbed part of the activation of manganese, gold, and indium foils and in fair agreement with the fraction of fissions below the cadmium cutoff. This calculation is a sensitive test of the assumed self-shielding of the uranium-fission cross section in the energy range below 300 ev. The effective fission cross section was calculated theoretically for an assumed resonant structure, which in turn was deduced from activation measurements on stacks of U\textsuperscript{235} foils in the assembly and from time-of-flight measurements. Good agreement is also obtained for the fraction of fissions and of gold activations removed by a heavy B-10 shield.

4. Values of \( \nu F_H \) measured for U\textsuperscript{235} and Pu\textsuperscript{239} are in the correct ratio \( \nu_{\text{pl}}/\nu_{\text{Pu}} = 1.18 \) within 3 per cent for both the center and outside edge of the assembly.

5. Absolute values of \( \nu F_H \) and \( F_L \) measured in the assembly agree best with theory for an assumed value...
of the "dollar" of \( \Delta K = 0.0089 \). The theoretical value of the dollar, taking into account the greater reactivity value of delayed neutrons due to their lower energy, is 0.0087. This does not take into account the small additional contribution of beryllium (\( \gamma, n \)) neutrons produced by fission-product gamma radiation. This contribution, however, is less than 0.005, so that the agreement is still good within 3 per cent.

6. A theoretical calculation of \( F_L \) for thick gold inside a B-10 shield in the reactor agrees with an experimental determination within 10 per cent. The theoretical calculation involves a correction for the two-way transmission of the shield and for the "sink effect" produced by the presence of the B-10 shield, as the thickness is increased, since the spectrum of absorptions has a higher average energy for the thick stacks. The drop in alpha for six plutonium foils, as compared with one, is quite striking, especially in the outer edge of the assembly. A rough extrapolation of the plutonium measurements to an infinitely thin foil gives a value of alpha between 0.6 and 0.8 at the edge of the assembly, where the spectrum corresponds approximately to that of the 100-ev median-energy Hanford experiment (compare with Fig. 1, based on multi-group calculations by R. Ehrlich). It is to be expected that plutonium would show more influence of foil thickness than \( U^{235} \) since it is not already surrounded by an environment of other plutonium foils. By the same token 0.020-in. plutonium foils in an all-plutonium assembly would have an effective alpha comparable with that of two or more isolated disks. Thus the value of alpha for an actual assembly would be somewhat lower than the value measured for an isolated 0.020-in. disk.

Measurements have also been carried out on \( U^{235} \) and plutonium disks inside a B-10 shield at the center of the reactor. The median fission energy inside the shield was calculated to be as high as 0.2 mev for plutonium and 50 kev for \( U^{235} \). In the case of \( U^{235} \), 53 per cent of the fissions were cut out by the shield, while the fraction was 50 per cent in the case of plutonium. In spite of this the reactivity change accompanying the insertion of either type of fuel is greater when it is inserted inside the boron shield than when it is inserted without the shield in an equivalent position. Interpretation in terms of alpha involves a correction to \( \nu F_B \) arising from capture in the B-10 shield and a theoretical correction to \( F_L \) to take account of the difference in absorption spectrum shown in gold, \( U^{235} \), and plutonium. The most acceptable numbers at present lead to \( \sigma = 0.05 \) for \( U^{235} \) and \( \sigma = -0.08 \) for plutonium; the latter, of course, is physically impossible. At any rate it may be concluded that alpha for plutonium is negligible and alpha for \( U^{235} \) is near 0.15. By difference it is possible to compute the average value of alpha for the fissions which are eliminated by the B-10 shield. These are predominantly below 2000 ev. The average values then become 0.8 for plutonium and 0.5 for \( U^{235} \). The most certain inference from the data is the ratio of 1 + \( \alpha \) for plutonium and \( U^{235} \), which gives

\[
\frac{1 + \alpha_{238}}{1 + \alpha_{235}} = 0.87 \pm 0.06 \tag{5}
\]

It would thus appear that alpha falls off more rapidly with energy for plutonium than for \( U^{235} \).

Wigner\(^{12}\) has worked out the details of a theory of the resonance structure of plutonium or \( U^{235} \) which would qualitatively explain the type of behavior suggested by the above experiments. According to this

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Location</th>
<th>Thickness, in.</th>
<th>Alpha</th>
</tr>
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<tbody>
<tr>
<td>( U^{238} )</td>
<td>Center</td>
<td>0.020</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.040</td>
<td>0.28</td>
</tr>
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<td></td>
<td></td>
<td>0.080</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.120</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.160</td>
<td>0.16</td>
</tr>
<tr>
<td>( Pu^{239} )</td>
<td>Center</td>
<td>0.020</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.040</td>
<td>0.35</td>
</tr>
<tr>
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<td></td>
<td>0.080</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.120</td>
<td>0.24</td>
</tr>
<tr>
<td>( U^{238} )</td>
<td>Edge</td>
<td>0.020</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.040</td>
<td>0.26</td>
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<td>0.17</td>
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<td>( Pu^{239} )</td>
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<td></td>
<td>0.120</td>
<td>0.17</td>
</tr>
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</table>

which amounts to about 10 per cent. This calculation constitutes an especially sensitive test of the theoretical values of \( F \) used in the high intermediate energy range for estimating \( F_L \) for plutonium and \( U^{235} \).

The critical assembly also permits measurements of the influence of fuel geometry. There is evidence that at least a part of the capture lies in resonances which are separate from fission resonances. The most reasonable interpretation of this is that the fission width varies by a large factor from resonance to resonance while the radiation width remains more or less constant. Hence capture and fission will be self-absorbed differently, and plausible theoretical assumptions indicate that alpha should decrease with increasing thickness. This effect has been observed for \( U^{235} \) and plutonium in both the center and outside spectrum of the intermediate critical assembly, and the results for various numbers of disks are summarized in Table 2 (compare with the data given by Stewart\(^{10}\)). The values in the table allow for a small change of \( F_L \).
theory the fission width, $\Gamma_f$, is assumed to vary widely from level to level while the radiation width, $\Gamma_r$, remains relatively constant. The neutron width also fluctuates but remains uncorrelated with the fission width and increases on the average as the square root of the energy. In this picture the contribution to alpha comes preferentially from the levels having a small fission width and hence a small total width, since $(\Gamma_{\text{av}}^r) < (\Gamma_{\text{av}})^r$. At higher energies, however, owing to the increase of $\Gamma_n$, neutron reemission competes with fission and gamma emission but does so preferentially in the resonances having large capture. Thus the value of alpha averaged over a number of levels might be expected to decrease rapidly with energy above the energy at which $\Gamma_n \sim \Gamma_r$. For both types of fuel this may be expected to occur between 1 and 10 kev, but nearer the upper value. There is some indication from time-of-flight experiments that the level spacing, and hence the average neutron width, may be larger for plutonium than for $U^{235}$, leading to a lower cutoff energy. This theoretical picture seems to be consistent with the known facts about alpha and is supported both by the large self-absorption effects, as indicated in Table 2, and by the boron-shielded danger-coefficient experiments. Partial confirmation should come from the higher-energy Hanford experiments, and more conclusive confirmation should come from danger-coefficient measurements in a faster critical assembly which will be carried out in the near future as soon as the fissionable material becomes available.

**CHOICE OF NEUTRON SPECTRUM**

For evaluating breeding potentialities only two loadings of the WMA reactor will be discussed in this section: an intermediate loading, corresponding to

![Fig. 1 — Intermediate-spectrum atomic ratio of Be to $U^{238}$, 32:1.](image)

32 beryllium atoms per fuel atom, in which the alpha experiments described above were carried out, and a fast loading containing no beryllium in the core except that in the interstices between matrix tubes, corresponding to only 2.5 beryllium atoms per atom of fuel. The critical masses are about 60 and 130 kg of $U^{238}$, respectively. With these two loadings it is possible to cover the complete range of neutron spectra from 100-ev median energy to 100 kev or more. It happens that the spectrum near the reflector of the fast loading has about the same median energy as the spectrum at the center of the intermediate loading.

The neutron spectra of these two reactors are summarized in Figs. 1 and 2. These figures are graphs of the integral spectrum of fissions, i.e., the abscissa is energy and the ordinate is percentage of
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of independent capture and fission resonances indicates \( \bar{\alpha} = 0.18 \) for uranium and \( \bar{\alpha} = 0.15 \) for plutonium in the fast assembly, giving \( \eta = 2.12 \) and \( \eta = 2.57 \), respectively. These calculations represent only guesses at the present time, but the hypothesis on which they are based gives reasonably good agreement with experiment for (1) values of effective alpha with actual foil geometry, (2) variation of foil fission activation with stacked foils of \( U^{235} \) and plutonium in center and outside spectra of critical assembly, (3) variation of effective alpha with foil thickness in both positions, (4) the boron-shield alpha experiment, and (5) level density from differential measurements of the fission cross section. The main influence of fuel geometry, i.e., self-absorption, is already accounted for in the critical assembly measurements. The influence of peak fuel temperatures in the fuel capsules is not large, never accounting for more than 10 per cent increase in alpha. The interpretation of self-absorption data is based on a theory developed by G. M. Roe.

The value of alpha is smaller for the fast loading not only because of the faster spectrum but also because the high fuel density results in selective self-absorption of capture resonances. For the actual geometry of the WMA reactor the fuel density for the fast loading produces self-absorption equivalent to a foil thickness of 0.12 in. (see Table 2).

The curves are for \( U^{235} \) assemblies; no corresponding calculations have been carried out for plutonium of independent capture and fission resonances indicates \( \bar{\alpha} = 0.18 \) for uranium and \( \bar{\alpha} = 0.15 \) for plutonium in the fast assembly, giving \( \eta = 2.12 \) and \( \eta = 2.57 \), respectively. These calculations represent only guesses at the present time, but the hypothesis on which they are based gives reasonably good agreement with experiment for (1) values of effective alpha with actual foil geometry, (2) variation of foil fission activation with stacked foils of \( U^{235} \) and plutonium in center and outside spectra of critical assembly, (3) variation of effective alpha with foil thickness in both positions, (4) the boron-shield alpha experiment, and (5) level density from differential measurements of the fission cross section. The main influence of fuel geometry, i.e., self-absorption, is already accounted for in the critical assembly measurements. The influence of peak fuel temperatures in the fuel capsules is not large, never accounting for more than 10 per cent increase in alpha. The interpretation of self-absorption data is based on a theory developed by G. M. Roe.

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The values of alpha for the intermediate loading may be taken from the critical assembly measurements, with some slight additional correction for self-absorption in the case of plutonium. Estimated volume averages may be taken as 0.3 for \( U^{235} \) and 0.4 for plutonium, substantially the same as the center values. These give \( \eta = 1.92 \) and \( \eta = 2.11 \), respectively.

For the fastest assembly the data are less certain, but a theoretical calculation based on the hypothesis

![Image](https://via.placeholder.com/150)

*Fig. 2—Fast-spectrum atomic ratio of Be to \( U^{238} \), 2.5:2.*

The distribution of fissions will be quite similar, with the plutonium assemblies showing a somewhat higher percentage of fissions in the very fast group above 0.5 mev and a substantially lower percentage in the very low group from 1 ev down to thermal. This comparison has been given for a somewhat slower spectrum.\(^\text{11}\)

The diagrams show the distributions for the center, for the outside, and for the volume average are indicated by separate curves. The corresponding curve for the 100-ev median-energy Hanford alpha experiment is shown in Fig. 1 for comparison. These curves are based on theoretical calculations, but the cross sections used have been adjusted for self-absorption and for alpha to give a good fit with experimental spectrum measurements.

<table>
<thead>
<tr>
<th>Energy (KeV)</th>
<th>Fraction of Fissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.0</td>
</tr>
<tr>
<td>500</td>
<td>0.9</td>
</tr>
<tr>
<td>1000</td>
<td>0.8</td>
</tr>
<tr>
<td>1500</td>
<td>0.7</td>
</tr>
<tr>
<td>2000</td>
<td>0.6</td>
</tr>
<tr>
<td>2500</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Fraction of Fissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

\(...\text{continued...}\)
The spectrum at the center of the fast loading, as shown in Fig. 2, represents the fastest spectrum attainable in a fast power breeder having a specific power of the order of 2000 kw/kg and employing sodium as the primary coolant. The 2.5 atoms of beryllium per atom of fuel, which result from the filling of the interstices between matrix tubes, are equivalent in moderating power to 7.5 atoms of sodium. Thus the tables are for a loading which is critical at operating temperature with average burn-up conditions (5 per cent of the fuel fissioned on the average over the whole reactor, 10 per cent in those rods just ready to be unloaded). Table 3 is for the intermediate (32:1) loading, and Table 4 for the fast (essentially 2.5:1) loading. These compositions are fairly typical of what might be used in a production-type power breeder.

### Table 3 — Variable-spectrum Reactor, Intermediate Loading

<table>
<thead>
<tr>
<th>Region</th>
<th>Constituent</th>
<th>Volume %</th>
<th>Atomic ratio referred to U²³⁵ in core</th>
<th>Atomic ratio referred to natural uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>U (94%)</td>
<td>4.177</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>44.13</td>
<td>30.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>4.131</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Void</td>
<td>3.135</td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>33.21</td>
<td>5.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>11.18</td>
<td>4.43</td>
<td></td>
</tr>
<tr>
<td>Reflector</td>
<td>Be</td>
<td>70.90</td>
<td>65.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>20.92</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>7.38</td>
<td>4.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Void</td>
<td>0.87</td>
<td>5.16</td>
<td></td>
</tr>
<tr>
<td>Fast breeder</td>
<td>U</td>
<td>49.41</td>
<td>1.00*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>7.76</td>
<td>0.402</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Void</td>
<td>1.21</td>
<td>0.315</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>31.77</td>
<td>0.363</td>
<td></td>
</tr>
<tr>
<td>Slow breeder</td>
<td>U</td>
<td>38.70</td>
<td>1.00*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>41.25</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Void</td>
<td>0.40</td>
<td>0.200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>15.45</td>
<td>0.198</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>4.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Atomic ratios in blanket are normalized to natural uranium rather than core.

The relative contributions of the various substances to the total structural absorption are estimated as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Intermediate</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe, %</td>
<td>46</td>
<td>51</td>
</tr>
<tr>
<td>Ni, %</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Cr, %</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>Ti, %</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Na, %</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Impurities, %</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

Estimated total absorption by structural material and coolant for the two loadings is illustrated in Tables 5 and 6. These estimates are based on theoretical multigroup calculations (carried out by R. Ehrlich) using assumed cross sections for the elements. It is indicated that 50 per cent of the structural absorption is below 300 ev in the core of the intermediate design and 90 per cent for the reflector, whereas time-of-flight experiments show that there are no resonances below 1000 ev in any of the major structural elements.
FEASIBILITY OF PLUTONIUM BREEDING

Thus 1/ν absorption extending upward from the thermal cross section is used to estimate the reflector absorption in the intermediate loading. For the core the assumption is taken as a judicious compromise between the 1/ν assumption and values of σₚ/σᵣ deduced from danger-coefficient measurements in the center of the critical assembly, corrected for inelastic scattering. The danger coefficients give twice as much absorption as the 1/ν law, presumably owing to the contribution of resonances in the high-intermediate-energy region.

For the fast loading nearly 90 per cent of the structural absorption is below 3000 ev in the reflector and breeder regions, so that, again, the 1/ν extrapolation from thermal is a reasonable assumption. For the core, values of σₚ/σᵣ for the structural elements as measured by D. J. Hughes for fission-spectrum neutrons are employed, interpolation being resorted to where actual measurements were not available.

The tables also show estimated structural absorption for a plutonium reactor. These are guesses only and should not be taken as seriously as the results for U²³⁵. Estimates are given for leakage from the blanket. The large leakage is mainly due to the coolant channels in the fuel-rod breeder sections; it would be reduced to less than 0.06 neutron per fission if the fuel rods were extended so that the total thickness of uranium were the same on the ends as on the sides. This was avoided in the present design in order to facilitate handling of rods and also to permit a higher flux in the experimental graphite region beneath the reactor.

The total structural absorption of nearly 0.14 neutron per core fission in the intermediate assembly is rather large. Of this, the core portion may be regarded as the price of specific power, and the reflector portion may be charged to special precautions to ensure the mechanical reliability of the control and safety system. Until more data are available on the stability of beryllium under irradiation in the presence of sodium, it was thought unwise to place major reliance on it as a structural part of the control and safety rods. From the viewpoint of optimum breeding performance, it should be emphasized that the shortest doubling time is obtained not with the reactor having the best neutron economy but rather with the reactor having the maximum product of breeding gain times specific power. Assuming that the possible specific power is proportional to the absorption by structural material and coolant, it may be shown that the product is a maximum when there is a sufficient amount of structural material to reduce the breeding gain to half its value in the absence of structural material. The amount of structural material in the present design probably falls short of this optimum at least for the fast spectrum, but the specific power is also less than would be desirable in an ultimate breeder.

FISSION PRODUCTS

Since the fissions in both the intermediate and fast designs are produced by neutrons having a wide range...
of energies, it is virtually impossible that any single fission product could be as significant as Xe\(^{135}\) is in a thermal reactor. The xenon cross section is remarkable, not only because the resonance is nearly at thermal energy (about 0.1 ev), but also because its height is nearly equal to the maximum theoretical height of a resonance at that energy. The range of energy covered by such a resonance is negligible compared with the range covered by the neutron absorption in an intermediate or fast reactor. Rough estimates of the xenon absorption in the intermediate and fast spectra, using the Oak Ridge cross-section data and neglecting the cross section above 0.5 ev, indicate

\[
\frac{\int \nu \sigma_{\text{Xe}}}{\int \nu \sigma_f} \approx 150 \quad \text{for intermediate}
\]

\[
\frac{\int \nu \sigma_{\text{Xe}}}{\int \nu \sigma_f} < 10 \quad \text{for fast}
\]

For the fast assembly the main contribution comes from the region near the reflector. These values are to be compared with

\[
\frac{\int \nu \sigma_{\text{Xe}}}{\int \nu \sigma_f} = 6000
\]

for a thermal reactor. These numbers mean that for corresponding xenon absorptions the reactor would have to have between 50 and 600 times the specific power of a thermal reactor. Xenon might absorb about 2 per cent per fission at a specific power between 12,000 and 120,000 kw/kg, i.e., it is negligible at any reasonably obtainable specific power.

On the other hand, it might be expected that in the intermediate region, over a range of energy covering many resonances, the cumulative absorption of all the stable fission products may be appreciable compared with the effective fission cross section after 10 per cent burn-up. To test this point an extensive program of measurements has been carried out in the critical assembly by the danger coefficient method (by H. Schulz and G. Dessauer) and by irradiation of selected elements in an intermediate flux produced by x-ray bombardment of a beryllium block of proper dimensions (by I. Dearley). The information gained from this program will be set forth in detailed reports now in preparation. The significant results are summarized in Fig. 3 (analysis by G. Dessauer), which shows a graph of the partial contribution of each of the stable fission products to the reactivity of the intermediate critical assembly for a total of 1 mole of such fission products. The results are based only on measurements in the center spectrum. In general it is found that odd-A isotopes absorb more than even-A isotopes. An attempt was made to take this into account in preparing Fig. 3, therefore the ordinate shown represents the absorption of a fictitious stable element having the isotopic composition corresponding to fission-product yields rather than natural abundance. The elements 43 and 61, which are missing from the diagram, are both long-lived radioactive products. They are assumed to give the same contribution to the poisoning as their daughters and so are not added to the total contribution. This assumption is reasonable because they are, like their daughters, odd-A isotopes, and the measurements indicate that absorption changes very slowly with A. Several interesting facts appear from this curve. The elements having largest fission yields are magic-number elements and have abnormally small cross sections. The largest contribution comes from two elements near but not at the maxima in the yield: samarium and ruthenium. These account for about 50 per cent of the total absorption. The total danger coefficient of 1 mole of stable fission products is 7.2 cents per mole, including the effect of burn-out of the high cross-section products. This corresponds to

\[
\frac{\int \nu \sigma_s}{\int \nu \sigma_f} = 0.16
\]

in the central spectrum of the intermediate assembly.

<table>
<thead>
<tr>
<th>Region</th>
<th>(^{235}\text{U}) reactor absorptions per core fission</th>
<th>(^{239}\text{Pu}) reactor absorptions per core fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>0.043</td>
<td>0.043</td>
</tr>
<tr>
<td>Reflector</td>
<td>0.082</td>
<td>0.10</td>
</tr>
<tr>
<td>Breeder</td>
<td>0.030</td>
<td>0.04</td>
</tr>
<tr>
<td>Leakage from blanket</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Total</td>
<td>0.22</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Region</th>
<th>(^{235}\text{U}) reactor absorptions per core fission</th>
<th>(^{239}\text{Pu}) reactor absorptions per core fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>0.031</td>
<td>0.021</td>
</tr>
<tr>
<td>Reflector</td>
<td>0.020</td>
<td>0.028</td>
</tr>
<tr>
<td>Fast breeder</td>
<td>0.017</td>
<td>0.024</td>
</tr>
<tr>
<td>Slow breeder</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td>Leakage from blanket</td>
<td>0.06</td>
<td>0.085</td>
</tr>
<tr>
<td>Total</td>
<td>0.14</td>
<td>0.17</td>
</tr>
</tbody>
</table>
The central spectrum is somewhat faster than the average spectrum of the reactor, so that the fission-product absorption may be underestimated by this exclusive of xenon. The value in the actual intermediate spectrum may be slightly higher than Eq. 8 but much closer to it than Eq. 9. Equation 8 certainly sets

\[
\frac{\sigma_s}{\sigma_f} = 0.65
\]  

(9)

Fig. 3 — Partial contribution of stable fission products to the reactivity effect of 1 mole of total fission products in the center of intermediate critical assembly. Total poisoning, 7.69 cents per mole.
At 5 per cent average fission burn-up the reactor contains about 0.107 mole of fission products per mole of fuel, resulting in an average neutron loss of 0.0175 neutron per fission. In no case may the number be expected to exceed 0.02, even for the intermediate loading. Similar calculations for plutonium indicate about 30 per cent greater total fission-product absorption.

In evaluating overall breeding or conversion performance, a compromise must be made between reprocessing losses and neutron losses due to fission products. If the fuel is reprocessed after too little burn-up, reprocessing losses are excessive, but, if the fuel is carried to too high burn-up, fission-product poisoning is excessive. The optimum fractional burn-up is given by

$$p = \sqrt{\frac{1}{\beta}}$$

where $f = \text{fraction of fuel lost in reprocessing}$

$$\beta = \frac{\sigma_f}{\sigma_t} \quad \text{for average fission product}$$

$p = \text{fractional burn-up}$

Assuming $f = 0.01$, appropriate when reprocessing to metal is considered, and $\beta = 0.18$, $p = 0.24$. Under these conditions the total loss is doubled over the neutron losses alone and is thus equivalent to 0.09 neutron per fission. For reprocessing to oxide a value of $f = 0.001$ might be obtained, giving $p = 0.075$, with a total loss equivalent to 0.028 neutron per fission. The design objective of 10 per cent burn-up is thus seen to be reasonable from the reprocessing standpoint, resulting in an equivalent neutron loss of 0.118 per fission in the worst case and 0.028 in the best.

HEAVY ISOTOPES

If it is assumed that the life of the KAPL reactor is not more than 10 years, it is estimated that the maximum loss from higher isotopes is only 0.02 per fission for the intermediate and 0.003 for the fast loading. Although this is not very significant for the present design, the effect of fuel isotopes merits discussion in connection with ultimate breeder designs.

In a true breeder it is the isotopes of plutonium, chiefly $\text{Pu}^{240}$ and $\text{Pu}^{241}$, which are of interest. They are of special importance because they cannot be separated from the fuel and therefore accumulate in successive reprocessing cycles until a certain equilibrium is reached in which the rate of production of each isotope is balanced by its destruction by neutron absorption or by natural decay. In the latter the isotope is transformed to a different chemical element which can be removed by reprocessing if desirable.

It is the breeding gain of the fuel of equilibrium isotopic composition rather than that of $\text{Pu}^{239}$ which is of real significance for the long-range breeding and power program, although the time scale for attainment of equilibrium isotopic content amounts to several doubling times. In this connection the fission properties of $\text{Pu}^{240}$, $\text{Pu}^{241}$, and to some extent $\text{Pu}^{242}$ are of importance. The only information available is on the thermal-neutron properties of $\text{Pu}^{240}$ and $\text{Pu}^{241}$, and this is still quite unreliable. The indications are that $\text{Pu}^{240}$ does not fission to an appreciable extent at thermal energies, but $\text{Pu}^{241}$ does. On the other hand, there is some evidence that $\text{Pu}^{240}$ has a moderately high fission cross section at high energies. Although $\text{Pu}^{241}$ is fissionable, it appears to have a rather high capture cross section leading to $\text{Pu}^{242}$ at thermal energies. The 10-year beta decay of $\text{Pu}^{241}$ also competes with fission and reduces the benefits from its fission properties.

Let it be assumed that $\text{Pu}^{240}$ has no fission. As the isotopic composition of the fuel changes, the effective breeding gain changes uniformly with recycling, approaching an equilibrium value as the isotopic-fuel composition reaches equilibrium. If $\text{Pu}^{241}$ has the same values of $\nu$ and $\sigma$ as $\text{Pu}^{239}$, and if its beta decay is neglected, then the ultimate breeding ratio is the same as that of pure $\text{Pu}^{239}$. The contribution of $\text{Pu}^{241}$ to the breeding ratio is proportional to the value of $\sigma$ for $\text{Pu}^{239}$, so that, if $\sigma$ is sufficiently small, the properties of the higher isotopes are of little or no consequence.* This is probably the case for the fast loading. Too little is known about the cross sections to say more than this. It is expected that, with samples of plutonium produced in thermal reactors which are very rich in higher isotopes, it will be possible to determine the fission and capture properties of these isotopes in the range of neutron spectra available in the KAPL-WMA reactor.

The situation in the case of $\text{U}^{235}$ is somewhat different since the third isotope, $\text{U}^{237}$, has a very short half-life and hence disappears as $\text{Np}^{237}$, which is removed or can be removed in the chemical processing. Thus, only the properties of $\text{U}^{234}$ are of importance. The maximum effect of $\text{U}^{234}$ will be to double the effective value of $\sigma$ for $\text{U}^{235}$ for fuel which has undergone an infinite number of reprocessings. Thus, ultimately the additional loss per fission due to $\text{U}^{234}$ will amount to 0.3 in the intermediate loading and 0.18 in the fast loading. This is of no importance for the KAPL reactor, however, since even half equilibrium, i.e., a loss per fission of 0.15 in the intermediate loading, is reached only in a period of 23 years. If it is assumed that the life of the reactor is not more than 10 years, the maximum loss per fission at the end of this period is only 0.02, even for the intermediate loading, and 0.003 for the fast loading, as indicated previously.

*For a quantitative discussion of this problem see the article "Secular Equations for Breeding."
BERYLLIUM EFFECTS

On the basis of the \((n,\alpha)\) cross section for beryllium, measured by Allen,²⁹ about 4 per cent of the neutrons released in fission may be absorbed in beryllium in the intermediate loading. Since this effect depends upon the competition between slowing down and absorption in the beryllium, it is nearly independent of spectrum and amounts to a loss of about 0.10 neutron per fission. Countering this is a gain of neutrons arising from the \((n,2n)\) reaction which has an effective energy threshold in the laboratory system of 1.8 mev. There is evidence²⁹ that the gain in neutrons from the \((n,2n)\) reaction exceeds the loss from the \((n,\alpha)\) reaction so that there is a net gain in \((n,2n)\) due to the presence of beryllium which might amount to as much as 0.10 neutron per fission. Measurements in the intermediate spectrum of the critical assembly indicate that the danger coefficient of beryllium falls in line with what may be expected from its slowing-down properties alone; although such discrepancies as exist indicate a slight net advantage from the \((n,2n)\) reaction. The safest assumption is probably to ignore both the \((n,\alpha)\) and \((n,2n)\) reactions in beryllium and assume that they compensate each other.

The \((n,\alpha)\) reaction leads eventually to \(\text{Li}^6\) which has a very high absorption cross section. The \(\text{Li}^6\) comes to equilibrium when the number of neutrons lost to it is equal to the number of neutrons lost to the \((n,\alpha)\) reaction itself. This effect doubles the potential neutron loss due to the \((n,\alpha)\) reaction to a value of about 0.2 neutron per fission. However, it takes of the order of 10 years of continuous operation at full power for the \(\text{Li}^6\) to approach equilibrium, and the average loss to this isotope in the first cycle amounts to only 0.005 neutron per fission. The main influence of this effect may be to necessitate occasional reprocessing of the permanent beryllium in the reactor and replacement of control and safety rods. The beryllium matrix in the blanket, which cannot be removed, will not show appreciable build-up of \(\text{Li}^6\) because it is in a lower flux and because, owing to inelastic scattering in natural uranium, most of the neutrons are below the effective \((n,\alpha)\) threshold.

FAST FISSIONS IN NATURAL URANIUM

Between 20 and 30 per cent of the total heat generation in the reactor originates from fissions of \(\text{U}^{235}\) and \(\text{U}^{238}\) in the fertile material of the blanket. The \(\text{U}^{238}\) fissions involve the destruction of fuel and must be added to the total destruction of fuel in the denominator of the formula for conversion ratio. The \(\text{U}^{238}\) fissions, on the other hand, do not constitute fuel destroyed, and the extra neutrons which they produce are absorbable in \(\text{U}^{238}\) to produce additional plutonium. Since these extra neutrons do not involve expenditure of fuel, they constitute a particularly valuable contribution to the neutron economy. The effect on breeding performance is as though the effective value of \(\nu\) were increased for \(\text{U}^{235}\), both in the core and in the blanket.

Measurements in the intermediate critical assembly with a solid natural-uranium blanket indicate that there are about 16 per cent as many fissions in \(\text{U}^{238}\) in the blanket as there are fissions of \(\text{U}^{235}\) in the core. These fissions result in a net production of 0.22 extra neutron per fission in the core, assuming \(\nu = 2.5\) for \(\text{U}^{238}\). Comparison with the theoretical multigroup calculations for the critical assembly of this composition indicates that the large magnitude of the fast-fission effect in the blanket can only be obtained if the inelastic cross section of natural uranium for fission neutrons is assumed to be substantially smaller than was formerly believed. The effective value deduced from the experiments of Snell¹² was \(\sigma_i = 2.2\) barns, whereas the present measurements are only consistent with \(\sigma_i = 1.4\) barns. A similar value is obtained from the ratio of \(\text{U}^{235}\) to \(\text{U}^{238}\) fissions observed in the middle of the blanket if it is assumed that the neutron spectrum has reached equilibrium there, an assumption for which there is some experimental evidence but no proof.

Because of its importance to the over-all breeding performance of the reactor, the magnitude of the inelastic scattering has been investigated by a different type of experiment. In this experiment (carried out by G. Dessauer) a rather large region of the core was loaded with a mixture of enriched and natural uranium and the ratio of \(\text{U}^{235}\) to \(\text{U}^{238}\) fissions at the center of this region was determined. Assuming that the leakage into or out of the central part of this modified region can be neglected, the value of the effective inelastic scattering cross section can be calculated directly from the ratio of fissions. This experiment gives a lower limit to the value of \(\sigma_i\) for natural uranium of 2.2 barns, in agreement with Snell's experiments. The discrepancy between this experiment and the results on the critical-assembly blanket has not been resolved. However, the experiment is much more direct than the two blanket measurements, since one of the latter involves comparison between an integrated experiment and a rather elaborate theoretical calculation, while the other is based on the unproved assumption of equilibrium. Further experiments to resolve the discrepancy are planned.

Theoretical calculations for the fast loading of the reactor give a value of only 0.09 fast fission per core fission in the actual blanket design, which contains considerable sodium, iron, and beryllium, as compared with a computed value of 0.17 for a solid undiluted blanket. Both these calculations are based on \(\sigma_i = 1.6\).

The actual contributions to breeding gain of the fissions in the blanket involve a rather complicated
discussion because of the close interrelation between $^{235}U$ fissions and $^{238}U$ fissions. For example, the fast neutrons arising from $^{235}U$ fissions produced by slow primary leakage neutrons result in additional $^{238}U$ fissions, and, conversely, some of the fast neutrons produced in $^{238}U$ fissions, after being inelastically scattered and degraded in energy, finally produce $^{235}U$ fissions. Thus the two types of fissions may not be regarded as independent, and reduction in the number of $^{238}U$ fissions, for example, by the use of a depleted blanket, will also result in a reduction of the number of $^{235}U$ fissions and hence of conversion ratio or breeding gain. Typical results are illustrated in Table 7, which shows the net increase in conversion ratio resulting from one primary $^{235}U$ fission per leakage neutron or one primary $^{238}U$ fission per leakage neutron. A primary fission is simply a fission produced by a neutron which leaked out of the core rather than by a secondary neutron arising from a fission in the blanket. The influence of three different factors is shown in the table. The quantity $\sigma_i$ is the inelastic scattering per atom of $^{238}U$ from above to below the $^{235}U$ fission threshold. In principle, it should include the moderating influence of structural materials and coolant. The quantity $p_{2s}$ is the relative probability that a neutron degraded below the fission threshold of $^{235}U$ will produce a fission of $^{238}U$. The effectiveness of $^{235}U$ and $^{238}U$ fissions is also influenced by the conversion ratio of the reactor in the absence of fissions in the blanket, i.e., the so-called "core" conversion ratio. The table shows values for a core conversion ratio of 1 and a core conversion ratio of 1.3. A number of general qualitative conclusions can be drawn from an examination of this table.

1. A $^{238}U$ fission is from two to four times as valuable as a $^{235}U$ fission, hence the most desirable design of reactor would involve the maximum leakage of fast neutrons into the blanket, i.e., neutrons above the fast-fission threshold of $^{235}U$.

<table>
<thead>
<tr>
<th>$\sigma_i$</th>
<th>$p_{2s}$</th>
<th>Core conversion ratio</th>
<th>$^{235}U$</th>
<th>$^{238}U$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.1</td>
<td>1.0</td>
<td>1.77</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.0</td>
<td>1.42</td>
<td>2.72</td>
</tr>
<tr>
<td>2.2</td>
<td>0.1</td>
<td>1.0</td>
<td>1.09</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.0</td>
<td>0.88</td>
<td>2.18</td>
</tr>
<tr>
<td>1.4</td>
<td>0.1</td>
<td>1.3</td>
<td>1.50</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.3</td>
<td>1.30</td>
<td>3.44</td>
</tr>
<tr>
<td>2.2</td>
<td>0.1</td>
<td>1.3</td>
<td>0.79</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1.3</td>
<td>0.61</td>
<td>2.76</td>
</tr>
</tbody>
</table>

2. Increasing the core conversion ratio increases the value of primary $^{235}U$ fissions and decreases the value of primary $^{238}U$ fissions.

3. Increasing the effective inelastic scattering enhances the importance of $^{238}U$ fissions relative to $^{235}U$ fissions but decreases the net value of both substantially.

4. Decreasing the value of $p_{2s}$ decreases the effectiveness of both $^{235}U$ and $^{238}U$ fissions.

The value of $p_{2s}$ as a function of energy is shown in Table 8 for a blanket having the approximate composition of the KAPL-WMA reactor. Also shown in the table is the quantity $\int \sigma_i / \xi_{2s}$ evaluated from just below the fast-fission threshold for the slow breeder region of the reactor. Relatively few neutrons in the blanket are absorbed below the energy for which this integral is approximately 1, about 1000 ev in the present example.

By examination of Table 8 it is possible to draw some additional qualitative conclusions regarding the most desirable composition of the blanket. The addition of small amounts of moderator or inelastic scattering material to the blanket is seen to be disadvantageous in two ways. In the first place, the effective value of $\sigma_i$ is increased, thus reducing the effectiveness of both primary $^{235}U$ and $^{238}U$ fissions. In the second place, neutrons which are degraded below the fission threshold are moderated into an energy region in which $p_{2s}$ is smaller than it is immediately below the fast-fission threshold and in the energy region to which inelastic scattering in the uranium itself degrades the neutrons. The moderator has an additional disadvantageous effect which does not appear clearly from examination of the table. The dilution of fertile material with moderator, or indeed with any scattering material, results in reduced self-shielding and therefore in increased resonance absorption in $^{238}U$ and thus in a smaller value of $p_{2s}$. The only advantage of the addition of moderator is that it increases the absorbability of neutrons in natural uranium and therefore decreases the over-all weight.

### Table 8 - Relative Probability of $^{238}U$ Fission in the Blanket as a Function of Neutron Energy

<table>
<thead>
<tr>
<th>Energy group*</th>
<th>$p_{2s}$</th>
<th>$\int \sigma_i / \xi_{2s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 - 3</td>
<td>0.071</td>
<td>0.057</td>
</tr>
<tr>
<td>3 - 4</td>
<td>0.063</td>
<td>0.128</td>
</tr>
<tr>
<td>4 - 6</td>
<td>0.044</td>
<td>0.362</td>
</tr>
<tr>
<td>6 - 8</td>
<td>0.037</td>
<td>0.818</td>
</tr>
<tr>
<td>8 - 12</td>
<td>0.103</td>
<td>1.954</td>
</tr>
<tr>
<td>12 - 20</td>
<td>0.374</td>
<td></td>
</tr>
</tbody>
</table>

*Expressed in terms of $u = \ln (100^2 / E)$. 

**H. Brooks**
FEASIBILITY OF PLUTONIUM BREEDING

and possibly also the size of the blanket needed to capture all the neutrons.

There is one circumstance in which the addition of moderator to the blanket might be beneficial. If enough moderator is added, the neutrons are degraded to the energy region below 1000 volts, where it is seen from Table 8 that $p_{2s}$ increases rapidly with decreasing energy. This rapid increase is due to resonance self-shielding in the $^{238}$U. The ideal moderator for this purpose is a hydrogenous material since its scattering cross section for fission neutrons is small and therefore does not contribute very much to $\sigma_t$, but at the same time its moderating power for degraded neutrons is large so that they enter the energy region where $p_{2s}$ is large. In addition to this, hydrogen gives large moderation for a given scattering power and thus gives a minimum reduction in the self-absorption effect from dilution. For the examples shown in Table 7, calculations (by H. A. Bethe) indicate that the addition of about 0.2 to 0.3 hydrogen atom per atom of fertile material would add between 0.5 and 0.8 to the numbers under the $^{235}$U and $^{238}$U columns, which amounts to an increase of between 0.2 and 0.3 in the total contribution to the conversion ratio. This possibility will receive further evaluation theoretically, but it is doubtful whether it can be incorporated in the present reactor design.

The information which has been developed so far shows that the present design of breeding blanket is not the optimum for obtaining the maximum benefit from the fast-fission effect. The two most undesirable features of the present design are the use of a thick beryllium reflector region separating the core and blanket and the incorporation of beryllium in the matrix of the so-called "slow-breeder" region. The reflector is needed in the present design for achieving adequate safety and control, especially sufficient safety to ensure adequate cooling of the reactor under emergency conditions by the stand-by cooling system. In the fast loading the beryllium reflector also results in the saving of approximately 50 per cent of the total critical mass in comparison with a reactor which is surrounded immediately by the natural-uranium breeding blanket without a reflector. The loading of a fast reactor having the same specific power potentiality as the present core, but without the reflector, would involve of the order of 170 kg of critical material. The beryllium in the slow-breeder region was introduced originally to save on the total weight of natural uranium and to keep the total thickness of the blanket to a minimum. These purposes do not appear to be essential at present, but in the meantime the beryllium matrix has become a rather essential structural element in the design.

SUMMARY

A summary of the estimated losses and gains for various effects and for both $^{235}$U and plutonium reactors is shown in Table 9 for the intermediate loading, and in Table 10 for the fast loading. The contribution from the fast-fission effect in neutrons per fission is adjusted to give the computed conversion ratio when substituted in the ordinary conversion ratio formula. In the case of the plutonium reactor the destruction of $^{239}$Pu is treated as equivalent to the destruction of $^{239}$Pu for the purpose of calculating the breeding ratio. The net conversion and breeding ratios are shown at the end of Tables 9 and 10.

The final conclusion of this analysis is that for the reactor as actually constructed the conversion ratio of the intermediate loading will be less than one, while there will be a slight gain of the order of 10 per cent for the fast loading. The corresponding breeding ratios which are estimated when the reactor is loaded with plutonium instead of $^{235}$U as fuel are about 1.1 in the case of the intermediate plutonium reactor and 1.5 in the case of the fast plutonium reactor. Because of present uncertainties regarding the performance of the mixed blanket, these figures are to be regarded as tentative.

From the standpoint of an ultimate power breeder very much more optimistic figures than shown in Table 10 may be attainable, especially if full advantage is taken of the fast-fission effect. Elimination of the moderating reflector and the blanket beryllium in the
WMA design will result in reduced structural absorption and greatly enhanced fast fissions at the price of substantial increase in critical mass and size. For a plutonium fast breeder of this type breeding ratios of 2.0 or breeding gains of 1.0 appear to be feasible. Furthermore a reasonable extrapolation of the present contemplated WMA reactor structure to plutonium indicates a possibility of a specific power of the order of 800 watts per gram. Taken together these figures would give doubling times which would be of substantial practical interest.

ACKNOWLEDGMENTS

Many individuals have contributed to the work, and it is difficult to acknowledge them all. The measurements of alpha by spontaneous fission counting were carried out under the direction of Dr. W. R. Kanne and were by F. A. White and I. H. Dearnley, especially. The work in the critical assembly was carried out mostly by Dr. H. B. Stewart. The method of measuring $F_a$ was devised by Dr. H. Hurwitz, Jr., and the detailed multigroup calculations for the assemblies were carried out by Dr. R. Ehrlich. The fission-product work by activation was carried out by Dr. I. H. Dearnley, while the fission-product danger coefficients in the critical assembly were measured by H. F. Schulz. The interpretation of the fission-product work was done by Dr. G. Dessauer. The experimental work on fast fissions in $^{239}$Pu was done by Dr. T. M. Snyder and Dr. G. Dessauer. I am indebted to many of my colleagues, especially Dr. Hurwitz and Dr. Snyder, and also to Prof. H. A. Bethe for fruitful theoretical discussions.

REFERENCES


May 1950
Vanadium as a Possible Structural Metal in Nuclear Reactors

By Alan U. Seybolt
Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York
Report MEMO-AUS-4

INTRODUCTION

In recent months there has been considerable activity in the field of the metallurgy of vanadium, both inside and outside AEC installations. The interest in this metal shown by various AEC laboratories has been prompted by the possible use of vanadium as a structural material in a fast reactor. For this application its low-capture cross section for fission neutrons coupled with properties such as high melting point, high ductility, and good alloying characteristics with uranium (absence of brittle intermetallic compounds) make it an interesting material.

The main object of this report is to review briefly the present status of vanadium metallurgy, particularly in relation to its possible use in nuclear reactors.

NUCLEAR PROPERTIES OF VANADIUM

Vanadium consists almost entirely of a single isotope, $V^{51}$, which upon capturing a neutron leads to a 3.9-min activity. Because of this its cross section can be readily measured by activation. For fission neutrons the measurements of Hughes give a value of 2.2 millibarns, which means that vanadium in this region has a capture which is only about 0.001 the fission cross section of plutonium. This value has been more or less confirmed by activation measurements made in the Los Alamos fast reactor by Hall and Hall. This is the lowest fission-neutron cross section of any metal in the first transition series, so far as is known on the basis of present incomplete data. Capture due to the $(n,p)$ reaction amounts to only 0.2 millibarn. Measurements of the danger coefficient in the Los Alamos fast reactor indicate that the inelastic-scattering cross section of vanadium is quite small, probably again the smallest of any element in the first transition series. Because of its influence on the fast fissions in $U^{235}$ small inelastic scattering is a desirable property of a structural material. Unfortunately the transport cross section of vanadium is also quite small, about 2.5 barns, making it a weak diluent for a fast reactor. This latter factor, however, influences only the critical mass and does not affect the breeding gain of such a reactor.

From the standpoint of the allowable amount of vanadium in a fast reactor, up to 50 atoms of vanadium per atom of plutonium could be used in such a reactor if 5 per cent absorption by structural material is allowed.

When slower spectra are discussed, vanadium does not appear so attractive since the thermal cross section, and consequently the $1/v$ part of the epithermal cross section, is rather large. Way and Haines quote a value of 4.5 barns, while Hughes et al. give a value of 5.5. The latter value would allow a dilution ratio of only 5 atoms of vanadium to 1 atom of $U^{235}$ in a thermal reactor.

METAL STATISTICS

Abundance

While vanadium is generally regarded as a rare metal, data on its occurrence in the earth's crust show it to be more abundant than copper, zinc, or lead. In fact, Clarke shows its occurrence to be approximately equal to the sum of the three common metals mentioned above, as indicated in Table 1.
Vanadium is very widely distributed, but it does not seem to occur in massive deposits except in a few localities, principally in Colorado, Utah, and Arizona, where it is found in sandstone formations, and in Mina Ragra, Peru. Only in Colorado and Peru are ores mined solely for the vanadium content.

The ores in the United States are principally carnotite and roscoelite. Carnotite, of particular interest because of its uranium content, is a uranium potassium vanadate containing approximately 54 per cent \( \text{UO}_2 \) and 18 per cent \( \text{V}_2\text{O}_5 \).

### Production of Vanadium

The production of vanadium\(^5\) in the United States from 1942 to 1946 was as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1942</td>
<td>2220</td>
</tr>
<tr>
<td>1943</td>
<td>2800</td>
</tr>
<tr>
<td>1944</td>
<td>1770</td>
</tr>
<tr>
<td>1945</td>
<td>1446</td>
</tr>
<tr>
<td>1946</td>
<td>636</td>
</tr>
</tbody>
</table>

Second only to the United States in vanadium production is Peru with the following figures:

<table>
<thead>
<tr>
<th>Year</th>
<th>Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1941</td>
<td>1000</td>
</tr>
<tr>
<td>1942</td>
<td>1000</td>
</tr>
<tr>
<td>1943</td>
<td>800</td>
</tr>
<tr>
<td>1944</td>
<td>510</td>
</tr>
</tbody>
</table>

The United States, however, has consistently been the world's largest producer.

### Cost

In recent years ferrovanadium has been selling for about $2.80 per pound of contained vanadium. This suggests that the price of the pure metal will probably never be as low as $2.80 per pound, but it could conceivably be not more than two or three times this much if an efficient reduction process were developed.

### Major Uses

The current consumption of vanadium may be divided into two categories: metallurgical and nonmetallurgical. Of the approximately 95 per cent consumed in metallurgical uses, about 50 per cent is used in the production of high-speed tool steel, and about 45 per cent is used in other tool steels and alloy steels and for deoxidation and degasification. The remaining 5 per cent is used nonmetallurgically in catalysts, pigments, etc.

### PROPERTIES OF VANADIUM

Most of the known physical properties of metallic vanadium are given in Table 2.

#### Chemical Reactivity: Corrosion

Like zirconium and titanium, vanadium is sensitive to embrittlement by gases of the atmosphere and hydrogen. It appears to be particularly sensitive to oxygen, which apparently diffuses through vanadium exceptionally rapidly; about 0.07 per cent oxygen is sufficient to render the metal so brittle that it cannot be cold-worked. Nitrogen also hardens it, but nitrogen diffuses through vanadium much more slowly and hence is not so dangerous a contaminant as oxygen. Hydrogen also renders the metal glass-brittle, but no definite information is available as to how much hydrogen may be tolerated.

There is not much quantitative information available on the corrosion resistance of vanadium to aqueous solutions or sodium, but what is known is favorable. About 30 days in liquid sodium at 500°C caused no appreciable attack. Similarly, vanadium appears to be quite resistant to dilute nonoxidizing acids; it is readily attacked by nitric acid in all concentrations. Its resistance to high-temperature water is not known.

### METHODS OF PREPARATION

Pearson,\(^8\) in a recent review of the metallurgy of vanadium, has discussed the methods of preparation exhaustively; hence there is no need to repeat it here. Calcium reduction of the pentoxide has been shown at KAPL and elsewhere to be a reliable source of metal of sufficiently high purity to be satisfactory as a base of engineering alloys or as a pure metal for structural purposes. Other methods can, and probably will, be developed. However, the calcium-reduction technique properly scaled up to produce about 20 lb of...
metal in one reduction should suffice for the immediate future unless unforeseen large-scale uses become urgent.

SOURCES OF PURE VANADIUM

For many years the Vanadium Corp. of America has supplied small amounts of vanadium metal, reported to be of high purity, more or less as a convenience to experimenters who needed only a few grams of metal; its lack of ductility suggests that it undoubtedly contained rather large amounts of oxygen. The Westinghouse Electric Corporation has made pure vanadium in small amounts in the past and lately has been doing more work on the preparation of the powdered metal by calcium reduction of \( \text{V}_2\text{O}_5 \) (reference 8) followed by consolidation by regular powder-metallurgy techniques. This metal appears to be of good quality but is made in small quantities and, as far as is known, only for their own experiments.

Union Carbide & Carbon Corp. Research Laboratories have been making vanadium metal in recent months and are apparently prepared to sell metal of about 99.5 per cent purity in lots of about 50 lb. Because this metal has only very recently become available, it has not been possible as yet to ascertain its properties.

The Knolls Atomic Power Laboratory has made several pounds of calcium-reduced metal of approximately 99.5 per cent purity, most of which has been ductile. However, it is not in a position to supply enough metal for an experimental program to any other site but could do this in cooperation with others if it seemed desirable.

Batelle Memorial Institute has been exploring some of the properties of pure vanadium in cooperation with KAPL but has no plans to produce vanadium in quantity. The uranium-vanadium phase diagram, shown in Fig. 1, was outlined at Battelle.

In summary, there is at present no commercial source of metal of proven quality. It may be that the metal prepared by Union Carbide will be satisfactory for metallurgical work in AEC programs; the status of this source should be established very soon. However, it is likely that the AEC will want to establish more than one supplier for pure ductile vanadium.

USE OF VANADIUM IN REACTORS

There are two possible applications of vanadium in fast reactors: (1) as a structural material and (2) as a fuel diluent. Where the fuel would be in contact with vanadium, the two applications tend to overlap. It may be repeated that it is not only the nuclear properties (discussed above) which make vanadium an interesting metal but also its other properties such as high melting point, formability, corrosion resistance, and good alloying characteristics with uranium.

The discussion which follows is concerned only with the use of vanadium as a fuel container or fuel diluent. These applications appear to impose more stringent requirements than its use only as a structural material.

Vanadium-Uranium Alloying Behavior

The vanadium-uranium constitutional diagram, as determined by Saller and Rough, \(^{11}\) Battelle Memorial Institute, is shown in Fig. 1. While the diagram has not been determined with precision, the general nature of the system is clear. It will be noted that there are no intermetallic compounds; hence any composition from pure uranium to pure vanadium is workable.
This is indeed a fortunate circumstance. There are very few uranium binary diagrams, if any, that are as simple as this one.

One feature of the constitution, however, is undesirable. It will be noted that any alloy richer in vanadium than the composition of the eutectic will freeze out primary vanadium surrounded by the eutectic structure rich in uranium. The complications caused by this feature of the constitution will be referred to later.

Vanadium as a Fuel Container: Vanadium Tubing

The Superior Tube Co. has succeeded in drawing vanadium tubing as small as 60 mil (I.D.) by 7.5 mil (wall). The uranium could be placed inside such small tubes in the form of wires and then bonded to the vanadium by melting or perhaps by diffusion bonding below the melting point of uranium. The last technique would probably involve drawing the tubing over the fuel structure in order to secure a close contact between the two. Other techniques could undoubtedly be considered. A major problem involved in this type of construction is the extent of the diffusion of uranium into the tube wall which would occur during either initial fabrication or pile operation. A radiation test conducted under simulated reactor operating conditions would be required to ensure the safeness of any particular fuel arrangement. In the meantime diffusion experiments should be conducted in the laboratory to find out the extent of diffusion under nonirradiation conditions.

Fission-product gases such as krypton would be generated during fuel burn-up, and enough void space must be allowed to take care of the gas pressure developed.

Vanadium Alloy

As an alternative to the tubing design outlined above, a vanadium-uranium alloy containing perhaps 20–40 per cent uranium by volume could be used, with the expectation that the fission gas would be retained within the alloy in the same way as contemplated for the aluminum alloy in the MTR reactor. Here, the question of the structure of the alloy is of interest, and, as mentioned above, the ordinary cast alloy would contain islands of essentially pure vanadium surrounded by a sea of uranium-rich eutectic. This structure is just the reverse of what is desired because of the following considerations: it has been speculated that less radiation damage would result in an alloy containing enriched uranium if the latter were segregated into islands separated by a relatively large volume of non-fissionable material. That is, radiation would damage the uranium portion of the alloy selectively, provided the dimensions of the islands and channels around the islands were large compared with the fission-product range. Thus uranium in the channels or matrix would be expected to seriously weaken the material, causing general swelling and fragmentation. On the other hand, if the uranium is restricted in location to the islands, these would still be held in place and restrained from expansion by the ductile matrix. The only way such a structure can be obtained is by powder metallurgy techniques in which the structure is largely determined by the relative volumes of the two metals. Since vanadium would be present in larger amount by volume, on the average more fuel would be surrounded by vanadium than vice versa. This is predicated on sintering the powder alloy at a temperature which is not high enough to melt uranium. A few weeks' work at KAPL has not solved this problem, but it is thought that the desired structure can be obtained by proper attention to fabrication details.

Another possibility which may offer an easier solution is to use a three-component alloy where a third metal ties up the uranium in the form of a high-melting alloy such as U₃Si₄. The main advantage of such an alloy would be to create a second phase rich in uranium which would be relatively insoluble in solid vanadium. In this manner the desired structure of a continuous phase of ductile vanadium would be achieved more readily owing to the stability of the compound.
Here again powder-metallurgy methods would be required. It should be emphasized that this discussion of possible uses of vanadium in reactors is very incomplete and is mainly illustrative of techniques which have been under consideration from time to time at KAPL. None of these techniques has been adequately developed and some have hardly been investigated. With the recent change in emphasis in program at KAPL, it appears unlikely that much development work on vanadium-containing fuel elements will be done in the near future because the Navy reactor, with its much slower spectrum, will be given precedence. However, because some laboratories are interested in a fast reactor, it appeared desirable to set forth some thoughts on possible uses of vanadium in such a reactor and to give a brief summary of the metallurgy of vanadium so that others might take advantage of this experience.

SUMMARY

Vanadium is a new metal of interest as a possible structural material in nuclear reactors having a fast-neutron spectrum. The current shortage of pure (99.5%) ductile metal will probably be overcome within a few months, when experimental lots of a few pounds should be readily available.

Vanadium can be easily fabricated into sheet, wire, and tubing with approximately the same precautions against atmospheric contamination as are used with zirconium. Fortunately it forms no brittle alloys with uranium; hence uranium-vanadium structures for fuel rods present no unusual fabrication difficulties. However, much additional work will be required before a complete evaluation of its potentialities in the atomic-energy field can be made.

ACKNOWLEDGMENTS

The author is indebted to Dr. Harvey Brooks for the section on the nuclear properties of vanadium.

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April 1950
Fabrication of Uranium Wire

By R. E. Anderson, J. M. Taub, and D. T. Doll
Los Alamos Scientific Laboratory

Report LAMS 967

ABSTRACT

A procedure for the fabrication of uranium wire was developed. The method consisted in swaging 0.500-in.-diameter silver-plated uranium rod to 0.042-in. diameter. The swaged rod was annealed in vacuum at 400°C after each 75 per cent reduction in area. Reduction from 0.042-in. diameter was accomplished by wire-drawing, using Aquadag as a lubricant. The wire was annealed in vacuum at 400°C after each 75 per cent reduction in area.

Wire was produced to 0.0033-in. diameter in tuballoy and to 0.010-in. diameter in enriched uranium (U\textsuperscript{235}). There was no apparent difference in workability between natural uranium and U\textsuperscript{235}.

INTRODUCTION

The work described was undertaken to satisfy a request for uranium wire of 0.010 ± 0.002-in. diameter in depleted uranium (U\textsuperscript{235}), normal uranium (tuballoy), and enriched uranium (U\textsuperscript{235}).

A search of the literature showed that Edelmann\textsuperscript{1} had produced tuballoy wire of 0.020-in. diameter by swaging and short lengths of 0.013 to 0.014-in. diameter by drawing. The major difficulties encountered in his work were pointing, lubrication, and lack of proper equipment. Considerable failure of the wire was encountered when the drawing operation was started because the Vaughn commercial drawing machine had a drawing speed that was too high (around 900 in./min). A machine was constructed to provide a drawing speed of 40 in./min.

Thompson\textsuperscript{4} drew uranium wire to 0.012-in. diameter through sapphire dies by employing a copper electroplate 0.0005 in. thick. The chief objection to the procedure was the short life of the plate. The use of lubricants did not appear to be as effective as the copper plate in permitting ease of drawing.

Cleaves\textsuperscript{3} drew uranium wire to 0.030-, 0.020-, and 0.010-in. diameters. He also employed a copper plate 0.0005 to 0.001 in. thick. At small diameters, 0.015 to 0.010 in., it became necessary to replate after each pass. The wire was annealed in helium at 600°C after each 10 per cent, or at most 15 per cent, reduction in diameter.

Annealing experiments at Battelle\textsuperscript{5} indicated that cold-drawn uranium rod could be annealed in the region of 480°C. Tests at M.I.T.\textsuperscript{5} were made to relate annealing temperature with the per cent of reduction by cold-rolling. The curve of the data shows that increased reduction from 15 to 45 per cent does not decrease the temperature of recrystallization and indicates that reduction beyond 45 per cent would not further decrease it. This work showed 450°C as the recrystallization temperature beyond 15 per cent reduction.

The present work does not represent a complete investigation. The pressure of time required that wire be produced without an extensive examination of the variables concerned.

EXPERIMENTAL WORK

Earlier investigations indicated that a process to fabricate small-diameter wire could be developed. It
appeared that a metal-coated uranium rod could be processed to wire by swaging and wire-drawing in suitable steps with intermediate anneals. It remained to establish a procedure.

The metal stock consisted of 0.500-in.-diameter normal-uranium extruded rod (thought to be a extruded) and cast 0.500-in.-diameter rods in both high-purity uranium (tuballoy) and enriched uranium (U²³⁵). Table 1 lists the carbon and spectrographic analyses of these materials.

Each rod was machined to remove oxide and to secure a smooth surface for electroplating. The rod was then plated with silver to about 0.003 in.* As a silver plate tends to spall unless annealed,¹⁶ the plated rod was heated at 600°C in vacuum to "set" the plate. The silver plate served two purposes in that it protected the uranium from oxidation during annealing and also acted as a lubricant in drawing.

An earlier investigation⁸ indicated that uranium could be successfully worked in the region of 300°C. Silver-coated rods were heated in a silicone oil bath to 300°C and swaged. The procedure gave satisfactory results for rod greater than 0.250 in. in diameter. For rod of 0.250-in. diameter or less, the dissipation of heat from the rod during swaging was sufficiently rapid to cause the warm-swaging operation to approach cold-forming. There was also considerable tendency for the silver coat to rupture.

It was found that the metal could be cold-swaged from 0.500-in. to 0.042-in. diameter (99 per cent reduction in area) without intermediate anneal. Temperature determinations on the rod immediately after cold-swaging showed temperatures ranging from 120 to 200°C. This evolution of heat during working may have helped to secure the very high reduction. However, rod so treated showed end splitting (Fig. 1) and a metal structure which appeared fibrous.

Silver-coated tuballoy rod was cold-swaged from 0.500-in.diameter to 0.012-in. diameter. The rod was immediately annealed whenever there was a tendency for the cold-worked rod to flash in the swaging dies. The flashing occurred when some 80 per cent reduction in area was obtained and indicated that a softening treatment was required.

Because of the character of the swaging operation, a variation of 0.001 in. was found in wire passed through the 0.012-in. swaging die. In the smaller sizes flashing occurred, resulting in a poor surface condition and fracture of the wire. To prevent the formation of surface irregularities resulting from swaging small-diameter wire (and because swaging long lengths of rod is tedious and time-consuming), it was decided to perform the first reductions by swaging and finish by wire-drawing, starting with the largest die feasible with available equipment. A 0.042-in.-diameter wire-drawing die was selected as the starting point for wire-drawing.

A few tensile and hardness tests were made to establish a satisfactory annealing temperature for cold-reduced metal. These tests were made on 0.117-in.-diameter wire which had been cold-reduced from 0.250-in. bar (93 per cent reduction in area). From the data thus acquired and from other sources,⁴ the annealing temperature of 400°C was selected for wire reduced 75 per cent in area.

In pointing wire for drawing it was possible to swage a point for those dies in the range of 0.042 to 0.014 in. For dies less than 0.014 in., the points had to be prepared by hand-sanding. Other methods, such as grinding and electroetching, were not suitable because of the nonuniformity or pitting of the metal and failure of the point on drawing. Considerable care was required to prepare satisfactory points by sanding. Best results were obtained by clamping the wire 1 in. from the end so that uniform removal of metal could be

Copper plates and copper jackets were tried as a protective covering for the uranium rod. Neither of these methods was as satisfactory as the silver plate. The copper plate appeared to work harden at a different rate than the uranium and would spall unless annealed frequently. The copper-jacketed rod was swaged in the 550 to 600°C temperature range. The jacket failed by peeling while reducing ¾-in.-diameter rod to ⅛-in. diameter. Because of the pronounced plasticity of the metal in the 550 to 600°C range, the metal tended to twist with the swaging dies and form a helical shape. As a result of the twisting, oxidation of the tuballoy, and the difficulty of handling hot material, the method was not pursued.

Silver-plated uranium rod of 0.500-in.diameter was reduced by warm-swaging (250 to 300°C) and by cold-swaging (room temperature).

*Copper-plating process will be furnished to interested persons upon request.

<table>
<thead>
<tr>
<th>Element</th>
<th>High-purity cast</th>
<th>Extruded</th>
<th>Cast U²³⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>120 - 110</td>
<td>900</td>
<td>150</td>
</tr>
<tr>
<td>Silicon</td>
<td>60</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Iron</td>
<td>25</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>Manganese</td>
<td>20</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>Magnesium</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cobalt</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Calcium</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>5</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

*All other elements for which values were obtained in spectroscopic analysis showed less than 5 ppm.
Fig. 1—Example of end splitting in rod cold-swaged from 0.500 in. to 0.042 in. without intermediate anneal. Magnification, approximately 20x.

Fig. 2—Photograph showing samples of rod and wire in various stages of reduction.
obtained. This length of wire was sufficient to thread
the die so that the point could be grasped with a pair
of needle-nose pliers and drawing could be started.
By hand-starting, a length of wire could be drawn
which would enable clamping the wire in the drawing
block.

Some effort was directed toward securing informa-
tion relative to the forces required in wire-drawing.
The comparison was made between silver-coated and
bare tuballoy and in respect to several lubricants. The
data secured were not sufficiently complete and were
too scattered to provide reliable conclusions. How-
ever, an evaluation of such data as were secured indi-
cated that silver-coated wire drew better than plain
wire, and that Aquadag was the most suitable lubri-
cant. A soap mixture reduced the drawing force to
about the same value as Aquadag, but it was not as
readily applied to the wire as Aquadag.

The annealing of rod or wire was performed in an
induction-heated vacuum furnace. Metal was charged
to the furnace at room temperature. The furnace was
evacuated and heated to 400°C. Charge and furnace
were then permitted to cool to room temperature. Time
at annealing temperature (from 30 min to 12 hr)
did not appear to help or hinder subsequent working.
It is questionable whether complete recrystalliza-
tion occurred to permit subsequent working.

Annealing at 600°C, a procedure used in previous
drawing projects,4,5 was satisfactory for metal which
had been lightly cold-worked (10 to 15 per cent reduc-
tion in area). However, this 600°C temperature tends
to embrittle metal which had been extensively cold-
worked (75 per cent reduction in area). No investiga-
tion was made to determine the cause of embrittle-
ment.

It was found that a drawing rate of 40 in./min per-
mitted the heat generated to be dissipated, and injury
to the wire was not encountered. High-speed drawing
(900 in./min as provided by one machine) generated
considerable heat and appeared to contribute to the
rupture of the silver plate. Drawing rates other than
those noted were not studied.

Based upon the work thus far performed, the pro-
cedure outlined below has proved successful in pro-
ducing wire 0.005 in. in diameter. Examples of the
original bar, swaged rod, and drawn wire are shown
in Fig. 2. It is thought that smaller wire can be made.
Also further study of the variables concerned in the
process might be beneficial in improving the present
method.

1. The uranium-metal rod stock should be machined
to provide a surface free from oxide and smooth in
countour and then electroplated with silver to a thick-
ness of about 0.003 in. The plated bar is heated at
600°C in vacuum to set the plate and prevent spalling
during fabrication.

2. Reduction of the rod can be accomplished by
swaging, with intermittent anneals at 400°C in vacuum
recommended when a 75 per cent reduction of area
has been achieved. (It is only necessary to heat the
metal to the annealing temperature and furnace cool.)
Successive reductions by swaging and drawing, with
intermittent anneals as required, can be employed to
fabricate wire to 0.005 in. in diameter. It is suggested
that the reduction of area made in any single pass be
not more than 35 per cent for swaging and not more
than 20 per cent in drawing.

3. For purposes of lubrication in drawing, Aquadag
of a paste consistency has been found suitable. The
paste is introduced in the die throat before threading
the wire.

4. A slow drawing speed is recommended to prevent
separation of the silver coat from the wire and to
prevent detriment to the coat itself. A drawing rate
of 40 in./min has been found satisfactory.

ACKNOWLEDGMENT

Considerable assistance in the work of the project
was received from C. Hercher and R. Osborn in re-
spect to the machining of required specimens.

Electroplating, electropointing, and stripping of
plated coatings was performed by the Electrochemis-
try Section under the supervision of J. Gore, Section
Leader, aided by R. Seegmiller and A. Fox.

The experimental work in wire fabrication, culmi-
ning in the adoption of a recommended procedure,
was carried out by R. Anderson, G. Andrews, and
G. Sweeney.

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October 1949
Fabrication of Large Beryllia Crucibles

By W. E. Hauth and H. A. Wilhelm
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Iowa State College, Ames, Iowa
Report ISC-117

ABSTRACT

A method for the production of a large thin-walled beryllium oxide crucible for metal melting and casting is described. The piece is formed by jolt-packing in a graphite mold, it is fired in an induction furnace. The important factors in overcoming warpage and cracking are the use of electrically fused beryllia grain and the proper particle-size distribution of the grain to give a close-packed system. An addition of 1.5 per cent of CaO is made to the beryllia to produce a hard abrasion-resistant crucible at a firing temperature of approximately 1900°C. Crucibles formed by this method undergo about 3 to 5 per cent firing shrinkage and have a porosity of roughly 20 per cent.

The crucible fabrication procedure described below arose from the need for a crucible suitable for thorium melting and casting, in conjunction with the metallurgy program of the Ames Laboratory. The selection of beryllium oxide as the crucible material was thus dictated by the metal being processed. Since the need for a crucible was urgent, the emphasis of the work described was on the production of a satisfactory finished product rather than on the fabrication process itself. Therefore many of the conditions of manufacture, for example, the firing temperature, were not rigorously determined, reproducibility being the desired feature. However, large thin-walled crucibles were produced without cracking and with little or no warpage, and it is believed that the procedure used can be specified in sufficient detail to enable its duplication in any laboratory.

CRUCIBLE FORMING

The crucible is formed by the jolt-pack method in a two-piece graphite mold. The details of the mold are shown in Fig. 1. The mold consists of a graphite form in which a graphite mandrel is inserted. The mold and mandrel are assembled by inserting a graphite plug, 3 1/8 in. in diameter by 2 1/8 in. long (not shown in Fig. 1), in the opening in the bottom of the mold. The mandrel is then placed in position on this plug and is thereby centered in the mold. The cavity between the mold and the mandrel is filled with the oxide grain and is jolt-packed on a compressed-air jolter. As the mix compacts, successive additions of grain are made to keep the annular space filled. This process is continued until no further decrease in volume is obtained with continued jolting. The top is finished by pressing it with a graphite ring which fits around the mandrel. This ring also acts to hold the top grain in place while the mandrel is being removed. The mandrel is removed by first inserting a rod through the 1/4-in. drill hole shown in Fig. 1 and then lifting with a chain hoist. The mandrel is in the form of a hollow shell to reduce its weight. However, the openings at the top and bottom of the mandrel are smaller than the main cavity in order to strengthen these sections.

It has been found that two very important factors in the formation of large thin-walled crucibles, free from cracking and warping, are the type of beryllium
oxide grain used and the particle-size distribution of the grain. The initial attempts to produce the crucibles were made with sintered beryllium oxide. However, the firing operation produced large shrinkages and, almost without exception, severe warping and cracking of the crucible walls. Although particle sizing improved the behavior of this grain, suitable crucibles could not be made consistently from the sintered beryllium oxide. Since it was thought that the large shrinkage obtained on firing was primarily responsible for the defects in the fired piece, electrically fused beryllia was tried in order to decrease this factor. It was found that the use of fused beryllium oxide did decrease the firing shrinkage markedly, with a resultant reduction in warping and a decided decrease in the amount of cracking.

Further improvements in the crucible walls were obtained by experimentation with the particle-size distribution in an attempt to secure a close-packed system. Such a distribution is highly desirable because of the extent and varying thickness of the crucible walls and because of the method of forming. As is generally known, unless a close-packing mix is used the jolting will tend to segregate the particles, causing a variation in the density of packing. In the case of beryllia-ware fabrication by the jolt-pack method, such segregation will result in differential shrinkage. The experimentation with the particle-size distribution was necessarily limited by the relative availability of various grades of the fused oxide. Since a considerable quantity of a size finer than 325 mesh was available, this size was taken as a base, and varying quantities of coarser grains were added until a suitable distribution was obtained. The particle-size distribution now being used is given in Table 1. Undoubtedly a number of other combinations would perform equally well, the important property being that a close-packed system results. A quantity of lump fused beryllium oxide was recently ground at the Metallurgy Project at Massachusetts Institute of Technology, where ap-
proved equipment is available for the crushing, grinding, and screening of beryllia. It was found that the distribution of grain sizes obtained approximated that given in Table 1, with the exception of the finer than 325-mesh fraction. Therefore, it was necessary to reprocess only a small portion of the grain to obtain the proper ratios of the various fractions.

period. The refiring to which the crucible is subjected in use is sufficient to prevent this deterioration.

Firing

After the grain has been jolt-packed sufficiently, the mandrel is carefully removed, and the mold, con-

An investigation was made of the effect on the increase in strength of the crucible made by the addition of varying percentages of calcium oxide to the beryllia. The addition which appeared to show the best results, giving a hard abrasion-resistant surface at a firing temperature of approximately 1900°C, was 1.5 wt. % calcium oxide. Although the unreacted particles of CaO tend to rehydrate slightly and cause some chipping or scaling, this occurs only after a period of several months and then only if the crucible has not been used and has been exposed to the air for this period. The crucible, is placed in an induction furnace for firing. The mold is inserted in a 1/2-in. wall thickness graphite susceptor tube which is separated from the outer quartz tube by 1/16 in. of carbon insulation. This unit is used in conjunction with a movable coil powered by a 40-kW mercury-arc gap converter. This assembly is shown in cross section in Fig. 2.

The firing is begun at a power setting of about 18 kw, with the coil positioned so that the center of the coil is opposite the top of the crucible. This position is maintained until the temperature is 1100°C (ap-
proximately 1.5 hr), during which time the power setting is increased to 32 kw. Then the coil is slowly lowered until, for the final 0.5 to 0.75 hr, the center of the coil is positioned at the bottom of the crucible mold. The maximum power input during the later stages of the firing is 36 to 38 kw. The total firing time is approximately 3.5 hr.

The final firing temperature has not been accurately determined. The temperature readings are taken on the reflection of the sight-tube opening in a mirror (Fig. 2). An accurate calibration of the system is not possible, however, since the firing is done in air and the sight is taken through considerable flame and vapor. The maximum temperature reading obtained under these conditions, but corrected for the effect of the mirror (approximately 50°C), is 1900 to 1925°C. Although this value may be in error by a considerable amount, it gives sufficient indication of the temperature to permit reproducible firing conditions. The furnace is allowed to cool, and the crucible can then be easily removed from the mold.

It should be mentioned that sufficient ventilation should be provided to remove the beryllia vapors, which are developed in the later stages of the firing operation, in order to ensure the safety of the operator.

**CRUCIBLE PROPERTIES**

The beryllia crucible obtained by the method described above is true in shape, without cracking, and relatively hard and strong. It has a 3\% in. diameter hole in the bottom through which the molten metal is drained during casting. The linear shrinkage during firing is approximately 3 to 5 per cent. The final piece has an outside diameter of 8\% in., with a wall thickness of 1/16 in. The porosity of the fired crucible is approximately 20 per cent.

At the present time no effort has been made to reclaim the material from broken, used crucibles. This is due primarily to the lack of properly ventilated facilities for crushing, grinding, and screening of beryllia. However, when this equipment becomes available, it is planned to reuse this grain by recrushing and grinding the used pieces. The ground material will be chemically treated to remove some of the contamination caused by the melt and then sized and reformed into crucibles. By this procedure very little new oxide would be necessary to maintain the requirements of the metallurgical process.

September 1950
Problems in the Use of Molten Sodium as a Heat Transfer Fluid

By Leo F. Epstein and Clifford E. Weber
Knolls Atomic Power Laboratory, General Electric Company
Schenectady, New York
Report KAPL-362

PART I

ABSTRACT

Corrosion of materials by liquid sodium is discussed in detail. The available experimental static- and dynamic-corrosion data from various laboratories engaged in this work are tabulated. Theories of corrosion are considered, as well as special topics such as the effects of oxygen and radiation. The paper concludes with a discussion of other problems in sodium technology: mass transfer, carburization, diffusion bonding, purification of sodium, and similar subjects.

III. CORROSION BY LIQUID SODIUM

A. INTRODUCTION

The successful use of liquid sodium as a heat-transfer fluid is at the present time limited only by the nature of its reactions with other substances. The physical properties of this material are satisfactory, but its corrosion characteristics and the tendency of metals to bond together under sodium present problems. Zinn has stated that, so far as the Argonne National Laboratory (ANL) sodium-potassium-alloy-cooled fast reactor (CP-4) is concerned, a surface-corrosion rate of greater than approximately 0.01 in. per year cannot be tolerated. Throughout this paper sodium-potassium alloy is referred to as (NaK). Type 347 stainless steel meets this condition and, furthermore, does not show diffusion bonding (welding) in NaK up to 650°C. Low-carbon steel, on the other hand, cannot be used above about 450°C. The Argonne reactor will not be operated above approximately 400°C, however, because of the α-to-β transformation in uranium at 665°C and the danger of welding of metals under stress in valves, pumps, and similar components.

Thus, it will be seen that, at present, corrosion and welding phenomena are important limiting factors in determining the operating temperatures and, consequently, the thermodynamic efficiency of an alkali metal-cooled power-producing reactor. As a result a great deal of effort has been expended in obtaining the corrosion data necessary for proper engineering design; this work will be discussed in the sections which follow.

It has become customary in liquid-metal-corrosion studies to express the corrosion rate $R_T$ in milli-
grams of weight gain (+) or loss (−) per square centimeter of material per month of exposure (mg/cm²-month), at the temperature T. For materials which lose weight, the "penetration rate" 𝑃_𝑇 is often used also; it is generally expressed in engineering units as the surface thickness lost in mils/year. The relation of these two measures of corrosion is given by

\[ P_T (\text{mils/year}) = R_T (\text{mg/cm}^2\text{-month}) \times (4.72/\rho) \]  

where \( \rho \) is the density of the material in g/cm³. For metals which gain weight owing to the formation of an oxide film, as is true in many cases, an effective penetration rate may be computed; this is the rate at which the metal surface is converted into the oxide. It also is expressed in mils/year. Where the weight gain is due entirely to oxygen pickup and the oxide contains \( Q \) grams of oxygen per gram of metal, the effective penetration rate is

\[ P_T (\text{mils/year}) = R_T (\text{mg/cm}^2\text{-month}) \times (4.72/Q) \]  

The value of \( Q \) may readily be computed from the stoichiometric formula of the oxide. The value of \( P_T \) obtained in this way is essentially the weight loss which would be observed if all the oxide layer were subsequently to be removed in some way. The trouble with this computation is that the formula for the oxide in the film usually is not known with certainty. For example, at the Knolls Atomic Power Laboratory (KAPL) the most stable oxide, thermodynamically, is generally assumed so that in stainless steel the nickel, iron, and other constituents are ignored, and the effective penetration rate computed is as though the oxide film were all Cr₂O₃. This procedure is, however, very crude and should be employed with caution.

In general it may be said that the computation of penetration rates from weight-change data is a risky procedure unless the mechanism of the weight loss is clearly understood. It is altogether wrong, for example, to compute \( P_T \) from \( R_T \) by the formulas above when the weight loss is due essentially to the removal of interstitial components of the system. Another common, although obviously dangerous and unreliable, practice used in the interpretation of corrosion data is the extrapolation of short time tests to relatively long periods. Again this is valid only when the factors affecting the variation with time are clearly understood. The equations which will permit this extrapolation are developed for a few simple cases in later sections.

1. Organic Materials

Many organic substances are known (paraffin hydrocarbons, ether, etc.) which are resistant to the reducing action of sodium at room temperature; in fact sodium is an excellent dehydrating agent for such materials. Compounds containing halogens, unsaturated groups, labile hydrogen, etc., are not stable even under these mild conditions. At the elevated temperatures at which sodium is useful as a heat-transfer fluid, even the substances normally thought of as stable to this material are pyrolyzed and converted into products which react readily. In some cases these processes may actually be catalyzed by the sodium.

A few materials have been found which can stand liquid alkali metals under relatively mild conditions. Thus at the Babcock & Wilcox Co. (BW), neohexane (2,2 dimethylbutane) and Dow Corning Corp. 550 silicone oil have been used with NaK at temperatures below 100°C for prolonged periods. The silicones are quite useful in this respect. Silicone rubber has been found to be useful as a gasketing material, and the use of Dri-film in systems containing sodium has been suggested to slow down the reaction with glass surfaces and absorbed or adsorbed moisture. In a nuclear reactor where interactions with radiation are important, the instability of organic compounds in sodium is enhanced. In general the use of organic compounds in the presence of hot liquid sodium should be avoided.

Tests on the reactions of relatively pure organic materials in sodium or NaK have been carried out at ANL and KAPL, mostly in a search for suitable materials for use as gland packings. Teflon (tetrafluoroethylene polymer) is drastically attacked at temperatures as low as 200°C. Dow Silastic 180, a silicone rubber, showed a corrosion rate of -350 mg/cm²-month when tested at ANL at 200°C for 144 hr in NaK containing 56 per cent sodium. At KAPL some General Electric Co. silicone rubbers (e.g., G. E. Nos. 268A, 274, 275B, 154, 12602) were found to retain their flexibility after 96 hr at 250°C. As far as could be found from Project literature this is the most severe treatment that has been given an organic compound without serious attack. Rubbers, natural and synthetic, either disintegrated completely or lost all resemblance to an elastomer under these conditions.

The Mine Safety Appliance Co. (MSA) has studied the resistance of protective clothing and similar equipment to splashes of sodium and NaK at elevated temperatures. The data, which are only qualitative, are summarized in Table 1.

2. Inorganic Materials

The reactions between sodium and certain inorganic compounds were considered in Part I of this paper. The notes which follow are concerned for the most part with reactions of sodium and certain materials showing promise as ceramic and thermal insulating materials. In many cases it is possible to predict whether a given substance will or will not react with sodium from an examination of the relative free energies of formation of the metallic oxide and Na₂O.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Thus from Table 16 of Part 1 it would be expected that the oxides of those elements whose free energy of formation per mole per atom of oxygen is more negative than the free energy of formation of Na₂O would not be reduced by sodium. The alkaline earth oxides, Al₂O₃, TiO₂, ZrO₂, and UO₂, are examples of oxide materials resistant to sodium by this criterion. From Table 16, Part I, SiO₂ appears to be a border-line case, but experiment has shown that fused quartz is rapidly attacked by sodium, particularly when it is in a finely divided form.

<table>
<thead>
<tr>
<th>Table 1 — Resistance of Protective Materials to Sodium and NaK</th>
<th>Resistance to sodium</th>
<th>Resistance to sodium-potassium alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>At 350°C</td>
<td>At 550°C</td>
</tr>
<tr>
<td>Chrome leather</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Laminated bakelite</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Skull protector</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Rubber gloves</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Face shield</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Goggles (safety glass)</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Goggles (plain glass)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wool</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cotton</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Goggles (cast-hardened glass)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Goggles (plain glass)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Argonne has carried out a few experiments on the attack of NaK on a number of types of glass. Their results with NaK containing 56 per cent sodium in static corrosion tests are shown in Table 2. It has been found at KAPL that the attack of glass is accompanied by a significant rise in the oxygen content of the sodium, and, if the process proceeds very far, there is a marked darkening of the glass. Consequently the use of glass containers for sodium or NaK should be avoided for temperatures above about 250°C. High-silica minerals behave somewhat like SiO₂ itself, the most stable materials in this class apparently being those in which the stoichiometric balance between basic and acidic oxides is such that the material is virtually equivalent to a neutral salt in composition. In the search for sodium-resistant thermal-insulating materials for use at KAPL, most mineral wool and glass compositions (which are essentially silicate-silica mixtures) have been found to be attacked. A few substances of this type which have shown some resistance are being explored further.

In the consideration of ceramics for use with sodium, the resistance to corrosion appears to be highly dependent upon the porosity, mode of firing, binder, and similar factors. Thus while single-crystal Al₂O₃ (synthetic sapphire) is only slightly affected, alumina compacts made from the powdered material are often rapidly attacked. In some cases the liquid apparently seeps into the interstices of the ceramic mass where it may react and combine with some of the constituents of the material, so that there is an over-all weight gain. With other substances the reaction with sodium results in water-soluble compounds. On treatment with water to remove excess sodium prior to weighing, these are dissolved out, so that in corrosion tests these materials show weight losses. Massive graphite in sodium falls into a powder, possibly owing to the penetration of the sodium atoms into the lattice with swelling, until disintegration occurs. Apparently similar effects are noted with many ceramics; for example, ThO₂, UO₂, U₃O₈, mycalex, porcelain, and such materials pulverize in this way under sodium.

Another kind of attack is noted with ZrO₂. Crucibles made of this material, which by itself should be quite resistant to oxygen-free sodium, are often formed using a silicate binder which is retained throughout the firing process. On exposure to sodium or NaK this binder is drastically attacked; this results in high corrosion rates. In addition, when oxygen is present as Na₂O, there may be some attack on ZrO₂ due to the formation of zirconates.

Asbestos has been tested by BW and has been found to be satisfactory as a packing material in NaK containing 80 per cent potassium up to about 165°C, but it is not usable at temperatures of 200°C and higher. At ANL it has been found that mica resisted the attack of NaK containing 56 per cent sodium for 10 days at 200°C, but, owing to the entrance of conducting fluid into the interstices of the solid, it lost virtually all its electrical insulating properties after exposure for 30 days at 400°C.
LEO F. EPSTEIN AND CLIFFORD E. WEBER

Some work has been done on the reactions of sodium with the hard substances like Carboloy, useful as valve-seat materials and in similar applications. These substances are made of carbides, some of which should be thermodynamically stable to sodium, probably must await the development of a need for these substances. The sections which follow will be concerned principally with the corrosion of pure metals and alloys by sodium.

Table 2—Static Corrosion of Glass in NaK

<table>
<thead>
<tr>
<th>Glass</th>
<th>Temperature, °C</th>
<th>Time of exposure, hr</th>
<th>Corrosion rate, mg/cm²/month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali resistant</td>
<td>400</td>
<td>72</td>
<td>-30</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>72</td>
<td>Disintegrated</td>
</tr>
<tr>
<td>Pyrex</td>
<td>300</td>
<td>72</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>72</td>
<td>-12</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>48</td>
<td>-320</td>
</tr>
<tr>
<td>Vycor</td>
<td>400</td>
<td>48</td>
<td>-500</td>
</tr>
</tbody>
</table>

Table 3—Static Corrosion of Inorganic Compounds by Liquid Alkaline Metals

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL (NaK, 56% Na)</th>
<th>KAPL (Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, °C</td>
<td>Time, hr</td>
</tr>
<tr>
<td>BeO</td>
<td>600</td>
<td>144</td>
</tr>
<tr>
<td>MgO</td>
<td>200</td>
<td>144</td>
</tr>
<tr>
<td>Single-crystal Al₂O₃</td>
<td>600</td>
<td>144</td>
</tr>
<tr>
<td>Alumina*</td>
<td>1800°C</td>
<td>243</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>90 per cent Al₂O₃, plus clay and feldspar flux, fired at about 1800°C or somewhat higher</td>
<td>243</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Silicate binder</td>
<td>600</td>
</tr>
<tr>
<td>Carbolyt</td>
<td>Tungsten carbide, with Co binder</td>
<td>500</td>
</tr>
</tbody>
</table>

*Other alumina ceramics yield R values varying from -0.2 to +0.5 mg/cm²-month in similar tests (KAPL).

B. CORROSION OF METALS AND NONMETALLIC ELEMENTS BY SODIUM

Introductory Remarks

The corrosion of metals by liquid sodium and NaK has been the subject of intensive investigation since 1945, with the major result to date being the demonstration of the complexity and difficulty of the problem. Many elements appear to be soluble in liquid sodium, although quantitative data on the solubilities are meager. The available data are shown in Fig. 1 and are summarized in Appendix C. The soluble metals, which would, of course, be drastically corroded by sodium, are of considerably less interest than those which are relatively insoluble and, therefore, suitable for consideration as structural materials in sodium-filled systems. For these insoluble substances the observed corrosion effects are small and the test re-
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Results are difficult to obtain and interpret. A factor of 10 in the measurement of a corrosion rate $R_T$ is quite good agreement on samples of the same material run in the same or different laboratories, although in any given group much better reproducibility of results is usually attained. This fact will be less astonishing, perhaps, if it is noted that the net weight changes observed in these corrosion tests are often of the order of tenths of a milligram after weeks or months of exposure; also, the treatments required to remove excess sodium from the solid sample may vary considerably from one experiment to another. Furthermore it appears that corrosion rates of metals in sodium are highly dependent on the surface condition of the solid and the impurities (particularly oxygen and perhaps carbon) in the sodium. In view of this superfluity of variables, it perhaps is not surprising that the art of liquid-metal-corrosion testing is in a crude state and an understanding of the mechanisms of corrosion perhaps even less advanced.

Metals which have been immersed in sodium may either gain or lose weight, and the explanation of this simple observation requires a careful consideration of the details of the corrosion processes. While electrical fields are known to produce measurable effects in liquid and solid alloys (references 78, 90, 114, and 115), the reactions observed in corrosion by sodium are quite different from the electrolytic phenomena which are largely responsible for corrosion in aqueous solution (references 11, 15, 31, 32, 88, 107, 112, 117, 123, and 128). It appears that many different kinds of reaction, rather than electrochemical, may be responsible for the observed effects in sodium. It is useful to think of the primary process as one of solution, with the liquid sodium acting as the solvent; in addition, however, the strong reducing action of this material, the universal presence of Na$_2$O with its tendency to be reduced by some metals and to oxidize others, and other factors complicate the picture considerably.

To illustrate these facts, consider the three materials iron, stainless steel, and beryllium immersed in sodium of low-oxygen content (well filtered or distilled material). Iron always loses weight; initially this appears to be due to solution of impurities, carbon in particular. Then the iron itself dissolves, and the rate of weight loss is determined by the equilibrium solubility and the so-called "specific solution
rate" of the material, which in turn varies with the oxygen content of the sodium as well as the temperature. Stainless steels of the 18-8 type almost always gain weight. It is known that when Cr₂O₃ is present on the surface of stainless steel it is not reduced by sodium,¹⁴ so that the reaction

\[ 2\text{Cr} + 3\text{Na}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{Na} \]  

may occur under these conditions, contrary to the predictions of thermodynamics based on measurements of bulk-phase properties. The resulting Cr₂O₃ layer is relatively adherent, and the increase in weight may be attributed to the take-up of oxygen from the Na₂O present. An alternate hypothesis involves the actual soaking up of sodium by the steel. There is some indication that this may occur based on Na²² tracer experiments in which Davis²⁵,⁵¹ concluded that there was actual alloying of stainless steel and sodium. It is possible that this pickup of sodium by the metal may rather be due to a relatively insoluble salt-like compound (Na₆-O-Cr₂O₃, perhaps) on the steel. Whatever the mechanism, the results of the corrosion tests and the tracer experiments are in approximate agreement as to the magnitude of the weight change, a result that is somewhat confusing. Up to the present time the critical experiments which would determine which of these factors (the interaction with Na₂O or the alloying with sodium) is the more important in the corrosion of stainless steel have not been carried out.

Beryllium is one of the metals which can readily reduce Na₂O, the reaction

\[ \text{Be} + \text{Na}_2\text{O} \rightarrow \text{BeO} + 2\text{Na} \]  

occurring at 500°C with a ΔF° of about -45 kcal. The solubility of beryllium in sodium, on the other hand, seems to be quite low. Consequently the first effect of sodium on beryllium to be expected and which has, in fact, been observed is the conversion of some of the beryllium to BeO with consequent weight gain. The resulting BeO film, however, unlike the Cr₂O₃ film on stainless steel in sodium or the Al₂O₃ film formed on aluminum in air, is not adherent (see Sec. II B-2). Because of its rather friable nature, it tends to spall off, particularly in dynamic systems where the flowing sodium tends to erode it. Thus beryllium sometimes exhibits a weight loss. It is possible for these two effects to balance one another exactly so that no net weight change is observed; therefore when weight remains constant, it is necessary to decide whether this is due to cancellation of opposing effects or to low solubility in sodium and the absence of significant amounts of Na₂O in the fluid.

NOTE: Generally speaking, oxide films tend to be adherent, while when the molar volume of the oxide is approximately equal to the atomic volume of the metal from which it is formed, so that the quantity in Eq. 4a is close to unity. Table 4 is of interest in this connection.

\[ E = \frac{1}{n} \frac{M_{\text{metal}}}{A} \frac{P_{\text{metal}}}{P_{\text{oxide}}} \]  

where \( n \) = number of metal atoms per molecule of oxide, \( M \) = molecular weight oxide, \( A \) = atomic weight metal, \( P_{\text{metal}} \) = density of metal, \( P_{\text{oxide}} \) = density of oxide.

<table>
<thead>
<tr>
<th>Metal and oxide</th>
<th>n</th>
<th>A</th>
<th>M</th>
<th>( P_{\text{metal}} )</th>
<th>( P_{\text{oxide}} )</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be (BeO)</td>
<td>1</td>
<td>9.02</td>
<td>25.02</td>
<td>1.85</td>
<td>3.02</td>
<td>1.70</td>
</tr>
<tr>
<td>Cr (Cr₂O₃)</td>
<td>2</td>
<td>52.01</td>
<td>152.02</td>
<td>6.92</td>
<td>5.21</td>
<td>1.94</td>
</tr>
<tr>
<td>Al (Al₂O₃)</td>
<td>2</td>
<td>26.97</td>
<td>101.94</td>
<td>2.7</td>
<td>3.5-3.9</td>
<td>1.3-1.5</td>
</tr>
</tbody>
</table>

The values of E in Table 4 are in good agreement with the well-known strong adhesion of oxide films to aluminum and the poor adhesive characteristics of BeO. The data for chromium suggest that the oxide films should not be adherent to this metal. This is in fact true when chromium is massively oxidized, i.e., under these conditions the oxides tend to spall off badly. With relatively mild oxidation, however, the films on stainless steel are known to be extremely adherent. Chromium, however, can form a lower oxide CrO, and, if it is assumed that this rather than Cr₂O₃ is produced in direct contact with the metal on reaction with Na₂O in the presence of sodium, E will be significantly lower. If, for example, it is assumed that \( \rho_{\text{CrO}} = 6.0, \rho_{\text{CrO}_2} = 1.5, \) which is very close to the value for Al₂O₃, a further point to be kept in mind is the fact that the adhesion of Cr₂O₃ to stainless steel may be improved over its adhesion to chromium by the presence of the iron and nickel in the system and that these substances may strengthen the bond by formation of compounds, such as iron and nickel chromites.

These three examples illustrate the complexity of the subject and may account for the fact that in spite of the several years of work in a large number of laboratories the amount of useful basic data is still small, although a rather substantial body of engineering test results are available. Most of the work has been done at ANL, KAPL, the Naval Research Laboratory (NRL), MSA, and BW, with NaK alloys rather than sodium, but to date comparatively few essential differences between these liquids have been observed with respect to corrosion, and in the discussion which follows the equivalence of these materials will be assumed. A possible exception to this statement is type 310 stainless steel, which is reported to show weight gains consistently in sodium and 50-50 NaK over a temperature range up to 650°C and shows weight losses in eutectic NaK, containing about 80 per cent potassium at 760°C.

With these preliminary remarks on the corrosion of metals by sodium, we shall proceed to an examination of the available data and the conclusions to be drawn from them. Two types of corrosion testing are considered. In the so-called "static" experiments a metal sample is immersed in liquid sodium in an inert at-
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

mosphere at constant temperature for a specified time, after which, change in weight and other properties are observed. In these tests saturation or chemical equilibrium is often achieved in the time required for the test, so that beyond this point no significant changes occur in the properties of the system. For use in heat-transfer systems the "dynamic" corrosion tests are somewhat more informative and useful.

static-corrosion tests, as previously described. For many metals only the results of these tests are available at present. There are, however, certain very serious limitations and objections to this type of test. The final experimental value for the corrosion rate is often the net result of a large number of competing reactions, and in many cases important details are obscured by side reactions. Thus, for example, the

The dynamic tests are carried out by immersing the metal sample in a stream of flowing sodium, which may be in motion in a closed circuit owing either to thermal convection or mechanical pumping. One part of the system, the "hot zone," where the sample is located, is maintained at a temperature \(\Delta T\) degrees above that of the "cold zone." The sample is examined for weight change, alteration of metallographic characteristics, etc., after exposure, as in the static tests.

C. CORROSION OF METALS BY SODIUM IN STATIC SYSTEMS

1. Introductory Remarks

In order to determine the relative stability of metals in sodium, most investigators have first carried out influence of a third substance on the corrosion rate is in many cases large. In the tables which follow, where the data are definite and clear-cut, this effect has been indicated. In these tests when a sample is removed from sodium, it is necessary to clean off the excess sodium before reweighing. This is usually done with water or alcohol, and the lack of reproducibility of the data may be due, to a considerable extent, to details of this procedure. Precautions against the presence of oxygen contamination, either from the sodium or the inert gas blanket, are necessary in all this work. Whenever oxygen enters the picture it almost always increases the corrosion rate. Other elements—carbon, in the case of ferrous alloys, arising from free carbon or the presence of higher carbon steels, iron in the presence of nickel alloys, nickel in the presence of copper alloys—often show similar

Fig. 2—Argonne NaK static-corrosion test setup.
Large effects, some of which will be apparent in the tables. Discrepancies between the work of various laboratories in most cases must be attributed to these factors, e.g., the data on molybdenum, tantalum, and niobium (columbium).

Four laboratories have done principal static-corrosion work with sodium and NaK alloys: ANL (Kelman et al., KAPL (Vandenberg et al.), MSA (Jackson, Tidball, and coworkers), and BW (Piotter and Young, references 5, 6, 8a, 8b, 8c, 105). A large number of different NaK alloys, from pure sodium to pure potassium, have been used; as will be seen from the tables, however, the precision of the work does not allow clear differentiation between the corrosion rates for these liquids on most materials, as far as static corrosion is concerned. In preparing the data which follow, experiments in which there was clear indication of impure liquid or of other accidental error were not used. When several experiments were carried out under supposedly identical conditions, so that only statistical errors were present, the several data were averaged. This procedure is admittedly crude (and may conceal some miscellaneous details), but it has been followed uniformly for the work of all the laboratories and is considered to provide a fair basis for comparing the data. As has previously been pointed out, all corrosion figures may be in error by a factor of as much as 10, and engineering design should allow sufficiently large safety factors to take this, as well as the presence of possible contaminants, into account. When experiments resulted in no weight change within the error of weighing, the notation "2" has been used, followed by a sufficient number of zeros to indicate the order of precision of the measurements.

2. Comparison of Static Corrosion Test Data (R_T in mg/cm²-month)

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>KAPL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, °C</td>
<td>Time, hr</td>
</tr>
<tr>
<td>Uranium</td>
<td>200†</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
</tr>
<tr>
<td>U-Al alloy (40 per cent U)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>660</td>
<td>164</td>
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<td>U-Al alloy (31 per cent U)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>167</td>
</tr>
<tr>
<td>Thorium</td>
<td>200</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
</tr>
<tr>
<td>Beryllium§</td>
<td>200</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>156</td>
</tr>
</tbody>
</table>

*All ANL experiments in 56 per cent sodium - 44 per cent potassium alloy purified by deoxidation with uranium chips. All KAPL data for sodium purified by gettering with beryllium or calcium.
†In container of same material.
In presence of beryllium, niobium, molybdenum, nickel, and ferrous alloys.
§Extruded material only. Sintered beryllium soaks up liquid metal into the pores.
Table 6 — Ferrous Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL a</th>
<th>KAPL a</th>
<th>MSA b</th>
<th>BW c</th>
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<tbody>
<tr>
<td></td>
<td>T, °C</td>
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<td>hr</td>
<td>R T</td>
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<td>Armco iron</td>
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<td>+0.06</td>
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<td>-0.2</td>
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</tr>
<tr>
<td></td>
<td>400</td>
<td>144</td>
<td>-0.2</td>
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<td>SAE 1020 steel</td>
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<td>144</td>
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<td>500</td>
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<td></td>
<td>600</td>
<td>144</td>
<td>-1.0</td>
<td>600</td>
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<tr>
<td></td>
<td>800</td>
<td>144</td>
<td>+0.7</td>
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</tr>
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<td>SAE 1095</td>
<td>600</td>
<td>144</td>
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</tr>
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<td>SAE S2100 steel</td>
<td>450</td>
<td>144</td>
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<tr>
<td>(ball-bearing steel)</td>
<td>800</td>
<td>144</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>Wrought iron</td>
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<td>825 (b.p.)</td>
<td>100</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(56% Na)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56% Na)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(100% Na)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56% Na)</td>
<td>760</td>
</tr>
<tr>
<td>SAE 1018 steel</td>
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<td>144</td>
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<td>500</td>
</tr>
<tr>
<td>Stainless steel</td>
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<td>144</td>
<td>+0.3</td>
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</tr>
<tr>
<td>(type 302)</td>
<td>600</td>
<td>144</td>
<td>-0.4</td>
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<td>(type 303)</td>
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<td>892 (b.p)</td>
<td>500</td>
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<td></td>
<td>(100% Na)</td>
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<td>(type 310)</td>
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<td>871</td>
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<td></td>
<td>850</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>+1.1</td>
<td>500</td>
</tr>
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<td></td>
<td>600</td>
<td>144</td>
<td>+2.7</td>
<td>500</td>
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<tr>
<td>Stainless steel</td>
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<td>144</td>
<td>+0.00</td>
<td></td>
</tr>
<tr>
<td>(type 340)</td>
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<td></td>
<td>850</td>
<td>185</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>600</td>
<td>144</td>
<td>+3.7</td>
<td></td>
</tr>
<tr>
<td>(type 321)</td>
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</tr>
<tr>
<td>5% Cr-0.5% Mo steel</td>
<td>500</td>
<td>184</td>
<td>+0.1</td>
<td></td>
</tr>
<tr>
<td>5% Cr-0.5% Mo-0.5% Ti steel</td>
<td>500</td>
<td>169</td>
<td>-0.1</td>
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</tbody>
</table>
Table 6 (Continued)

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>KAPL</th>
<th>MSA</th>
<th>BW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T. °C</td>
<td>Time, hr</td>
<td>R_T</td>
<td>T. °C</td>
</tr>
<tr>
<td>High-speed steel&lt;sup&gt;1&lt;/sup&gt;</td>
<td>500</td>
<td>166</td>
<td>+0.04</td>
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<tr>
<td>High-temperature steel&lt;sup&gt;2&lt;/sup&gt;</td>
<td>500</td>
<td>168</td>
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<tr>
<td>2% Cr-1% Mo steel</td>
<td>500</td>
<td>184</td>
<td>+0.1</td>
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<td>Worthite&lt;sup&gt;3&lt;/sup&gt;</td>
<td>500</td>
<td>169</td>
<td>+0.2</td>
<td>760</td>
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<tr>
<td>Croloy 2-½&lt;sup&gt;4&lt;/sup&gt;</td>
<td>500</td>
<td>184</td>
<td>+0.5</td>
<td>760</td>
</tr>
<tr>
<td>Croloy 5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>500</td>
<td>180</td>
<td>+0.9</td>
<td>760</td>
</tr>
<tr>
<td>Croloy 7&lt;sup&gt;6&lt;/sup&gt;</td>
<td>500</td>
<td>184</td>
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<tr>
<td>Croloy 9&lt;sup&gt;7&lt;/sup&gt;</td>
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<td>184</td>
<td>+0.3</td>
<td>760</td>
</tr>
<tr>
<td>9% Ni steel</td>
<td>500</td>
<td>184</td>
<td>+0.6</td>
<td>760</td>
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<tr>
<td>Hadfield's Mn steel</td>
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<td>144</td>
<td>-1.3</td>
<td>760</td>
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<tr>
<td>(1 to 1.5% C — 10 to 15% Mn)</td>
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<td></td>
<td></td>
<td>760</td>
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<tr>
<td>Nitralloy G&lt;sup&gt;6&lt;/sup&gt;</td>
<td>300</td>
<td>144</td>
<td>-4.0</td>
<td>760</td>
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<tr>
<td>Sicromo 5S&lt;sup&gt;8&lt;/sup&gt;</td>
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<td>144</td>
<td>-4.0</td>
<td>760</td>
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<td>Fernico</td>
<td>300</td>
<td>144</td>
<td>-4.0</td>
<td>760</td>
</tr>
<tr>
<td>Fe-P brazing alloy</td>
<td>500</td>
<td>336</td>
<td>+0.3</td>
<td>760</td>
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</tbody>
</table>

<sup>1</sup>All ANL experiments in 56 per cent sodium—44 per cent potassium alloy purified by deoxidation with uranium chips. All KAPL data on sodium purified by gettering with beryllium or calcium.

<sup>2</sup>MSA samples were tested in a number of different NaK alloys and in pure metal. The weight per cent sodium is shown in parentheses in the time column. Oxygen content of NaK was not controlled, and these results may all be high.

<sup>3</sup>All BW samples were tested in NaK containing 20 per cent sodium.

<sup>4</sup>No additional metals in system.

<sup>5</sup>In presence of other ferrous alloys, uranium, thorium, aluminum bronze, beryllium, nickel, niobium, or molybdenum.

<sup>6</sup>Wrought iron: 0.5 per cent carbon, 0.04 per cent manganese, 0.126 per cent phosphorus, 0.03 per cent nitrogen, remainder iron.

<sup>7</sup>See also Table 13.

<sup>8</sup>Very slight weight gain after 5000 hr.

Designation: Cr, C, Mn, S, P, Si, Mo,

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr,</th>
<th>C,</th>
<th>Mn,</th>
<th>S,</th>
<th>P,</th>
<th>Si,</th>
<th>Mo,</th>
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</thead>
<tbody>
<tr>
<td>2-½</td>
<td>2.25</td>
<td>0.15</td>
<td>0.3-0.6</td>
<td>0.045</td>
<td>0.03</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.15</td>
<td>0.3-0.6</td>
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<td>0.03</td>
<td>0.5</td>
<td>0.55</td>
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<td>7</td>
<td>7</td>
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<td>0.3-0.6</td>
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<td>0.03</td>
<td>0.5-1</td>
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<td>9</td>
<td>9</td>
<td>0.15</td>
<td>0.3-0.6</td>
<td>0.03</td>
<td>0.03</td>
<td>0.5-1</td>
<td>1</td>
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</tbody>
</table>

<sup>9</sup>Nitralloy G: 0.4 per cent carbon, 0.5 per cent manganese, 1 per cent aluminum, 0.3 per cent silicon, 1.5 per cent chromium, 0.2 per cent molybdenum, remainder iron. Samples had nitrided surfaces.

<sup>10</sup>Sicromo 5S: 1.5 per cent silicon, 5 per cent chromium, 0.5 per cent molybdenum.

<sup>11</sup>Fernico: 54 per cent iron, 28 per cent nickel, 15 per cent cobalt.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Table 7 — Nickel-base Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>KAPL</th>
<th>MSA</th>
<th>BW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, °C hr</td>
<td>Time,</td>
<td>T, °C hr</td>
<td>Time,</td>
</tr>
<tr>
<td>Nickel</td>
<td>200 144 -0.15</td>
<td>500 144-168</td>
<td>0.1</td>
<td>825 (b.p.) 100 (56% NaK) 50.00</td>
</tr>
<tr>
<td></td>
<td>450 144 -0.04</td>
<td>600 185 -0.1</td>
<td>825 (b.p.) 500 (56% NaK) -3.9</td>
<td></td>
</tr>
<tr>
<td>Ni-Mn brazing rod</td>
<td>600 144 -0.3</td>
<td>600 144 -0.2</td>
<td>600 144 -0.08</td>
<td></td>
</tr>
<tr>
<td>Invar (31% Ni-Fe alloy)</td>
<td>600 144 -0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inconel</td>
<td>600 144 -0.5</td>
<td>500 144-2850</td>
<td>-0.04</td>
<td>825 (b.p.) 100 (56% NaK) -26</td>
</tr>
<tr>
<td></td>
<td>600 144 -2.2</td>
<td>700 144 -5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monel</td>
<td>600 144 -2.3</td>
<td>500 125-168</td>
<td>-0.6</td>
<td>825 (b.p.) 500 (56% NaK) -8</td>
</tr>
<tr>
<td>Nichrome</td>
<td>600 144 -0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hastelloy A</td>
<td>600 144 -0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hastelloy B</td>
<td>600 144 -0.2</td>
<td>500 168 -0.15</td>
<td>760-870 500 (56% NaK) -99</td>
<td></td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>600 144 -0.9</td>
<td>500 168 -0.2</td>
<td>760-870 500 (34% NaK) -5.1</td>
<td></td>
</tr>
<tr>
<td>Hastelloy D</td>
<td>600 144 -0.15</td>
<td>500 168 -0.1</td>
<td>600 165 -2</td>
<td></td>
</tr>
<tr>
<td>Alnico 5</td>
<td>500 168 +0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inco alloy No. 83</td>
<td>500 166 +0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inco alloy No. 77</td>
<td>500 166 -0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inco alloy No. HF 4095</td>
<td>500 165 -0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel welding rod</td>
<td>500 166 +0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo brazing alloy (90-90 and 60-40)</td>
<td>500 720 -0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo brazing alloy (50-50)</td>
<td>500 336 +2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-P brazing alloy (90-10)</td>
<td>500 336 +2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1ANL experiments, except as noted, in 56 per cent sodium—44 per cent potassium alloy purified by deoxidation with uranium chips. All KAPL data for sodium purified by gettering with beryllium or calcium.
2MSA samples were tested in a number of different NaK alloys and in pure metal. The weight per cent is shown in parentheses in the time column. Oxygen content of NaK was not controlled, and these results may all be high.
3All BW samples were tested in NaK containing 20 per cent sodium.
4In presence of iron and ferrous alloys.
5In absence of iron alloys.
6In eutectic NaK (23 per cent sodium—77 per cent potassium) in the presence of iron alloys.
7In eutectic NaK (23 per cent sodium—77 per cent potassium) in the absence of iron alloys.
8When A/V = 2 cm⁻¹.
9When A/V = 0.3 cm⁻¹.
10In presence of nickel.
11No other metallic components present.

Nichrome: The Nichromes are Ni-Cr alloys containing varying amounts of iron and other constituents. A typical analysis is that for Nichrome IV: 83 per cent nickel, 16 per cent chromium, 0.8 per cent iron, 0.5 per cent manganese, 0.2 per cent silicon.

Nominal composition of Hastelloys:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Ni, %</th>
<th>Fe, %</th>
<th>Mn, %</th>
<th>Mo, %</th>
<th>Other, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50</td>
<td>20</td>
<td>1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>60</td>
<td>7</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>7</td>
<td>20</td>
<td>Cr, 18; W, 6</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>85</td>
<td>2</td>
<td></td>
<td>Cu, 3; Si, 10</td>
<td></td>
</tr>
</tbody>
</table>

Alnico 5: 8 per cent aluminum, 14 per cent nickel, 24 per cent cobalt, 3 per cent copper, remainder iron.

Inco alloys:

<table>
<thead>
<tr>
<th>No.</th>
<th>No. HF 4085</th>
<th>No.</th>
<th>No. HF 4085</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn, %</td>
<td>0.3</td>
<td>1.9</td>
<td>Zr, %</td>
</tr>
<tr>
<td>Si, %</td>
<td>0.25</td>
<td>2.3</td>
<td>C, %</td>
</tr>
<tr>
<td>Ti, %</td>
<td>0.065</td>
<td>0.08</td>
<td>Ni, %</td>
</tr>
<tr>
<td>Mg, %</td>
<td>0.068</td>
<td>0.10</td>
<td>Ni to make 100%</td>
</tr>
</tbody>
</table>

Nickel welding rod: 2.9 per cent tantalum, 0.89 per cent aluminum, 0.58 per cent silicon, 1.0 per cent magnesium, 0.02 per cent carbon, remainder nickel.
Table 8 — Copper-base Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>KAPL</th>
<th>BWb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$, °C</td>
<td>Time, hr</td>
<td>$R_T$</td>
</tr>
<tr>
<td>Phosphorus-deoxidized</td>
<td>200</td>
<td>144</td>
<td>−0.3</td>
</tr>
<tr>
<td>Copper</td>
<td>450</td>
<td>144</td>
<td>−0.07</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>−2.5</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>−85</td>
</tr>
<tr>
<td>Beryllium copper</td>
<td>600</td>
<td>144</td>
<td>+2.4</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>−1.4</td>
</tr>
<tr>
<td>Aluminum bronze</td>
<td>600</td>
<td>144</td>
<td>−0.4</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>−0.1</td>
</tr>
<tr>
<td>Brass</td>
<td>200</td>
<td>144</td>
<td>−0.4</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>+34</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>144</td>
<td>−230</td>
</tr>
<tr>
<td>Super nickel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cupro nickel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel silver</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambraloy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver-bearing copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Everdur</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trodaloy No. 11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*ANL experiments, except as noted, in 56 per cent sodium–44 per cent potassium alloy purified by deoxidation with uranium chips. All KAPL data for sodium purified by gettering with beryllium or calcium.

†All BW samples were tested in NaK containing 20 per cent sodium.

‡Electrolytic copper undergoes serious intergranular attack.

§In vessel containing 63 ml of NaK.

In presence of nickel, all copper-base alloys (except aluminum bronze) are drastically affected by the presence of this substance in the same system.

In presence of ferrous and nickel alloys.

In presence of nickel only.

Super nickel: 70 per cent copper, 30 per cent nickel.

Cupro nickel: 80 per cent copper, 20 per cent nickel.

Nickel silver: 65 per cent copper, 18 per cent nickel, 17 per cent zinc.

Ambraloy: 75 per cent copper, 20 per cent nickel, 5 per cent zinc.

Ambraloy: 95 per cent copper, 5 per cent aluminum.

Everdur: 95.8 per cent copper, 3.1 per cent silicon, 1.1 per cent manganese.

Table 9 — Refractory Metals

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>KAPL</th>
<th>BW (NaK, 80°, Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$, °C</td>
<td>Time, hr</td>
<td>$R_T$</td>
</tr>
<tr>
<td>Niobium</td>
<td>600</td>
<td>144</td>
<td>−1.1</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>600</td>
<td>144</td>
<td>+0.00</td>
</tr>
<tr>
<td>Tantalum†</td>
<td>450</td>
<td>144</td>
<td>−0.6</td>
</tr>
<tr>
<td>Titanium</td>
<td>600</td>
<td>144</td>
<td>−2.5</td>
</tr>
<tr>
<td>Wolfram (tungsten)</td>
<td>400</td>
<td>144</td>
<td>+0.00</td>
</tr>
<tr>
<td>Zirconium</td>
<td>600</td>
<td>144</td>
<td>+0.6</td>
</tr>
<tr>
<td>Vandium</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*ANL experiments, except as noted, in 56 per cent sodium–44 per cent potassium alloy purified by deoxidation with uranium chips. All KAPL data on sodium gettered with beryllium or calcium.

†Extremely sensitive to oxygen.

‡The oxide film on titanium was flaky and nonadherent on removal from the NaK bath.
Table 10 — Other Metals and Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL(^{a,b})</th>
<th>KAPL(^{a})</th>
<th>MSA(^{a})</th>
<th>BW(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hr R(_T)</td>
<td>hr R(_T)</td>
<td>hr R(_T)</td>
<td>hr R(_T)</td>
</tr>
<tr>
<td>Aluminum 2S</td>
<td>200 144 ±0.00</td>
<td>400 168 -2</td>
<td>538 200 -13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 144 +0.6</td>
<td>500 168 -3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum 3S(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum 24S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum 52S(^d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>800 144 +0.6</td>
<td>500 168 -0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stellite No. 1(^e)</td>
<td>600 144 -0.06</td>
<td>500 168 +0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stellite No. 6(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stellite No. 12(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stellite No. 21</td>
<td>450 168 -30</td>
<td>760 -870 500</td>
<td>(56% NaK) -11</td>
<td></td>
</tr>
<tr>
<td>Multimet N-155(^f)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitallium(^f)</td>
<td>500 184 +6</td>
<td>760 -870 500</td>
<td>(56% NaK) +90</td>
<td></td>
</tr>
<tr>
<td>Tantung(^f)</td>
<td>500 720 -0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)ANL experiments in 56 per cent sodium-44 per cent potassium alloy purified with uranium chips. KAPL data on sodium gettered with beryllium or calcium. BW data in 20 per cent sodium-80 per cent potassium alloy. MSA samples as shown in time column.

\(^{b}\)Silver, gold, platinum, and silicon are drastically attacked by NaK according to ANL.

\(^{c}\)3S-O, -8H, and -H samples gave -5.0, -3.5, and -2.6. The figure given in the table is the mean of these three.

\(^{d}\)Similar small heat-treatment effects were noted with other aluminum alloys, but the differences are all negligible.

\(^{e}\)In presence of iron alloys.

\(^{f}\)Composition of Stellites and Multimet:

<table>
<thead>
<tr>
<th></th>
<th>Co, %</th>
<th>Cr, %</th>
<th>W, %</th>
<th>Ni, %</th>
<th>Other, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stellite No. 1</td>
<td>43</td>
<td>34</td>
<td>14</td>
<td></td>
<td>To make 100</td>
</tr>
<tr>
<td>Stellite No. 6</td>
<td>55</td>
<td>33</td>
<td>6</td>
<td></td>
<td>To make 100</td>
</tr>
<tr>
<td>Stellite No. 12</td>
<td>47</td>
<td>34</td>
<td>10</td>
<td>1.5-3.5 C 0.2-0.35</td>
<td></td>
</tr>
<tr>
<td>Stellite No. 21</td>
<td>To make 100</td>
<td>25-30</td>
<td></td>
<td>Mo 4.5-6.5</td>
<td></td>
</tr>
<tr>
<td>Multimet N-155</td>
<td>19-23</td>
<td>19-23</td>
<td>1.5-3.5</td>
<td>19-23</td>
<td>Fe 2 max.</td>
</tr>
</tbody>
</table>

\(^{f}\)Vitallium: 26 per cent chromium, 5.7 per cent molybdenum, 3 per cent nickel, 2 per cent iron, 0.32 per cent manganese, 0.31 per cent carbon, remainder cobalt.

\(^{e}\)Tantung: 45-50 per cent cobalt, 27-32 per cent chromium, 14-19 per cent wolfram, 2-7 per cent tantalum plus niobium, 2-4 per cent carbon, 2-5 per cent iron, 1-iron, 1-per cent manganese.
NOTE. Additional results were reported by KAPL after the preparation of the bulk of the tables above, using calcium-gettered sodium. These results are shown in Table 11. All R_T values are good to about ±0.03 mg/cm²-month. A review of the current status (May 1950) of the KAPL sodium studies is given by Koenig. 117

Table 11 — Newer Static-corrosion Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>T, °C</th>
<th>Time, hr</th>
<th>R_T, mg/cm²-month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>500</td>
<td>730</td>
<td>-0.04</td>
</tr>
<tr>
<td>(type 347)</td>
<td>500</td>
<td>168</td>
<td>-0.06</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>500</td>
<td>730</td>
<td>-0.05</td>
</tr>
<tr>
<td>(type 347, plated with 0.0005 in. Cr)</td>
<td>500</td>
<td>168</td>
<td>-0.05</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>500</td>
<td>730</td>
<td>-0.05</td>
</tr>
<tr>
<td>(type 347, plated with 0.0005 in. hard Cr over 0.0005 in. Ni)</td>
<td>500</td>
<td>168</td>
<td>-0.02</td>
</tr>
<tr>
<td>Nitrided stainless steel</td>
<td>500</td>
<td>730</td>
<td>-0.32</td>
</tr>
<tr>
<td>(type 347)</td>
<td>500</td>
<td>168</td>
<td>-1.79</td>
</tr>
<tr>
<td>QM Be</td>
<td>500</td>
<td>730</td>
<td>-0.15</td>
</tr>
<tr>
<td>40% Ni-60% Mn</td>
<td>500</td>
<td>730</td>
<td>-0.09</td>
</tr>
<tr>
<td>80% Ni-20% Mn</td>
<td>500</td>
<td>730</td>
<td>-0.30</td>
</tr>
<tr>
<td>OFHC copper</td>
<td>500</td>
<td>730</td>
<td>-0.06</td>
</tr>
<tr>
<td>Zirconium</td>
<td>500</td>
<td>730</td>
<td>-0.24</td>
</tr>
<tr>
<td>Titanium</td>
<td>500</td>
<td>168</td>
<td>-0.52</td>
</tr>
</tbody>
</table>

3. Theory of Static Corrosion

Even the simple static corrosion test is complicated by numerous side reactions and involved phase-interaction phenomena.

Work at KAPL on the mechanism of static corrosion by sodium has been largely guided by the experience available in the General Electric Co. on the corrosion of metals by liquid mercury. 40, 118 Corrosion by mercury was found to be due essentially to solution of the metal. In this and the following sections, this vastly over-simplified concept will be applied to the available data on liquid sodium.

Theories of the rate of solution of solids in liquids all go back to the original work of Noyes and Whitney. 106 In recent years this work has been continued by a number of workers (references 68 to 74, 136, and 151).

Applied to this problem these theories lead to the expression

\[
\frac{dS}{dt} = \alpha \frac{A}{V} (S^0 - S)
\]

which upon integration yields

\[
R_T = \frac{W_T}{\alpha T}
\]

where \( S^0 \) = the amount of solute present in the solvent at time \( t \), when \( A \) cm² of a solid surface are exposed to \( V \) cm³ of liquid.

\[
S = S^0 \left[ 1 - \exp \left( -\frac{\alpha t}{V} \right) \right]
\]

where \( \alpha \) = the specific solution rate constant, expressed in velocity units (cm/sec in the cgs system).

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Applied to this problem these theories lead to the expression

\[
\frac{dS}{dt} = \alpha \frac{A}{V} (S^0 - S)
\]

which upon integration yields

\[
R_T = \frac{W_T}{\alpha T}
\]

where \( W_T \) is the total loss in weight of the specimen in a time \( t \). But the quantity of solute disappearing from the solid surface is that in solution and

\[
W_T = -S_T V \rho_S^0
\]

where \( \rho_S^0 \) is the density of the solvent if \( S_T \) is expressed in weight-ratio units (grams of solute per gram of solvent or parts per million by weight). Introducing the value of \( S_T \) from Eq. 6

\[
R_T = -S_T V \rho_S^0 \left[ 1 - \exp \left( -\frac{\alpha T}{V} \right) \right]
\]

The initial value of \( -R_T \) is \( -\alpha S_T \rho_S^0 \). This value decreases exponentially with time. Static tests are usually run to saturation equilibrium, where \( t \gg (V/\alpha T) \) so that there is virtually no weight change after this time. Under these conditions Eq. 9 reduces to

\[
R_T \approx -S_T V \frac{\rho_S^0}{\alpha T}
\]

It should be noted that this asymptotic expression for \( R_T \) is not a time-independent measure of the corrosion rate but that the product of \( R_T \) and \( t \) is a constant for
any given temperature and geometry. This constitutes a serious flaw in the reporting of static-test data in that $t$ enters into the equation. Different metals should not only be compared under the same conditions as to $T$ and $A/V$ but also as to total exposure time.

The best test data for the dependence of $R_T$ on $t$ come from the BW experiments on type 310 stainless steel at 760°C; these results are shown in Table 12.

In the last column of Table 12 are shown values of $R_T$, computed from the empirical equation

$$R_T = \frac{S \rho_T}{A t} \left[ 1 - \exp \left( -\alpha T \frac{A}{V} \right) \right]$$

where $t$ is in hours. The constants in this equation were obtained by fitting the experimental data at the 200- and 1500-hr points. The agreement is quite satisfactory for all values of $t$, considering the accuracy of the experimental results.

The Babcock & Wilcox Co. has also carried out a series of extremely interesting tests on corrosion rates in NaK (containing 20 per cent sodium) at 760°C, as a function of time. These rates were compared with the corrosion rates of samples exposed to argon gas for the same time and temperature. The data are summarized in Table 13. The corrosion observed in argon in some cases can probably be attributed to residual impurities in the gas. This juxtaposition of corrosion data in NaK and an inert gas illustrates rather strikingly the relatively small $R_T$ values encountered with liquid alkali metals. With the single exception of type 316 stainless steel (which can probably be attributed to experimental error), all the materials considered show a decrease of the corrosion rate in NaK with time, as in the case of the type 310 stainless steel, above. This may be taken to indicate that equations of the general form of Eqs. 9 or 11 are valid for a considerable number of materials.

The fundamental constants in static corrosion are $\alpha_T$ and $S^\circ_T$. Greater insight into the nature of static corrosion would be possible if care were taken to measure $A/V$ and if enough points were obtained to compute these constants. The resulting data could then be compared directly with equilibrium solubility and solution-rate data, which can be obtained in independent experiments. Considerable experimental deviation would probably occur, however, owing to other variables entering into consideration.

In the above paragraphs it was assumed that the container used in the static tests was inert compared with the sample. This can never be entirely true, and in practice it is customary whenever possible to carry out the test in a container fabricated from the same material as the sample itself. The equations for this case can be derived quite simply.
LEO F. EPSTEIN AND CLIFFORD E. WEBER

Let the subscript s refer to the sample and c to the container. Then

\[ W_s = -RT_A s t \]
\[ W_c = -RT_A c t \]  

For large values of \( t \) corresponding to Eq. 10

\[ R_T = \frac{-S^2 V}{(A_s + A_c)} t \]  

It should be noted that in isothermal static systems when the mechanism of action of the liquid on the solid metal is simple solution, as described above, it should be possible to reduce the corrosion to a negligibly low value by presaturating the fluid with solid at the temperature of operation before introducing it into the system. Cases of this sort, however, where no variations of temperature occur, are rare in practice, and this device has found relatively little use. It should, however, be kept in mind as a possible solution of the corrosion problem under conditions where it can be carried out appropriately.

The most important mechanism for weight gains in corrosion is perhaps the formation of an adherent oxide film. In this case a simple analysis may also be formulated for positive RT values. Let \( p \) be the number of grams of oxygen per 100 grams of sodium initially present, so that the total weight of oxygen present in the system is \( (pV/100) \) grams of oxygen. This Na\(_2\)O is assumed to react with the metal M according to either of the equations

\[ aM + bNa_2O \rightarrow M_2O_b + 2bNa \]  
\[ aM + (b + x)Na_2O \rightarrow xNa_2O\cdot M_2O_b + 2bNa \]  

The latter reaction would be expected, for example, with strongly acidic oxides like ZrO\(_2\) and TiO\(_2\), which can form well-characterized salts with the alkali metal oxides. For short test periods \( R_T \) may be affected by a number of factors, such as the rate of reaction of Na\(_2\)O and the metal, the rate of diffusion of the oxide through the liquid, the rate of solution of solid Na\(_2\)O in the liquid, and may have almost any finite value. While this case is subject to analysis, the results are complex and the resulting development is only descriptive and qualitative. If the test period is long so that the reaction goes to completion, all the oxygen in the system may be adherent to the metal as \( M_2O_b \) or the mixed oxide. The increase in weight of the metal W will then be given by

\[ W = -pV \frac{\rho^2}{100} \]  

The apparent rate (exact only for a uniform oxidation rate) corresponding to this is

\[ R_T = \frac{-pV \rho^2}{100 A_t} \]  

or for the case of a container of the same material as the test sample, rather than an inert container,

\[ R_T = \frac{pV \rho^2}{100 (A_s + A_c)} t \]  

It will be noted from this equation that the quantity \( R_T(A_s + A_c)/V \) should be constant, all other factors being equal. The ANL results in Table 14 give enough data to test this relation in only one case (type 347 stainless steel, \( t = 144 \) hr, \( T = 600^\circ C, \) NaK, 56 per cent sodium). The results, while not startlingly good, show that the quantity \( R_T(A_s + A_c)/V \) is more nearly constant than \( R_T \) itself.

Table 14—Dependence of Corrosion Rate on the Surface to Volume Ratio

<table>
<thead>
<tr>
<th>( R_T ) mg/cm(^2)-month</th>
<th>( (A_s + A_c)/V ) cm(^{-1} )</th>
<th>( R_T(A_s + A_c)/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.05</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>+1.1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

It is quite possible that the reaction of Eq. 13 does not go to completion but stops with the formation of a stable salt-like compound of the form Na\(_2\)O-M\(_L\)O\(_b\) according to Eq. 14; this fact, however, does not change the quantitative formulation of \( R_T \). The validity of the assumption of a completely insoluble adherent oxide is somewhat questionable. Also it is conceivable that the oxidation reaction, which leads to a positive \( R_T \), and the solution of the metal in sodium may occur simultaneously. The relative rates of these two processes, plus any weight losses due to solution or spalling off of the oxide films, can consequently lead to a whole range of values for \( R_T \). As a matter of fact, while positive weight changes are usually found with type 347 stainless steel, when the sodium is highly purified to remove Na\(_2\)O, this material tends to lose weight (see Sec. III-C-2), and it may be supposed that for \( p \), vanishingly small, the solution mechanism is the more important.

For a heterometallic system where mass-transfer effects are of importance (see Sec. IV-A), an entirely different mechanism of weight change is possible. This type of phenomenon is especially prominent with systems in which there is strong interaction between the constituents involved. In most cases the resulting compound-formation or solid-solution surface layers are adherent, but a few examples of nonadherent intermetallic reaction products have been observed. From
USE OF MOLten Sodium As A heat transfer fluid

the arguments previously developed it will be apparent that this situation may then result in positive, zero, or negative values of \( R_T \).

From these relations it is plain that the static test has serious disadvantages from a fundamental point of view. Some of these are:

1. For long test periods the apparent corrosion rate varies inversely with the duration of the run, all other factors being equal.
2. To obtain significant changes in sample weight, the container should be inert to action of the solvent or made of the same material as the sample, and the area of the exposed surface of the container, as well as the sample, should be taken into account. No foreign substances should be present in the system.
3. In the case of metals which can reduce \( \text{Na}_2\text{O} \), positive, negative, or zero weight changes may be observed depending upon the oxygen content of the sodium, the adherent characteristics of resulting surface layers, and the relative rates of the solution and reduction processes.
4. The isothermal static test does not reproduce the conditions of flow and varying temperatures encountered in a heat-transfer system.

In order to avoid some of these problems and to obtain a realistic measure of corrosion under conditions which more nearly resemble those in systems of engineering importance, the static experiments have been used essentially as screening tests, to be followed, for materials of interest, by the dynamic tests. The following sections discuss the nature of these experiments and some of the results which have been obtained. It should not be supposed from these comments that the static test has no practical use other than preliminary corrosion observations. Its speed and relative simplicity make it quite useful for a number of different applications. Thus, for example, Van-denberg at KAPL uses short-time static-corrosion tests on type 347 stainless steel to monitor the amount of oxygen and other impurities in sodium, the idea being that corrosion is much more sensitive to small amounts of some of these constituents than any known method of chemical analysis. Other applications, similar in principle, are conceivable.

4. Miscellaneous Topics in Static Corrosion

a. Vapor-phase Corrosion Studies. A few laboratories have investigated static corrosion by vapors of sodium and NaK as well as by the liquid metals. These tests were carried out in a static-corrosion pot, with the sample suspended in the gas space above the liquid; the temperature used was the boiling point of the fluid and the pressure generally at or close to 1 atm. Experimental work along these lines has been conducted by MSA, Si80, Si8a and BW. The data are summarized in Table 15; the liquid corrosion rate is also given for comparison. All the BW studies were carried out at 760°C for 200 hr in NaK containing 20 per cent sodium.

These data are relatively old and were obtained at a time when purification procedures and handling technique were relatively crude, which may explain some of the discrepancies which will be noted in this table. They are perhaps rather too meager to warrant drawing quantitative conclusions. Vapor corrosion should show a number of effects not observed in the liquid, e.g., because of the relative nonvolatility of \( \text{Na}_2\text{O} \)

<table>
<thead>
<tr>
<th>Material</th>
<th>Time, ( \text{hr} )</th>
<th>( T, ^\circ\text{C} )</th>
<th>Alloy, ( % \text{Na} )</th>
<th>Vapor phase, ( R_T, \text{mg/cm}^2\text{-month} )</th>
<th>Liquid phase, ( R_T, \text{mg/cm}^2\text{-month} )</th>
<th>Vapor phase, ( R_T, \text{mg/cm}^2\text{-month} )</th>
<th>Liquid phase, ( R_T, \text{mg/cm}^2\text{-month} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel (type 304)</td>
<td>100</td>
<td>625</td>
<td>56</td>
<td>2.3</td>
<td>59</td>
<td>&gt;0.01</td>
<td>0.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>500</td>
<td>625</td>
<td>56</td>
<td>3.9</td>
<td>2.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Inconel</td>
<td>500</td>
<td>692</td>
<td>100</td>
<td>2.5</td>
<td>3.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Stainless steel (type 310)</td>
<td>500</td>
<td>760</td>
<td>0</td>
<td>0.9</td>
<td>5.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>SAE 1020 steel</td>
<td>500</td>
<td>760</td>
<td>56</td>
<td>20.0</td>
<td>3.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>500</td>
<td>760</td>
<td>56</td>
<td>28.9</td>
<td>7.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Hastelloy B</td>
<td>500</td>
<td>760</td>
<td>56</td>
<td>10.3</td>
<td>5.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Multimet (N-155)</td>
<td>500</td>
<td>760</td>
<td>56</td>
<td>20.0</td>
<td>3.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Stellite No. 21</td>
<td>500</td>
<td>760</td>
<td>56</td>
<td>-20</td>
<td>-11</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*See references 33, 80, 82, and 149.
many of the reactions with this material which contribute essentially to liquid-phase corrosion occur to a much smaller extent in the vapor. There is evidence that other complicating reactions also occur, so that it is not yet possible to derive exact numerical data on the relation between liquid- and vapor-phase corrosion.

At present, vapor-phase corrosion by sodium is perhaps of secondary importance. In mercury-vapor turbines and similar applications where the solid material comes into contact with both the liquid and vapor, the gas-phase reactions may play the dominant role. At the present time the upper temperatures at which structurally useful materials may be used with sodium and NaK are fixed by welding and similar factors (see Sec. IV-B). But, if materials resistant to this welding phenomenon become available in the future, the temperature may be limited by the vapor-phase rather than the liquid-phase corrosion. So far as the mechanisms of these reactions are concerned, there are many competing processes which may occur in liquid-alkali metal systems, and it is always possible to formulate some kind of reasonably plausible explanation for the observed effects. How valid these hypotheses may be in any given case must await further study and more experimental data.

b. Changes in Metallographic Appearance and Mechanical Properties on Exposure to Liquid Alkali Metals. Weight changes of materials exposed to liquid alkali metals may be of far less importance than changes in other properties. Consequently, practically all the laboratories engaged in liquid-metal corrosion studies have supplemented weight-change determinations with metallographic examination and investigation of other properties such as hardness, variation in chemical composition, tensile strength, yield strength, stress corrosion, and ductility.

Microscopic examination has clarified some of the details of the corrosion process; sometimes there is uniform attack on the material while in other cases the greatest change is observed in the intergranular constituents. (This is true, for example, of types 302, 304, and other unstabilized stainless steels in sodium or NaK containing significant amounts of oxygen, at least.) Grain growth, precipitation, recrystallization, diffusion (and in some cases removal) of constituents, and almost any phenomenon observed with metallic systems have, for one material or another, been found to occur with substances exposed to sodium or NaK. In many cases these changes are purely thermal and are also seen in blank samples exposed to inert-gas atmospheres for the same time and temperature. By and large there have been relatively few clear-cut metallographic changes that can be positively attributed to the action of the liquid metal. An extremely wide range of phenomena is observed in this work, some unexplained to date, and the original data on the specific material of interest should be consulted for details.

The literature on this subject contains a great deal of discussion of the macroscopic appearance of samples exposed to sodium and NaK. Frequently, identical samples after the same treatment have shown wide variations in appearance, although the R values were almost the same, with some surfaces showing heavy dark coatings while others came out quite bright and shiny. Appearance in this case is a rather deceptive criterion since a film only 400 A thick on a metal is clearly visible. However, if such a film of Cr2O3 is assumed on a surface of 1 cm2, its volume is only $4 \times 10^{-5}$ cm3. Using the macroscopic density of Cr2O3, 5.2 g/cm³, the weight change amounts to only 0.02 mg/cm², which is hardly detectable on an ordinary sample (about 10 cm² in area) using an analytical balance.

Chemical analysis has tended to confirm the results of metallographic examination. There is little or no evidence for selective attack on the constituents of an alloy, except when these occur predominantly as intergranular impurities (see the sections on carburization and mass transfer below).

Figure 4 shows the effect of prolonged exposure to NaK at 760°C on the mechanical properties of a number of materials, as compared with exposure to argon gas at the same temperature for the same time. As can be seen, no significant changes in mechanical properties which can be attributed to the action of the liquid metal have been observed in materials which show generalized attack; although such changes might be expected a priori in some cases. For example, in a tensile test with stainless steel, if the oxide film is thick and brittle and causes surface cracks during loading, the ductility and strength of the composite bar might be expected to be lowered. Since these surface films are known to be quite thin, it is understandable that their effects on the over-all mechanical properties of massive specimens, for example, standard test bars, are quite beyond the limits of observation by ordinary test methods. For the KAPL reactor, however, some of the structural materials will be used in very thin sections (of the order of 0.005 to 0.030 in. thick) in order to minimize thermal stress and keep the weight of structural material to a minimum to prevent neutron absorption. It is conceivable that these samples will show changes of the type postulated above. Mechanical tests on thin samples are currently in progress. Preliminary observations were made by Carrkeker and Vandenberg on 0.015-in. type 347 stainless-steel wire: (1) untreated, (2) exposed to liquid sodium for three to four months at 500°C, and (3) sealed in argon and subjected to the same temperatures as the sample exposed to sodium. Essentially no difference in tensile-strength and elongation was found in these tests.
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Materials for which the principal corrosive action is removal of alloy constituents, on the other hand, show marked changes in properties on exposure to sodium or NaK. Low-carbon steels, for example, are almost completely decarburized by relatively short exposures (of the order of 1 week) to sodium or NaK at temperatures in the 500 to 700°C range; the carbon probably ends up as solid suspended in the liquid sodium. Removal of the carbon permits the growth of large grains in the metal, and the resulting coarse structure is significantly weaker than the steel which has been subjected to the same time and temperature treatment, without the decarburizing action of the alkali metal (see Table 16).

Experiments on the effect of deformation on corrosion have yielded essentially negative results. At ANL, numerous static experiments were carried out with metal samples which had previously been stressed to failure in tension. On exposure to NaK at 200°C, where the resulting strains were not completely annealed out, there was some indication that with these samples there was selective attack at the points of greatest strain. Vandenberg at KAPL has tested samples under continuous stress (bending) in sodium at 500°C and has observed no significant differences between these and unstressed samples.

If the oxide films which are of such importance in the behavior of many materials have densities and...
coefficients of thermal expansion significantly different from those of the base metal, successive heating and cooling of the sample would be expected to lead to poor adhesion and spalling off of the oxide films. Such thermal-cycling tests under sodium have been carried out at KAPL with type 347 stainless steel, but the results have been negative, i.e., there was no significantly greater increase in corrosion and no observable tendency for the oxide film to become porous or non-adherent. Further extensive tests along these lines are planned.

The effects of exposure to alkali metals on the physical properties of a few materials are summarized in Table 16, which is taken from an ANL report. The results are typical of observations made at other laboratories.

The Babcock & Wilcox Co. has made similar tests on type 316 stainless steel in NaK (20 per cent sodium) and in air, after short periods of exposure.

<table>
<thead>
<tr>
<th>Material</th>
<th>Treatment</th>
<th>Specimen No.</th>
<th>Tensile strength, psi</th>
<th>Yield point, psi</th>
<th>Yield strength, psi (0.04% offset)</th>
<th>Per cent elongation in 2 in.</th>
<th>Per cent reduction of area</th>
<th>Hardness (Rockwell B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold-worked</td>
<td>As received</td>
<td>1</td>
<td>108,000</td>
<td>70,000</td>
<td>18.7</td>
<td>52.0</td>
<td>83.5</td>
<td></td>
</tr>
<tr>
<td>low-carbon steel</td>
<td>At 600°C for 1 hr</td>
<td>1</td>
<td>70,000</td>
<td>63,500</td>
<td>35.9</td>
<td>74.0</td>
<td>44.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days in argon</td>
<td>1</td>
<td>59,800</td>
<td>39,000</td>
<td>33.5</td>
<td>80.0</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In NaK alloy,</td>
<td>1</td>
<td>59,200</td>
<td>38,000</td>
<td>36.7</td>
<td>78.0</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>As received</td>
<td>1</td>
<td>125,400</td>
<td>79,000</td>
<td>10.1</td>
<td>76.0</td>
<td>92.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>124,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>At 600°C for 1 hr</td>
<td>1</td>
<td>88,800</td>
<td>48,000</td>
<td>31.2</td>
<td>74.0</td>
<td>54.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days in argon</td>
<td>2</td>
<td>91,800</td>
<td>48,000</td>
<td>31.2</td>
<td>72.0</td>
<td>61.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In NaK alloy,</td>
<td>1</td>
<td>91,800</td>
<td>48,000</td>
<td>31.2</td>
<td>74.0</td>
<td>61.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days at 600°C</td>
<td>2</td>
<td>90,400</td>
<td>43,000</td>
<td>31.2</td>
<td>76.0</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>As received</td>
<td>1</td>
<td>119,600</td>
<td>64,000</td>
<td>57.0</td>
<td>80.0</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td>(type 302)</td>
<td>2</td>
<td>122,400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>At 600°C for 1 hr</td>
<td>1</td>
<td>127,600</td>
<td>62,000</td>
<td>53.1</td>
<td>76.0</td>
<td>87.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days in argon</td>
<td>2</td>
<td>122,800</td>
<td>62,000</td>
<td>53.1</td>
<td>74.0</td>
<td>87.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In NaK alloy,</td>
<td>1</td>
<td>122,000</td>
<td>64,000</td>
<td>50.0</td>
<td>66.0</td>
<td>84.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days at 600°C</td>
<td>2</td>
<td>117,400</td>
<td>63,000</td>
<td>47.6</td>
<td>54.0</td>
<td>86.0</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>As received</td>
<td>1</td>
<td>121,600</td>
<td>47,000</td>
<td>46.8</td>
<td>74.0</td>
<td>82.0</td>
<td></td>
</tr>
<tr>
<td>(type 347)</td>
<td>2</td>
<td>118,200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>At 600°C for 1 hr</td>
<td>1</td>
<td>123,000</td>
<td>63,000</td>
<td>43.3</td>
<td>72.0</td>
<td>82.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 days in argon</td>
<td>2</td>
<td>123,800</td>
<td>63,000</td>
<td>43.3</td>
<td>72.0</td>
<td>81.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 17 — Effect of Exposure of Type 316 Stainless Steel in Air and NaK on Mechanical Properties

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Test fluid</th>
<th>Ultimate tensile strength, psi</th>
<th>Elongation in 2 in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>538</td>
<td>Air</td>
<td>63,750</td>
<td>52.5</td>
</tr>
<tr>
<td>538</td>
<td>NaK</td>
<td>63,500</td>
<td>52.0</td>
</tr>
<tr>
<td>760</td>
<td>Air</td>
<td>36,000</td>
<td>61.5</td>
</tr>
<tr>
<td>760</td>
<td>NaK</td>
<td>36,000</td>
<td>66.5</td>
</tr>
</tbody>
</table>

After the specimens had reached the desired temperature, a soaking period of 1 hr was allowed to ensure equilibrium conditions prior to applying the load. Note that these tests, unlike those mentioned above, were carried out at high temperatures while the samples were immersed in the NaK. The results obtained are shown in Table 17. The last column of Table 17 shows no significant change in the ductility of samples exposed to NaK. On the other hand, using type 347 stainless steel, Vandenberg at KAPL has found that in slow deformation (stress-rupture tests), the time, and therefore the strain, to rupture is considerably greater in samples exposed to sodium than it is for those heated in air, so that with this material there is an increase in ductility. In all probability this effect is not due to the sodium, per se, but to the exclusion of oxygen from the system.

c. Oxygen Sensitivity in Static Systems. In the preceding sections frequent reference has been made to the sensitivity of metallic corrosion in liquid alkali...
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

metals to the presence of oxygen. This element almost always tends to increase the absolute magnitude of the corrosion rate, whether it be positive or negative. Because of the chemical reactivity of sodium and oxygen, it is to be expected that the oxygen is present almost entirely as $\text{Na}_2\text{O}$, and it is in this form that it acts to accelerate corrosion; although in many laboratories order of 0.01 wt. % oxygen. The purification of sodium will be discussed in a later section. For the time being it is sufficient to point out that careful filtration, distillation, or "gettering" with a more reactive metal all give material of approximately this oxygen content. Using this as the starting material, oxygen has been added as gaseous $\text{O}_2$ or as $\text{Na}_2\text{O}_2$ (which sub-

Table 18 — ANL Oxygen Sensitivity Tests
(In NaK containing 56 per cent sodium; 144-hr test at 600°C, except as noted for aluminum. Oxygen added as $\text{O}_2$ gas.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_T$, mg/cm²-month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen added, %</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>0.5</td>
</tr>
<tr>
<td>SAE 1020 steel</td>
<td>1.7</td>
</tr>
<tr>
<td>Invar</td>
<td>3</td>
</tr>
<tr>
<td>Monel</td>
<td></td>
</tr>
<tr>
<td>Aluminum bronze</td>
<td>0.0</td>
</tr>
<tr>
<td>Beryllium copper</td>
<td>-1</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2.0</td>
</tr>
<tr>
<td>Wolfram (tungsten)</td>
<td>2.0</td>
</tr>
<tr>
<td>Inconel</td>
<td>0.4</td>
</tr>
<tr>
<td>Aluminum 28</td>
<td>0.7</td>
</tr>
<tr>
<td>(tested at 450°C)</td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>+3</td>
</tr>
<tr>
<td>Beryllium</td>
<td>+0.0</td>
</tr>
<tr>
<td>Thorium</td>
<td>+4.4</td>
</tr>
<tr>
<td>Chromium and chromium-containing alloys</td>
<td>Increased $R_T$</td>
</tr>
<tr>
<td>Niobium (columbium)</td>
<td>-1</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>-0.05</td>
</tr>
<tr>
<td>(type 347)</td>
<td></td>
</tr>
<tr>
<td>Tantalum</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

*See reference 126.

it is customary to speak of the percentage of oxygen rather than the percentage of $\text{Na}_2\text{O}$ in the liquid. Since the publication of Part I of this paper further experiments have suggested that the figure of 0.3 per cent $\text{Na}_2\text{O}$ for the equilibrium solubility at about 125°C, previously quoted, may be too high, probably by a factor of 10 at least.

Several studies of the effect of oxygen addition on static corrosion have been made at various sites. Usually the initial oxygen content of the liquid metal, while not accurately known, is low, possibly of the consequently reacts with sodium and is reduced to $\text{Na}_2\text{O}$ in the oxygen sensitivity tests which have been carried out.

Quantitative data on the effect of oxygen on static corrosion are meager. The data from ANL in Table 18 are typical and have been confirmed, qualitatively at least, by work at KAPL and MSA.

In considering the nature and mechanism of oxygen-accelerated corrosion, it is convenient to divide metals into two classes: (1) those which thermodynamically can reduce $\text{Na}_2\text{O}$, according to Eqs. 13 and 14,
and (2) those which do not reduce Na₂O. The first group is somewhat simpler to consider and will be examined first.

As was pointed out in Sec. II-B-6 of Part I of this paper, whether a metal can or cannot reduce Na₂O to sodium depends on the relative magnitudes of the free energy of formation per atom of oxygen of the metal oxide compared with that of Na₂O. From Table 16 of Part I, using this purely thermodynamic criterion, the elements listed in Table 19 would be expected to react in this way with Na₂O. In Table 19 an attempt has been made to divide the elements into those which form basic oxides and those which form acidic oxides, with the amphoteric bases occupying an intermediate position. Whether these oxides should act more nearly basic or acidic in the presence of the strong base Na₂O has been indicated. The first group, the base formers, would be expected to reduce Na₂O. Equation 14 might be quite important in the acid-forming class. (The use of the terms acid and base applied to proton-free systems above differs from the commonly used Brønsted concept of acidity. It is, however, a useful point of view and is still frequently employed.)

Several large groups stand out in the table, e.g., the alkaline earth metals, the alkali metals lithium and potassium, and the rare earths. A conspicuous and important omission from this table is the probably acidic element chromium. At 500°C the free energy of formation of Cr₂O₃ is -215 kcal/mole, so that the free energy per mole per atom of oxygen is -72 kcal. Since ΔFº for Na₂O is -75, chromium in bulk should not reduce Na₂O. However, Weber and Fisher⁴ at KAPL have shown that when stainless-steel samples are oxidized by flaming in air the resulting oxide films are clearly visible owing to interference colors. These films which have been identified as largely Cr₂O₃ by electron-diffraction studies are not removed on exposure to sodium at 500°C for as long as 360 hr. Apparently Cr₂O₃ (under these conditions) is not reduced by sodium, and consequently it would appear that under similar conditions chromium can be oxidized by Na₂O. Whether the discrepancy is due to errors in the thermodynamic data on Cr₂O₃ and Na₂O (after all, the difference of only 3 kcal is well within the experimental error), the free energy of solution of chromium in the alloy, the formation of stable lower oxides, or the surface free energy of the oxide layers is not clear; the facts of the case, however, seem quite definite.

The reactions which produce oxygen sensitivity in materials which ordinarily gain weight in sodium are heterogeneous and complex, but the following factors...
will determine the magnitude of the effect of oxygen on corrosion:

1. The free energy of formation of the metal oxides compared with Na$_2$O, and the free energy of formation of saltlike sodium oxide—metal oxide compounds.
2. The rate of reaction of Na$_2$O with the metal.
3. The diffusion rates of Na$_2$O and sodium passing through surface films into the metal or the diffusion rate of the metal in the opposite direction.
4. The molal volume, crystal type, and coefficient of thermal expansion of the oxide or salt films which may be formed, relative to the base metal influence the adhesive strength of the resulting films and, along with the permeability of these films to sodium, metal, and Na$_2$O, determine whether they remain tightly bound to the metal and protective in nature (like chromium oxide on stainless steel) or fragile and nonprotective (like beryllium oxide on beryllium).

For these materials, therefore, the oxygen sensitivity may be explained on the basis of Eqs. 13 and 14.

It must be remembered that the solution reaction and possibly others occur simultaneously with the Na$_2$O reactions. For many substances these competing reactions appear to lead to a threshold oxygen content below which there is no effect, e.g., between 0.5 and 1 per cent for nickel, 1 to 3 per cent for molybdenum, etc. (These threshold values are rather deceptive quantitatively; there may be relatively little correlation between the amount of oxygen added and the amount actually present, owing to interaction with the other constituents of the system.) Uranium and beryllium, as might be expected for such strongly reducing substances, are, on the other hand, extremely sensitive to even small traces of oxygen. These effects seem to complicate the picture to the point where experimental measurements rather than theoretical studies must be depended upon for the final answers.

For materials which cannot reduce Na$_2$O, an entirely different explanation of oxygen sensitivity apparently is required. The best evidence on the nature of this process appears to be the KAPL studies on the solubility of iron in sodium. In this work a vessel made of iron was filled with sodium which was stirred at the temperature of measurement. Samples of the liquid were taken as a function of time and analyzed for iron by a colorimetric procedure accurate to at least ±0.5 ppm. In this way the approach to saturation could be checked. Such measurements were carried out at about 325°C with 0, 0.5, and 1 per cent oxygen added as Na$_2$O$_2$ to sodium initially containing from 0.01 to 0.07 wt. % oxygen. The measurements were extremely crude quantitatively, but the resulting curves of $S_T$ vs. t had the general form shown in Fig. 5.

The equilibrium solubility, $S_T$, was not significantly changed by the addition of oxygen within these limits, although the initial slope of the curves was greatly altered. From Eq. 6 the initial slope of these curves is

\[
\left( \frac{dS}{dt} \right)_{t=0} = \alpha_T \frac{A}{V} S_T^2
\]

and, since $A/V$ and $S_T^2$ were identical in these experiments, it is evident that it is the specific solution rate constant $\alpha_T$ which is sensitive to the presence of the oxygen. The apparatus used was designed to obtain equilibrium (long time) values of $S$ rather than the initial (short time) values, and the precision of the data for small $t$ values is so poor that it is not possible to establish the exact functional relation between $\alpha$ and $p$, the oxygen content of the sodium. There is some indication that the $\alpha$ vs. $p$ curve, extrapolated to low values of the oxygen content, passes through the origin, so that the relation is probably of the form $\alpha = Kp^n$. The value of $n$ is still undetermined, but some rather intuitive theoretical considerations suggest that it is unity. The implications of the $\alpha$ vs. $p$ curve passing through the origin are rather striking; from Eq. 9, when $\alpha = 0$, $R_T = 0$. Thus this hypothesis suggests that in pure sodium, when there is no Na$_2$O present, corrosion rates for materials which normally lose weight by solution become vanishingly small. (The same conclusion, it will be noted, can be derived for the case of positive $R_T$ values, on the basis of the oxide film hypothesis.) This deduction, while interesting and thought provoking, is based on a somewhat risky extrapolation of relatively poor data and may be in error by an appreciable amount; that is, $\alpha$ may have the form

\[
\alpha = \alpha_0 + Kp + \ldots
\]
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this problem. The techniques required to carry out these measurements on iron and other relatively insoluble metals will be most exacting. Analytical methods (quite beyond the limits of normal chemical analysis) for hundredths and possibly thousandths of a part per million are required. Radioactive tracer techniques will immediately come to mind as a possible solution. Experiments with relatively soluble metals might also be of value in elucidating the mechanisms involved and would be much easier to carry out.

D. CORROSION OF METALS BY SODIUM AND NaK IN DYNAMIC SYSTEMS

1. Introductory Remarks

The limitations of the static-corrosion test for liquid metals to be used in a heat-transfer system have been discussed in detail above. These factors have led to the use of the so-called "dynamic" or "harp" tests. A typical thermal-convection harp is shown in Fig. 6. Harps of this type apparently were first used to study liquid-metal corrosion by mercury in tests carried out by Nerad and his associates at the General Electric Co. Research Laboratories in the middle and late 1920's. The importance of dynamic-corrosion measurements may be appreciated from the fact that the development of the titanium-magnesium inhibition technique for ferrous metals in mercury required the expenditure of about 1000 of these harps and approximately 100 man-years of effort.

In the sections which follow, the symbols \( R_T \) and \( P_T \) will be used to represent the dynamic-corrosion and penetration rates analogous to the corresponding static quantities. In pumped systems the flow velocity can be determined from the pump characteristics and the geometry of the system. For thermal-convection harps the following analysis, due to Lockhart, may be used. Notation and symbols are the same as those in Part I of this paper. Consider the somewhat idealized loop shown in Fig. 7. Note that the cold zone must always be located at a higher level than the hot zone to obtain circulation.

The difference in hydrostatic pressure between the hot and cold zones is

\[
- \int_0^h \rho g \, dz = (\rho_c - \rho_h)gh
\]

But

\[
\rho_c - \rho_h = -\rho \beta_0 \Delta T
\]  

(20)

where the subscript 0 refers to the temperature \( T_0 \). Thus

\[
\Delta p \equiv \rho \beta_0 \Delta T
\]
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Opposing the hydrostatic force is the frictional force of the fluid against the pipe walls. According to the Fanning equation\(^\text{\textsuperscript{2}}\) for smooth pipes with no sharp corners

\[
\Delta p = \int_0^L \left(2f \rho v^2 \frac{D}{D} \right) dx
\]

(21)

where \(f\) is the so-called dimensionless "friction factor" and \(x\) is the distance measured around the loop. Then, since in the steady state these two expressions for \(\Delta p\) must be equal,

\[
\Delta p \approx \rho \beta h \Delta T \approx 2f v^2 \frac{L}{D}
\]

(22)

Simplifying this equation gives

\[
v^2 = \frac{g \rho D}{2} \left(\frac{D}{L}\right) \frac{\Delta T}{f}
\]

(23)

It has been found empirically\(^\text{\textsuperscript{7}}\) that for Reynolds numbers between 5000 and 200,000 (which covers the range of interest to this discussion) the friction factor can be represented by

\[
f = 0.046 \text{Re}^{-\frac{1}{5}} = 0.046 \left(\frac{\rho}{\mu}\right)^{-\frac{1}{5}} v^{-\frac{1}{5}} D^{-\frac{1}{5}}
\]

(24)

where \(\text{Re}\) is the Reynolds number, as defined in Part I. Combining Eqs. 23 and 24 and using the mean temperature \(T_o\) to determine \(f\), it follows that

\[
v^{\frac{1}{5}} \approx \frac{g \rho D}{0.0882} \left(\frac{\rho}{\mu}\right)^{-\frac{1}{5}} \left(\frac{D^2 h}{L}\right) \frac{\Delta T}{f}
\]

(25)

If there are no heat losses, the heat input into the system, \(q\), required to maintain the temperature difference \(\Delta T\) may be computed from the mass-flow velocity and is given by

\[
q_{\text{min}} \approx 4 \int \rho \frac{C_p}{D} \Delta T
\]

(26)

In general this is the minimum value for \(q\). In a practical harp, heat losses through the insulation, thermal convection to the surroundings, and so forth, may raise the amount of heat which must be supplied to the system considerably above this value.

Taking a typical harp with \(T_o = 500^\circ\text{C}\), \(D = 1\) cm, and \(L = 100\) cm, so that
\(\rho_o = 0.832\text{ g/cm}^3\)
\(\beta_o = 2.88 \times 10^{-4}\text{ (C)}^{-1}\)
\(\mu_o = 2.3 \times 10^{-3}\text{ poises}\)
\(C_{p_o} = 0.302\text{ cal/g-C}\)

and using these constants, \(v\) has been computed as a function of \(h\) and \(\Delta T\), as shown in Fig. 8. Similarly the minimum power consumption \(q_{\text{min}}\) is plotted on

Fig. 8 — Flow velocity in a sodium-filled thermal-convection harp. \(T_o\), 500°C; \(D\), 1 cm; \(L\), 100 cm.

Fig. 9 for the same system. These formulas give quite good agreement with experiment, perhaps better than might be expected, and the approximations and averaging processes used in their derivation undoubtedly involve some compensation of error.

Fig. 9 — Minimum power consumption in a sodium-filled thermal-convection harp. \(T_o\), 500°C; \(D\), 1 cm; \(L\), 100 cm.

It is never possible for \(h/L\) to be greater than about \(\frac{1}{2}\) for a thermal convection loop, and usually it is much smaller than this. For the system described above, a maximum flow velocity of 31.5 cm/sec (1.0 ft/sec) can be attained; this would require at least 2.6 kw of heat. In general then the flow velocities attainable in
a system of this sort are small, and pumped loops are required if the effect of large values of \( v \) is to be studied. In an attempt to increase the value of \( v \), some laboratories have used quite large harps, sometimes 10 to 15 ft in height. Another device which has been used is to employ smaller sized tubing in the hot zone of the harp, thus effectively increasing the linear-flow velocity in this region. Even so, flow velocities greater than 1 or 2 ft/sec are difficult to obtain in thermal-convection systems; moreover, these velocities can be much more readily achieved in a considerably more compact unit by using one of the centrifugal or electromagnetic pumps designed for use with sodium and NaK. In any case, according to present concepts, as will appear presently, the flow velocity in a harp has only a small effect on \( R_T \) for most materials.

Experimenters who have used harps will appreciate the fact that the model discussed above is highly idealized and seldom realized in practice. The high degree of localization of the hot and cold zones which is assumed cannot be achieved because of the conduction of the pipe walls and similar factors; also the hot and cold zones are frequently spread over a considerable length of the loop. Actual systems are not always constructed throughout of piping of uniform diameter, in which case the above formulas must be corrected. Ideally a harp should be made of a material completely inert to the test fluid, and the sample should be placed at the hottest point in the system. Since there apparently are no metals completely inert to sodium and NaK, the next best design is to make the harp of the same material as the sample itself, in which case the calculation of \( R_T \) involves only a correction for the relative area of the sample and the harp walls, as in the case of static corrosion. Actually neither of these simplified cases has been used consistently. Several samples are often strung over a considerable length of the hot zone, and frequently these are of different materials so that the effect of one metal upon the corrosion of another, noted in the discussion of static corrosion in heterometric systems, may be significant. Under these circumstances it is not difficult to understand why the reproducibility of dynamic-test results has been poor, and why theories of the dynamic-corrosion process must be content with order-of-magnitude agreement with the observed \( R_T \) values.

From the KAPL work, thermal-convection dynamic-corrosion data are available on only two materials, extruded beryllium and SAE 1010 steel. Some emphasis has been placed on another type of test in moving liquid, the so-called "Whirligig," designed to supplement the available harp data. The sample is immersed in the sodium and rotated at high speed. This is an isothermal experiment designed to determine the effect of velocity on corrosion and the protective action of oxide films. These tests were carried out with beryllium at 500°C. The data obtained are shown in Table 20. The product \( tR_T \) has been computed from these data. According to Eq. 10 this quantity should then be independent of time and should show the effect of velocity on the corrosion of beryllium. It will be seen that \( tR_T \) is almost directly proportional to \( v \) for this material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Time, months</th>
<th>Peripheral velocity, ft/sec</th>
<th>( R_T ), mg/cm²-month</th>
<th>( tR_T ), mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be (QT)</td>
<td>0.233</td>
<td>10</td>
<td>-10</td>
<td>-2.3</td>
</tr>
<tr>
<td>Be (premium)</td>
<td>0.425</td>
<td>10</td>
<td>-7</td>
<td>-3.0</td>
</tr>
<tr>
<td>Be (extruded)</td>
<td>3.29</td>
<td>20</td>
<td>-1.5</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

With type 347 stainless steel the effect of thermal cycling as well as high flow velocities was examined. A Whirligig setup in which the peripheral velocity was 18 ft/sec was cycled 24 times between 200 and 600°C for a period of 216 hr. This yielded a corrosion rate of 0.89 mg/cm²-month. Since this is of the same order of magnitude as the static-test results at 600°C, it appears that flow velocity up to this value of 18 ft/sec, at least, does not affect the corrosion of stainless steel, as may be predicted from the adherent nature of the oxide films on this material.

In dynamic as in static corrosion a distinction must be made between materials which lose weight and those which gain weight. The latter case is somewhat simpler; for materials which form tightly adherent oxides, \( R_T \) and \( R_T \) should be identical for long-time experiments. The flowing fluid might, a priori, be expected to abrade and erode away portions of these oxide films. In practice erosion has been observed only in the case of very loosely bound oxides, BeO on beryllium for example. Nerad has pointed out that even when net flow rates are quite high the velocity profile in a tube results in a virtually stagnant layer at the solid-liquid interface, so that only the most sensitive systems should show an increase of the corrosion rate with flow velocity. This remark applies strictly only to the streamline-flow region (Re < 2100), but even when there is turbulent flow due to high velocities or sharp edges or corners the dependence upon velocity should not be very great, although it has been observed and is significant in some cases.

For materials which lose weight, the physical picture, as in the static-test case, is one of solution. In the hot zone the material dissolves in the liquid, tending towards saturation. When this body of fluid, saturated at \( T_0 + \Delta T/2 \) reaches the cold zone \( T_0 - \Delta T/2 \), precipitation occurs. On the next cycle the process is repeated, so that the accumulated effect after pro-
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The possibility of the coolant system plugging in a nuclear reactor, with subsequent overheating and possible catastrophe (not a high-order explosion) must always be kept in mind. It will be noted that this trouble can occur only when large amounts of metal are dissolved, i.e., with materials with large $R_T$ values. For many substances of importance such large corrosion rates occur only when there are considerable amounts of oxygen in the system, so that there is an intimate connection between plugging and the presence of Na$_2$O. Of course, with enough oxygen in the system plugs of Na$_2$O itself can, and accidentally have, often been formed. It is to avoid these plugging difficulties that the extensive corrosion tests and the intensive search for corrosion-resistant structural materials have been carried out. How serious this plugging problem can become may be illustrated from the history of the mercury-boiler development. In the first system, built before the development of the titanium-magnesium inhibitor technique, the operating conditions were approximately $T_0 = 480^\circ$C, $\Delta T = 15$ to $20^\circ$C, and penetration rate about 4 mils/year. This system plugged and became inoperative in about one year, after which it was found that some 2000 lb of metal had been corroded away. Modern developments have reduced this by a factor of at least 100 in the case of mercury systems, and it would appear that $R_T$ values of 0.1 mil/year or less are needed before a sodium or NaK-filled reactor system can be operated with assurance of safety. That this corrosion rate is attainable and feasible from an engineering standpoint, providing proper care is taken, will appear in the sections which follow.

longed test is quite large. (Note that presaturation of the liquid in such a dynamic system is ineffective in inhibiting corrosion in the hot zone, since the advantages to be gained by pretreatment disappear after the first cycle around the closed loop.) The net effect then is to remove material from the sample in the hot zone and transport it elsewhere. “Elsewhere” in this case is a necessarily vague and indefinite term. A number of possibilities may be considered, as follows:

1. The particles of metal come out of solution and are deposited on the walls of the cold zone, where they are tightly adherent. This is the simplest but seems to be the least likely of all possibilities. It must be remembered, however, that a small crystal of metal deposited from solution may serve as a nucleation center for further deposition, and all the solid may come out in this region. For prolonged operation of a heat-exchange system, for example, this might be undesirable, since enough metal could conceivably be deposited in the tubes to seriously affect their flow and heat-transfer characteristics, particularly when narrow annuli or small-diameter pipes are used.

2. The particles of metal which come out of solution in the cold zone continue to float around in suspension owing to Brownian motion and the flow of the liquid. The suspension would become more and more concentrated as the process continued, and it is conceivable that the particles might agglomerate and grow to a size large enough to plug the system. Note that in this case, contrary to the conditions in (1) above, the plugging might occur in any part of the system rather than only in the cold zone.

3. There is one peculiarity of sodium and NaK which permits a third possibility. Pieces of metal in contact under sodium tend to weld together if the temperature is high enough (diffusion bonding, cf. Sec. IV-B). Thus a dilute suspension of metal might circulate freely until it reached the hot zone. There the increased Brownian motion would result in an increase in the number of collisions between particles and between particles and the wall. The tendency towards welding then might cause aggregation and plugging in the hot zone.

4. There is still another possibility, perhaps the most optimistic of all. The particles of solid precipitated in the cold zone may be small enough to remain in suspension. When these are carried into the hot zone, they may, because of their smaller size, dissolve at a rate fast compared with the bulk metal. In this way the system walls would be protected. It seems unlikely, however, that this is the process which occurs, since, if it did, no appreciable differences between dynamic- and static-corrosion rates should be observed, whereas, in fact, there are quite significant differences, as a comparison of the dynamic- and static-rate tables will show.

In this discussion of the various possible fates of the metal which dissolves, the things that may happen have been listed; it should be apparent, however, that no clean-cut answer to what will happen in any given system is possible at the present time. In harps operated at KAPL at about 700°C deposition of metal crystals occurred in the hot zone suggesting that mechanism (2) or (3) is important. However, the ANL work on welding indicates that this phenomenon is sharply temperature-dependent and should not occur with stainless-steel components, say, much below 600°C.
### Dynamic-corrosion Data Table

#### Table 21 — Thermal-convection Dynamic-corrosion Test Data

<table>
<thead>
<tr>
<th>Material</th>
<th>ANL</th>
<th>RSA</th>
<th>KAPL I</th>
<th>KAPL II</th>
<th>BW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of tests</td>
<td>Mean ( R_T ), mg/cm²-month</td>
<td>No. of tests</td>
<td>Mean ( R_T ), mg/cm²-month</td>
<td>No. of tests</td>
</tr>
<tr>
<td>Armco iron</td>
<td>15</td>
<td>0.050</td>
<td>1</td>
<td>-0.71</td>
<td>9</td>
</tr>
<tr>
<td>SAE 1010 steel</td>
<td>27</td>
<td>0.096</td>
<td>2</td>
<td>-0.94</td>
<td>1</td>
</tr>
<tr>
<td>SAE 1020 steel</td>
<td>25</td>
<td>0.086</td>
<td>2</td>
<td>-0.94</td>
<td>1</td>
</tr>
<tr>
<td>Stainless steel (type 304)</td>
<td>21</td>
<td>0.022</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Stainless steel (type 316)</td>
<td>20</td>
<td>0.011</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Stainless steel (type 347)</td>
<td>19</td>
<td>0.005</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium bronze</td>
<td>9</td>
<td>0.025</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>8</td>
<td>0.002</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Tantalum</td>
<td>13</td>
<td>0.150</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Beryllium</td>
<td>2</td>
<td>0.2</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Stellite 21</td>
<td>1</td>
<td>0.2</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Stellite 6</td>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Multimet</td>
<td>1</td>
<td>1.2</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Synthetic Sapphire</td>
<td>1</td>
<td>0.70</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Carboley Company, Inc.</td>
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<td>0.48</td>
<td>1</td>
<td>-0.80</td>
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</tr>
<tr>
<td>Cemented carbides</td>
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<td>0.23</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Firth Sterling Steel &amp;</td>
<td>1</td>
<td>0.23</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Carbide Corporation</td>
<td>1</td>
<td>0.23</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
<tr>
<td>Cemented carbides</td>
<td>1</td>
<td>0.23</td>
<td>1</td>
<td>-0.80</td>
<td>1</td>
</tr>
</tbody>
</table>

*Note: 18 per cent wolfram, 4 per cent chromium, 1 per cent vanadium, remainder iron.
1 In presence of nickel.
*IA per cent wolfram, 1 per cent carbon.
*SLM single-crystal Al₂O₃.
*Approximate composition of Firth-Sterling cemented carbide samples:
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3. Theory of Dynamic Corrosion

a. Introduction. Modern theories of the solution of solids in liquids are all based on Eqs. 5 and 6 and are concerned with the evaluation of the specific solution-rate constant \( \alpha_T \) and the factors which influence it. In aqueous solutions and the more common nonaqueous solvents, it has been found (with a few rather important exceptions) that \( \alpha_T \) may be expressed by the relation

\[
\alpha_T = kD_T^n
\]  
(26a)

where \( D_T \) is the rate of diffusion of the solute in the liquid. It may be remarked, anticipating the results of Sec. III-D-3, that the experimental evidence indicates that corrosion by liquid alkali metals is primarily dependent on properties other than \( D_T \). The diffusion theory will nevertheless be developed in some detail since the technique of obtaining the equations and the way in which they fail to explain the observed data with sodium may be of interest and value.

Since the dependence of \( D_T \) on \( T \) can be expressed by an Arrhenius type equation \( D = D_0 \exp \left( -\frac{Q}{RT} \right) \), the temperature dependence of \( \alpha_T \) can be written

\[
\log \alpha_T = A - \frac{B}{T}
\]  
(27)

The exponent \( n \) in Eq. 26a is \( \frac{1}{2} \) according to the theory of Chilton and Colburn\(^{25} \) and Colburn\(^{26} \) \( \frac{4}{5} \) according to the theory of King,\(^{29} \) 0.83 in the experimental work of King\(^{26} \) on the solution rates of metal in benzoic acid, and 0.70 in studies by King and Cathcart\(^{29} \) on magnesium in acids. The exact value between the limits 0.67 to 0.83 does not appear to be critical. The two theories are equivalent, except in detail. Physically it is assumed that the boundary layer of the fluid in contact with the solid becomes saturated with the solute very quickly, and the rate-determining factor is the rate at which the solute moves by diffusion through this boundary layer into the bulk of the fluid. The derivation of Eq. 26a applied to aqueous solution has been made by King and Howard\(^{27} \) using the analogy between mass and heat transfer and applying the empirical heat-transfer relations suggested by Colburn\(^{24} \) and Chilton and Colburn.\(^{25} \) The following development of the equation for \( \alpha_T \) due to Brooks\(^{19} \) at KAPL is, physically, completely equivalent to, and perhaps somewhat simpler than, the development of King and Howard.

Brooks begins with the McAdams heat-transfer equation (Eq. 18 of Part I of this paper) and substitutes the values of the Reynolds, Nusselt, and Prandtl numbers in terms of physical constants of the fluid.

In this equation, the thermal diffusivity \( \kappa = k/\rho C_p \) and the kinematic viscosity \( \nu = \mu/\rho \). Note that the coefficient 0.023 in this equation is dimensionless and dependent only on the assumptions as to the nature of the turbulent-fluid flow. In the material transport analogy, \( \kappa \) is replaced by the diffusion coefficient \( D \) and \( \rho C_p \) is replaced by \( \alpha (A/V) \). Then \( \alpha (A/V) \) is the concentration increase transported into the fluid per unit concentration difference between a film in contact with the solid and the bulk liquid. In a harp this film is assumed to be saturated at the high temperature \( T_0 + \Delta T/2 \), since the basic postulate of this development is that solution and precipitation of the solute occur instantaneously in the boundary layer. The concentration of solute in the hot zone is then \( S_{rT} + \Delta T/2 \), and the bulk liquid contains a concentration corresponding to the low temperature equilibrium solubility \( S_{rT} - \Delta T/2 \), so that the concentration difference is \( S_{rT} + \Delta T/2 - S_{rT} - \Delta T/2 \) which can be written as \( (dS/dT) \Delta T \). The value of \( \Delta T \) is taken to be small. Then

\[
\frac{D}{
\frac{h}{\kappa (\rho C_p)} = 0.023 \left( \frac{(D^2)^{0.2}}{\nu} \left( \frac{\nu}{\kappa} \right)^{0.4} \right)
\]  
(28)

Substituting this and the other relations above in Eq. 28,

\[
R_{rT + \Delta T/2} = -0.023 \left( \frac{D^2}{\nu} \right)^{0.2} \left( \frac{\nu}{D} \right)^{0.4} \left( \frac{dS}{dT} \right)_{rT + \Delta T/2} \Delta T
\]  
(29)

where all the physical constants should be computed at the hot zone temperature, \( T_0 + \Delta T/2 \), although the computation is quite insensitive and \( \kappa \) could be used instead without significant error. From this equation \( \alpha = kD^{0.4} \). If the exponent of the \( \nu/\kappa \) term in the heat-transfer equation is taken as \( \frac{1}{2} \) (see remark under Eq. 18, Part D, \( n = \frac{1}{2} \) in agreement with the Chilton and Colburn derivation. All the constants in this equation except the diffusion coefficient \( D \) and the temperature coefficient of the equilibrium solubility \( dS/dT \) are properties of the solvent only. To check this theory of dynamic corrosion against experimental data on \( r_T \) in sodium or NaK, it is first necessary to determine the values of these parameters.

There appear to be no direct measurements in liquid sodium of the diffusion coefficient \( D \), although such data would be highly desirable. There is, however, a fairly extensive body of measurements on diffusion of metals in other molten-metal systems: copper, \( ^{79,127} \), mercury, \( ^{113,114,115,145} \), tin, lead, bismuth, iron, \( ^{102} \) and aluminium.\(^{12,120,127} \) An examination of the data indicates that for these six liquid-metal solvents over the tem-
temperature range 7 to 700°C and over a wide range of concentrations \( D \) varies only between the limits 0.52 and \( 7.5 \times 10^{-5} \text{ cm}^2/\text{sec} \). The average of over one hundred \( D \) values which could be found in the literature for the temperature range up to 700°C is about \( 2 \times 10^{-5} \text{ cm}^2/\text{sec} \), and this value may be taken as typical of all metals in liquid-metal systems and applied to the case of metals in liquid sodium.

b. Comparison of Experimental Data on Dynamic Corrosion with Results of Diffusion Theory. From Appendix C, the equilibrium solubility of iron in sodium for the range 225 to 500°C is given by

\[
S^2_T = -1.1 + 0.02767T_C \quad (30)
\]

where \( S^2_T \) is in parts per million. Then \( dS^2/dT = 0.02767 \text{ ppm}/°C \). For this analysis it will be convenient to consider a harp with the characteristics of the ANL system:

- \( v = 45 \text{ cm/sec} \)
- \( T_C = 500°C \)
- \( \Delta T = 150°C \)
- \( D = 2.5 \text{ cm} \)
- \( L = 550 \text{ cm} \)

so that at \( T_0 \):

- \( \rho = 0.844 \text{ g/cm}^3 \)
- \( \mu = 2.58 \times 10^{-3} \text{ poises} \)
- \( \nu = 3.06 \times 10^{-3} \text{ cm}^2/\text{sec} \)
- \( dS^2/dT = 2.33 \times 10^{-4} \text{ g/cm}^2\cdot°C \)

Using these constants:

\[
\frac{R_{450°C}}{D_{450°C}} = \frac{-57 \text{ mg/cm}^2\cdot\text{month}}{3.84 \times 10^{-4} \text{ cm}^2/\text{sec}}.
\]

or using 7.85 g/cm³ as the density of iron, this is equivalent to a penetration rate

\[
P_{450°C} = 34 \text{ mils/year}
\]

Taking the lowest value of \( D \) appearing in the literature, \( D = 0.5 \times 10^{-4} \), the calculation yields \( R_{450°C} = -25 \text{ mg/cm}^2\cdot\text{month} \). If \( R_T \) varies not as \( D^{0.8} \) but as \( D^{0.5} \) (the largest value for the exponent in the literature), this low value for \( D \) yields \( R_{450°C} = -17 \text{ mg/cm}^2\cdot\text{month} \).

Experimentally, \( R_{450°C} \) for iron, according to the ANL data, is \(-0.076 \) (the weighted mean of the values for Armco iron and SAE 1020 steel). Thus this theory yields values of \( R_T \) which appear to be a hundred to a thousand times too great. There are at least two other objections to this formulation. It will be noted from Eq. 29 that the corrosion rate should be proportional to the \( \nu_{20} \) power of the fluid velocity, i.e., it should be nearly linear. While studies of \( R_T \) as a function of \( v \) have not been carried out over a very wide range of velocities, such experiments as have been conducted show \( R_T \) to be nearly independent of \( v \) except for oxygen-sensitive systems. Also the temperature coefficient of \( R_T \) should be considered. From Eq. 29, \( R_T \) is proportional to \( (D^{0.5}/\nu)^{0.4} \), and these, practically speaking, the only temperature-dependent terms. Then

\[
\frac{R_{500°C}}{R_{450°C}} = \left[ \frac{D_{500°C}}{D_{450°C}} \right]^{0.2} \left( \frac{\nu_{450°C}}{\nu_{500°C}} \right)^{0.4}
\]

Introducing the values of \( \nu_{450°C} = 3.06 \times 10^{-3} \) and \( \nu_{500°C} = 2.84 \times 10^{-3} \),

\[
\frac{R_{500°C}}{R_{450°C}} = 1.03 \left[ \frac{D_{500°C}}{D_{450°C}} \right]^{0.5}
\]

Now we may consider two extreme cases: (1) The temperature coefficient of \( D \) is substantially 0, so that \( D_{500°C} = D_{450°C} \); then \( R_{500°C} \) would be 3 per cent greater than \( R_{450°C} \). (2) Since the activation energy of diffusion is of approximately the same order of magnitude as that for viscosity, \( D_{500°C}/D_{450°C} = \nu_{500°C}/\nu_{450°C} = 0.93 \); if this were true, \( R_{500°C} \) would come out about 8 per cent less than \( R_{450°C} \). In either case this theory predicts only a very small temperature coefficient for \( R_T \). Actually, by extrapolation of such meager experimental evidence as is available on \( dR_T/dT \), it is estimated that \( R_{500°C} \) is two or three times as great as \( R_{450°C} \).

Thus there seem to be three facts predicted by the theory which are at variance with experiment: (1) \( R_T \) as computed from Eq. 29 is a hundred to a thousand times greater than the experimental value; (2) the diffusion theory predicts that the corrosion rate is proportional to the \( \nu_{20} \) power of the flow velocity, whereas there seems to be very little dependence on this factor; and, finally, (3) the diffusion hypothesis leads to a practically zero temperature coefficient for the corrosion rate (no greater than \( dS^2/dT \) for example), while, experimentally, temperature has been found to have a marked effect on this parameter. While there is some uncertainty about the value of \( D \) and its temperature coefficient as used in this calculation, it does not seem likely that better values of these constants could affect the final conclusions enough to resolve the discrepancies noted above between experiment and theory. The available evidence, therefore, is that dynamic corrosion in liquid-alkali metals is not diffusion-limited. There are numerous examples, even in aqueous solution, where other processes have been found to determine the solution rate; thus King and Abrahamson found that for iron in HNO₃ at large velocities, high salt concentration, and low nitrate concentration the corrosion rate "... is in whole or part controlled by a slower reaction perhaps of a chemical nature at the metal surface." Also, for the corrosion of zinc and magnesium by acetic acid in alcohol–water mixtures it was found that "... when more than 45 per cent alcohol is present ... the rate
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is partly or entirely controlled by some other than the normal diffusion process. It should be noted also that the above conclusions indicate that in diffusion-controlled corrosion \( R_T \) should be essentially independent of \( v \) and that the temperature coefficient of solution tends to be higher for non-diffusion-controlled corrosion. These deductions have been amply substantiated experimentally for aqueous solutions.

c. Rate of Solution as the Limiting Process in Dynamic Corrosion. Since the corrosion process in sodium does not appear to be diffusion-limited, an alternative formulation must be developed. Such a theory has been worked out by Brooks of KAPL. In this development, instead of assuming that the liquid boundary layer next to the solid is saturated and that the slow step is the diffusion of the solute into the bulk of the fluid (as in the diffusion-limited case), it is postulated that the diffusion step is fast compared with the initial rate of solution, so that the liquid boundary layer is not saturated. This process will be referred to as “solution-rate limited” in contrast to the diffusion-limited process described above. The assumption that equilibrium solubility is not attained is quite reasonable; with iron in liquid sodium at about 400°C, periods of about 2 hr are necessary to obtain saturation. (For mercury on the other hand, Marshall and Norton²⁸ state, “...at room temperature, mercury passed over wetted iron attained its equilibrium solubility in a few seconds”; thus, corrosion in this system is probably diffusion-limited.)

With this hypothesis the maximum corrosion rate is given by (cf. Appendix A for the derivation of this result)

\[
R_{T,AT/2} = -\frac{\alpha}{2} \frac{dS}{dT} \Delta T \left[ 1 + \left( \frac{2\alpha}{\pi D_v} \right)^{1/4} \right]^{1/2} \tag{31}
\]

In using this equation, one should note that the constants \( \alpha \) and \( dS/dT \) are taken at \( T_0 \), the mean temperature of the system. This equation, unlike Eq. 29 for the diffusion case, is quite sensitive to the temperature at which the parameters are determined. To see the differences between Eqs. 29 and 31, consider a harp with the same characteristics as the ANL unit used as an example above. Experimentally, in the range 225 to 500°C, measurements at KAPL²⁸ have yielded the equation

\[
\log \alpha_T \text{(cm/sec)} = -0.007 - \frac{2388}{T_K} \tag{32}
\]

for iron in sodium saturated with Na\(_2\)O at about 125°C (that is containing 0.01 to 0.03 per cent oxygen). This result is obtained by extrapolation of \( S_T \) vs. \( t \) curves, using Eq. 6, and is of a very low precision; the probable error in \( \alpha \) from Eq. 32 is at best 30 per cent and may be as great as 100 per cent. From the magnitude of \( \alpha_T \), compared with the rate of evaporation of iron into a vacuum, it may be concluded that only a small fraction of the atoms on the iron surface, of the order of \( 10^{-10} \), perhaps, are effective in the solution reaction; or, in other words, the accommodation coefficient for iron atoms on an iron surface in sodium is much less than unity. From Eq. 32 the energy of activation of the process is about 11 kcal/mole and at \( T_0, \alpha_{300°C} = 6.7 \times 10^{-8} \text{ cm/sec} \).

An examination of Eq. 31 will show that \( R_T \) should increase with the flow velocity \( v \). However, this effect is vanishingly small for all practical pur-
Thus the difficulties with the diffusion-limited theory development.

In aqueous solution, when the rate process is not complicated by passivity reactions at the metal-liquid interface, e.g., passivity reactions in the case of iron in HNO₃ at high ionic strengths, esterification reactions in acetic acid–alcohol–water mixtures. It is reasonable, therefore, to ask whether the iron-sodium system there is similar evidence for chemical reaction. The oxygen-sensitivity experiments previously described suggest rather strongly that the rate-determining reaction in this system may be

FeO (on surface) + 2Na₂O (surface) = 2Na₂O·FeO (surface)

Further experiment is needed, however, to check this hypothesis. It may be noted that it seems equally likely that the rate of wetting of metals by sodium (see Sec. IV-E) is similarly dependent on a reaction of this kind.

Essentially the same process can be described in terms which are more physical than chemical by saying that there is a film which lowers the “work function” for removal of iron atoms from the surface. This suggests the familiar case (so important in modern electron-tube technology) of the increased emission of electrons by tungsten when the surface is coated with thorium or BaO. It is well known that caesium metal on tungsten also has the same effect (“caesiated” filaments) on the electronic work function. This in turn suggests that the film inhibiting the passage of iron from the solid into the solution may be sodium itself adsorbed on the surface of the metal. Careful measurements of $\alpha$, as a function of temperature and oxygen content, for iron and other materials would go far toward determining whether the theory of dynamic corrosion developed here is correct. Note also that $R_T$ as a function of the oxygen content of the sodium can be obtained from the dependence of $\alpha$ on $p$, since it has been established that $\alpha$ is essentially independent of $p$.

For materials which gain weight in sodium owing to the formation of oxide films, the picture is similar to the static-corrosion case leading to positive $R_T$ values. The initial behavior of the $R_T$ vs. $t$ curves is influenced by the same confusion of factors as entered into the static measurements, plus the additional complication of the fluid-flow velocity. For a long time, after all the oxygen initially present has been taken out of solution

$$+R_T = R_{T_0}$$

i.e., the positive dynamic-corrosion rate is exactly equal to the static-corrosion rate at the mean harp temperature for the same period of time $t$. As noted above, the protective action of oxide films and the nonadherence of these layers in some cases may complicate the situation further, and the over-all result may be considerably different from the answer developed from the simple picture of the process given here.

The only data which appear to be suitable for testing this theory are harp tests conducted at BW on type 310 stainless steel for 5000 hr. In these tests, which were carried out in a harp made of the same material as the samples, the specimens were suspended along the whole range of the hot and cold zones, and the temperatures were measured at each sample. Since the coldest part of the system was always at $34^\circ$C, $\Delta T$ is in every case the difference between the sample temperature and this figure. The data are given in Table 22. Note that the temperatures given are slightly different from those given in the original report.\[14\]
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The data of Table 22 are plotted in Fig. 11 where the radius of each circle is equivalent to a weight change of 0.2 mg, the probable error in weighing. It will be observed that $R_T$ is remarkably constant and independent of $\Delta T$. The mean corrosion rate is $+0.0130$ mg/cm²-month, even including the two "wild" points. The theory developed above predicts that for these long-time tests $R_T$ should be independent of $\Delta T$ and should be equal to $R_{T_0}$ at 5000 hr. In this case $T_0$ is $470^\circ$C, a temperature at which no static-corrosion measurements appear to have been made with type 310 stainless steel. To make the comparison between theory and experiment, log ($R_T t$) was plotted as a function of $T$, using the ANL, MSA, and KAPL data on type 310 stainless steel from the table in Sec. C-2. The resulting adequately straight line, covering the range 500 to $650^\circ$C, could readily be extrapolated to yield the value $R_{470^\circC} = +0.016$ mg/cm²-month. The agreement between this value and the mean $R_T$ computed above is remarkable, much better than there is any reason to expect from the extremely oversimplified model on which it is based.

The behavior of the static- and dynamic-corrosion rates with time is shown in Fig. 12. These curves show that for positive weight changes there is little to choose between the static- and dynamic-corrosion tests; for negative weight changes, however, $R_T$ is to be preferred to $R_T$ because of the tendency toward saturation in the latter case, as well as the fact that a harp more nearly reproduces the working condition of a heat-transfer system. For these reasons, except for the other uses previously mentioned, the static test should be looked upon as essentially a method of screening and eliminating materials with an unsatisfactory high corrosion rate in the liquid metal, and the ultimate criterion of corrosion resistance should always be a dynamic test under conditions as close as possible to those under which the material is to be used.

4. Oxygen Sensitivity in Dynamic Systems

The most extensive quantitative study of the effect of oxygen on dynamic corrosion is the MSA data on mild steel. In harps of the type previously described,
Experimentally, $R_{355^\circ C}$, the corrosion rate when there was no added oxygen, is $0.94 \text{ mg/cm}^2\text{-month}$. Using this value and determining the proportionality constant $C$ and the initial oxygen concentration of the NaK, $p_0$, by the method of least squares (weighting the points proportional to the added oxygen content), $C = 226$ and $p_0 = 0.004$ per cent, a quite reasonable figure. Then

$$R_{355^\circ C} = -226 \ p$$

with a probable error of $0.11 \text{ mg/cm}^2\text{-month}$. This work offers quite good confirmation of the previously hypothesized functional form for $\alpha$ and, in fact, leads to

$$\alpha_{460^\circ C} = 0.0676 \ p \text{ cm/sec}$$

for the effect of oxygen in NaK on iron. (This result is derived on the assumption that $dS/dT$ for iron in NaK containing 56 per cent sodium is the same as it is in pure sodium.) Further extensive experiments of this type would be extremely informative and are badly needed; other materials and temperatures should also be investigated. It should be noted that this is perhaps one of the simplest and most direct ways of determining $\alpha$, providing $dS/dT$ data are available.

E. RADIATION CORROSION

The effect of radiation on corrosion of materials to be used in nuclear reactors is most important and no doubt will be thoroughly investigated in the future. Preliminary work at KAPL indicates that the effects are small in structural materials but may be extremely large in uranium which is undergoing fission, owing to the removal of protective oxide films and consequently greatly increased values of $\alpha$.

A simple and rather attractive physical theory of radiation damage in nonfissionable materials can be formulated by assuming that the particles produced in the reactor ($\beta$ particles, neutrons, or fission products) at high energies collide with atoms of the material under consideration. This then produces a first generation of recoil atoms, which in turn may collide with more atoms in the stationary lattice to produce second generation displacements, and so on. The cumulative effect, therefore, is to accelerate the transport of atoms from the solid into the liquid metal and thus speed up the corrosion process.

The energetics of this problem are such that the effects to be observed vary essentially as the mass of the particle under consideration. Thus fission products, when present, should enormously accelerate the corrosion phenomenon, compared with, say, neutrons. However, the range of fission-product particles is relatively short, and few will penetrate the structural elements of the system sufficiently to cause trouble. Except for uranium corrosion, therefore, corrosion induced by fission-product radiation should be of comparatively little importance and may be ignored when only structural materials are considered.

The light-weight $\beta$ particles produced in fission can take part in two competing reactions when they strike a lattice of stationary atoms: they may react with the outer-shell electrons, producing ionization, or they may impart all or part of their energy to the nucleus itself, producing a displacement. In this competition the ionization process is by far the more probable, and the effects of pure $\beta$ radiation on materials are quite small, although they have been reported.28,105

The important effects to be expected are primarily due to the neutrons, except for the one noted above with respect to fission products. In the paragraphs which follow, therefore, the main attention will be devoted to corrosion effects produced by neutron bombardment. The calculations have been made for iron, and this material will be considered in the illustrative examples, but the extension to other materials can readily be made. For example, stainless steel and other ferrous alloys which show weight gains in sodium corrosion due to oxide-film formation may show an additional effect on neutron bombardment. The oxide films, which are somewhat protective in nature, may be knocked off. The resulting bare metal would then be expected to behave rather like iron. Consequently, with these alloys the radiation-corrosion effect, in the absence of additional oxygen, should be of the same order of magnitude as that calculated below for pure iron.
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In static corrosion, bombardment of an iron sample with neutrons would not be expected to change the equilibrium solubility. The iron knocked off the surface in excess of the quantity required to attain saturation equilibrium might rapidly reprecipitate. If this occurred at the same site from which the iron originated, there would be no change in the corrosion rate on prolonged exposure. If, on the other hand, the reprecipitation process occurred on the walls of the containing vessel rather than on the specimen, there might be an increase in the corrosion rate. The problem can be treated by the so-called "displacement" method, studied by Ozernoff, among others. The neutron flux, \( n_v \), will give rise to an isotropic matter flux, \( j \), for any given material, where \( j \) is the number of displaced atoms passing through a unit surface per unit time at the specified flux. Thus, on the basis of this hypothesis, to obtain the maximum static-corrosion rate under irradiation, \( R_R \), all other conditions being the same, it would be necessary only to add a term \( j M/N_o \) (where \( M \) is the molecular weight of the material, and \( N_o \) is the Avogadro number) to the rate in the absence of radiation \( R \). From Ozernoff's calculations

\[
j = \frac{1}{6} (n_v) \sigma_d \xi N_i \langle R_i \rangle \]

(34)

where \( \sigma_d \) = neutron scattering cross section of the material

\( N_i \) = number of the \( i \)th generation recoil atoms produced per neutron

\( \langle R_i \rangle \) = average range of an \( i \)th generation recoil atom

\( d \) = atomic density, number of atoms of material per unit volume

The original paper should be consulted for details of the calculations, but the final conclusion is that, for iron,

\[
j = 2.9 \times 10^{-4} (n_v) \text{ iron atoms/cm}^2\text{-sec} \]

(35)

The uncertainties in this computation are such that the constant in this relation may be off by a factor of 10 or more.

This method of computing \( R_R \) assumes that the rate-of-solution term is unimportant, i.e., it refers to long-time tests (see Eq. 10). It is to be expected, however, that \( \alpha \) will, in fact, be a function of the flux, so that deviations from the result given above would show up in short-time experiments. The high-energy particles on passage through the material pass their energy on to the lattice and produce local "thermal spikes," narrow regions where the temperature may be far in excess of the ambient. Brooks\(^{18}\) has shown that it is possible to compute \( f(T, n_v, T_o) \), the fraction of the volume of a solid at which the temperature is \( T \), when the neutron flux is \( n_v \) and the ambient temperature is \( T_o \). Since the specific solution rate constant \( \alpha \) has the form

\[
\alpha = \alpha_0 e^{-Q/RT} \]

(36)

and is consequently highly dependent on temperature, the value of \( \alpha \) under neutron irradiation, \( \alpha_R \), will be given by

\[
\alpha_R(T_o, n_v) = \int_{T_o}^{T} \alpha(T) f(T, n_v, T_o) \, dT \]

(37)

Using Eq. 36 for the temperature dependence of \( \alpha \) for iron, however, the difference between \( \alpha_0 \) and \( \alpha \) is negligible for neutron fluxes so far attainable, i.e., less than \( 10^{13} \). Consequently, no observable radiation effects are to be expected in a static system, other than that noted above, with iron at least. For other materials, however, where the energy of activation of \( \alpha \) is considerably greater than it is for iron, such effects may appear.

For the case of dynamic corrosion of iron by sodium, it is also simpler to treat the problem by assuming \( \alpha \) to be unaltered by the radiation and to use the displacement formulation. In Appendix B, equations are developed for the dynamic-corrosion rate \( R_R \) under neutron irradiation on this assumption. It is shown that the effects depend not only on the value of the neutron flux in the heat-transfer loop but also on its spatial distribution about the loop. If the flux is represented by

\[
n_v = (n_v)_k \exp \left[ -\beta x (L - x) \right] \]

(38)

where \( (n_v)_k \) = the flux at the hottest point in the system, taken as the origin for the parameter \( x \)

\( L \) = the total length of the loop, so that \( 0 < x < L \)

\( \beta = \) a constant of the system which fixes the rate at which the flux falls off around the loop

From this equation the minimum flux will occur at \( x = L/2 \) and will be given by

\[
(n_v)_{\min} = (n_v)_k \exp \left( -\frac{\beta L^2}{4} \right) \]

(39)

Then

\[
R_R/R = 1 - \frac{M}{N_o R} \frac{av \beta L}{2\sigma_o} \int_0 \]

(39a)

For a sodium-filled iron harp, with the characteristics of the KAPL reactor, i.e., \( T_o = 350^\circ C \) and \( \Delta T = 100^\circ C \) so that \( R = 1.69 \times 10^{-4} \) gram of iron/cm\(^2\)-sec or 0.44 mg/cm\(^2\)-month and \( L = 100 \text{ cm} \), Eq. 39a reduces to
The ratio \( \frac{R_R}{R} \) has been computed as a function of the logarithm of the maximum flux \((\nu)\), for various values of \( \beta \). These data are shown in Fig. 14.

From the curves it will be observed that the dynamic-corrosion rate increases rather rapidly with the flux for all values of \( \beta \). Since for most reactors the portion of the heat-transfer loop which is irradiated is quite small, \( \beta \) will have a relatively high value. These curves would be rather more alarming if it were not for (1) the uncertainties in Eq. 35, which may yield values of \( j \) which are too great; (2) the fact that, owing to the restoring processes discussed in Sec. D-1, the values of \( R_R \) (as well as \( R_B \)) computed above are maximum rather than most probable rates.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

The results here are probably of little more than qualitative significance and suggest that radiation corrosion may be a significant factor in presently contemplated reactors and will be more important as higher flux units are constructed.

F. SOME UNSOLVED PROBLEMS IN SODIUM CORROSION

In addition to the problems presented in the preceding sections there appear to be a number of unsolved problems in alkali metal corrosion. These will be listed here, more or less briefly, as a guide to future investigation.

The question of the effect of added constituents on the corrosion of a metal by sodium is important. The transport of material from one metal to another when two dissimilar samples are immersed in the liquid is discussed in some detail below. The, perhaps, equally important effect of dissolved materials in the sodium has hardly been touched in these investigations. Raw brick sodium contains trace amounts of a large number of elements in the 0- to 100-ppm range; for example, a typical analysis on Du Pont brick sodium (interior of brick) by the General Electric workers gave the results shown in Table 23. The results of a spectroscopic analysis made by the Ethyl Corp. on material which they manufacture for use in their processes are also included.

Possibly some of these impurities will elude the purification processes used with sodium. What these materials, in trace amounts, do to corrosion is completely unknown. Some, it is suspected, are innocuous, while others may be like oxygen in that extremely small amounts are effective in modifying corrosion rates. For example, Na₂S might behave similarly to Na₂O. Liquid mercury is sensitive to traces of dissolved impurities, and it seems reasonable to expect that other liquid metals will also be markedly affected by small amounts of additives. The practical utilization of mercury in turbines, for example, is completely dependent upon the addition of as little as 1 ppm of titanium and 20 ppm of magnesium to the mercury. With these additives there is virtually no corrosion of the ferrous alloys which are used in boiler construction; without them, corrosion rates as high as 90 mg/cm²-month (50 miles/year) have been observed. Trace constituents in liquid metals may act as corrosion inhibitors (like titanium and magnesium in mercury) or corrosion accelerators (like oxygen in sodium), and the study of their behavior should be quite informative.

It has been suggested elsewhere that virtually no changes in mechanical properties of solids upon exposure to purified sodium or NaK have ever been observed. If proper purification procedures are not employed, it is conceivable that at high temperatures impurities might be selectively extracted from liquid sodium and taken up by the solid-metal constituents of the system. The effect of these impurities on physical and mechanical properties could conceivably be very great. Numerous examples are known in metallurgy where trace impurities drastically alter the properties of metals. Some examples are:

1. The presence of 2 ppm of H₂ causes serious embrittlement in iron.²
2. A 50 per cent increase in the critical shear stress is caused by 0.1 ppm of silver in mercury at -60°C.

3. At room temperature 99.95 per cent pure zinc dissolves completely in 10 per cent HCl. In the same time, under identical conditions, "chemically pure"

<table>
<thead>
<tr>
<th>Element</th>
<th>Quantity, ppm by weight</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.5 - 2</td>
<td>109</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>108</td>
</tr>
<tr>
<td>Bi</td>
<td>0</td>
<td>111</td>
</tr>
<tr>
<td>Ca</td>
<td>100 - 300</td>
<td>111</td>
</tr>
<tr>
<td>Cd</td>
<td>0</td>
<td>111</td>
</tr>
<tr>
<td>Cl</td>
<td>100</td>
<td>104a</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
<td>108</td>
</tr>
<tr>
<td>Fe</td>
<td>5 - 10</td>
<td>103</td>
</tr>
<tr>
<td>K</td>
<td>1350</td>
<td>108</td>
</tr>
<tr>
<td>Mg</td>
<td>50</td>
<td>108</td>
</tr>
<tr>
<td>Mn</td>
<td>Trace, &lt;1</td>
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</tr>
<tr>
<td>N</td>
<td>1</td>
<td>111</td>
</tr>
<tr>
<td>Ni</td>
<td>2 - 4</td>
<td>111, 103</td>
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<tr>
<td>P</td>
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<td>111, 103</td>
</tr>
<tr>
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<tr>
<td>Sr</td>
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<td>108</td>
</tr>
<tr>
<td>Ti</td>
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<td>103</td>
</tr>
<tr>
<td>H</td>
<td>40 - 80</td>
<td>104</td>
</tr>
</tbody>
</table>

zinc (99.99 per cent) loses 53 per cent by weight, and "spectroscopically pure" zinc loses only 0.02 per cent.

4. One part per million of phosphorus in copper lowers the electrical conductivity by 0.06 per cent.³

Numerous other examples of this type are well known, e.g., boron in steel.⁴ Whether or not similar effects will result from the reaction of metals and impurities extracted from sodium is completely unknown at the present time.

No attempt will be made here to go into the many and varied problems which arise in the design of equipment and the engineering details of components for use in systems containing liquid alkali metals. It is sufficient here to point out that a large-scale technology of sodium or NaK requires the development of suitable pumps, level indicators, flowmeters, valves,
packing and gasketing materials, bearings, leak detectors, and similar devices. Considerable progress has been made along these lines, but many problems still remain unsolved. The original reports of the various laboratories engaged in this work should be consulted for details.

Other unsolved problems will be apparent in the sections which follow.

IV. SPECIAL TOPICS IN SODIUM TECHNOLOGY

A. MASS TRANSFER

In previous sections the problems of the corrosive action of sodium on a pure metal in dynamic and static systems were considered as examples of solution and mass transfer. These are special cases of a general situation since most systems contain more than two components. Thus, if metals, alloys, and nonmetals are mixed with sodium, a number of reactions may take place at competing rates and finally yield a system in chemical equilibrium. In such a case the liquid sodium may act as a solvent and medium for diffusion, the end result being transfer of materials through the sodium until a state of minimum free energy is attained in the system.

A particular case, for purposes of illustration, is the rapid formation of a brittle iron-aluminum intermetallic compound on the surface of an iron strip placed near a strip of aluminum in a sodium bath. The mechanism consists in solution of the aluminum in the sodium, diffusion through the liquid, and reaction at the iron surface. In a previous section it was shown that corrosion in sodium is dependent on the solubility $S$ and the rate of solution $\alpha$. In a multicomponent heterogeneous system the reactions will also depend on the diffusion constants $D$ (for any particular species through sodium) and the thermodynamic activity of the components. At equilibrium the most stable system will be that in which each component is in its most thermodynamically stable state and the activities of each species are everywhere equal. An additional, but completely unsolved, factor in these mass-transfer effects is the role that oxide or other films, present on the solid, may have in determining the rate of interaction. A number of reactions have been observed resulting from mass transfer either through or into sodium. Some are technically important and will be discussed in the following sections.

1. Mass Transfer Upon Immersion of Dissimilar Metals in Sodium

The reactions which occur when two dissimilar, pure metals or alloys are immersed in sodium at temperatures in the range 300 to 600°C would probably be susceptible to exact calculation if sufficient basic data were available. Two of the best examples in the literature are the formation of an iron-nickel solid solution on the surface of nickel specimens immersed in sodium in an iron container, and the extremely rapid formation of the brittle intermetallic compounds between aluminum and iron or aluminum and the components of stainless steel with sodium as a solvent.

In the case of the aluminum, static tests on small aluminum specimens immersed in a large volume of sodium in an iron container showed little or no corrosion during a test period of the order of one week. However, with a reduced volume of sodium and a small sodium annulus (10 to 20 mils) the aluminum sample was drastically attacked, the stable iron-aluminum compound forming on the surface of the iron. This effect is not prevented or inhibited by presaturation of the sodium with aluminum.

Another illustration of the interaction of metals in sodium is the formation of what appears to be an intermetallic compound of nickel and calcium on the surface of the nickel. The sodium-calcium system is of particular interest to KAPL in that the addition of calcium to sodium to remove the last traces of oxygen chemically is under consideration. However, calcium cannot be used when nickel or high-nickel alloys are present in the system.

The rate determining step, or steps, in the above reactions is not known, and in general the number of variables may be quite large, e.g., for the aluminum-iron system the thermodynamics of compound formation, like

$$3\text{Al (in Na)} + \text{Fe (in Na)}$$

$$\rightarrow \text{Al}_3\text{Fe (on the Fe surface)} $$ (40)

the free energy of formation of iron-aluminum solid solutions; the solubilities, rates of solution ($\alpha$), and diffusion coefficients ($D$) of iron and aluminum in sodium and in each other may all be of importance. For this system the transfer of aluminum to the iron surface (rather than in the opposite direction) is probably due to the higher solubility of aluminum in sodium, compared with the iron, but lack of detailed studies on this and similar mass-transfer reactions reduces any detailed consideration of these effects to little more than speculation.

2. Decarburization, Denitrification, and Related Phenomena

Metals in sodium may interact not only with other metals but also with impurities present in the metals or the liquid. In addition to interactions due to mass migration through the solvent, discussed previously, a constituent of the metal may be more stable in the pure state (either in solution in sodium or as a solid)
than as an impurity or alloying element. This appears to be the case with carbon in steels. Carburization and decarburization of steels in the absence of sodium is well known, and recently both reactions have been observed to take place with specimens immersed in sodium. The decarburization reaction was observed at ANL with NaK alloy and mild-steel (SAE 1020) specimens.\(^{13,14,42}\) Other data show that sodium acts in the same fashion.\(^{15,16}\) These observations are based, for the most part, upon metallographic examination. The decarburization takes place rapidly, and it appears that much of the initial loss in weight of carbon steels immersed in sodium may be due primarily to decarburization and not to solution attack of the iron. There is no evidence for the solution of carbon in the sodium, but the carbon may concentrate in the sodium as dispersed particles, which is in agreement with the reported lack of compound formation between sodium and carbon. While potassium and the heavier alkali metals form compounds with carbon,\(^{141}\) workers at ANL have not observed any such compound formation in NaK, and they state that the final state after decarburization appears to be a dispersion of carbon in the NaK alloy. No satisfactory method of analysis for carbon in sodium or NaK has been worked out as yet, but studies are in progress at several laboratories.

The metallurgical consequences of the decarburization of carbon steels are well known. At temperatures of interest in heat-transfer systems, as low as 350 to 450°C, decarburization results in extensive grain growth and the tensile and yield strengths are drastically reduced. This is perhaps one of the most important factors favoring the choice of stabilized alloy steels over low-carbon steels for use in sodium-cooled systems. In static tests carried out at BW on SAE 1020 steel,\(^{142,150}\) no decarburization by NaK alloy was observed while low-chromium steels (2 to 9 percent chromium) were decarburized, although a zone of relatively high-carbon concentration formed near the surface. By further experiments on mild steel the contradiction will probably soon be resolved. The chromium-steel data may involve carburization phenomena to be discussed later. On the basis of all other available evidence, however, low-carbon steels are decarburized by NaK or sodium, contrary to the BW results.

The mechanism of the decarburization of steels by sodium or NaK alloys is not known and has received relatively little attention, but the phenomenon may be examined for consistency with known thermodynamic and kinetic data. Assuming that the end state is carbon dispersed in sodium, the reaction may be written as

\[
C (\text{in Fe}) + Na \rightarrow C \text{(dispersed in Na)} + Na \text{(saturated with C and Fe)} \quad (41)
\]

where the free energy change for the reaction must be negative.

Data are available on the free energy change for the reaction

\[
\text{Fe}_2\text{C} (\beta) + 3\text{Fe} (\alpha) + C (\alpha \text{ graphite})
\]

\[
\Delta F_{500^\circ C} = -2020 \text{ cal/mole} \quad (42)
\]

The carbide is unstable,\(^{55}\) and thermodynamically this decomposition reaction can occur. These data can be applied to the sodium case if the dispersed carbon is assumed to be in equilibrium with \(\beta\) graphite. Since the solubility of carbon in \(\alpha\) iron is very low at 500°C (an assumed average of the experimental decarburization temperatures) having a value\(^{35,124}\) of 0.006 wt. %, this amount may be neglected. In the region from saturation up to the average carbon content of the steels exposed to sodium (which will be taken as 0.2 wt. %), the variation of the partial molar free energy (or activity) of dissolved carbon with concentration may also be disregarded. Stanley\(^{150}\) has measured the diffusion constant of carbon in \(\alpha\) iron at 500°C, and from these data the rate of decarburization of a finite slab has been calculated, assuming diffusion of carbon through the solid to be the rate-determining step. The rate of diffusion of carbon in \(\frac{1}{9}\) in. thick specimens of SAE 1020 steel is such that nearly complete decarburization can occur in about 200 hr. This result has been confirmed by experiments on this steel at KAPL.\(^{122}\) Data from ANL show complete decarburization of SAE 1020 sheet specimens to a depth of 20 mils at 500°C in 312 hr.\(^{35}\) Therefore, the observed data on decarburization in sodium are consistent with the thermodynamic and diffusion-rate data.

The details of the mechanism of the interaction at the interface are not known. The reaction may conceivably involve formation of an unstable sodium-carbon compound or such factors as nucleation and grain growth of the carbon in the sodium. An additional factor which may be of importance is the presence of oxygen in the sodium so the reaction of carbon with Na\(_2\)O at the solid-liquid interface may play a significant role.

The consequences of decarburization as related to dynamic- and static-corrosion rates have not received much attention since the total corrosion rate of metals in sodium has been the objective of most investigators to date. However, if both decarburization and solution of iron occur during exposure of mild-steel specimens, the total corrosion rate is the sum of the solution rate for iron and the rate of decarburization. In other words, the total rate \(R_T = (\Delta W_i + \Delta W_c)/At\), where \(\Delta W_i\) is the weight loss of iron, \(\Delta W_c\) is the weight loss of carbon, \(A\) the area of the surface, and \(t\) the time interval. It is important to separate these two
effects, solution and decarburization, in attempting to correlate the dynamic- and static-corrosion rates theoretically by the methods previously discussed. A specific example is the change in the total dynamic-corrosion rate $R_T$ with time of SAE 1020 steel specimens. Theory predicts, if solution were the only process occurring, that the rate should be independent of time. The data are shown in Table 24.

Table 24 — Nak Harp Test Data at 450°C

<table>
<thead>
<tr>
<th>Duration, days</th>
<th>Corrosion rate, $R_T$, mg/cm²-month</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>-0.35</td>
</tr>
<tr>
<td>28</td>
<td>-0.16</td>
</tr>
<tr>
<td>30</td>
<td>-0.31</td>
</tr>
<tr>
<td>42</td>
<td>-0.14</td>
</tr>
<tr>
<td>167</td>
<td>-0.03</td>
</tr>
<tr>
<td>168</td>
<td>-0.07</td>
</tr>
<tr>
<td>182</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

These data in Table 24 indicate that the rate is constant for the Armco iron (which is essentially carbon free) but decreases for the carbon steel. The rates are in good agreement for long times where $\Delta W_m$ may be large compared to $\Delta W_p$, since the source of carbon is limited. These data suggest that the long-time weight changes observed in the carbon steel are essentially due to solution and that the initial short-time effects are largely due to the decarburization phenomena. It can be seen that a detailed balance of all the constituents of a system is necessary. Weight changes alone, without metallographic analysis, might lead to altogether erroneous conclusions about the nature of the corrosion process. The problems of decarburization and the mechanisms involved are still far from solved and leave room for a great deal of interesting research.

The converse of decarburization of steel has also been observed (see references 49, 132, 149, and 150). Chromium alloy steels in sodium, when exposed to carbonaceous material, tend to pick up carbon. Vendenberg has shown that plain carbon steel in the system can act as the source of carbon. However, carburization has also been observed in the absence of known carbon sources, suggesting that carbon may occasionally be present as an impurity in sodium, possibly as the free element, or it may arise from decomposition of hydrocarbons or inorganic carbonates.

With type 347 stainless steel in the presence of large amounts of carbon this material precipitates at the grain boundaries, presumably as a complex niobium–iron carbide, and, as the niobium is used up, subsequently as a mixed iron–chromium carbide. The result is a general surface embrittlement of the stainless steel. Typical data are as follows: Static runs were carried out exposing type 347 stainless-steel specimens to sodium at 500°C for approximately one month, the source of carbon being the steel container in one case and SAE 1020 steel test strips in another. In both tests the surface layer was carburized to a depth of about 4 mils and became very brittle. Figure 15 shows the altered grain structure, while Fig. 16 shows the intergranular cracks which result upon bending the material. Failure occurs between the grains owing to the brittle nature of the precipitated carbide. Micro-hardness tests showed the surface layer to have a Knoop hardness in the affected zone of 1190 compared to 565 in the core of the sample. Chemical analyses of a 10-mil-deep surface layer of the specimen (the minimum thickness that could be machined off) compared with a sample from the core gave the results shown in Table 25. Assuming that the composition of this layer is the same as the core in the region 4 to 10 mils deep, the average composition in the 4-mil surface layer is 0.35 per cent carbon.

Technically it may be very important to keep carbon away from stainless steel–sodium systems in order to prevent the observed embrittlement, particularly when thin sections of steel are used. Thermodynamically the chromium carbides are stable towards decomposition to carbon, in contrast to the iron and nickel carbides. No data are available on the thermodynamic stability of the carbides of niobium, and there is some question as to their composition. However, they are almost certainly more stable than the chromium carbides, since niobium in stoichiometric excess is added to stainless steel to prevent formation of the complex iron–chromium carbides. The data on the free energies of formation of the carbides given in Table 26 are taken from Kelley.

Referring again to Table 25 it can be seen that the nitrogen normally present in stainless steel was also reduced upon exposure to sodium and practically completely removed in the 4-mil surface layer. This removal of nitrogen may well be important. The role of nitrogen in 18-8 stainless steels has been reported to be the stabilization of the austenitic phase.
Fig. 15—Cross section of carburized type 347 stainless steel showing altered surface zone and unaffected core.
A detailed analysis of this phenomenon leads to the conclusion that sodium plays an important, but secondary, role in the bonding, the extent of the welding being primarily a function of the diffusion rates, which are known to vary exponentially with tempera-

Original Magnification 250×

Fig. 16—Section of carburized type 347 stainless steel showing intergranular cracks caused by bending embrittled material.

zation is not known at present. The diffusion rate of nitrogen in stainless steel can be estimated from data on the diffusion coefficient of nitrogen in austenitic iron. It can be shown that the rate of diffusion is sufficient to account for the denitrification observed. Fortunately, from a technological point of view, removal of nitrogen has not been observed in the absence of an accompanying carburization reaction. Why this is so is not known at present.

B. DIFFUSION BONDING OF METALS IN SODIUM

The formation of solid-phase bonds between metals in intimate contact at an elevated temperature is a well-known phenomenon and has been the subject of a recent survey by Kittel. This bonding or diffusion welding has been observed with metals immersed in either sodium or NaK alloy, the principal work in this field of sodium technology having been carried out at ANL (see references 2, 4, 75, 76, 83, 99, and 99b). However, the total contact area and the nature of the surfaces in contact are also important variables, since impurities or oxide films on the surface may inhibit or prevent bonding. The sodium present in the small space between the two surfaces can play a dual role in the process; first, it may act as a reducing agent (in some cases) to convert oxide films present to base metal; and, second, it may act as a solvent bridge permitting transfer of metal atoms through the liquid, crystal growth occurring at and near the surfaces of contact, although this effect may be of lesser importance. A quantitative comparison of welding, with and without sodium present, is difficult and has not been made. The sodium does appear to accelerate bonding, particularly in the case of iron, while an inhibiting oxide film seems to be present on stainless-steel samples.

The engineering consequences of welding in sodium are quite important and may constitute one of the most serious limitations on the temperature of operation of
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

Data on a series of experiments in which the contact area and pressure were varied\textsuperscript{9,40} to determine the relative importance of these variables are given in Table 29.

Table 27 — Welding of Metals under NaK as a Function of Temperature

<table>
<thead>
<tr>
<th>Interface</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>U-Fe</td>
<td></td>
<td></td>
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<tr>
<td>U-Mo</td>
<td></td>
<td></td>
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<tr>
<td>U-Ni</td>
<td></td>
<td></td>
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<tr>
<td>U-Ta</td>
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<td></td>
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<tr>
<td>U-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Zr</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>U-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
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<tr>
<td>Ni-Be</td>
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<tr>
<td>Ni-Mn</td>
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<tr>
<td>Mo-Nb</td>
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<tr>
<td>Fe-347</td>
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<td></td>
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</tr>
</tbody>
</table>

\*D, phase layers observed.  
\*I, no phase layers formed.  
\*II, irregular layer observed, possibly resulting from impurities.

Based on these engineering data, there apparently is no problem in choosing structural materials for operation of a liquid-sodium or NaK-alloy coolant system at temperatures below 600°C. Type SAE 347 stainless steel has good welding resistance; and, with materials such as Stellite, good resistance at localized points of intimate contact such as valve seats.

Table 26 — Free Energy of Formation of Metallic Carbides

<table>
<thead>
<tr>
<th>T, °C</th>
<th>C_{r}C_{n}</th>
<th>Cr_{n}C_{r}</th>
<th>Fe_{r}C_{n}</th>
<th>Ni_{r}C_{n}</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-12,480</td>
<td>-10,050</td>
<td>4610 (a)</td>
<td>9870</td>
</tr>
<tr>
<td>100</td>
<td>-13,300</td>
<td>-10,430</td>
<td>4340 (a)</td>
<td>8790</td>
</tr>
<tr>
<td>200</td>
<td>-14,400</td>
<td>-10,930</td>
<td>3358 (b)</td>
<td>8660</td>
</tr>
<tr>
<td>300</td>
<td>-15,500</td>
<td>-11,430</td>
<td>3247 (b)</td>
<td>8570</td>
</tr>
<tr>
<td>400</td>
<td>-16,600</td>
<td>-11,940</td>
<td>2623 (b)</td>
<td>8460</td>
</tr>
<tr>
<td>500</td>
<td>-17,700</td>
<td>-12,440</td>
<td>2020 (b)</td>
<td>8350</td>
</tr>
<tr>
<td>600</td>
<td>-18,800</td>
<td>-12,940</td>
<td>1463 (b)</td>
<td>8240</td>
</tr>
<tr>
<td>700</td>
<td>-19,990</td>
<td>-13,450</td>
<td>970 (b)</td>
<td>8130</td>
</tr>
</tbody>
</table>

Data on the extent of the interaction of a number of metallic couples\textsuperscript{27} are given in Table 27. These data represent an incomplete survey of a number of couples and show little welding at temperatures below 600°C in a time interval of six days. Similar data\textsuperscript{28,29} more directly applicable to engineering design have been obtained by loading specimens under 5000 psi pressure and immersing them in NaK alloy for periods of from one week to three months. The data are given in Table 28, expressed as "welding resistance." The lower temperature (450°C) can be considered a desirable operating temperature for presently contemplated reactors.

Based on these engineering data, there apparently is no problem in choosing structural materials for operation of a liquid-sodium or NaK-alloy coolant system at temperatures below 600°C. Type SAE 347 stainless steel has good welding resistance; and, with materials such as Stellite, good resistance at localized points of intimate contact such as valve seats.

Sizable operating temperature for presently contemplated reactors.

Data on a series of experiments in which the contact area and pressure were varied\textsuperscript{9,40} to determine the relative importance of these variables are given in Table 29.

Table 27 — Welding of Metals under NaK as a Function of Temperature

<table>
<thead>
<tr>
<th>Interface</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Ta</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-Zr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Ta</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Zr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-Ta</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta-Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta-Zr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-Zr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\*D, phase layers observed.  
\*I, no phase layers formed.  
\*II, irregular layer observed, possibly resulting from impurities.
can be obtained to temperatures as high as 600°C. Mild steel will weld at 450°C and is an unsatisfactory material. The welding is probably accelerated by the decarburization and resultant grain growth. No welding has been shown for the uranium-nickel or uranium-347 stainless steel couples up to temperatures of 450°C.

The shear strengths for a number of bonds formed after immersing specimens in NaK alloy at 650°C for six days are given in Table 30.

The relative strengths of the bonds are dependent, of course, on the type of interaction. If a brittle intermetallic compound is formed, the breaking strength may be quite low. Again iron-iron proves to be the worst offender; welding occurs at a rapid rate to give a bond as strong as the metal itself. It is reported that iron-iron specimens are completely bonded after 144 hr at 600°C.

### Table 28 — Welding Resistance of Metals under NaK

<table>
<thead>
<tr>
<th>Material</th>
<th>Welding resistance At 450°C</th>
<th>Welding resistance At 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ni</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Ni-347 stainless steel</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>U-Ni</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Monel-Ni</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>U-347 stainless steel</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>304 stainless steel - 304 stainless steel</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Mild steel-mild steel</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Stellite No. 1-No. 6</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>No. 1 stellite-Ni</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Monel-347 stainless steel</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>No. 6 stellite- 347 stainless steel</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

### Table 29 — Strength of Metal Bonds after Welding in NaK

<table>
<thead>
<tr>
<th>Material</th>
<th>Contact area, sq. in.</th>
<th>Loading, psi</th>
<th>Test time, days</th>
<th>Temp., °C</th>
<th>Breaking force, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ni</td>
<td>0.0064</td>
<td>4040</td>
<td>30</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>347 stainless steel-Ni</td>
<td>0.065</td>
<td>4040</td>
<td>20</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.065</td>
<td>4040</td>
<td>62</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>0.4421</td>
<td>578</td>
<td>40</td>
<td>600</td>
<td>645</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.058</td>
<td>2240</td>
<td>5</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.058</td>
<td>4480</td>
<td>22</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>Mild steel-mild steel</td>
<td>0.058</td>
<td>4480</td>
<td>33</td>
<td>600</td>
<td>Very slight</td>
</tr>
<tr>
<td>Stellite No. 1-No. 6</td>
<td>0.058</td>
<td>4480</td>
<td>62</td>
<td>600</td>
<td>Very slight</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0064</td>
<td>3930</td>
<td>30</td>
<td>450</td>
<td>2250</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.0064</td>
<td>3930</td>
<td>33</td>
<td>450</td>
<td>233</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0495</td>
<td>5180</td>
<td>14</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.0495</td>
<td>5180</td>
<td>47</td>
<td>600</td>
<td>621</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0495</td>
<td>5180</td>
<td>7</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.0495</td>
<td>5050</td>
<td>28</td>
<td>600</td>
<td>1420</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0495</td>
<td>5050</td>
<td>17</td>
<td>600</td>
<td>2730</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.0064</td>
<td>4000</td>
<td>8</td>
<td>600</td>
<td>Very slight</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0064</td>
<td>4000</td>
<td>20</td>
<td>600</td>
<td>Very slight</td>
</tr>
<tr>
<td>347 stainless steel - 347 stainless steel</td>
<td>0.0064</td>
<td>4000</td>
<td>62</td>
<td>600</td>
<td>2800</td>
</tr>
<tr>
<td>347 stainless steel-Ta</td>
<td>0.0064</td>
<td>4000</td>
<td>8</td>
<td>600</td>
<td>466</td>
</tr>
</tbody>
</table>
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

The activation energies for diffusion are of interest in estimating the rate of interaction or, expressed in other terms, the penetration rate as a function of temperature. These energies have been investigated for the couples uranium-molybdenum, uranium-nickel, and sodium-potassium alloy to thin sections of a jacketing material. For design purposes it is convenient to extrapolate penetration rates; this can be done to a first approximation using the simple parabolic equation

\[ x^2 = kt \]  

where \( x \) is the thickness of the alloy layer, \( k \) the reaction-rate constant, and \( t \) the time. It should be noted that the more general equation

\[ x^n = kt \]  

should apply, as shown by Lustman and Mehl, with the value of \( n \) varying over wide limits, depending on the detailed mechanism of the bonding process. Assuming simple diffusion to be the rate-determining step, \( n \) is equal to 2, and the values of \( x \) for a period of one year are shown in Table 32. From the data of Table 32, the penetration rate can be quite appreciable at 500°C for thin nickel and stainless-steel couples.

Additional data on solid-state bonding and penetration rates are needed before fuel elements such as the KAPL capsule (in which uranium will be contained in a small cylinder with a wall thickness of 5 to 10 mils) can be designed with any degree of assurance. The possibility of an unknown induction period in the experiments to date may modify the data appreciably, since diffusion could then occur at an even faster rate. A second, and as yet unresolved, problem is the possible acceleration of the diffusion of uranium during irradiation due to neutron and fission-product bombardment. In addition radiation may tend to destroy protective oxide films which normally inhibit welding.

C. SODIUM PURIFICATION METHODS

In previous sections the large and pernicious effect of oxygen in sodium on corrosion has been described in considerable detail. This immediately raises the problem of how to eliminate this impurity. There appear to be three alternative methods: (1) distillation, (2) filtration, and (3) chemical reaction ("gettering"). All three are being examined intensively. Distillation was used by Bennett and is being employed at the present time in the "Genie" Project (the General Electric sodium heat-transfer system being studied under a Navy contract). While plans for the purification plant for the KAPL reactor are still somewhat fluid, the greatest reliance is currently being placed on controlled filtration or a system using calcium metal to getter the sodium. At ANL it is apparently felt that satisfactory purity can be achieved by filtration, and current studies at KAPL, NRL, and else-

Table 30 — Shear Strengths in Metal Couples Welded under NaK

<table>
<thead>
<tr>
<th>Couple</th>
<th>Shear strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-U</td>
<td>6,100</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>5,400</td>
</tr>
<tr>
<td>Fe-347 stainless steel</td>
<td>15,400</td>
</tr>
<tr>
<td>Ni-347 stainless steel</td>
<td>16,300</td>
</tr>
<tr>
<td>Zr-347 stainless steel</td>
<td>1,070</td>
</tr>
<tr>
<td>Zr-U</td>
<td>10,500</td>
</tr>
<tr>
<td>Zr-U</td>
<td>5,300*</td>
</tr>
</tbody>
</table>

*Diffused one day only.

Table 31 — Diffusion Couple Activation Energies

<table>
<thead>
<tr>
<th>Couple</th>
<th>Penetration, mils</th>
<th>Temp., °C</th>
<th>Activation energy, cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Ni</td>
<td>0.27</td>
<td>500</td>
<td>19,000</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>U-Mo</td>
<td>0.038*</td>
<td>500</td>
<td>46,000</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>U-347 stainless steel</td>
<td>0.40</td>
<td>500</td>
<td>16,000</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

*Extrapolated.

Table 32 — Penetration of Uranium as a Function of Temperature

<table>
<thead>
<tr>
<th>Couple</th>
<th>Penetration, mils/year</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Ni</td>
<td>2.1</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>600</td>
</tr>
<tr>
<td>U-347 stainless steel</td>
<td>3.1</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>600</td>
</tr>
<tr>
<td>U-Mo</td>
<td>0.29</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>600</td>
</tr>
</tbody>
</table>

and uranium against SAE 347 stainless steel. The rates are for the total maximum diffusion layer thickness formed after six days contact in NaK. These rates are given in Table 31. The penetration of uranium into a metal is of particular interest in reactors in which uranium may be thermally bonded with sodium or sodium-potassium alloy to thin sections of a jacketing material. For design purposes it is convenient to extrapolate penetration rates; this can be done to a first approximation using the simple parabolic equation

\[ x^2 = kt \]  

where \( x \) is the thickness of the alloy layer, \( k \) the reaction-rate constant, and \( t \) the time. It should be noted that the more general equation

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</tr>
<tr>
<td>Zr-347 stainless steel</td>
<td>1,070</td>
</tr>
<tr>
<td>Zr-U</td>
<td>10,500</td>
</tr>
<tr>
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<td>5,300*</td>
</tr>
</tbody>
</table>

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<tr>
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<tbody>
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<td>U-Ni</td>
<td>0.27</td>
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</tr>
<tr>
<td></td>
<td>1.1</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>U-Mo</td>
<td>0.038*</td>
<td>500</td>
<td>46,000</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>U-347 stainless steel</td>
<td>0.40</td>
<td>500</td>
<td>16,000</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

*Extrapolated.

Table 32 — Penetration of Uranium as a Function of Temperature

<table>
<thead>
<tr>
<th>Couple</th>
<th>Penetration, mils/year</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Ni</td>
<td>2.1</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>600</td>
</tr>
<tr>
<td>U-347 stainless steel</td>
<td>3.1</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>600</td>
</tr>
<tr>
<td>U-Mo</td>
<td>0.29</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>600</td>
</tr>
</tbody>
</table>
where indicate that carefully filtered sodium or NaK is very nearly as free of oxygen as material prepared by the other procedures.

In the sections below, the available information on these three methods of purification will be reviewed.

1. Distillation

From the data on the vapor pressure of sodium and the rather more uncertain values of NaK given in Tables 8 and 14 of Part I of this paper, it might be supposed that the separation of NaK from sodium by distillation is comparatively simple. Actually this process is complicated by the limited solubility of NaK in sodium and by some somewhat puzzling deviations from the simple-solution laws.

To analyze this problem, let \( x \) be the mole fraction of NaK in the liquid and \( y \) the mole fraction in the vapor. Now by Dalton’s law of partial pressures

\[
\frac{y}{P_{\text{Na}_2\text{O}}} = \frac{x}{P_{\text{Na}_2\text{O}} + P_{\text{Na}}}.
\]

In general \( P_{\text{Na}_2\text{O}} < P_{\text{Na}} \), and the partial pressure of sodium over the mixture is approximately equal to the vapor pressure of pure sodium, i.e., \( P_{\text{Na}} = P_{\text{Na}}' \). So

\[
y = \frac{P_{\text{Na}_2\text{O}}}{P_{\text{Na}}} \times x.
\]

Now, if the solution is saturated with NaK at all times during the distillation, the partial pressure of NaK is equal to the vapor pressure of pure NaK, i.e.,

\[
P_{\text{Na}_2\text{O}} = P_{\text{Na}_2\text{O}}' \times
\]

\[
y = \frac{P_{\text{Na}_2\text{O}}'}{P_{\text{Na}}} \times x.
\]

At the normal boiling point of sodium, \( 892 \degree C \), \( P_{\text{Na}}' = 760 \text{ mm Hg} \), and, from Eq. 29 of Part I of this paper, \( P_{\text{Na}_2\text{O}}' = 13.7 \text{ mm Hg} \). So that if the distillation were carried out at this temperature from a solution containing excess solid NaK, from Eq. 47, \( y = 13.7/760 \) or 0.0180. This calculation then leads to the conclusion that the distillate will contain 69.6 x 0.0180 or 1.25 per cent oxygen. Since the equilibrium solubility of NaK in sodium is not believed to reach this value, even at this very high temperature (although conclusive evidence on this point is lacking), it appears clear that atmospheric-pressure distillation of sodium containing solid NaK should lead to a distillate richer in oxygen than the starting material. It should be noted also that multiple-plate distillation will not help the purification process in this case.

Now, if the original solution is not saturated at the temperature of distillation, \( P_{\text{Na}_2\text{O}} = P_{\text{Na}_2\text{O}}' \). If the solution is assumed to follow Henry’s law up to the saturation concentration, \( x_s \).

When the analysis is carried through as before, the distillate will contain

\[
69.6 \times \frac{P_{\text{Na}_2\text{O}}}{P_{\text{Na}}} \times x_s = 1.25 \times x_s \quad \text{wt. \% oxygen}
\]

This is what would be expected from a single-plate distillation. For an n-plate column, the final product will contain

\[
\left( \frac{1.25}{P_s} \right) P \quad \text{wt. \% oxygen}
\]

where \( P_s \) is the wt. \% oxygen present at saturation at the temperature of distillation and \( P \) is the initial wt. \% oxygen in the sodium.

The degree of purification to be expected by low-pressure (vacuum) distillation could be computed in the same way. Unfortunately the data on the equilibrium solubility of NaK in sodium as a function of temperature are meager, and the vapor pressure data on NaK are extremely doubtful. Furthermore there is always the possibility that the simple-solution laws used above do not apply, and the system NaK-Na is complicated by azeotropism.

Experimentally, the study made by Lee at MSA seems to lead directly to the following conclusions:

1. In atmospheric-pressure distillation of sodium, carefully filtered at 150 to 175 \degree C, the NaK passes off first, so that the still-pot residue is leaner in oxygen than the initial feed or the distillate.

2. The distillate uniformly contains 0.01 to 0.03 wt. \% oxygen.

3. Lee feels that “there is no reason to expect that sodium containing less than 0.01 wt. \% oxygen cannot be produced consistently. After the initial distillation and removal of sodium oxide, the pure sodium can be drained off. However, certain other undesirable impurities may exist which will require distillation of the sodium even after sodium oxide has been removed.”

The results described under (1) above are somewhat anomalous. The starting material in these experiments is saturated with NaK at a low temperature; if, as is to be expected, the solubility increases with increase of temperature, at the normal boiling point of sodium the solution should, therefore, be undersaturated, and Eq. 48 should apply, or, if the NaK vapor pressures are correct, Eq. 50 should apply. The quantity \( n \) in this work is approximately 4 in this work. In this case \( p = p_s \) at about 160 \degree C, and from Eq. 50

\[
\text{Wt. \% oxygen in distillate} = 2.4 \left( \frac{P_{\text{Na}_2\text{O}}(\text{at } 160 \degree C)}{P_s(892 \degree C)} \right)^{\frac{1}{n}}
\]
For the distillate to be richer in oxygen than the feed therefore, \(2.4/\left[ P_{N_2O} \right]^{1.25} \) must be less than 1, and \( P_{N_2O} \) is probably less than 0.01 wt. %. While this is by no means impossible, it appears to be an extremely high value for the solubility considering the fact that \( P_{N_2O} \) is probably less than 0.01 wt. %.

Experimentally (cf. comments on the work by Buncel and Kohlraush, Sec. B-1, Part I) there is some indication that the estimated vapor-pressure data for \( P_{N_2O} \) may be in error by a considerable amount. If \( P_{N_2O} \) at 892°C is a factor of 10 less than the value used, carrying through the analysis as before, it appears necessary that \( P_{N_2O} \) be 0.125 wt. % for the vapor to be richer in oxygen than the feed. This last figure seems quite reasonable, but the large decrease in \( P_{N_2O} \) is somewhat difficult to accept. The final resolution of this difficulty must await better data on the vapor pressure of \( N_2O \) and its solubility in sodium as a function of temperature.

Lee's last remark, (3) above, brings up a very important point: the removal of impurities other than \( N_2O \) from sodium by distillation. While commercial sodium brick is relatively pure, it may contain carbon (as carbonate, organic carbon, and free carbon), which, as has been discussed above, is known to have a deleterious effect on stainless steels, plus other impurities which may or may not influence the corrosion, metallurgical properties, or nuclear behavior of the system. If these impurities are relatively nonvolatile compared with sodium, distillation appears to be the most feasible method of eliminating them.

Because of the uncertainties in other purification procedures which have been suggested for sodium, project Genie has decided upon distillation, discarding "tops" and "bottoms," as its purification method. The Genie still is designed for semicontinuous operation at atmospheric pressure. Filtered sodium in 200-lb batches is distilled until 15 per cent of the metal has passed over. This top fraction is expected to be richer in \( N_2O \) and is discarded. The remaining still-pot residue is then transferred to a second still, operated under similar conditions, where the bulk of the sodium is distilled off for use, leaving only about 15 per cent bottom residue to be discarded. A flow sheet for the Genie still, designed to produce pure sodium and NaK by blending the material thus prepared with purified potassium, is shown in Fig. 17. The complexities which a distillation process involves are clear from this drawing.

While distillation has some obvious advantages, it is also subject to real limitations. First, distillation is relatively expensive and cumbersome, compared with other purification methods. Second, the feasibility of removal of \( N_2O \) from sodium by distillation, while strongly indicated by studies which have been made to date, has not been demonstrated on a large scale. The limitations of the mercury-amalgamation technique for determining oxygen in sodium (cf. Sec. B-1, Part I) are such that following the course of the oxygen through the various stages of the distillation procedure is difficult. Finally, a sound basis for engineering design of a distillation system can be established only when \( P_{N_2O} \) and the vapor-liquid equilibrium diagram of the system \( NaO-Na \) are known as functions of temperature. While techniques for measuring these quantities will no doubt be exacting, the profits from such a study would appear to be extremely worth while.

2. Filtration

The simplest and most inexpensive method of purification is filtration. The common source of large quantities of sodium is the bricks, cast in air, as furnished by the Electrochemical Department of the E. I. du Pont de Nemours & Company. As received, the bricks are covered by a mixed oxide-hydroxide-carbonate layer contaminated with hydrocarbons used to lubricate the molds during casting. The analysis of this sodium is given in Sec. III-F. At the concentrations listed it is felt that no impurities other than oxygen and carbon will affect the operation of the KAPL reactor. This is based on the lack of corrosion in sodium of this type used under oxygen- and carbon-free conditions.

In the past, standard practice in purification of a charge of liquid sodium for experimentation has been to melt bricks in a tank, allowing the surface impurities to settle or float to the liquid surface. In withdrawing the charge, filters have been used in most cases to remove larger particles, and filters have been included in designs for other purification systems as a preliminary purification step. Until recently filtration only has not been considered as the primary purification process at KAPL. Neglecting other constituents for the present, oxygen will be discussed as the principal impurity and used as a basis for comparing filtration with the other two methods, gettering and distillation. (It may be remarked in passing that distillation appears to be the only feasible method of removing minor soluble nonvolatile constituents, should this removal prove necessary.)

In the past a large amount of data were accumulated, suggesting that filtered sodium contained undesirable amounts of oxygen (greater than 0.01 wt. %). With present techniques, filtered sodium has been shown to contain less than this amount. The reader should bear this point in mind in reading older reports and literature on this subject. Samples of sodium taken from melt tanks, static pots, and large engineering systems showed 0.03 to 0.06 wt. % oxygen.\(^{49,50,89}\) Corrosion tests using filtered sodium also showed more attack than sodiumgettered with calcium.\(^{130}\) In addition preliminary sodium oxide solubility experi-
ments described in the first part of this paper indicated an equilibrium solubility at the melting point of 0.07 ± 0.03 wt. % oxygen in solution. However, based on data to be mentioned later, it appears that fine particles of sodium oxide in suspension which passed through the sampling filters in these solubility experiments account for the low accuracy, a possibility which was recognized and feared in reporting the data. The filters used were made of sintered stainless steel and had average pore sizes ranging from 5 to 165 μ. Passage of a relatively large amount of sodium through a filter seemed to plug up the pores and result in a filter cake which was considerably more effective than a fresh filter in removing oxide.

2. The accuracy in the oxygen analytical procedure has been increased.
3. Generally improved asepsis is now employed, so far as oxygen is concerned, in handling and sampling liquid sodium.
4. Proper precipitation (aging) and settling techniques to remove sodium oxide before use are now being utilized.

These factors can best be taken up separately. The first, better sampling techniques, is important since continued sampling of sodium and better understanding of the method appears to be giving better reproducibility. Without experimental proof it would seem that present data might run as much as 0.02 wt. % oxygen lower than the past samples. This could account for a large portion, but probably not all, of the discrepancy in the oxygen content of melted, or melted and filtered, sodium.

The second point, improvement in analytical techniques, has pushed the absolute accuracy in weight per cent oxygen from ±0.01 wt. % down to at least ±0.005 and possibly ±0.001 wt. %. Neither improvement in technique is sufficient to account for the high oxygen values found in the solubility work, suggesting a higher solubility at higher temperatures or the presence of finely divided solid oxide.

The third factor obviously is important.

The sudden production of oxygen-free (less than 0.01 wt. %) sodium even without filtration requires explanation. Data are still being accumulated, but the following factors appear significant:

1. Better and more accurate sampling techniques for the oxygen analyses are available.
previously mentioned, samples taken from near the center of a melt tank without filtration showed less than 0.01 wt. % oxygen. In this case the bulk sodium was allowed to stand overnight before sampling. This phenomenon has been called "aging"; it is assumed that the finely divided sodium oxide present as a dispersion coagulates and either settles to the bottom or floats to the surface when held above the melting point for a period of some hours. The exact time required for this process to occur has not yet been definitely established. The role that agitation plays is not understood, but apparently once the oxide has coagulated it is not dispersed by violent agitation, since aged sodium was agitated and at temperatures less than 220°C the oxygen content remained less than 0.01 wt. %.

Corrosion tests with type 347 stainless steel on this carefully prepared and filtered sodium have shown nearly as little attack as has been observed with the best calcium-gettered runs to date, less than +0.05 mg/cm²-month. However, corrosion tests have also indicated a settling effect with agitated sodium for which, unfortunately, oxygen data are not available. In one run, a melt tank of sodium (with a crust of oxide on the surface) was agitated for 1 hr and then a portion withdrawn for static-corrosion tests on stainless-steel specimens. Specimens suspended in the sodium gained weight slightly (+0.16 mg/cm²-month), but a specimen resting on the bottom of the stainless-steel static pot was attacked at a rate approximately a hundred times as great (+14 mg/cm²-month). This has been interpreted as a settling effect in which a relatively small amount of dispersed oxide settled from the large bulk of the sodium and was concentrated on the bottom of the container.

More data are definitely needed before the aging phenomena can be verified as real and, in particular, shown not to be due to improvements in handling, sampling, and analyzing sodium. However, it does appear that large amounts of oxygen can be dispersed in sodium for moderate lengths of time (several hours), based on the previously mentioned solubility experiments. In that case the experimental conditions may have been ideal for creating a dispersion (i.e., addition of oxygen at high temperatures, with good agitation, so that the oxide first formed is dispersed in a very finely divided condition), and these conditions may be reproduced in general practice.

To summarize the status of purification by filtration, this procedure may be completely adequate, using the apparently effective but as yet inconclusively established technique of properly aging the sodium. In this case filtration may not even be necessary but would be used to ensure uniformity and remove larger particles of impurities. Such a procedure would be by far the least expensive method, should it be reliable. It should be mentioned that filtration and even simply melting to produce gross segregation of the solid impurities from the liquid have been successfully used to prepare sodium for other engineering uses such as in the valves of internal combustion engines. The need for other more complex treatments may well be less urgent when standards of practice are not based on use in a nuclear reactor.

3. Chemical Reaction (Gettering)

Any chemical reaction in which sodium oxide in sodium is either reduced to metallic sodium or tied up as an insoluble or nonreacting compound should constitute a basis for the purification of sodium on an engineering scale, assuming oxygen to be the critical impurity. (Other constituents such as trace amounts of chloride, carbon, and calcium will probably not be removed by such treatment.) The class of reaction that has received the most attention to date at KAPL is that in which sodium oxide is reacted with a metal and reduced to sodium, the metal being oxidized. Such metals have been referred to as "getters" by some workers in the field owing to the resemblance to vacuum-tube techniques. An essential condition for the use of a getter metal is that the free energy of formation of its oxide per atom of oxygen must be significantly greater than the free energy of formation of Na₂O.

In Table 33 the free energy change for the reaction

\[
\frac{a}{b} M + \text{Na}_2\text{O} = \frac{1}{b} \text{M}_2\text{O}_3 + 2\text{Na}
\]

has been tabulated for a number of possible materials. The data have been abstracted from Table 16 of Part 1 of this paper and arbitrarily edited to throw out met-
als whose thermal cross sections for absorption of neutrons is known to be greater than 10 barns. On the basis of the evidence given in Sec. III-A, chromium or stainless steel might also be considered as possible getters, even though the available free energy data are not encouraging.

Since the rate at which the gettering reaction occurs is not known, this quantity must be determined experimentally. In the absence of data, it is generally best to carry out the reaction at as high a temperature as possible.

A second class of compounds offers a somewhat different means of removing oxygen from sodium, namely, through direct combination. For example, SiO$_2$ may react with Na$_2$O in the following manner:

$$\text{SiO}_2 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 \quad \Delta F^\circ = -70 \text{ kcal} \quad (53)$$

Aluminum oxide may also tie up sodium oxide in this manner, and further investigation may suggest additional compounds.

In addition to the thermodynamic characteristics, the following properties must be considered in selecting a getter for sodium purification:

1. Nuclear. If the sodium is to be used in a nuclear reactor, the getter should not have a high neutron cross section over the neutron-energy spectrum contemplated, so that the amount dissolving in the sodium will not contribute appreciably to the neutron loss of the system. Also, the capture products should not be long-lived, with associated high-energy-\(\gamma\) activity.

2. Metallurgical. The getter should not interact with the system materials to form undesirable alloys or intermetallic compounds. An example of this is the formation of the nickel-calium compound.$^{47}$

3. Chemical. Getter materials can arbitrarily be classified into two groups, those which are appreciably soluble in sodium and those which are relatively insoluble. The soluble getters probably will react more readily with Na$_2$O in solution, but they will be carried into the reactor in the coolant stream and consequently their nuclear properties will be more important. It may be advantageous to carry out a temperature cycle with soluble getters in which the reaction takes place at a high temperature and the charge is cooled to a low temperature for filtration of the sodium, thus removing a fraction of the soluble getter. Such a system is under consideration at KAPL, using calcium, which has a high temperature coefficient of solubility.

The insoluble getters are perhaps most readily adaptable to a constant-flow purification system, particularly so if the reaction products adhere to the surface. Uranium, while probably not useful for reactor-sodium purification, is an example of this group of getters and has been tried experimentally at ANL to purify NaK alloy.$^{48}$

It is of interest to determine the limiting degree of purification that can be expected using chemical reaction to remove sodium oxide. From Eq. 52 the equilibrium constant of the reaction is

$$K = \frac{1}{(\text{Na}_2\text{O})} \quad (54)$$

where (Na$_2$O) represents the concentration of sodium oxide in solution in the sodium (expressed as moles of oxygen per 100 grams of sodium) and the other constituents are present at unit activity since they are solids or liquids in excess. Since

$$\Delta F^\circ = -RT \ln K \quad (55)$$

then

$$(\text{Na}_2\text{O}) = \exp \frac{\Delta F^\circ}{RT} \quad (56)$$

If calcium is used as a getter at 500°C, the equilibrium concentration of oxygen in the sodium will be $$(\text{Na}_2\text{O}) = e^{-77} \text{ moles of oxygen per 100 grams of sodium},$$ which is equal to $8 \times 10^{-17}$ wt. \(\%\) oxygen, an entirely negligible amount. In a dynamic system the oxygen content may be far from its equilibrium concentration and the degree of decontamination much less. However, the product should be much purer than that obtained by distillation.

Numerous experimental approaches have been followed to determine the desirability and practicability of pretreatment of sodium by chemical reaction. A comparison has been made of the behavior of gettered sodium and untreated filtered sodium with respect to oxygen content, attack on metals, and the nature of the metal surfaces after exposure. Unfortunately exact data are not yet available in many cases.

A few semiquantitative measurements have been made at KAPL on the oxygen content of sodium before and after treatment with calcium. The results have been promising, indicating successful purification. In these experiments excess oxygen as Na$_2$O was added to sodium contained in a stainless-steel vessel.$^{49}$ Subsequently, calcium in stoichiometric excess to the oxygen was added and the system heated to 400°C. The liquid was cooled to about 150°C before sampling, and stainless-steel filters with an average pore size of about 30 \(\mu\) were used to prevent contamination with particles of calcium oxide or solid calcium. The residual oxygen content was found to be 0.003 wt. \(\%\) oxygen after treatment, whereas similar untreated samples generally contained 0.03 to 0.10 wt. \(\%\) oxygen. It was necessary to modify the standard amalgamation procedure for oxygen analysis$^{44}$ to include analysis for calcium oxide present in the sample, since this oxide titrated along with sodium oxide, giving erroneously high results.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

The determination of the factors which establish the ultimate oxygen content of gettered sodium will probably be difficult and time-consuming, but the engineering tests should also yield these data. At present ±0.003 wt. % oxygen is about the lower limit of sensitivitv of oxygen analyses and the sampling techniques are not too satisfactory or reproducible, which makes a detailed study of gettering extremely troublesome.

Magnesium has been used in a slightly different approach as an oxygen getter for the determination of oxygen in sodium. Preliminary data indicate that the method is feasible and also furnish some information on the completeness of reaction of a getter with oxygen and sodium. Experimentally, magnesium turnings were reacted with sodium at 300°C to form magnesium oxide from the sodium oxide present. The amount of magnesium oxide formed was determined by distilling off excess magnesium and sodium. On the basis of the data obtained, the oxygen present in the triple-distilled sodium was 0.003 wt. % in agreement with other methods. In one run a known large excess of oxygen was added to the sodium and the recovery was 60 per cent. The incomplete recovery was probably due to factors susceptible to control, and additional experiments are required.

Another method of evaluating calcium gettering, which has been followed at KAPL, is based on the sensitivity of the corrosive attack of sodium on stainless steel to the oxygen content. In static-corrosion tests there is generally a slight gain in weight of SAE type 347 stainless steel due to the formation of a light-grey oxide film on the surface of the metal. This is always the case for untreated sodium. With calcium-gettered sodium the film formation is much less and in most cases the surface after test is still bright and shiny. The weight gains are smaller and in a few tests the specimens decreased slightly in weight. These lowered corrosion rates are the basis of the plan to pretreat sodium before use in the KAPL reactor, since in this system many thin sections of stainless steel will be used. The latest available data (April 1950) from these tests indicate the results shown in Table 34.

Table 34 — Comparison of Corrosion Rates of Filtered and Calcium-gettered Sodium
(500°C, 730 hr, type 347 stainless steel)

<table>
<thead>
<tr>
<th>Sodium treatment</th>
<th>Sample pretreatment</th>
<th>(R_T), mg/cm²-month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aged and filtered</td>
<td>Alcohol cleaning</td>
<td>+0.13 ± 0.03</td>
</tr>
<tr>
<td>Aged and filtered</td>
<td>Electrolytic</td>
<td>+0.07 ± 0.03</td>
</tr>
<tr>
<td>Calcium-gettered</td>
<td>Alcohol cleaning</td>
<td>+0.04 ± 0.03</td>
</tr>
<tr>
<td>Calcium-gettered + 0.01 wt. %</td>
<td>Alcohol cleaning</td>
<td>+0.02 ± 0.03</td>
</tr>
<tr>
<td>Calcium-gettered + 0.01 wt. %</td>
<td>Electrolytic</td>
<td>+0.02 ± 0.03</td>
</tr>
<tr>
<td>Calcium-gettered + 0.03 wt. %</td>
<td>Alcohol cleaning</td>
<td>+0.18 ± 0.03</td>
</tr>
<tr>
<td>Calcium-gettered + 0.03 wt. %</td>
<td>Electrolytic</td>
<td>+0.10 ± 0.03</td>
</tr>
</tbody>
</table>

The results in Table 34 have led to the following conclusions:

1. Aged and filtered sodium was not so noncorrosive to type 347 stainless steel as calcium-gettered sodium. It appears therefore that calcium gettering is a more effective method of removing oxygen from sodium than aging and filtering.

2. When the oxygen content which can be gettered by residual calcium is exceeded, measurable corrosion occurs.

3. The corrosion rate was higher for alcohol cleaning than for electrolytic cleaning when there was sufficient oxygen present to cause a measurable attack. This agrees with previous results.

Some of the best data on chemical treatment of sodium or NaK alloy have been obtained at MSA using various solid getter metals. The tests were run in a standard thermal-convection hump with mild-steel (SAE 1020) samples. The positive effect of oxygen on corrosion has been discussed in a previous section, but some of the data will be repeated here for comparison. The data are tabulated in Table 35. The amount of getter metal added is expressed as the percentage of the theoretical amount required to combine with the oxygen added. The first group of tests show the deleterious effect of oxygen and the complete inhibition due to magnesium. Zirconium (similar results have been observed with titanium) does not appear as good as magnesium, and the difference is probably due to the relative insolubility compared with magnesium, suggesting that liquid-phase getters are more suitable.
In addition to the MSA experiments tabulated in Table 35, the order of addition of the oxygen and magnesium metal was inverted. In this case the oxygen was added before the getter. In contrast to the previous experiments, the getter was not effective. The corrosion was not reduced but even appeared to be accelerated. The reason for the lack of effectiveness of magnesium under these conditions is not apparent. Possibly the magnesium became covered with a film of adherent magnesium oxide which inhibited the gettering action. Additional work in this field is required.

The general effectiveness of chemical pretreatment of sodium has been demonstrated at least qualitatively, and, since such a treatment appears more reproducible and yields sodium with a lower oxygen content than filtration (on the basis of present data), engineering studies have been initiated at KAPL on the treatment of sodium on a bench and pilot-plant scale. Batch-by-batch treatment and continuous treatment employing calcium are being investigated. In the batch system the sodium will be held in contact with excess solid calcium at approximately 400°C for the required period of time and then cooled to about 125°C to precipitate out most of the dissolved calcium. In this manner most of the calcium can be removed by filtration before passing the sodium into the reactor, since the solubility is about 0.048 wt.% at 125°C compared to 1.8 wt.% at 400°C. Data are available from the Du Pont Company showing the filtration of the precipitated calcium to be practical.

Table 35 — MSA Experiments on Use of Getter Metals to Purify NaK

<table>
<thead>
<tr>
<th>Experimental conditions:</th>
<th>Corrosion rate, $R_T$</th>
<th>Treatment mg/cm²-month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure, dynamic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test material, mild steel (SAE 1020)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration, 500 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, 1000°F (538°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid metal, NaK (66 wt. % potassium)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>0.1 wt. % O₂</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>0.1 wt. % O₂</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>150 wt. % Mg-0.1 wt. % O₂</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>150 wt. % Mg-0.1 wt. % O₂</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>150 wt. % Zr-0.1 wt. % O₂</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>150 wt. % Zr-0.1 wt. % O₂</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

*Oxygen added as sodium peroxide.

is attained at the lower temperature, the residual calcium in the system will not be harmful in the KAPL reactor. However, because of the metallurgical incompatibility of calcium with some metals such as nickel, highly insoluble metals such as zirconium may be desirable for other systems.

D. SOURCES OF IMPURITIES AND ESTIMATED TOLERANCE LEVELS FOR SODIUM SYSTEMS

In this section an effort will be made to apply the principles developed in previous paragraphs to a typical full-scale sodium system. In addition, some of the problems and observations made to date on experimental large-scale systems will be included. It should be pointed out that all the data are preliminary, and the interpretations presented are necessarily incomplete. This section should be considered more as an outline of the approach being followed at KAPL rather than as a guaranteed procedure to follow for successful operation with sodium. The KAPL point of view is perhaps somewhat conservative, and, moreover, many of the following interpretations are the opinions of the authors. A typical coolant system considered for the KAPL power-breeder reactor will be used as an example since tolerance levels for impurities will depend on the size and shape of the system.

To date, large-scale sodium or NaK alloy systems have been successfully operated at many sites: KAPL, ORNL, ANL, MSA, and BW. It appears that, if reasonable asepsis is maintained with respect to oxygen and water, no difficulties are encountered in operation. In the earlier days of sodium technology a large amount of time was spent in the development and refinement of techniques for handling this material. These large systems tended to plug at first, and large amounts of a black so-called "crud" were often observed to form on or in the sodium at both KAPL and ANL. For example, at KAPL McMahan has operated a low-carbon-steel system holding about 300 gal of sodium. The sodium used was commercial brick from the Du Pont Company and, after melting, was filtered through fine (about 200 mesh) screen. As the system was operated, large amounts of the black solid accumulated on the surface. This was repeatedly removed by skimming, and eventually it stopped forming. This material is highly pyrophoric and appears to be a mechanical mixture of sodium and sodium oxide.

Chemical analysis has shown that this material contains about 98 per cent sodium and 2 per cent oxygen, with a trace of iron present. The oxygen content of the sodium in the system was observed to drop from about 0.06 to 0.01 wt. % over the course of the black-crud removal. Along similar lines at ANL, a thermal-convection system was observed to plug partially upon addition of about 0.2 wt. % oxygen and completely plug upon addition of 0.5 wt. % oxygen.
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

As discussed in a previous section, the oxygen sensitivity of sodium systems is well recognized. Unfortunately insufficient data are available on long-term tests with large sodium systems from which an extrapolation can be made to the operating life of a reactor-coolant system, based on this factor. In particular, the degree of purity required is not known precisely. Several surveys of the contamination problem at KAPL have been prepared.30,35,116

Now let us discuss contamination in a typical sodium system. The approximate parameters of this system are:

<table>
<thead>
<tr>
<th>Structural material</th>
<th>Type 347 stainless steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum sodium temperature</td>
<td>400°C</td>
</tr>
<tr>
<td>Minimum sodium temperature</td>
<td>300°C</td>
</tr>
<tr>
<td>Sodium volume</td>
<td>800 ft³</td>
</tr>
<tr>
<td>(2.7 x 10⁷ cm³)</td>
<td></td>
</tr>
<tr>
<td>Helium volume</td>
<td>2000 ft³</td>
</tr>
<tr>
<td>(5.7 x 10⁷ cm³)</td>
<td></td>
</tr>
<tr>
<td>Sodium-steel interfacial area</td>
<td>4500 ft²</td>
</tr>
<tr>
<td>(9.2 x 10⁶ cm²)</td>
<td></td>
</tr>
<tr>
<td>Sodium-helium interfacial area</td>
<td>200 ft²</td>
</tr>
<tr>
<td>(1.0 x 10⁵ cm²)</td>
<td></td>
</tr>
<tr>
<td>Weight of stainless steel</td>
<td>200 tons (2 x 10⁸ g)</td>
</tr>
</tbody>
</table>

Besides old shoes, mice, and rubber gloves which should be removed in the first clean-up, there may be other impurities remaining in the system. The ones considered of importance for which tolerance limits have been set are tabulated below. The upper limit set for carbon is the total integrated amount over life of the unit.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Upper limit in the coolant system, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>220</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>None</td>
</tr>
<tr>
<td>Oxygen (water)</td>
<td>100</td>
</tr>
<tr>
<td>Carbon</td>
<td>2</td>
</tr>
</tbody>
</table>

Hydrogen. The upper limit on the amount of hydrogen which can be tolerated is fixed by nuclear considerations, based on the neutron-moderating effect of hydrogen.

Nitrogen. Practically indefinitely large amounts of nitrogen can be tolerated in the coolant system since no reaction takes place with the sodium. In addition, no reaction will occur due to radiation in the absence of oxygen and moisture. For practical purposes the nitrogen content of the helium blanket will be controlled since it has a much higher cross section for neutron absorption than helium and, in addition, calcium may be present in the sodium, and formation of calcium nitride is undesirable.

Oxygen (water). The maximum amount of oxygen that can be tolerated depends upon corrosion considerations. At present an upper limit of 0.01 wt. % oxygen from any source, oxygen, water, or oxide impurities, appears safe.

Carbon. The amount of carbon from any source that can be tolerated is not known exactly, since the precise effect of this impurity on stainless steel and the rates of reaction are not known. However, the carburization effect previously mentioned can be serious. The provisional upper limit on carbon in the tabulation above is fixed as the amount of carbon necessary to react with one-half the niobium normally present in a 1-mil-thick layer of type SAE 347 stainless steel. On this basis the maximum amount tolerable is 2 ppm. This figure may be very conservative, and work is underway at KAPL to obtain a more realistic evaluation of the effect of carbon.

Having discussed the impurities which should be controlled, it is pertinent to discuss the various sources of these impurities. It should be noted that the figures quoted below are simply those in use at KAPL; in general, such quantities as the amount of oxygen permissible in the inert-gas blanket will depend on the size and geometry of the system and on the repurification rate of the reactor sodium which in itself is necessarily dependent on the rate of contamination.

1. Sources of Oxygen
   a. As an Impurity in Helium. At KAPL a limit of 20 ppm of oxygen in the helium-gas blanket has been established. The gas represents one of the biggest potential sources of oxygen.
   b. As Present in Water Vapor in Helium. The KAPL limit is -40°C with the dewpoint at 200 psi gauge.
   c. From Oxide Films Present on Stainless Steel in Contact with Sodium. It can be shown that the average film thickness of oxide would have to be of the order of 100,000 A to give a marked increase (of the order of 0.02 wt. %) in the oxygen content of the sodium even if the oxide film is completely reduced by the sodium. Since the films on bright and shiny stainless steel are probably of the order of 700 to 1000 A thick,24 visually clean surfaces should be more than satisfactory for exposure to sodium. In addition static tests indicate no reducing action of sodium on the oxide films on stainless steel.42 From these comments it can be seen that it is possible to overemphasize the importance of thin oxide films on stainless steel.
   d. Diffusion from and through Stainless Steel into Sodium. A potentially large source of contaminant oxygen is the oxides normally present in the stainless
steels derived from process slag and similar sources, probably of the order of 0.1 to 0.01 wt.%. In addition the diffusion of atmospheric oxygen through the steel walls of the system must be considered. Very little data are available on the diffusion of oxygen in steels, but, based on the work of Bramley, the amount diffusing appears insignificant. For Armco iron at 1000°C the diffusion constant \( D = 7.5 \times 10^{-10} \text{ cm}^2/\text{sec} \) was found. The well-known Langmuir-Dushman equation

\[
D = \frac{E}{hN} e^{-E/kT} \tag{57}
\]
can be solved for \( E \) and \( D_0 \) where \( D_0 = Ed^2/hN \), \( d \) = lattice parameter for \( \gamma \) iron (3.65 \times 10^{-8} \text{ cm}) \), \( h \) = Planck's constant, and \( N \) = Avogadro's number. Then solving the equation, \( E = 53 \text{ kcal} \) and \( D_0 = 0.75 \text{ cm}^2/\text{sec} \). Taking the lattice spacing to be about the same in austenitic stainless steel as in \( \gamma \) iron, solution of the diffusion equation for a semi-infinite slab shows diffusion of oxygen to be insignificantly small at temperatures as high as 600°C. The use of an inert atmosphere such as the KAPL helium blanket to encase the sodium system will eliminate the trace amount of oxygen contamination by diffusion through steel.

2. Sources of Carbon

There are perhaps three important sources of carbon in a system of the type considered here.

a. Helium. Carbon may be formed by the decomposition of hydrocarbons present as an impurity in this gas.

b. Sodium. Sodium may contain free carbon as an impurity arising from the manufacture of the material; or contamination during operation may occur from decomposition of hydrocarbon oils and greases used in some parts of the system; or formation of carbonate carbon produced by reaction with \( \text{CO}_2 \) from the air.

c. Air. The air, which must always be assumed to leak into the system to a greater or lesser extent, contains about 0.03 vol. % \( \text{CO}_2 \). This, on reaction with sodium, could yield free carbon.

A detailed consideration of the KAPL system shows that the carbon tolerance for both the helium and sodium is small, of the order of 10 ppm. The contamination from air will depend, of course, on the degree of leak-tightness which can be achieved in the system.

In concluding this section it appears that with reasonably clean components a sodium system will give satisfactory performance. There are impurities such as oxygen, water, and possibly carbon which may be detrimental and require purity control. However, the problem of purification does not appear to be insurmountable and, indeed, may not be difficult.

E. WETTING OF SOLIDS BY LIQUID SODIUM

In the early project experiments with NaK alloy and sodium, the surfaces of metals immersed at high temperatures in the liquid alkali metal and later removed were observed to be uniformly wet with a film of the liquid metal. This wetting did not occur at room temperature or at the melting point of sodium but only after heating. De-wetting did not take place upon cooling. This spreading of sodium over a surface has been referred to as "wetting" rather than the observation of the contact angle at the liquid-solid interface, where a contact angle of less than 90 deg is customarily taken as the wetting criterion. However, the spreading of a liquid on a solid surface and the contact angle are closely related. It can be shown that the condition for spreading of liquid A on surface B is

\[ W_{AB} > 2\gamma_A \tag{58} \]

when \( W_{AB} \) is the work of adhesion between the liquid A and the surface B and \( 2\gamma_A \) is the work of cohesion between the liquid A and its vapor. However, \( \gamma_A \) is numerically equal to the surface tension of the liquid. For an extensive treatment of spreading of liquids on solids see the monograph by Burdon. In the technology of liquid-alkali metal-cooled reactors and heat-transfer systems wetting may play an important role. For example, the liquid metal may be used as a thermal bonding agent to ensure good heat transfer across small annuli, since liquid sodium (or NaK alloy) wetting the solid will penetrate into microscopic cracks. On the other hand, in the unwetted state the sodium will not flow into small openings, owing to its high surface tension. A second consideration is the heat-transfer coefficient from a solid surface in contact with sodium. At the heat fluxes now under discussion for nuclear reactors, which are made possible by the use of an efficient coolant like sodium, the film drop for a surface wetted by sodium may be significantly lower than that for an unwetted surface. Mannal and coworkers at KAPL are investigating heat-transfer coefficients in experiments designed to measure this quantity as a function of the temperature. The magnitude of the effect will be determined as well as the wetting temperature. Only preliminary experiments have been reported to date, but there is an indication that a measurable change in the heat-transfer coefficient, \( h \), occurs at the wetting temperature.
A third manifestation of wetting which may be of technological importance is the spreading of sodium on a solid, in particular its tendency to creep up a surface. For example, sodium may creep up a wall, penetrating a gas seal designed to prevent escape of sodium vapor. This phenomenon is due to capillary action of the type described by Smoluchowski and Parker and is a function of the solid-liquid contact angle. In their work they observed creep to be a function of the roughness of the metal surface and the shape and direction of the grooves; the creep of liquid silver on a steel surface was negligible when the surface was highly polished. This represents a condition where the contact angle is close to, but not equal to, zero. Mannal and coworkers are carrying out similar experiments on liquid sodium. They are studying creep as a function of the angle of the groove on the surface of a metal, varying this over wide limits.

A study of spreading on a flat highly polished surface is also underway, and it is concluded that the contact angle of sodium against stainless steel in the wet condition is close to, but not quite equal to, zero. From the variation of time necessary for the sodium to rise a fixed distance up the metal grooves as wetting occurs an activation energy of the order of 20 to 25 kcal/mole has been obtained. The rate-controlling reaction has not been isolated as yet. In addition an analysis of the data indicates that the surface tension of sodium at 500°C is about 200 dynes/cm, in agreement with data given in Part I of this paper. There appears to be a limiting height at any given temperature to which the liquid will rise in grooves of depth d and base angle 2β, given by

$$ h = \frac{2\gamma_L (\csc \beta \sin \beta)}{\rho_L g d} $$

(59)

where $\gamma_L$ and $\rho_L$ are the surface tension and density of the liquid, respectively. For sodium at 500°C and higher, d = 0.025 cm, and $\beta = 60$ deg, $h \approx 2.5$ cm.

As previously mentioned, it appeared in preliminary experiments that there was a characteristic temperature for wetting of a solid by sodium or NaK. In general, without careful surface preparation most solids are not wet at room temperature or at the melting point of sodium, but as the temperature is slowly raised wetting occurs. This phenomenon has been reported for a number of solids. Practically all metals and even ceramics are found to be wetted if the temperature is high enough, say, 500°C. Later work by Mannal and coworkers and Winkler and Vandenberg has shown that there is no single characteristic wetting temperature and that the observed temperature is highly dependent on the nature of the solid surface and is largely a function of contamination. These results are consistent with data by Marshall and others on the wetting of a freshly broken surface of iron by mercury at room temperature and the same observation of Weber on the wetting of iron by sodium near the melting point. In both cases wetting occurred rapidly at the fresh interface which was formed by breaking a sample immersed in the liquid to obtain a fresh oxide-free surface. Winkler and Vandenberg have shown the wetting temperature of most metal and some nonmetallic surfaces to be dependent on the grease and other surface impurities present on the solid. In their measurements the sodium level was alternately raised and lowered on a ribbon of the material being tested through which a known electrical current was passed. The sodium was heated at a uniform rate, and when wetting occurred the total current increased owing to passage through the sodium clinging to the wire when the sodium level was lowered. The sodium forms a parallel electrical circuit, giving a lower voltage drop. In every case observation of the ribbon after cooling showed that wetting had occurred, as indicated by the change in the electrical resistance. The method is very sensitive and reproducible and moreover is experimentally simple. Data are given in Table 36. Samples labeled "clean"

### Table 36—Results of Wetting Experiments at KAPL

<table>
<thead>
<tr>
<th>Material</th>
<th>As machined</th>
<th>Machine oil</th>
<th>Silicone oil</th>
<th>Oxide coating</th>
<th>Clean</th>
</tr>
</thead>
<tbody>
<tr>
<td>(type 347)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>247–260</td>
<td>277</td>
<td>322</td>
<td>267–268</td>
<td>m.p. of Na</td>
</tr>
<tr>
<td>Low-carbon steel</td>
<td>260</td>
<td>286</td>
<td>281–289</td>
<td>392–426</td>
<td>m.p. of Na</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>306–333</td>
</tr>
</tbody>
</table>
in Table 36 had previously been wet by sodium and subsequently washed and dried. The wetting temperatures are much lower than those reported by previous workers and clearly show the effect of oil and oxide films.

Mannal and coworkers are examining wetting phenomena on surfaces exposed to sodium in a vacuum or a highly purified inert atmosphere. In their experiments, the samples are very carefully cleaned and degreased in vacuo and the surface degassed by induction heating to a very high temperature. They also find wetting to occur near or at the melting point of sodium on samples carefully cleaned in this manner. They plan further experiments to establish the factors which are important and the mechanism of the wetting phenomena. At present the data are incomplete and no detailed picture can be advanced. However, there appears to be a definite activation energy in the wetting reaction which is chemical in origin. The reaction may be desorption of an occluded gas or oil film, reduction of an oxide present on the surface, or a combination of these reactions.

The following observations should be explained by an exact theory of wetting:

1. Instantaneous wetting of iron occurs in NaK or sodium at low temperatures when the solid surface is freshly generated.

2. Metals whose oxides are either reducible or nonreducible are wetted by sodium and do not dewet upon standing unless they are subsequently exposed to oxygen. Uranium and beryllium are wet by sodium, although macroscopically their oxides are very stable towards reduction by liquid sodium. Nickel and iron whose oxides are readily reducible by sodium are wet quite as readily.

3. Ceramics and glasses are also wet by sodium. High-density beryllia, uranium oxide compacts, and uranium dioxide powder are wet by sodium and remain wet upon cooling.

4. There is an activation energy for wetting most surfaces, except those that are newly generated.

V. CONCLUSIONS

Sufficient time has elapsed since the publication of Part I of this paper so that it may be well to repeat the comments made in the Preface on the objectives which we have attempted to reach in this contribution. Basically we have tried to collect, correlate, and summarize the voluminous body of data scattered throughout the classified and open literature and to emphasize the places where experimental results do not exist and where further work is considered desirable. It is hoped that to some extent experimentalists will be guided by this survey in planning future work.

With the emphasis on problems, gaps in experimental knowledge, and theoretical interpretation, as in this paper, it is easy to lose sight of the tremendous body of data which has been obtained. It is probably correct to say that owing to its importance and the interest in its application to nuclear engineering more is known about liquid sodium and NaK at the present time than about any other liquid metal, with the possible exception of mercury.

ACKNOWLEDGMENTS

Many people have contributed to the preparation of this compilation, and the authors wish to express their thanks to the following members of the KAPL staff: H. Brooks, J. R. Low, J. P. Howe, L. P. Pekowitz, A. Savolainen, S. R. Vandenbergh, L. B. Vandenbergh, L. W. Dunbar, T. Trocki, and R. F. Koenig.


APPENDIX A

DERIVATION OF SOLUTION-RATE-LIMITED DYNAMIC-CORROSION EQUATIONS

Consider a harp of radius \( a = D/2 \) and length \( L \). Let \( S \) (g/cm\(^2\)) be the concentration of the harp material dissolved in the circulating fluid and \( S^0 \) be the equilibrium solubility. Then the rate of solution per unit length is given by

\[
\frac{\pi a^2}{2} \alpha (S^0 - S)
\]

where \( \alpha \) is the so-called "specific-solution-rate constant." The rate at which material deposits out of solution, per unit length, is

\[
\frac{\pi a^2 v}{dx} \frac{ds}{dx}
\]

where \( v \) is the flow velocity of the circulating fluid, and the distance \( x \) is measured around the loop, with the hottest point as the origin, so that \( L > x > 0 \). The net change of \( S \) with time is given by

\[
\frac{\pi a^2}{dt} \frac{dS}{dx} = 2\pi a \alpha (S^0 - S) - \frac{\pi a^2 v}{dx} \frac{dS}{dx}
\]
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

If \( v = 0 \), this reduces to the familiar static-solution-rate equation
\[
\frac{dS}{dt} = \alpha \frac{A}{V} (S^0 - S)
\]
In the steady state in a harp, \( dS/dt = 0 \) and
\[
\frac{dS}{dx} = \lambda (S^0 - S)
\]  
(2)
where
\[
\lambda = \frac{2\alpha}{av}
\]  
(3)
Now the mass-transfer rate per unit length of harp is
\[
R' = -\pi a^2 v \left( \frac{dS}{dx} \right)_{\text{max}}
\]
the minus sign signifying a weight loss from the harp walls and the mass-transfer rate per unit area, the usual method of expressing corrosion rates, is
\[
R = \frac{R'}{2\pi a}
\]
\[
= -\frac{1}{2} av \left( \frac{dS}{dx} \right)_{\text{max}}
\]  
(4)
In general \( S^0 \) and \( S \) will be functions of \( x \). Letting \( \xi \) be the value of \( x \) at which \( dS/dx \) is a maximum, then from Eq. 2
\[
\left( \frac{dS}{dx} \right)_{\text{max}} = \lambda [S^0(\xi) - S(\xi)]
\]
and
\[
R = -\frac{1}{2} av \lambda [S^0(\xi) - S(\xi)]
\]  
(5)
To find \( R \) it is necessary to solve Eq. 2 for \( S(x) \). The general solution to this equation is
\[
S(x) = e^{-\int \lambda dx} \left[ \int \lambda S^0(x) e^{\int \lambda dx} dx + C \right]
\]  
(6)
In general \( \lambda \) will also be a function of \( x \). Letting
\[
\phi(x) = \int \lambda(x) dx
\]  
(7a)
and
\[
I(x) = \int \lambda(x) S^0(x) e^{\int \phi(x)} dx
\]  
(7b)
then
\[
S(x) = e^{-\phi(x)} \left[ I(x) + C \right]
\]  
(8)
The constant of integration, \( C \), can be found from the fact that \( S(0) = S(L) \). Then
\[
C = -\frac{e^{-\phi(L)} I(L) - e^{-\phi(0)} I(0)}{e^{\phi(L)} - e^{\phi(0)}}
\]  
(9)
The condition that \( dS/dx \) be a maximum at \( x = \xi \) requires that \( (d^2S/dx^2)_{\xi} = 0 \). From this relation and Eqs. 8 and 9, the equation defining \( \xi \) can be found to be
\[
\left[ \frac{d}{dx} (\lambda S^0) \right]_{\xi} = \lambda^2(\xi) \left[ S^0(\xi) - e^{-\phi(\xi)} \left[ \frac{d}{dx} (\lambda S^0) \right]_{\xi} \right] + \lambda^2(\xi) I(\xi) + C_0
\]  
(10)
Equations 5 and 10 constitute a complete and general solution of this problem provided the integrals \( \phi(x) \) and \( I(x) \) can be evaluated and the solution to Eq. 10 for \( \xi \) can be found. In principle these operations can always be carried out, by numerical methods as a last resort, if necessary. In practice the evaluation of these functions is tedious and time-consuming, and for a complex temperature distribution it does not seem justified in the present state of this problem. The mathematics of the solution can be considerably simplified by taking \( \lambda \) as independent of \( x \) and equal to \( \lambda_0 \), the value at the mean temperature of the harp, \( T_0 \). This implies that the \( \Delta T \) for the system is small; this condition, however, does not seriously reduce the applicability of this result since harps are generally operated between comparatively small temperature limits. With this assumption, then, the basic equations reduce to
\[
R = -\frac{1}{2} av \lambda_0 [S^0(\xi) - S(\xi)]
\]  
(11a)
\[
C = -\frac{e^{-\lambda_0 L} I(L) - I(0)}{e^{\lambda_0 L} - 1}
\]  
(11b)
\[
\left( \frac{dS^0}{dx} \right)_{\xi} = \lambda_0 \left[ S^0(\xi) - e^{-\phi(\xi)} \left[ I(\xi) + C_0 \right] \right]
\]  
(11c)
\[
S(x) = e^{\lambda_0 x} \left[ I(x) + C_0 \right]
\]  
(11d)
One of the simplest temperature distributions which satisfies the required condition \( T(0) = T(L) \) is
\[
T(x) = T_0 + \frac{\Delta T}{2} \cos \frac{2\pi x}{L}
\]  
(12)
Over the small temperature interval from $T_o + AT/2$ to $T_o - AT/2$, the equilibrium solubility may be taken to be linear in the temperature so that

$$S'(x) = S'(T_o) + \frac{AT}{2} \frac{dS}{dT} \cos \frac{2\pi x}{L}$$

(13a)

But from Eq. 12, $T_o = T(L/4)$ so that

$$S'(x) = S'\left(\frac{L}{4}\right) + \frac{AT}{2} \frac{dS}{dT} \cos \frac{2\pi x}{L}$$

(13b)

The integral $I(x)$ then becomes

$$I(x) = \lambda_o \int e^{\lambda_o x} \left[ S'\left(\frac{L}{4}\right) + \frac{AT}{2} \frac{dS}{dT} \cos \frac{2\pi x}{L} \right] dx$$

$$= e^{\lambda_o x} S'\left(\frac{L}{4}\right) + \lambda_o e^{\lambda_o x} \left( \lambda_o \cos \frac{2\pi x}{L} + 2\pi \sin \frac{2\pi x}{L} \right)$$

where

$$\mu = \frac{\Delta T}{2} \frac{dS}{dT} \left[ \frac{\lambda_o^2}{\lambda_o^2 + \frac{2\pi^2}{L^2}} \right]$$

(14)

In this case it can readily be shown that $C = 0$ and

$$S(x) = S'\left(\frac{L}{4}\right) + \lambda_o \cos \frac{2\pi x}{L} + 2\pi \sin \frac{2\pi x}{L}$$

(15)

Substituting these results in Eq. 11c, it follows that

$$\xi = \frac{L}{2\pi} \tan^{-1} \left( -\frac{L \lambda_o}{2\pi} \right) = -\frac{\alpha_o L^2}{2\pi^2 \alpha_v}$$

(16)

Then

$$S(\xi) = S'\left(\frac{L}{4}\right)$$

and

$$S'(\xi) = S'\left(\frac{L}{4}\right) + \mu \left( \lambda_o + \frac{2\pi^2}{L^2} \right) \cos \frac{2\pi \xi}{L}$$

Substituting these relations in Eq. 11a

$$R = -\frac{\Delta T}{2} \alpha_o \frac{dS}{dT} \cos \frac{2\pi \xi}{L}$$

(17)

From Eq. 16, $\cos \left(\frac{2\pi \xi}{L}\right)$ can be found, and it follows that

$$R = -\frac{\Delta T}{2} \alpha_o \frac{dS}{dT} \left[ 1 + \left( \frac{\alpha_o L^2}{\alpha_v} \right)^{1/4} \right]$$

(18)

which is the equation quoted in the text. The term in brackets is practically unity for cases of practical importance, and it is of interest to note that the maximum corrosion occurs not at $x = 0$ where the temperature is a maximum but at $x = \xi$, as defined by Eq. 16, that is, a short distance downstream from the origin.

Example

Consider an iron harp filled with sodium operating with the temperature characteristics of the KAPL reactor, i.e., $T_o = 350^\circ$C and $AT = 100^\circ$C. From Eq. 32 of the text

$$\alpha_{250^\circ} = 1.45 \times 10^{-4} \text{ cm/sec}$$

and from Eq. 30

$$\left( \frac{dS}{dT} \right)_{250^\circ} = 2.33 \times 10^{-8} \text{ g/cm}^2 \text{ - }^\circ \text{C}$$

A flow velocity of 1250 gal/min, specified for the KAPL reactor, corresponds to

$$v = \frac{1250 \times 60}{3600} = \frac{418}{60} \text{ cm/sec}$$

Taking $L = 100$ cm and $a = 1$ cm, then

$$\frac{\alpha_L}{\alpha_v} \approx 1.10 \times 10^{-5}$$

and the square of this quantity is, in fact, negligible in comparison with unity, as stated above. Then from Eq. 18

$$R = -1.69 \times 10^{-16} \text{ g/cm}^3 \text{ - sec}$$

$$= -0.44 \text{ mg/cm}^2 \text{ - month}$$

The point of maximum corrosion from Eq. 16 will come at a distance

$$\xi = -1.8 \times 10^{-4} \text{ cm}$$

downstream from the origin, that is practically at the hottest point in the system.

APPENDIX B

THE EFFECT OF RADIATION ON DYNAMIC CORROSION

Letting $S_r$ be the concentration of solute under the influence of radiation, the problem is set up as in
APPENDIX A, except for the addition, due to the radiation, of a term. In a neutron flux \( n_v \), there will be a so-called "isotropic-matter flux" \( j \), owing to displacements of atoms through neutron bombardment and subsequent collision of the resulting high-energy atoms with stationary ones, until the energy is virtually all dissipated. The symbol \( j \) is, then, the number of atoms of the harp material passing through a square centimeter of surface per unit time. The net effect of the radiation on displacement of the harp material will be given by \( j M / N_o \), where \( M \) is its molecular weight and \( N_o \) is the Avogadro number. Then in the harp described in Appendix A the rate of solution per unit length is given by

\[
2\pi a \frac{M}{N_o} + 2\pi a \alpha(S^o - S_R)
\]

Carrying through the rest of the argument as above, the differential equation

\[
\frac{dS_R}{dx} = \lambda \left( S^o - S_R + \frac{j M}{N_o \alpha} \right)
\]

is obtained. Then, as in Eq. 4, the dynamic-corrosion rate under irradiation, \( R_R \), is given by

\[
R_R = -\frac{1}{2} av \left( \frac{dS_R}{dx} \right)_{\text{max}}
\]

The value of \( dS_R/dx \) is a maximum at a point \( x = \eta \), where \( (dS_R/dx)_{\eta} = 0 \). By differentiating Eq. 2 and setting the derivative equal to zero, we obtain the equation defining \( \eta \)

\[
\frac{(dS_R)}{(dx)}_{\eta} = \frac{(dS^o)}{(dx)}_{\eta} + \frac{M}{N_o \alpha} j'(\eta)
\]

where \( j'(\eta) = \frac{dj(x)}{dx} \) at \( x = \eta \). Combining Eqs. 3 and 4

\[
R_R = -\frac{1}{2} av \left[ \left( \frac{dS^o}{dx} \right)_{\eta} + \frac{M}{N_o \alpha} j'(\eta) \right]
\]

By differentiating Eq. 13b in Appendix A and introducing the value of

\[
\mu \left[ \lambda^2 + \left( \frac{2\pi}{L} \right)^2 \right] = \frac{R}{\alpha_o}
\]

it follows that

\[
\frac{R_R}{R} = -\frac{av}{2\alpha_o} \left[ \frac{2\pi}{L} \sin \frac{2\pi \eta}{L} + \frac{M}{N_o \alpha} j'(\eta) \right]
\]

Now if the flux distribution is chosen so that it is a maximum at the origin (where the temperature is also at the peak), it is to be expected that the largest radiation-corrosion effect will occur close to \( x = 0 \). On this basis we may take \((\eta/L) < 1\), so that

\[
\frac{R_R}{R} = -\frac{av}{2\alpha_o} \left( \frac{2\pi}{L} \right)^2 \eta - \frac{av}{2\alpha_o} \frac{M}{N_o \alpha} j'(\eta)
\]

Now to a first approximation

\[
\eta \approx \xi \approx -\frac{2\alpha_o \left( \frac{L}{2\pi} \right)^2}{av}
\]

Then

\[
\frac{R_R}{R} = 1 - \frac{M}{N_o \alpha} \frac{av}{2\alpha_o} j'(\xi)
\]

This equation will now be applied to a case which approximates the actual operating conditions of a heat transfer system in the reactor. Let

\[
j(x) = \beta e^{-\beta x (L-x)}
\]

that is, the matter flux distribution around the harp is represented by an error function, peaking at the origin and falling off to a minimum value of \( \beta e^{-\beta L/2} \) at a distance equal to \( L/2 \). In this case

\[
j'(x) = -\beta \beta \left( L-2x \right) e^{-\beta (L-x)}
\]

and

\[
j'(\xi) \approx j'(0) = -\beta \beta L
\]

Substituting this in Eq. 9

\[
\frac{R_R}{R} = 1 + \frac{M}{N_o \alpha} \frac{av \beta L}{2\alpha_o} \beta
\]

which is the formula discussed in the text.

APPENDIX C

SOLUBILITIES IN SODIUM

This section will summarize the known data on the solubilities of metals (plus a few nonmetals) in liquid sodium. The data are taken from Hansen except as noted.

Aluminum. No measurable solubility of solid aluminum in sodium recorded. Above the melting point..
of aluminum (657°C), the two liquids form a typical immiscible liquid pair.
Antimony. The solubility of solid antimony in liquid sodium is given by
\[ W = -7.1 + 0.0730T \]
up to 700°C (44 per cent antimony).
Arsenic. No data are available on solubility of solid arsenic in liquid sodium.
Bismuth. The solubility of bismuth in sodium is given approximately by
\[ W = -0.0129T + 1.33 \times 10^{-4}T^2 \]
up to 600°C (40 per cent bismuth).
Boron. It is stated that solid boron is not attacked by boiling sodium.
Cadmium. Cadmium forms a simple eutectic with sodium, containing 2.6 per cent cadmium and melting at 95.5°C. Up to 250°C (34 per cent cadmium) the solubility is given by
\[ W = 223 - 2.29T \]
Calcium. The solubility of calcium in sodium was measured at the Du Pont company. The data are in good agreement with those of Rinck and have been confirmed by measurements at KAPL. Up to 700°C (9.4 per cent calcium) the data can be represented by
\[ \log W = 2.5629 - \frac{1545.6}{T_K} \]
with a probable error of ±0.14 per cent.
Copper. No quantitative data are available. Copper has been recrystallized out of sodium solution at 550°C.\(^{37}\)
Gallium. No data on the solubility of liquid gallium in sodium are available.
Germanium. No quantitative data are available.
Gold. Gold lowers the melting point of sodium. The eutectic melts at 82°C and contains 22.5 per cent gold. The data may be represented by
\[ \log \left(1 - \frac{W}{100}\right) = 2.5094 - \frac{930.25}{T_K} \]
from the melting point of sodium down to the eutectic.
Indium. Forms a eutectic with sodium, melting at about 96.1°C and containing 1.2 to 2.0 per cent indium. There is some indication also of the formation of the compound InNa.
Iron. The solubility of iron in sodium has been measured at KAPL over the range 225 to 500°C. The results are that
\[ \log S_T = 1.8266 - \frac{558.5}{T_K} \]
where \(S_T\) is the solubility in parts per million by weight at temperature \(T\). Alternatively, the data can be represented by
\[ 10^6W = -1.1 + 0.02787T \]
The probable error in these measurements is ±1.8 ppm.
Lead. The lead-sodium system has been extensively investigated. The eutectic (97°C) lies very close to the pure sodium, and up to 40 per cent by weight of lead (250°C), the solubility is given by
\[ W = -25.6 + 0.282T \]
Lithium. The sodium-lithium eutectic contains about 0.5 per cent lithium, and the melting point of sodium is lowered about 2°C by this additive. Larger quantities of lithium raise the melting point. Liquid lithium is nearly immiscible with liquid sodium; at 162°C about 3 per cent lithium dissolves in sodium.
Magnesium. The magnesium-sodium eutectic lies very close to the pure sodium end. The solubility of magnesium in sodium is given approximately by
\[ W = -0.27 + 0.002773T \]
up to 700°C (1.67 per cent magnesium).
Mercury. The sodium-mercury system has been extensively studied. The eutectic lies at 60.5°C and contains 1.2 to 2.0 per cent mercury (21.5°C) and down to this point the solubility of mercury in sodium can be represented by
\[ \log \left(1 - \frac{W}{100}\right) = 1.5642 - \frac{579.85}{T_K} \]
Palladium. The melting point of sodium is lowered 0.4°C by the solution of 2.8 per cent palladium.
Platinum. Only trace amounts of platinum dissolve in liquid sodium, although sodium vapor has a strong corrosive effect on the metal. Up to 1.5 per cent platinum added to sodium does not affect the melting point. According to ANL, corrosive attack of platinum is drastic in liquid NaK.
Potassium. The phase diagram of the potassium-sodium system shows the existence of the unstable compound KNa. The solubility of potassium in sodi-
USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID

...um is nearly linear in temperature and may be represented by

\[ W = 57.1 - 0.586T \]

down to 7°C (53 per cent potassium).

Rubidium. The melting point of sodium is lowered by the presence of rubidium, and the solubility of rubidium in sodium is given approximately by

\[ W = 132.2 - 1.356T \]

down to 61°C (50 per cent rubidium).

Selenium. The solubility of selenium in sodium is given approximately by

\[ W = -8.4 + 0.0858T \]

up to 680°C (50 per cent selenium).

Silicon. Silicon is drastically attacked by NaK, according to ANL.

Silver. The solubility of silver in sodium is given approximately by

\[ W = -2.4 + 0.0180T + 7.007 \times 10^{-5}T^2 \]

up to 650°C (40 per cent silver). According to ANL, 50-50 NaK saturated with silver contains less than 10 ppm of the metal at room temperature.

Sulfur. The sulfur-sodium system has been extensively studied, but mostly at high sulfur contents, above the composition corresponding to Na$_2$S (41 per cent sulfur).

Tellurium. The solubility of tellurium in sodium is given approximately by

\[ W = -8.1 + 0.083T \]

up to 700°C (50 per cent tellurium).

Thallium. The thallium-sodium system has been quite thoroughly investigated. The eutectic occurs at 40.8 per cent thallium (64°C), and down to this point the solubility can be represented by

\[ \log \left(1 - \frac{W}{100}\right) = 2.2917 - \frac{849.5}{T_K} \]

Thorium. Grube and Botzenhardt studied the thorium-sodium system. These authors report that there is a eutectic at 93°C containing 25 per cent thorium, and that as much as 80 per cent thorium dissolves in sodium at 166°C. Hayes and Gordon, however, report that only traces of thorium (probably less than 0.1 wt. %) dissolve in sodium at 300°C. Foote and his associates at ANL also tried to dissolve thorium in 50-50 NaK and could find no appreciable solubility (120 hr, purified eutectic NaK, 600°C, upper limit of solubility = 25 ± 10 ppm). The difference between these results may be due to the presence of oxide films on the metal, although efforts were made to eliminate this factor in the work in America. In the case of uranium, which resembles thorium in its ease of oxidation and other respects, the solubility in mercury is ten to one hundred times greater when clean metal is used, prepared from the hydride, considerably higher than that of thorium in sodium. It would not be surprising if thorium in sodium behave similarly.

Tin. The solubility of tin in sodium is given approximately by

\[ W = 7.9 - 0.141T + 6.16 \times 10^{-4}T^2 \]

Uranium. The solubility of uranium in sodium is about 50 ppm at 300°C, although there are some indications that for uranium, as for thorium, the apparent solubility is dependent on the nature of the oxide films on the metal.

Further Kapl Results on Static Corrosion in Sodium

R. F. Koenig at KAPL in a memorandum entitled "Compatibility of Sodium with Various Materials under Static Conditions" (Memo-RFK-2) dated Sept. 11, 1950, has added some further test data which are presented here in order to bring this compilation up to date, insofar as possible.

"The purpose of this report is to present the latest results in a form most useful for engineering purposes. Since the answer to most compatibility questions depends somewhat upon the purity of the sodium tested, it seemed desirable to separate the data according to the method of purification used.

"Much of the data which follow is the result of single tests. Before any of the materials are adopted for a specific use, further tests should be made under conditions which simulate those of the application.

"It is intended to revise these tables as frequently as the acquisition of new data warrants."

The following is a key to the ratings used in the tables below. They apply only to static or comparable conditions.

1. Excellent, satisfactory for long periods of time in very thin sections.
2. Good, satisfactory for long periods of time in heavier sections (roughly \( \frac{3}{4} \) in. and above).
3. Poor, unsatisfactory for almost all applications at the temperature shown.
<table>
<thead>
<tr>
<th>Material</th>
<th>Temp., °C</th>
<th>Time, month</th>
<th>Average weight change, mg/cm²-month</th>
<th>Corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum, 99.99% pure</td>
<td>427</td>
<td>1</td>
<td>-31</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 3S</td>
<td>427</td>
<td>1</td>
<td>-19</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 243</td>
<td>427</td>
<td>1</td>
<td>-18</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 525</td>
<td>427</td>
<td>1</td>
<td>-19</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 75S</td>
<td>427</td>
<td>1</td>
<td>-27</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 750</td>
<td>427</td>
<td>1</td>
<td>-23</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum bronze T-224</td>
<td>427</td>
<td>1</td>
<td>-0.17</td>
<td>Excellent</td>
</tr>
<tr>
<td>Beryllium, extruded</td>
<td>500</td>
<td>1</td>
<td>+0.1</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Beryllium, sintered</td>
<td>500</td>
<td>1</td>
<td>+0.1</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Boron carbide</td>
<td>427</td>
<td>1</td>
<td>?</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Copper, OFHC in copper</td>
<td>400</td>
<td>1</td>
<td>-0.05</td>
<td>Excellent</td>
</tr>
<tr>
<td>Copper, OFHC in stainless steel</td>
<td>427</td>
<td>1</td>
<td>+0.16</td>
<td>Excellent</td>
</tr>
<tr>
<td>Durimet 20</td>
<td>427</td>
<td>1</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>Inconel X</td>
<td>500</td>
<td>1</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>Mechanite</td>
<td>427</td>
<td>1</td>
<td>+0.95</td>
<td>Excellent</td>
</tr>
<tr>
<td>Monel, S</td>
<td>427</td>
<td>1</td>
<td>+0.04</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel, L</td>
<td>500</td>
<td>1</td>
<td>+0.49</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ni-Mn, 40-60</td>
<td>500</td>
<td>1</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ni-Mn, 80-20</td>
<td>500</td>
<td>1</td>
<td>+0.23</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel resist</td>
<td>427</td>
<td>1</td>
<td>+1.5</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nitrided 347</td>
<td>500</td>
<td>1</td>
<td>-0.32</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tantung-Ni, 30-70</td>
<td>500</td>
<td>1</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tantung A166</td>
<td>500</td>
<td>1</td>
<td>-0.04</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tantung A171</td>
<td>500</td>
<td>1</td>
<td>-0.02</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tantung A192</td>
<td>500</td>
<td>1</td>
<td>-0.07</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tantung A166 spring</td>
<td>500</td>
<td>1</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>Titanium</td>
<td>500</td>
<td>1</td>
<td>+0.2</td>
<td>Excellent</td>
</tr>
<tr>
<td>Vanadium</td>
<td>500</td>
<td>½</td>
<td>-0.2</td>
<td>Excellent</td>
</tr>
<tr>
<td>V-2-B stainless steel (19% Cr-10% Ni-3% Si-3% Cu-3% Mo-0.1% Be)</td>
<td>500</td>
<td>½</td>
<td>?</td>
<td>Good</td>
</tr>
<tr>
<td>W-Ni</td>
<td>500</td>
<td>1</td>
<td>+0.02</td>
<td>Excellent</td>
</tr>
<tr>
<td>Zirconium</td>
<td>427</td>
<td>1</td>
<td>+0.12</td>
<td>Excellent</td>
</tr>
<tr>
<td>Zirconium</td>
<td>500</td>
<td>1</td>
<td>+0.2</td>
<td>Excellent</td>
</tr>
<tr>
<td>Zirconia porcelain</td>
<td>500</td>
<td>1</td>
<td>?</td>
<td>Poor</td>
</tr>
<tr>
<td>302 stainless steel</td>
<td>500</td>
<td>3</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>304 stainless steel</td>
<td>500</td>
<td>3</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>310 stainless steel (25% Cr-20% Ni)</td>
<td>500</td>
<td>4</td>
<td>-0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>316 stainless steel</td>
<td>500</td>
<td>3</td>
<td>-0.02</td>
<td>Excellent</td>
</tr>
<tr>
<td>321 stainless steel</td>
<td>500</td>
<td>3</td>
<td>-0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>347 stainless steel</td>
<td>500</td>
<td>3</td>
<td>-0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>416</td>
<td>427</td>
<td>1</td>
<td>+0.04</td>
<td>Excellent</td>
</tr>
<tr>
<td>440 C</td>
<td>427</td>
<td>1</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>52100</td>
<td>427</td>
<td>1</td>
<td>-0.03</td>
<td>Excellent</td>
</tr>
<tr>
<td>6-6-2 HSTS</td>
<td>427</td>
<td>1</td>
<td>-0.14</td>
<td>Excellent</td>
</tr>
<tr>
<td>18-4-1 HSTS</td>
<td>427</td>
<td>1</td>
<td>-0.08</td>
<td>Excellent</td>
</tr>
<tr>
<td>35-15 Ni-Cr</td>
<td>500</td>
<td>4</td>
<td>-0.04</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

*Good if decarburization can be tolerated.*
### Table 2 — Sodium Gettered by Calcium Additions to the Test Container

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. °C</th>
<th>Time, month</th>
<th>Average weight change, mg/cm²-month</th>
<th>Corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium, extruded</td>
<td>500</td>
<td>1</td>
<td>-0.2</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Beryllium, sintered</td>
<td>500</td>
<td>½</td>
<td>43 (2% Ca)</td>
<td>Poor</td>
</tr>
<tr>
<td>Nickel, A</td>
<td>500</td>
<td>½</td>
<td>118 (10% Ca)</td>
<td>Poor</td>
</tr>
<tr>
<td>Nickel, L</td>
<td>500</td>
<td>1</td>
<td>0.2 (0.1% Ca)</td>
<td>Excellent</td>
</tr>
<tr>
<td>347 stainless steel</td>
<td>500</td>
<td>1</td>
<td>0.07</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

### Table 3 — Aged and Filtered (5 μ) Sodium (probably 0.005 – 0.01 wt. % oxygen)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. °C</th>
<th>Time, month</th>
<th>Average weight change, mg/cm²-month</th>
<th>Corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum, 99.99% pure</td>
<td>427</td>
<td>1</td>
<td>-10</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 3S</td>
<td>427</td>
<td>1</td>
<td>-11</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 248</td>
<td>427</td>
<td>1</td>
<td>-10</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 52S</td>
<td>427</td>
<td>1</td>
<td>-9</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 75S</td>
<td>427</td>
<td>1</td>
<td>-12</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 750</td>
<td>427</td>
<td>1</td>
<td>-17</td>
<td>Poor</td>
</tr>
<tr>
<td>Inconel X</td>
<td>500</td>
<td>1</td>
<td>0.03</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel, L</td>
<td>500</td>
<td>1</td>
<td>0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>347 stainless steel</td>
<td>500</td>
<td>1</td>
<td>0.03</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

### Table 4 — Miscellaneous Early Sodium Treatments (probably 0.01 wt. % and higher oxygen)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. °C</th>
<th>Time, months</th>
<th>Average weight change, mg/cm²-month</th>
<th>Corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alnico 5</td>
<td>500</td>
<td>¼</td>
<td>+0.1</td>
<td>Excellent</td>
</tr>
<tr>
<td>Alumina</td>
<td>243</td>
<td>¼</td>
<td>0.0</td>
<td>Excellent</td>
</tr>
<tr>
<td>Al-U, 60–40</td>
<td>450</td>
<td>¼</td>
<td>-2.7</td>
<td>Good</td>
</tr>
<tr>
<td>Al-U, 69–31</td>
<td>500</td>
<td>¼</td>
<td>-220</td>
<td>Poor</td>
</tr>
<tr>
<td>Al-U, 90–40</td>
<td>710</td>
<td>¼</td>
<td>Dissolved</td>
<td>Poor</td>
</tr>
<tr>
<td>Aluminum alloy 2S</td>
<td>450</td>
<td>¼</td>
<td>-2.9</td>
<td>Good</td>
</tr>
<tr>
<td>Aluminum alloy 52S</td>
<td>450</td>
<td>¼</td>
<td>-3.5</td>
<td>Good</td>
</tr>
<tr>
<td>Aluminum cast, RR-1</td>
<td>450</td>
<td>¼</td>
<td>-33</td>
<td>Poor</td>
</tr>
<tr>
<td>B-G Aluminte</td>
<td>243</td>
<td>¼</td>
<td>+0.2</td>
<td>Excellent</td>
</tr>
<tr>
<td>Beryllia</td>
<td>500</td>
<td>¼</td>
<td>-0.04</td>
<td>Excellent</td>
</tr>
<tr>
<td>Beryllium, extruded</td>
<td>500</td>
<td>¼</td>
<td>Uncertain</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Beryllium, sintered</td>
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<td>¼</td>
<td>Uncertain</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Beryllium, vacuum-cast</td>
<td>500</td>
<td>¼</td>
<td>Uncertain</td>
<td>Probably excellent</td>
</tr>
<tr>
<td>Carbon, amorphous</td>
<td>243</td>
<td>¼</td>
<td>Dissintegrated</td>
<td>Poor</td>
</tr>
<tr>
<td>Haenium</td>
<td>243</td>
<td>¼</td>
<td>+0.3</td>
<td>Excellent</td>
</tr>
<tr>
<td>Haenium</td>
<td>500</td>
<td>¼</td>
<td>+58</td>
<td>Poor</td>
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**USE OF MOLTEN SODIUM AS A HEAT TRANSFER FLUID**
Table 4—(Continued)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp., °C</th>
<th>Time, months</th>
<th>Average weight change, mg/cm²-month</th>
<th>Corrosion resistance</th>
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<tr>
<td>Hastelloy B</td>
<td>500</td>
<td>¼</td>
<td>+0.1</td>
<td>Excellent</td>
</tr>
<tr>
<td>Hastelloy B</td>
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<td>¼</td>
<td>-0.5</td>
<td>Excellent</td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>500</td>
<td>¼</td>
<td>+0.2</td>
<td>Excellent</td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>600</td>
<td>¼</td>
<td>+0.5</td>
<td>Excellent</td>
</tr>
<tr>
<td>Hastelloy D</td>
<td>500</td>
<td>¼</td>
<td>-2.5</td>
<td>Good</td>
</tr>
<tr>
<td>Hastelloy D</td>
<td>600</td>
<td>¼</td>
<td>-2.5</td>
<td>Good</td>
</tr>
<tr>
<td>Inconel</td>
<td>500</td>
<td>¼</td>
<td>+0.01</td>
<td>Excellent</td>
</tr>
<tr>
<td>Micalex</td>
<td>243</td>
<td>¼</td>
<td>Disintegrated</td>
<td>Poor</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>500</td>
<td>¼</td>
<td>-0.1</td>
<td>Excellent</td>
</tr>
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<td>Monel K</td>
<td>500</td>
<td>¼</td>
<td>0.0 (in SS)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Monel K</td>
<td>500</td>
<td>¼</td>
<td>-0.4 (in Ni)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel A</td>
<td>500</td>
<td>¼</td>
<td>0.0 (in SS)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel D</td>
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<td>-0.08 (in Ni)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel L</td>
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<td>¼</td>
<td>+0.1 (in SS)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel L</td>
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<td>¼</td>
<td>-0.05 (in Ni)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nickel Z</td>
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<td>-0.15 (in Ni)</td>
<td>Excellent</td>
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<td>Niobium (Cb)</td>
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<td>Excellent</td>
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<tr>
<td>Sapphire, Linde</td>
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<td>-0.08</td>
<td>Excellent</td>
</tr>
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<td>Sichromo SS</td>
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<td>¼</td>
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<td>Excellent</td>
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<td>Stellite 1</td>
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<td>-0.3</td>
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<td>Stellite 6</td>
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<td>¼</td>
<td>+0.4</td>
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</tr>
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<td>Stellite 12</td>
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<td>+0.9</td>
<td>Excellent</td>
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<td>Titanium</td>
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<td>¼</td>
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<td>Excellent</td>
</tr>
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<td>Trodaloy 1</td>
<td>500</td>
<td>¼</td>
<td>-28</td>
<td>Poor</td>
</tr>
<tr>
<td>Uranium</td>
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<td>¼</td>
<td>-4</td>
<td>Good</td>
</tr>
<tr>
<td>Vitallium</td>
<td>500</td>
<td>¼</td>
<td>+6</td>
<td>*</td>
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<td>Worthite</td>
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<td>+0.19</td>
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<td>Zirconium</td>
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<td>Zirconium-nickel</td>
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<td>T-304 SS</td>
<td>500</td>
<td>¼</td>
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<td>Excellent</td>
</tr>
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<td>T-304 SS</td>
<td>710</td>
<td>¼</td>
<td>+1.9</td>
<td>Good</td>
</tr>
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<td>T-310 SS</td>
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</tr>
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<td>T-310 SS</td>
<td>710</td>
<td>¼</td>
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<td>Good</td>
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<td>T-316 SS</td>
<td>500</td>
<td>¼</td>
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<td>Excellent</td>
</tr>
<tr>
<td>T-316 SS</td>
<td>710</td>
<td>¼</td>
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<td>Good</td>
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<td>T-347 SS</td>
<td>500</td>
<td>¼</td>
<td>0.0</td>
<td>Excellent</td>
</tr>
<tr>
<td>T-347 SS</td>
<td>710</td>
<td>¼</td>
<td>+2.1</td>
<td>Good</td>
</tr>
<tr>
<td>5% Cr-0.5% Mo</td>
<td>500</td>
<td>¼</td>
<td>+0.11</td>
<td>†</td>
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<tr>
<td>5% Cr-0.5% Mo-0.5% Ti</td>
<td>500</td>
<td>¼</td>
<td>-0.1</td>
<td>†</td>
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<td>1018 LC steel</td>
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<td>¼</td>
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<td>†</td>
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<tr>
<td>B4A2A HR steel</td>
<td>500</td>
<td>¼</td>
<td>-0.84</td>
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<td>18-4-1 HSTS</td>
<td>500</td>
<td>¼</td>
<td>+0.04</td>
<td>Excellent</td>
</tr>
<tr>
<td>18-4-1 HSTS</td>
<td>600</td>
<td>¼</td>
<td>+0.3</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

*Uncertain because material was cast and large weight gain probably resulted from the absorption of sodium.

†Although there was negligible corrosion, there may have been some decarburization.
REFERENCES

33. L. F. Epstein, unpublished work.
42. H. A. Fremont, Sodium Contaminating Impurities in Helium, KAPL Memo HAF-1, Confidential, June 1, 1949.
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144. C. E. Weber and S. R. Vandenberg, unpublished work.


August 1950
A number of attempts have been made to determine the structure of the beta phase of uranium. These have been generally unsuccessful because of the difficulty encountered in obtaining adequate and reproducible x-ray diffraction patterns. Apparently little consideration has been given to the possible mechanism of the inversions, gamma to beta and beta to alpha, and the structural implications contained therein. The following speculative discussion is offered in the hope that the ideas may prove stimulating to those engaged in a study of the structure of beta uranium.

The gamma phase of uranium has the body-centered cubic structure, with the a axis equal to 3.43 Å. Alpha uranium, on the other hand, is orthorhombic with the following cell constants:

\[
\begin{align*}
a &= 2.852 \\
b &= 5.865 \\
c &= 4.945
\end{align*}
\]

Projections of the alpha-uranium structure on 001 and on 100 are given in Figs. 1a and 2a. Jacobs and Warren* have suggested that the structure is essentially a distortion of hexagonal close packing. While this is a perfectly reasonable point of view, the structure can be more logically considered a distortion of the gamma or body-centered phase in which the 110 plane of the body-centered cube becomes 001 of the orthorhombic structure and the 100 plane retains its orientation.

Projections of a body-centered cube on 110 and 100 are shown in Figs. 1b and 2b. The close relation between the structures of alpha and gamma uranium is obvious.

The rapidity of the two inversions, gamma to beta and beta to alpha, and their complete reversibility indicate that little structural change takes place. Because of the close relation between the gamma and alpha structures, it is of interest to inquire if there is any logical intermediate state in a transition from one to the other. Comparison of Figs. 1a and b, and 2a and b shows that there are two essential differences. In the first place, the interatomic distances have decreased. Second, there is a change in the angle between the cube edge and face diagonal (ϕ in Fig. 2b) from

45 deg to about 26 deg (φ in Fig. 2a), which causes a translation of the dotted circles of Fig. 1b to the left, as indicated by the arrows. These two changes might well be the two inversions gamma to beta and beta to alpha. Which change might correspond to which inversion remains to be determined. However, the apparently greater volume changes in the latter suggests that the decrease in the interatomic distances is the causative factor.

Fig. 1b. Body-centered cube projected on 110.

Fig. 2a. The structure of uranium projected on 100.

Fig. 2b. Body-centered cube projected on 100.
The Thermal Expansion Characteristics of Beryllium as Measured with a High Temperature Precision X-Ray Camera

By Paul Gordon
Massachusetts Institute of Technology, Cambridge, Massachusetts
Report MIT-PG-9

The desirability of accurately measuring the lattice parameters of beryllium at elevated temperatures has led to the design and construction of a high-temperature precision x-ray camera. The original goal of such measurements was to determine whether the subjection of beryllium to the intense radiation of nuclear piles would have an appreciable effect on its lattice dimensions or on its thermal-expansion characteristics. Investigation of the possible occurrence of this radiation damage has not yet been carried out. However, the thermal-expansion coefficients of beryllium have been measured up to 1000°C. It is the purpose of these notes to present the results of the measurements along with the corollary evidence they have provided against the occurrence of any allotropic transformation in beryllium up to 1000°C. Such a phase change has been reported several times in the literature.

The x-ray camera and vacuum apparatus used have been described in detail elsewhere. Briefly, a back-reflection symmetrical-focussing camera was constructed in such a way as to allow the removal of its rear segment, which ordinarily supports the specimen. The specimen was then held in place in the proper position for focusing by an adjustable arm extending from a post at the top center of the camera. Heat was supplied by a small cylindrical platinum-wound resistance furnace that enclosed the specimen and was held in position by the same support arm. Water cooling coils and beryllium-radiation shields were provided to keep the camera and film at room temperature. In order to minimize oxidation, the whole assembly was placed within a vacuum chamber in which pressures of 10⁻⁴ to 10⁻⁵ mm of Hg were maintained during the measurements. The temperature of the specimen was determined by a chromel-alumel thermocouple, the hot junction of which was spot-welded to the small beryllium cylinder, which contained the pressed-powder beryllium specimen.

The lattice parameters of three separate specimens prepared from the same lot of 97%-assay beryllium powder were measured at some 20 temperatures between 24 and 1013°C. The major impurity in the beryllium was oxygen, which, along with the other impurities, has been indicated to have little effect on the lattice constants of beryllium. From the curves of parameters or unit cell volume vs. temperature, the true coefficients

$$\frac{1}{x} \frac{dx}{dT}$$

and the mean coefficients

$$\frac{x_T - x_{25}}{x_{25}} \frac{1}{T - 25}$$

of thermal expansion were calculated. These coefficients are plotted as a function of temperature in Figs. 1 and 2. Consideration of the errors involved in the measurements and in the reading of tangent values from the parameter-temperature curves, indicates the following approximate limits of accuracy for the values shown in Figs. 1 and 2: for the true coefficients, no better than ±5% at the extremities of the temperature range investigated, but considerably less uncertainty at the intermediate temperatures; for the mean coefficients, ±5% at the lower temperatures, approaching ±0.3% as the temperature approaches 1000°C.
In the use of these expansion coefficients it should be remembered that, although the volume coefficients are applicable to beryllium specimens of any type, the linear coefficients can be applied rigorously only to single crystals where the direction of expansion with respect to the hexagonal axis is known. However, the values read from the curves may be used as very close approximations for extruded round rods of beryllium where the extrusion reduction in area was greater than about 6 or 8 to 1. It has been demonstrated that such material has a high degree of preferred orientation, the basal (0001) planes lying within about 6 or 7 deg of parallelism with the rod axis and randomly oriented about this axis. Thus, the longitudinal coefficient of thermal expansion for extruded rods is given very closely by the coefficient perpendicular to the hexagonal axis of the unit cell. The coefficient of radial thermal expansion for the rods is approximately the arithmetical average of those perpendicular and parallel to the hexagonal axis. For a polygrained specimen exhibiting no preferred orientation, the coefficient of linear thermal expansion in any direction may be taken as equal to

\[ \frac{2\alpha_\perp + \alpha_\parallel}{3} \]

where \( \alpha_\perp \) is the coefficient perpendicular to the hexagonal axis, and \( \alpha_\parallel \) is the coefficient parallel to the hexagonal axis.

On several occasions there have been reports in the literature claiming evidence for one or more allotropic changes in beryllium at various temperatures: Lewis found indications of such transformations at \(-45^\circ C\) and \(450^\circ C\); Noyce and Daane reported a phase change at \(730^\circ C\), but attempts to discern this transformation by Gordon and Kaufmann were negative; Jaeger, et al., claimed to have produced a high-temperature beryllium phase, for which they gave the crystal structure, by heating at \(630^\circ C\).
temperature. The only change in the patterns as a function of rising temperature was a gradual shifting of the lines toward lower angles as a result of the uniformly increasing dimensions of the unit cell. All new lines which appeared at the high-angle end of the films could be indexed exactly on the same hexagonal close-packed lattice. At 900 and 1000°C, two faint lines extraneous to this lattice did appear, but these were definitely proved to be BeO lines, since they corresponded precisely with the two strongest lines appearing on pure-BeO patterns made at the same temperatures and with the same radiation. Since for all the exposures made the specimens were at temperature for 4 to 7 hr, it seems highly probable that if there were, indeed, a stable high-temperature phase it would have formed in sufficient quantity to make its presence evident in the diffraction patterns. Anticipating the objection that the transformation may possibly have been inhibited by the impurities (largely oxygen) in the 97%-assay beryllium used, a sample of powder assaying 99.4% Be and containing practically no oxygen (about 0.2% Fe, 0.2% Al, 0.1% C, 0.1% Si by weight) was obtained and x-ray photograms made at 650 and 900°C. In neither case was there any indication of the formation of a high-temperature phase. It seems safe to conclude, therefore, that the hexagonal close-packed beryllium phase found at room temperature is stable at least up to 1000°C.

REFERENCES
2. P. Gordon, Preliminary studies of the physical metallurgy of beryllium, MDDC-1370.

November 1948
It is of interest to note that the data in this paper may be used to compute a heat of activation for recrystallization and growth.

After large amounts of cold work, there are probably so many nuclei available for growth that any additional ones formed during recrystallization are a negligible fraction of the total. In this case, the process of recrystallization can be represented by the relation

\[ \ln t = \ln \ln \left( \frac{1}{1-x} \right) + A + \frac{Q}{RT} \]

where \( x \) is the fraction recrystallized at time \( t \),

---

Figure 1.
Q is a heat of activation, T the absolute temperature, and A a constant.

The data in Tables 3 and 4 represent recrystallization of uranium cold rolled 85%.

The data in Table 3 may be plotted directly as shown in Fig. 1. Note that the data lie on straight lines, and that the heat of activation computed from these lines is in the range from 100,000 – 110,000 cal/mol.

The data in Table 4 may also be used by assuming that the same hardness represents the same amount of recrystallization. By plotting $\ln t$ against hardness using the data in Table 4, a family of curves is obtained, representing recrystallization at various constant temperatures. From these curves, points at constant hardness level can be obtained.

A series of points, so obtained, at a hardness level of 84 Rockwell G are also shown in Fig. 1. If there is a linear relation between hardness and extent of recrystallization, this level of 84 Rockwell G represents about 50% recrystallization.

It will be noted from Fig. 1 that the points obtained from Table 4 indicate substantially the same slope as the ones from Table 3. The extent of recrystallization indicated by the two methods is different, however; that is, the hardness curve representing 50% recrystallization almost coincides with the curve representing complete recrystallization, as indicated in Table 3.

Thus, while the determination of heat of activation appears to be relatively straightforward, it would seem that any additional information would require a more reliable method of estimating extent of recrystallization.
In the course of a search for a single crystal of graphite suitable for a study of radiation damage by single crystal x-ray diffraction techniques, certain observations have been made which raise a serious question as to the true crystal structure of graphite. Although the data are insufficient to warrant drawing of conclusions, the great importance of graphite—entirely aside from its use as a moderator—in chemistry and biology suggests that the experimental observations would be of general interest. The writer, in conjunction with Linus Pauling, has discussed the problem and it is anticipated that a detailed account will be published in the near future. For this reason, only a brief summary will be given here.

One of the most striking observations is that of the almost universal existence of twinning. It is rare indeed to find a crystal which does not display one or more twin laws. Obviously, in a structure with such loose bonding as between the layers of graphite, one must not overlook random rotations. Only those relations which appear repeatedly are considered of importance. One of the most prominent of these is that which relates individuals having parallel c axes by an angle of 25.5° (or 57.5°) degrees. That this is not due to random rotation is shown by the fact that it has been found to occur three times in one individual. Furthermore, it has been found in natural material from three locations in Canada and from Ceylon as well as in synthetic crystals collected at a blast furnace. The importance of this angular relation lies in the fact that it cannot be rationalized on the basis of a structure having the high hexagonal symmetry of graphite. There is no way in which regular hexagons of carbon atoms can be either reflected or rotated so as to produce individuals related by that amount. This suggests an asymmetry in the ring, from which it follows that the three C-C bond lengths of each carbon atom cannot be equal nor at 120 degrees.

A second observation concerns the relative intensities of certain reflections. It is observed that the intensities of 1010 and 1120 are about equal with, perhaps, the latter 10 to 20% stronger. Calculations on the basis of the accepted structure show that 1120 should be about four times as intense as 1010. It has also been occasionally found that certain of the symmetrically related reflections do not have equal intensities. The differences are very small and the possibility that they are spurious cannot be discounted. However, if they are real, hexagonal symmetry cannot exist.

The above observations led Pauling to suggest an alternative stacking of the adjacent carbon layers. Instead of being stacked as shown in Fig. 1, they are related as in Fig. 2. The new stacking, incidentally, has the added virtue of allowing all carbon atoms to have the same coordination. The new structure is orthorhombic and, in order to obtain the apparent hexagonal symmetry, pseudo-
hexagonal twinning must be postulated, a by no means improbable situation.

Calculated intensities on the basis of the new structure are in better agreement with observa-

tion than those from the old structure. However, satisfactory agreement cannot be obtained until one of the C–C bond lengths is shortened to 1.37 A and the other two increased to 1.44 A. (In the old structure all are 1.42 A.) Bond angles become 118 degrees and two of 121 degrees. This departure from 120 degrees provides a mechanism through reflection or rotation of adjacent layers for the appearance of the angularly related individuals noted above.

In regard to the magnitudes of the bond lengths, Pauling has suggested that, in a resonance system, bond numbers tend to be simple fractions with a preference for one-half. In this case, the carbon atom would have one bond of 1.39 A and two of 1.43 A, which are not far from those calculated.

The case for the new structure has not been proved as yet. Certain minor discrepancies exist. It is hoped to eliminate these when a crystal giving reliable intensity data has been located.

REFERENCES

2. Linus Pauling, personal communication.
3. Linus Pauling, personal communication.
LETTERS TO THE EDITORS

To the Editors:

I have just completed reading the Journal of Metallurgy and Ceramics and I would like to extend my compliments to you and the editorial board and to the contributors for what I think is the best job of information reporting and dissemination that I have yet seen within the Atomic Energy program. I cannot help feel that the extension of this sort of publication to other fields of activity within the Commission can do more to eliminate the reluctance of research scientists to participate in classified work than any other combination of assurances or policies which I can think of.

This was an exceptionally good idea and the execution of same is outstanding.

Donald G. Sturges
April 1, 1949
Hanford Operations Office
Hanford, Washington

To the Editors:

It has been called to my attention recently that the graph showing the stress and temperature combinations producing an arbitrary series of creep rates published on page 87 of the July, 1948, issue of the Journal is in error. A mistake in load on one of the creep tests run at 500°C was noted before publication of the data and corrected in all plots except the one in question, which, through oversight, was published in uncorrected form. I would appreciate it, therefore, if you would publish the attached corrected plot in your next issue.

D. W. Lillie, Asst. to Chief

Metallurgy & Materials Branch
Division of Research
United States Atomic Energy Commission
Washington, D. C.

Fig. 20—A semi-logarithmic plot for beryllium showing load to produce creep rates of 1.0, 0.1, 0.01, and 0.001 per cent per hour at temperatures between 500 and 1100°C.