EXPERIMENTAL INVESTIGATIONS OF THE REMOVAL OF SODIUM OXIDE FROM LIQUID SODIUM

By

G. Billuris

January 18, 1960
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EXPERIMENTAL INVESTIGATIONS OF THE REMOVAL
OF SODIUM OXIDE FROM LIQUID SODIUM

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. ABSTRACT</td>
<td>3</td>
</tr>
<tr>
<td>II. INTRODUCTION</td>
<td>4</td>
</tr>
<tr>
<td>III. SODIUM PLUG GROWTH INVESTIGATION</td>
<td>6</td>
</tr>
<tr>
<td>A. Experimental Program</td>
<td>6</td>
</tr>
<tr>
<td>B. Description of Test Facility</td>
<td>7</td>
</tr>
<tr>
<td>C. Test Procedures and Results</td>
<td>11</td>
</tr>
<tr>
<td>D. Discussion</td>
<td>18</td>
</tr>
<tr>
<td>IV. SODIUM PURIFICATION INVESTIGATIONS</td>
<td>22</td>
</tr>
<tr>
<td>A. Experimental Program</td>
<td>22</td>
</tr>
<tr>
<td>B. Description of Test Facility</td>
<td>23</td>
</tr>
<tr>
<td>C. Test Procedures and Results</td>
<td>30</td>
</tr>
<tr>
<td>D. Discussion</td>
<td>50</td>
</tr>
<tr>
<td>V. CONCLUSIONS</td>
<td>55</td>
</tr>
<tr>
<td>VI. REFERENCES</td>
<td>56</td>
</tr>
<tr>
<td>Figure No.</td>
<td>Title</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>III-1</td>
<td>Sodium Plug Growth Experiment - Schematic</td>
</tr>
<tr>
<td>III-2</td>
<td>Plug Growth Test Facility</td>
</tr>
<tr>
<td>III-3</td>
<td>Cold Finger with Sodium Oxide Deposits</td>
</tr>
<tr>
<td>IV-1</td>
<td>Sodium Purification Loop Flow Sheet</td>
</tr>
<tr>
<td>IV-2</td>
<td>Sodium Purification Test Loop</td>
</tr>
<tr>
<td>IV-3</td>
<td>Cold Trap Section</td>
</tr>
<tr>
<td>IV-4</td>
<td>Cold Trap Packings</td>
</tr>
<tr>
<td>IV-5</td>
<td>Cold Trap Deposit During Removal Operation</td>
</tr>
<tr>
<td>IV-6</td>
<td>X-Ray Views of Cold Trap Deposits</td>
</tr>
<tr>
<td>IV-7</td>
<td>Oxide Distribution in Cold Trap - Run No. 2</td>
</tr>
<tr>
<td>IV-8</td>
<td>Oxide Distribution in Cold Trap - Run No. 3</td>
</tr>
<tr>
<td>IV-9</td>
<td>Oxide Distribution in Cold Trap - Run No. 4</td>
</tr>
<tr>
<td>IV-10</td>
<td>Oxide Distribution in Cold Trap - Run No. 5</td>
</tr>
<tr>
<td>IV-11</td>
<td>Cold Trap Deposit From Run No. 4</td>
</tr>
<tr>
<td>IV-12</td>
<td>Typical Structure of Deposit From Run No. 4</td>
</tr>
<tr>
<td>IV-13</td>
<td>Cold Trap Deposit From Run No. 5</td>
</tr>
<tr>
<td>IV-14</td>
<td>Typical Structure of Deposit From Run No. 5</td>
</tr>
<tr>
<td>IV-15</td>
<td>Cold Trap (Double Screen Packing) Showing Oxide Growth With Time on Lower Screens</td>
</tr>
<tr>
<td>IV-16</td>
<td>Cold Trap (Double Screen Packing) Showing Oxide Deposits</td>
</tr>
<tr>
<td>IV-17</td>
<td>System Oxide Concentration vs Time</td>
</tr>
</tbody>
</table>
Experimental investigations were conducted to obtain additional information on the growth and characteristics of sodium oxide deposits in liquid sodium which could lead to system plugging. These investigations included the removal of sodium oxide from molten sodium by the cold trap method.

The experimental equipment consisted of two separate test facilities. One piece of equipment contained a cooled, stainless steel "plug growth" thimble that extended below the surface of the sodium in an eight inch diameter vessel. Impurities were added to the sodium before a given series of tests. Sixteen test runs were conducted with this facility to determine the relative operating effects of time, sodium temperature, temperature differential and agitation on the deposit growth. The deposits were described by their appearance, weight, hardness and chemical analysis. The other facility consisted of a cold trap purification unit installed in a forced circulation sodium loop. Sodium monoxide or peroxide was periodically added to the sodium in the in-stream dump tank whenever the oxide concentration in the operating loop was reduced below about 30 ppm. Five test runs were conducted to provide additional information for defining the mechanism of oxide removal and to determine the effects of various kinds of packing on the capacity and efficiency for oxide removal. The deposits were described by their appearance, weight, hardness and oxide distribution. The latter was obtained by chemical analysis of selected samples and an X-ray of the deposit.

The experimental data confirmed that the deposits are formed more rapidly with an increased amount of oxygen in the sodium, cooling of the deposit area and fluid agitation. In general, the deposits at 300°F appeared to be silver in color with patches of liquid adhering to irregular, crystalline-like structures. At room temperature the deposits were relatively hard and brittle and broken pieces of the structure appeared porous. During operation of the purification loop the apparent rate of solution of sodium oxide in sodium appeared to be much slower than the rate of removal in the cold trap. The data from the cold trap deposit indicated that up to 20 volume per cent sodium monoxide could be collected in the trap before significant flow restriction was apparent. The most effective packing material tested was knitted wire mesh. With any of the packings tested, and operating with a residence time of about 8 minutes or longer, the effluent sodium from the cold trap did not appear to be supersaturated with oxygen.
II. INTRODUCTION

In July 1958 the Atomic Power Equipment Department of the General Electric Company undertook a sodium technology program to experimentally determine the growth and characteristics of plugs formed by impurities in sodium, basic information on sodium oxide behavior and its removal by the cold trap method and the rate of diffusion of sodium oxide in liquid sodium. This report describes the work that was performed under the first two items above. The diffusion of sodium monoxide in sodium is described in a companion report by S. Siegel (1)*. The methods of analyzing impurities in sodium samples for all the investigations were reported by H. E. Perrine (2).

Operating experience obtained with circulating sodium systems during the last 15 years has indicated that deposits occur when oxide is present in the sodium, and localized regions are at lower temperature than the oxide saturation temperature. Many of the systems have been plugged with these deposits, particularly in the locations where the sodium is nearly stagnant and/or the flow cross section is smaller than the remainder of the system.

Various means of sodium purification including distillation, filtration, chemical reduction (gettering) and precipitation, were investigated during development of the U.S. Navy SIR project. Precipitation of the sodium oxide by cooling below the saturation temperature was found to be the most effective method of reducing the plugging tendency and the oxide level in a sodium system. The equipment which was developed to remove oxide was called a "cold trap" because the device functions in a manner similar to the more common laboratory cold trap which is used to remove trace impurities in a gas system by condensation or precipitation. Differential solubility of sodium oxide in sodium is the basis on which the cold trap functions. Oxide removal is accomplished by cooling the sodium below its oxide saturation temperature and promoting crystallization and retention of the oxide. Cold traps can be divided into two categories - natural (diffusion) and forced circulation (3). The diffusion unit is usually a small container attached to the sodium system and operated at a lower than system temperature. The forced circulation cold trap is usually located in a bypass line of the main sodium system. It consists basically of a heat exchanger to cool the sodium and an oxide collection chamber; in larger systems a regenerative heat exchanger is also used to minimize heat losses. All sodium cooled, nuclear power plants including SIR, SRE, EBR-II and the Enrico Fermi plant have used cold trapping as a method of sodium purification.

Relatively high oxide concentrations are frequently encountered upon filling a system with sodium and consequently cold trapping is usually employed prior to initial operation. Normally a sodium system is leaktight so that the sodium does not become contaminated during operation. Although precautionary methods are used, air and other impurities containing oxygen can leak into a system during refueling or component maintenance. Contamination

*Numbers in parenthesis refer to items in the Reference.
by other sources such as leakage from the high pressure water side of a steam generator could result in significant quantities of oxygen addition to the sodium. It is necessary, therefore, that the cold trap be capable of coping with these infrequent and potentially large oxide additions as well as maintaining a normally low oxide concentration.

At present cold trap design appears to be largely an art due to the paucity of design data. The information available does not provide enough correlation of design parameters to permit extrapolation with confidence to large scale units for central station power plant use. Previous cold traps have been somewhat susceptible to plugging, probably due to high initial oxide concentration in the influent sodium stream, startup conditions in the economizer favorable to deposit growth and lack of optimized cold trap design parameters. Under such conditions some of the cold traps have exhibited very limited capacity.

The earliest work on cold trap investigations was reported by Voorhees and Bruggeman in 1951 (4). The first cold traps which were tested employed stainless steel filter elements for mechanical retention of the solid oxide. Performance of the porous metal filters was unsatisfactory because of plugging attributed to crystal growth in the interstices of the filter. Subsequent tests showed that a cold trap packed with stainless steel wool was not as susceptible to plugging yet was effective in oxide removal. The available data suggested two possible mechanisms for removal of oxide by a cold trap:

a. As the sodium is cooled below the saturation temperature the oxides are precipitated, either throughout the stream or preferentially at the coldest surfaces so the effectiveness of oxide removal would be a function of the ratio of cold surface area to flow rate and flow characteristics as they affect the contact between the saturated stream and the cold surfaces.

b. As the sodium is cooled below its saturation temperature, oxide nuclei are produced throughout the stream, and crystal growth continues as the particles are carried along until removed by mechanical filtration. Oxide removal effectiveness would then be a function of the relative size of the oxide particles and effective passages of the filter and thus a function of crystal growth prior to filtration.

A more recent discussion of cold trap investigations by Gray, Neal and Voorhees (5) presents performance correlations and limited data on capacity. A summary of their results and conclusions follow:

a. Capacity data with a knitted wire mesh packed cold trap yielded a total recovered weight of 38.7 lb. of Na₂O in a cold trap volume of 2.0 ft³ corresponding to 13.8 volume percent. The cold trap was still operable when the testing was terminated.
b. The effect of residence times ranging from 3.0 minutes to 10.4 minutes was studied; residence times of 5 minutes or longer were recommended to provide high oxide removal efficiency.

c. This and the aforementioned data led the authors to believe that the principal method of oxide retention was due to crystal growth rather than filtration.

To provide a source of oxygen for these investigations both Na$_2$O$_2$ and Na$_2$O were added to the system. Considerable loss of oxygen was observed when Na$_2$O$_2$ was added; an average recovery of 63% oxygen was obtained with Na$_2$O$_2$ but nearly 100% recovery was realized when Na$_2$O was used.

This report describes the work contracted by Atomics International to provide a better understanding of sodium purification and the characteristics of solid deposits in sodium. Section III of this report describes plug growth and characteristics of sodium oxide deposits which could lead to system plugging. Section IV of this report describes cold trap investigation which were designed to provide additional information for defining the mechanism of oxide removal and determining the effect of packing on the capacity and efficiency for oxide retention. Sodium purification investigations covered by this program have been directed toward removal of sodium oxide by the forced circulation cold trap method.

III. SODIUM PLUG GROWTH INVESTIGATIONS

A. Experimental Program

The objective of this program was to investigate the growth and characteristics of plugs formed by impurities in sodium through the use of small scale laboratory equipment. When oxide is present in sodium systems it has been found from previous observations that plug formation occurs in localized regions which are at a lower temperature than the oxide saturation temperature, have a small cross sectional flow path and contain low velocity sodium.

The concept of a cold finger immersed in a pool of hot sodium saturated with sodium oxide was selected as a convenient, inexpensive means of simulating plug formation environment. This system simulates all of the above conditions except restricted flow path; therefore, while no plugging is likely, uninhibited growth of the plug deposit is anticipated.

The experimental program was directed primarily to investigations with sodium oxide as the principal impurity. Excess oxide was introduced into the system to provide makeup during operation. Natural convection was used during most tests to circulate the sodium and help maintain saturation of the oxide in the main body of sodium. Stirring provisions were incorporated in several runs to obtain comparative data for evaluating the effects of fluid agitation on plug growth. Deposition under these conditions is assumed to be controlled by diffusion of sodium oxide across the boundary layer between the bulk sodium and the cold finger surface.

Test runs were conducted to cover the following approximate range of conditions for the controlled variables:
Sodium temperature*-----------------------------500°F to 650°F
AT between sodium and cooling oil----------200°F to 400°F
Duration of test run----------------------1/2 week to 2 weeks
Sodium circulation------------------------Low velocity
Most runs: natural circulation
Few runs: stirred

Deposited material on the cold finger was analyzed to obtain measurements of total weight and concentration of sodium monoxide for each run. Other impurities such as calcium, potassium and lithium were periodically analyzed.

At the completion of the above tests two runs were made with lithium additions; for the final two runs calcium was also added as an impurity. The resulting deposits were analyzed for all added impurities.

Plans for crystal structure measurements, considered originally in the program, did not materialize due to difficulty in developing suitable equipment and techniques for preventing surface contamination of the sample during transfer and analysis. Similarly, carbon impurity investigations were not pursued due to difficulties in obtaining a satisfactory method for carbon analysis. These problems were reviewed with the customer. With his concurrence no further action was taken to perform the analysis.

B. Description of Test Facility

The sodium plug growth test facility is shown schematically in Figure III-1 and by the photographs in Figures III-2 and -3. The test section of the facility consisted of a removable, cooled thimble, or "cold finger", located in the upper portion of a heated sodium pool which was contained in a vessel constructed of 8 inch schedule 40 pipe about 16 inches long. The cold finger, attached to the top head by a flanged connection, extended into the vessel for a length of about 6 inches with the lower 2½ inches normally submerged in sodium. Constructed as a bayonet tube heat exchanger the cold finger consisted of a 1 inch diameter tube with a flat bottom head and a concentric inner tube ¾ inch diameter; the inner tube served as the inlet and the annulus between the two tubes served as the outlet line for flow of cooling oil to dissipate heat from the facility. A modification to facilitate sampling provided a removable 1/32 inch wall, split ring sleeve over the lower 2-1/2 inches of the cold finger. The vessel top cover contained a nozzle for gas and was provided with an opening for attaching a stirrer.

All materials that contacted sodium were constructed of type 304 stainless steel.

A coiled 1 KW electrical tubular heater, manually controlled by a variac, served as a "hot plate" for supplying heat to the bottom of the vessel. The entire vessel was covered with thermal insulation.

To facilitate removal and observation of plug growth samples in an inert atmosphere a Kewatmee dry box was provided around the upper portion of the sodium vessel. The vessel was inserted through a ten inch diameter opening in the bottom of the box; a 12 inch diameter flange welded to the upper

*These temperatures correspond to saturation values ranging from 77 ppm to 227 ppm oxygen.
FIGURE III-1, SODIUM PLUG GROWTH EXPERIMENT—SCHEMATIC
FIGURE III-3, COLD FINGER WITH SODIUM OXIDE DEPOSITS
portion of the sodium vessel was used for bolting the assembly to the dry box. Transite insulation, 3/4 inch thick, was inserted as a thermal barrier between the metal flange and the bottom of the box.

The dry box was fitted with rubber gloves, oil line connections, gas and vent connections and sealed penetrations for power supply lines to the motor driven stirrer and thermocouple connections for use with an immersion thermocouple in the oil side of the cold finger. A double door interchange compartment provided on the box permitted insertion and removal of tools and other equipment from the inert gas space without significant oxygen contamination.

The cooling system, shown schematically in Figure III-1, consisted of a small, forced circulation loop constructed essentially of carbon steel. Major components of the loop included the cold finger, pump and surge tank; interconnecting lines were constructed of 3/8 inch diameter 20 BWG tubing and 1/4 inch schedule 40 pipe. The system was designed to circulate cooling oil at a temperature of 230°F and a maximum flow of 1/2 gpm.

Flexible, metal hoses located within the dry box were used to connect the inlet and outlet cooling oil lines from box penetration fittings to the cold finger; these flexible lines facilitated removal of the cold finger at the end of each test run without draining the oil system. A Fisher and Porter Flowrator was used to monitor the coolant oil flow rate. Flow regulation was obtained by manual adjustment of a globe valve in the pump line discharge. Six chromel alumel thermocouples located on the sodium vessel, cold finger and cooling lines were connected through a selector switch to a panel mounted temperature recorder. Natural convection cooling with ambient air was used to dissipate up to 2000 Btu/hr from the uninsulated piping outside the dry box. "Mobiltherm 600", a Socony-Vacuum aromatic heat transfer oil, was used as the coolant fluid. Circulation was accomplished with a type HAIX Corley "Magnaflow" canned rotor centrifugal pump.

Argon from a compressed gas cylinder was supplied through a low pressure Matheson pancake regulator to the dry box, interchange compartment and sodium vessel. A NaK bubbler, located in the inlet gas line behind the dry box, was used to remove oxygen and moisture impurities from the argon cover gas.

For test runs 5 through 9, which used stirring, a rheostat-controlled, motor driven stirrer was installed through a packed bushing on top of the sodium vessel.

C. Test Procedures and Results

Initial operation consisted of charging the test vessel with approximately 20 pounds of commercial grade sodium at 250°F. After adding 10 grams of sodium peroxide powder (analytical reagent grade) the first test run was started.

A typical test run consisted of maintaining the sodium and oil temperatures at fixed values for a specified time interval. At the completion of a run the sodium was cooled to about 300°F and the cold finger with deposit was withdrawn from the test vessel into the dry box argon atmosphere. The
deposit was removed from the cold finger, placed in a clean test tube or
glass container, sealed, transferred from the dry box and sent to the
laboratory for chemical analysis. The normal operating procedure for a
test run is summarized below:

1. Heat was applied until the sodium temperature reached about 300°F.
Then a blank flange cover over the vessel opening was removed and a
weighed quantity of impurity added to the sodium and stirred manually
with a stainless steel rod while an argon bleed was maintained over
the sodium. A list of the quantity and type of impurities added for
the different test runs is shown in Table III-1.

2. Following the impurity addition the cold finger was reinstalled in the
sodium container, removable insulation blocks replaced on top of the
vessel and about 1 KW of heat supplied to the system.

3. When the sodium temperature reached 400°F, the cooling oil flow was
re-established. Initial flow was set at approximately 0.1 gpm; as
the sodium temperature increased the coolant flow was periodically
increased to maintain the cold finger oil in the temperature region
desired for test.

4. Nearly four hours heating time was required to raise the sodium tem­
perature to 600°F. As the test temperatures were approached, the oil
flow and heat input were manually adjusted to maintain the desired
conditions.

5. Temperatures and oil flow data were recorded twice daily during the
test run. Periodic manual adjustment of heater voltage and coolant
flow was required to maintain desired test conditions within ±10°F.

6. Prior to completion of a test run the dry box was purged for about
16 hours with argon to assist in providing a dry, oxygen-free atmos­
phere. Since pressure within the box did not exceed 1/4 inch water
head and because the box was not completely leaktight, prolonged
purging was necessary in order to purify the enclosed cover gas.

7. Near completion of a run the heater was turned off and the sodium
allowed to cool.

8. After about two hours, when the sodium temperature reached 300°F to
350°F, the coolant oil flow was discontinued and the cold finger
removed for sampling.

9. The specific steps in the sampling operation at the end of a test
run follow:
   a. Leather gloves were placed over the drybox rubber gloves to
      provide protection from the hot equipment.
   b. Insulation blocks were removed from vessel top.
### TABLE III-1

**SUMMARY OF DEPOSIT DATA**

<table>
<thead>
<tr>
<th>RUN</th>
<th>DURATION HOURS</th>
<th>TEMPERATURE $^\circ$F</th>
<th>SODIUM</th>
<th>COOLANT</th>
<th>SODIUM DEPOSIT Wt,g</th>
<th>Na$_2$O,g</th>
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<tr>
<td>1</td>
<td>187</td>
<td>540</td>
<td>265</td>
<td>6.6</td>
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<tr>
<td>2</td>
<td>240</td>
<td>565</td>
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<tr>
<td>3</td>
<td>260</td>
<td>575</td>
<td>225</td>
<td>3.5</td>
<td>2.31</td>
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<tr>
<td>4</td>
<td>264</td>
<td>580</td>
<td>280</td>
<td>3.4</td>
<td>2.35</td>
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<tr>
<td>5</td>
<td>140</td>
<td>560</td>
<td>250</td>
<td>4.5</td>
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<tr>
<td>6</td>
<td>265</td>
<td>555</td>
<td>215</td>
<td>7.5</td>
<td>3.58</td>
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<tr>
<td>7</td>
<td>250</td>
<td>565</td>
<td>245</td>
<td>8.1</td>
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<td>8</td>
<td>216</td>
<td>595</td>
<td>260</td>
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<td>640</td>
<td>240</td>
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<tr>
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<td>174</td>
<td>620</td>
<td>220</td>
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<td>1.20</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>162</td>
<td>625</td>
<td>220</td>
<td>7.4</td>
<td>0.76</td>
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</tr>
</tbody>
</table>

**Notes:**

1. Stirrer used for runs 5 through 9.
2. Removable cold finger sleeve used for runs 7 through 17.
3. NaK bubbler installed in cover gas line after run 7.
4. Excessive surface contamination observed upon removal of run 4 sample.
5. Impurity additions to sodium.
   - Na$_2$O$_2$: 10 g additions prior to runs 1, 6, 10; 15 g prior to run 2.
   - Na$_2$O: 10 g addition prior to run 13.
   - LiOH: 5 g prior to run 14; 50 g prior to run 15.
   - Ca: 10 g prior to run 16; 5 g prior to run 17.
6. Na$_2$O in deposit = (deposit weight)/100 x w/o Na$_2$O from Table III-2.
7. Run 11 was discarded due to faulty temperature measurements.
c. 1/4 inch nuts attaching cold finger flange to sodium vessel were removed.

d. The cold finger assembly was withdrawn, and the appearance of the deposit was noted from visual inspection. Figure III-3 illustrates the typical appearance of a sample at this stage.

e. The sample deposit was transferred into a previously cleaned and weighed container. The lower deposit obtained from the liquid phase region comprised the sample of primary interest in these investigations; the upper, gas phase deposit was analyzed in several runs and found to be predominantly oxide but no consistent results for other impurities were evident. Transfer to the sampling container was initially accomplished by scraping the deposit from the cold finger with a stainless steel spatula; pieces which dropped into a beaker located directly below the cold finger were transferred to the test tube using tweezers. In later tests which had a weighed, removable sleeve over the end of the cold finger tube (spring tension in the sleeve held the piece in place), sampling consisted of pulling off the sleeve and its adherent deposit and placing the entire assembly into a previously weighed bottle.

f. The sampling container was sealed and the access hole in the sodium vessel covered then the sealed sample was removed from the dry box through the interchange compartment.

g. The sample, including sleeve and container, was weighed to permit determination of the deposit weight by difference, then the sample was submitted to the laboratory for chemical analysis.

Initial tests utilized natural circulation for sodium agitation to help insure that the bulk sodium was near saturation conditions. Because deposition originally occurred at a much slower rate than anticipated, stirring provisions were incorporated to provide additional fluid circulation. During later test runs at higher temperature levels stirring was discontinued since a measurable deposit was obtained each week.

Deposited material on the cold finger was analyzed to obtain measurements of hardness, total weight, and concentration of oxide and other impurities such as calcium, potassium and lithium. Test runs were repeated for varying time intervals to evaluate growth rate. The effects of sodium temperature and temperature difference between the sodium and cold finger were investigated. In the final series of tests lithium and calcium were added as impurities to determine their influence on sodium deposit formation.

The cold finger deposit always contained two distinct regions — one corresponding to the gas phase and the other corresponding to the liquid phase (see Figure III-3). The upper, gas phase region deposit appeared as a white or gray white powder, solid at 300°F, loosely adherent and crumpling readily upon external contact. The lower, liquid phase region appeared as a silvery deposit with patches of liquid adhering to irregular, crystal-like structures. Although the gas phase samples were not considered part of the planned test program, some samples of this material were analyzed.
for oxygen and calcium; results shown in Table III-3 indicate no specific trends and are not discussed elsewhere. All future references to cold finger deposits refer specifically to the liquid phase region.

Plug growth test data are summarized in Table III-1. Results of chemical analyses of sodium plugs, bulk sodium and gas phase deposits are shown in Tables III-2 and 3. A summary of the $\Delta T$, $\Delta C$ and deposition rate calculations are shown in Table III-4. For samples prior to run 8, oxide determinations were obtained by titrating to the phenolphthalein end point for total basicity so these oxide results may include some carbonate or other impurity; later oxide determinations, described in "Collected Methods for Analysis of Sodium Metal" by H. E. Perrine (2), provided more reliable results due to correction for bicarbonates and improved free sodium detection.

The method of sampling used in the first six test runs introduced errors in both weight and oxide determinations because:

a. some residue remained on the cold finger or was lost.

b. trace amounts of oxygen and moisture in the box cover gas were present causing visible clouding on the sample surface.

c. an appreciable surface area of freshly cut sodium was exposed to the box atmosphere as a result of the scraping operation.

Several modifications were made to the operating procedure to alleviate the aforementioned difficulties. Before run 7 and thereafter a removable stainless steel split cylinder, of 1/32 inch wall thickness, was placed over the lower part of the cold finger and held in position by tension fit. Removal of this sleeve and the collected deposit (at the end of a test run) was faster and exposed considerably less sample surface to the box atmosphere. To minimize moisture and oxygen impurities in the gas a NaK bubbler was installed in the argon supply line to the dry box and test vessel prior to run 8. From visual observations subsequent test deposits showed less surface contamination during the sampling operation.

The sample from run 8 was used for approximate hardness measurements and therefore was not submitted for chemical analyses. A two inch diameter sample of cast commercial sodium was used for hardness measurements for comparison purposes. Using a ball impression technique described in more detail under Section IV-C the following impression diameters (average of two readings) and hardness values were obtained:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Impression Diameter, mm</th>
<th>Calculated Brinell Hardness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test No. 8 Deposit</td>
<td>4.46 av.</td>
<td>0.175</td>
</tr>
<tr>
<td>Commercial sodium</td>
<td>7.40 av.</td>
<td>0.057</td>
</tr>
</tbody>
</table>

Prior to run 14, 5 grams of LiOH were introduced into the test vessel. This was sufficient to increase the lithium concentration to 150 ppm in the bulk sodium (commercial sodium analyses 20 ppm Li) (6). Although duration and test conditions remained approximately the same as for the preceding
### TABLE III-2

**SODIUM PLUG DEPOSIT COMPOSITIONS***

<table>
<thead>
<tr>
<th>Run</th>
<th>NaO%, ppm</th>
<th>Ca,%</th>
<th>Li,%</th>
<th>K, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4**</td>
<td>0.37**</td>
<td>*</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>58.0</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>65.9</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>67.0</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>47.7</td>
<td>0.15</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>7</td>
<td>88.3</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>63.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>39.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>33.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>32.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>11.7</td>
<td>0.023</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>28.9</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>9.2</td>
<td>0.04</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>10.3</td>
<td>0.33</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

* Element not detected in analysis.
** Although reported, the results are not considered reliable.
*** See notes for Table III-1.

### TABLE III-3

**CHEMICAL ANALYSES FOR BULK SODIUM AND GAS PHASE DEPOSITS***

<table>
<thead>
<tr>
<th>Sample</th>
<th>NaO%, ppm</th>
<th>Ca,%</th>
<th>Li,%</th>
<th>Fe, ppm</th>
<th>Cr, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk Sodium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prior to test</td>
<td>-</td>
<td>0.0014</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>After run 16</td>
<td>0.005**</td>
<td>0.091</td>
<td>0.006</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Gas Phase Deposits</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run No. 3</td>
<td>34.7</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Run No. 4</td>
<td>100.</td>
<td>0.20</td>
<td>-</td>
<td>15.6</td>
<td>21.</td>
</tr>
<tr>
<td>Run No. 6</td>
<td>94.1</td>
<td>0.003</td>
<td>*</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Element not detected in analysis.
** Sodium sampling temperature was 380°F.
*** See notes for Table III-1.
**SUMMARY OF ΔT, ΔC AND DEPOSITION RATE CALCULATIONS***

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration (Week)</th>
<th>Ts°F</th>
<th>ΔT°F</th>
<th>ΔTs°F</th>
<th>ΔC II ppmO₂</th>
<th>Desposition Rate g Na₂O/wk</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.43</td>
<td>565</td>
<td>275</td>
<td>38</td>
<td>31</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>1.55</td>
<td>575</td>
<td>350</td>
<td>49</td>
<td>42</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>1.57</td>
<td>580</td>
<td>300</td>
<td>42</td>
<td>38</td>
<td>1.56</td>
</tr>
<tr>
<td>6</td>
<td>1.58</td>
<td>555</td>
<td>340</td>
<td>48</td>
<td>40</td>
<td>2.27</td>
</tr>
<tr>
<td>7</td>
<td>1.49</td>
<td>565</td>
<td>320</td>
<td>45</td>
<td>37</td>
<td>4.80</td>
</tr>
<tr>
<td>9</td>
<td>0.96</td>
<td>640</td>
<td>400</td>
<td>56</td>
<td>65</td>
<td>6.80</td>
</tr>
<tr>
<td>10</td>
<td>0.95</td>
<td>630</td>
<td>360</td>
<td>50</td>
<td>56</td>
<td>3.78</td>
</tr>
<tr>
<td>12</td>
<td>0.86</td>
<td>610</td>
<td>400</td>
<td>56</td>
<td>55</td>
<td>5.09</td>
</tr>
<tr>
<td>13</td>
<td>1.01</td>
<td>615</td>
<td>405</td>
<td>57</td>
<td>58</td>
<td>4.08</td>
</tr>
<tr>
<td>14</td>
<td>1.12</td>
<td>610</td>
<td>400</td>
<td>56</td>
<td>55</td>
<td>1.09</td>
</tr>
<tr>
<td>15</td>
<td>1.11</td>
<td>620</td>
<td>405</td>
<td>57</td>
<td>59</td>
<td>2.75</td>
</tr>
<tr>
<td>16</td>
<td>1.04</td>
<td>620</td>
<td>400</td>
<td>56</td>
<td>58</td>
<td>1.15</td>
</tr>
<tr>
<td>17</td>
<td>0.97</td>
<td>625</td>
<td>405</td>
<td>57</td>
<td>61</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*Temperature drop through the sodium film was estimated on the basis of ΔTₛ = 70 ΔT/500.

**Concentration gradient was determined on the basis of ΔC = saturation at Tₛ - saturation at (Tₛ - ΔTₛ).

***See Notes for Table III-1.

**TABLE III-5**

SOLUBILITY OF SODIUM MONOXIDE IN SODIUM-BASED UPON KAPL DATA (6)

<table>
<thead>
<tr>
<th>TEMPERATURE °F</th>
<th>SOLUBILITY ppm Oxygen</th>
<th>TEMPERATURE °F</th>
<th>SOLUBILITY ppm Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>10</td>
<td>480</td>
<td>65</td>
</tr>
<tr>
<td>300</td>
<td>11</td>
<td>490</td>
<td>71</td>
</tr>
<tr>
<td>310</td>
<td>12</td>
<td>500</td>
<td>77</td>
</tr>
<tr>
<td>320</td>
<td>14</td>
<td>510</td>
<td>84</td>
</tr>
<tr>
<td>330</td>
<td>16</td>
<td>520</td>
<td>92</td>
</tr>
<tr>
<td>340</td>
<td>18</td>
<td>530</td>
<td>100</td>
</tr>
<tr>
<td>350</td>
<td>20</td>
<td>540</td>
<td>108</td>
</tr>
<tr>
<td>360</td>
<td>22</td>
<td>550</td>
<td>116</td>
</tr>
<tr>
<td>370</td>
<td>24</td>
<td>560</td>
<td>125</td>
</tr>
<tr>
<td>380</td>
<td>27</td>
<td>570</td>
<td>134</td>
</tr>
<tr>
<td>390</td>
<td>30</td>
<td>580</td>
<td>144</td>
</tr>
<tr>
<td>400</td>
<td>33</td>
<td>590</td>
<td>154</td>
</tr>
<tr>
<td>410</td>
<td>36</td>
<td>600</td>
<td>164</td>
</tr>
<tr>
<td>420</td>
<td>39</td>
<td>610</td>
<td>175</td>
</tr>
<tr>
<td>430</td>
<td>42</td>
<td>620</td>
<td>187</td>
</tr>
<tr>
<td>440</td>
<td>46</td>
<td>630</td>
<td>200</td>
</tr>
<tr>
<td>450</td>
<td>50</td>
<td>640</td>
<td>213</td>
</tr>
<tr>
<td>460</td>
<td>55</td>
<td>650</td>
<td>227</td>
</tr>
<tr>
<td>470</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
runs, the deposited Na₂O decreased to 1/3 of previous values at similar operating conditions.

An additional 50 grams of LiOH were added before run 15. The resulting cold finger deposit, while representing an oxide weight increase of 250% compared to the initial lithium run, was less (by about 25%) than plug growths obtained in runs 10-13 without lithium addition. The deposits from both runs 14 and 15 showed lithium concentrations in the range of 1% - 2%.

In general, the deposits on the cold finger at 300°F appeared to be silver in color with patches of liquid adhering to irregular, crystalline-like structures. At room temperature the deposits were relatively hard and brittle with evidence of porosity similar to the cold trap deposits described in Section IV of this report; the data tabulated above indicates the significant increase in hardness (compared to relatively pure, commercial sodium) exhibited by these high oxide concentration sodium specimens.

D. Discussion

Although no quantitative correlations were expected to be drawn from the data, qualitative observations show that the results generally confirm expected trends in that greater deposition rates were obtained with increased bulk sodium temperature and increased temperature drop through the cold finger sodium film. This is reasonable based upon the assumed diffusion controlled process since the oxide concentration gradient, or driving force for diffusion, increases with temperature and temperature differential.

The following data from Tables III-1 and 4 indicate time and temperature effects on plug growth:

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration Hours</th>
<th>Tₛ °F</th>
<th>ΔTₛ °F</th>
<th>ΔC ppm 0₂</th>
<th>Plug Deposit g Na₂O</th>
<th>Deposition Rate g Na₂O/wk</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>240</td>
<td>565</td>
<td>38</td>
<td>31</td>
<td>1.68</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>260</td>
<td>575</td>
<td>49</td>
<td>42</td>
<td>2.31</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>264</td>
<td>580</td>
<td>42</td>
<td>38</td>
<td>2.35</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Comparing the data from runs 2, 3 and 4 it can be seen that increasing the test duration by 10% and the temperature conditions increases the Na₂O deposit by about 40%. Assuming the plug growth varies linearly with time, the observed weight increase apparently is primarily due to the increase in concentration gradient resulting from the change in temperature conditions. Both the calculated concentration gradients and average deposition rates for runs 3 and 4 are about 30% greater than for run 2.

If the sodium in the test vessel is not saturated with oxide although excess sodium oxide is present in the container, then mixing or stirring should aid in dissolving the oxide. Therefore, the deposition rate of sodium oxide should increase with increased agitation until the bulk sodium is saturated with oxide. Also, as a consequence of stirring, the sodium boundary layer through which diffusion occurs should decrease and thereby further increase the rate of deposition. Because of the possibility that natural circulation
relied upon for the initial runs, did not provide adequate fluid motion, a motor-driven stirrer was used for runs 5 through 9. A comparison of data from runs 3 and 6 shows that the stirrer was effective in improving the rate of oxide transfer. Another evidence of increased deposition from stirring was the noticeable increase in crystal growths perpendicular to the cold finger surface.

A removable cold finger sleeve to facilitate sampling was used for runs 7 through 17. Since runs 5 through 9 were conducted with stirring, the overlapping runs 7 and 9 yielded data for comparing time and temperature effects under the combination of stirring and improved sampling.

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration Hours</th>
<th>$T_s$ °F</th>
<th>$\Delta T_s$ °F</th>
<th>$\Delta C$ ppm $O_2$</th>
<th>Plug Deposit Na$_2$O, g</th>
<th>Deposition Rate g Na$_2$O/wk</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>250</td>
<td>565</td>
<td>27</td>
<td>37</td>
<td>7.15</td>
<td>4.80</td>
</tr>
<tr>
<td>9</td>
<td>161</td>
<td>640</td>
<td>33</td>
<td>65</td>
<td>6.52</td>
<td>6.81</td>
</tr>
</tbody>
</table>

Run 7 was operated for 55% longer time but yielded only 10% greater deposit than run 9. The reduced temperatures corresponding to a 40% decrease in concentration gradient for run 7 and a 30% decrease in deposition rate appears to account for the difference. The variation between calculated concentration gradients and deposition rates, with the deposition rate relatively less than expected for the higher temperature, may be due to changes in the boundary layer thickness.

Runs 10, 12 and 13 were conducted under essentially constant concentration gradient conditions. Data for these runs from Table III-4, are shown below:

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration Hours</th>
<th>$T_s$ °F</th>
<th>$\Delta T_s$ °F</th>
<th>$\Delta C$ ppm $O_2$</th>
<th>Deposition Rate g Na$_2$O/wk</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>159</td>
<td>630</td>
<td>50</td>
<td>56</td>
<td>3.78</td>
</tr>
<tr>
<td>12</td>
<td>144</td>
<td>610</td>
<td>56</td>
<td>55</td>
<td>5.09</td>
</tr>
<tr>
<td>13</td>
<td>170</td>
<td>615</td>
<td>57</td>
<td>58</td>
<td>4.08</td>
</tr>
</tbody>
</table>

A ±15% variation in plug growth rate value is apparent on the basis of a mean value of 4.3 g Na$_2$O/wk. This variation corresponds to ±1/2 g sampling weight error. Excessive surface contamination was observed when the sample from run 12 was exposed to the dry box which undoubtedly accounts for some of the variation in measured Na$_2$O.

Since deposition on the surface of the cold finger has been assumed to be controlled by diffusion of the oxide across the boundary layer between the bulk sodium and the surface, analysis of the test data is in order. The following estimate of the diffusion of Na$_2$O in sodium was calculated from typical plug growth data and compared with measured diffusion rates. The diffusion coefficient was calculated by using the steady state diffusion equation and estimating the film thickness and the temperature drop across the boundary layer. Using the dimensions of the experimental apparatus,
the characteristics of the deposit and operating conditions of run 13
(see Table II-1 and -4) and the oxide saturation data from Table III-5
the following information is available:

\[ A = \pi d z = \pi (1.125)(2.5) = 8.84 \text{ in}^2 \]

where \( d \) = diameter of cold finger
\( z \) = submerged length of cold finger

\[ T_B = 615^\circ F \text{ bulk sodium temperature} \]
\[ T_C = 210^\circ F \text{ cooling oil temperature} \]
\[ w/t = 4.08 \text{ g Na}_2\text{O/wk or } 1.74 \times 10^{-6} \text{ g oxygen/sec} \]

Estimated velocity and heat transfer coefficients are:

\[ v = 0.10 \text{ ft/sec, natural convection sodium velocity} \]
\[ h_s = 500 \text{ Btu/hr ft}^2 \text{ °F, sodium film heat transfer coefficient} \]
\[ k/f = 890 \text{ Btu/hr ft}^2 \text{ °F, wall thermal conductance} \]
\[ h_c = 90 \text{ Btu/hr ft}^2 \text{ °F, oil film heat transfer coefficient} \]
\[ U = \frac{1}{\frac{1}{500} + \frac{1}{90} + \frac{1}{890}} = 70 \text{ Btu/hr ft}^2 \text{ °F overall coefficient} \]

The temperature drop across the sodium film is given by

\[ \Delta T_s = \frac{q}{h_s A} = \frac{U(T_B-T_C)}{h_s} = \frac{70(615-210)}{500} = 57^\circ F \]

Relating sodium temperatures to concentrations from oxide solubility data in Table III-5,

\[ \frac{C_1}{\rho_1} = 181 \times 10^{-6} \text{ g oxygen/g sodium at } T_B = 615^\circ F \]
\[ \frac{C_2}{\rho_2} = 123 \times 10^{-6} \text{ g oxygen/g sodium at } T_B-\Delta T_s = 558^\circ F \]
\[ \rho_1 = 0.870 \text{ g/cc} \text{ and } C_1 = 0.157 \times 10^{-6} \text{ g/cc} \]
\[ \rho_2 = 0.882 \text{ g/cc} \text{ and } C_2 = 0.108 \times 10^{-6} \text{ g/cc} \]

The boundary layer thickness can be estimated by the following expression
derived by Eckhert (7) for a flat plate in axial flow over length \( x \):

\[ \delta = 1.5 \left( \frac{z^2}{\rho v^3} \right)^{\frac{1}{2}} \]

where:
\( \delta \) = average boundary layer thickness.
\( z \) = flow length = 0.208 ft.
\( v \) = sodium velocity = 0.1 ft/sec.
\( \rho \) = sodium density = 54.8 lb/ft\(^3\)*
\( \mu \) = sodium viscosity = 2.28 \times 10^{-4} \text{ lb/ft-sec}.*

thus
\( \delta = 1.5 \left[ \frac{0.208 \times 2.28 \times 10^{-4}}{0.10 \times 54.8} \right]^{\frac{1}{2}} = 4.26 \times 10^{-3} \text{ ft or } 0.130 \text{ cm} \)

*From physical property data tabulated in Liquid Metals Handbook, Sodium
NaK Supplement, TID 5277.
Substituting the above quantities into the steady-state diffusion equation

\[ \frac{w}{t} = \frac{DA(C_1 - C_2)}{\delta} \]

or rearranging

\[ D = \frac{(w/t)\delta}{A(C_1 - C_2)} = \frac{1.74 \times 10^{-6} \times 0.130}{8.84 (2.54)^2 0.49 \times 10^{-6}} = 8.1 \times 10^{-5} \text{ cm}^2/\text{sec at 587°F}. \]

This value compares favorably with the experimental data of Siegel and Epstein (1) where \( D = 8.9 \times 10^{-5} \text{ cm}^2/\text{sec at this temperature and therefore adds credence to this assumption.} \)

Sodium oxide was the principal impurity in the plug growth investigations. Composition of sodium deposits from 15 different runs are shown in Table III-2. One sample, from run 5, yielded no Na$_2$O results due to analytical difficulties in detecting the titration end point. The extremely low oxide content in the sample from run 1 is attributed to inadequate mixing of sodium with the added Na$_2$O$_2$ prior to test and hence the results from this run were discounted. Subsequent impurity additions were manually agitated with a stirring rod, before initiating test runs, in order to promote wetting and solution.

Other impurities, normally present in commercial sodium, were added in the last four runs. LiOH was introduced into the sodium for runs 14 and 15 and metallic calcium chips were added for runs 16 and 17. The low lithium concentration in samples 14 and 15, ranging from 1% to 2%, imply extremely low solubility and/or a flat solubility curve. From Table III-1 it can be seen that the samples did not materially decrease in total weight but the Na$_2$O content dropped sharply, especially for run 14 after the first LiOH addition.

Ten grams of calcium metal chips - equivalent to a concentration of 0.1% in the bulk sodium- were added for run 16 and an additional five grams were added for run 17. The results appeared to confirm predicted trends. Successive, significant decreases were observed in the deposited Na$_2$O presumably due to gettering action of the calcium and the extremely low solubility of CaO.

On the basis of visual observations, oxide analyses and comparisons with cold trap deposits described in the following section of this report it appears that the sodium plug growth was composed of a solid, porous structure with metallic sodium retained in a large portion of the interstices.
SODIUM PURIFICATION INVESTIGATIONS

A. Experimental Program

The objective of this program was to provide through engineering scale experiments additional information on sodium purification. The program was directed toward obtaining information which would better define the mechanism of oxide behavior and its removal by the forced circulation cold trap method.

Tests to compare the efficiency and capacity of various types of cold trap packings (including no packing) were considered as a means of more clearly establishing the mechanism of oxide removal. The packing provides surfaces for the formation of nucleating centers to promote crystallization of the oxide from the cooled sodium and may or may not act as a filter. The effective retention of the oxide with no packing, for example, would tend to support the mechanism of crystal growth on cold surfaces rather than mechanical filtration.

The size of flow passages or clearances in the packing has been established as a factor which influences cold trap performance. Mausteller (8) found that a 200 mesh screen in the cold trap outlet caused plugging. Voorhees and Bruggeman (4) earlier found that metal filters with an average pore size of 20 microns or smaller resulted in rapid plugging but steel wool (with an estimated average clearance of 1/16 inch) was not as susceptible to this difficulty. Knitted wire mesh packing used in most of the recent cold traps is similar to the steel wool in density and average clearances. Investigations described herein include the testing of knitted wire and other packings corresponding to flow passage clearance ranging from about 1/16 inch to 1/2 inch plus no packing.

Correlations of efficiency versus residence time are available from the previous short time tests where the residence time was determined at initial conditions. As significant quantities of deposit are accumulated in the cold trap, the residence time should decrease with time which may decrease the efficiency of oxide removal.

Cold trap orientation (upflow versus downflow, horizontal versus vertical) and variable cooled surface area were recognized as other possible factors in oxide deposition and cold trap performance. Since previous experience has shown successful cold trap operation for different orientation and cooling conditions, these variables were not studied during this program.

During the present experimental program, cold trap capacity and efficiency were investigated for different types of packing in an attempt to obtain more quantitative correlations of oxide removal and retention. Five different packing conditions - (a) unpacked, (b) knitted wire mesh as currently used on most cold traps, (c) lower density knitted wire mesh, (d) Raschig rings and (e) 1/4" wire mesh screens - were selected for test. The experimental facility for providing this information consisted of a 1/2" forced circulation loop. The cold trap test section was designed to permit capacity data with relatively short test runs and permit analysis.
for distribution and quantity of sodium oxide deposits. A large reservoir of oxide in the system was provided in an attempt to operate under continuous, steady-state conditions until the cold trap was filled with deposit. Oxide inventory was maintained by integration of sodium flow and differential oxide concentration (from plugging determinations) as a function of time. This was periodically checked against the weighed quantities of oxide added to the system. With a cold trap flow of 1/4 gpm the initial residence time is 5 minutes corresponding to the previously recommended design value (5). Assuming the ultimate oxide capacity is 20 lb/ft³ or 14 vol. % Na₂O, then about one pound of oxygen will have to be transferred to the cold trap. Therefore, approximately 100 hours of loop operation should be required to transport this amount of oxygen if the conditions are maintained at 1/4 gpm sodium flow, inlet saturation temperature at 600°F and a cold trapping (effluent) temperature of 300°F.

During initial loop operation it became obvious that the excess oxide did not dissolve rapidly enough in the system to supply the desired concentration in the sodium entering the cold trap. To improve this situation higher temperatures were maintained in the dump (oxide source) tank by by-passing some of the cold trap flow and supplying more heat to the tank. Each test run, therefore, required more time than indicated above due to curtailed flow through the cold trap. Due to loop design limitations, the bypass flow, normally through the plugging indicator, had to be eliminated while cold trap outlet plugging determinations were made. Consequently, these data were obtained infrequently and at best may not represent operating conditions. Thus, only approximate data on cold trap efficiency are available.

In order to provide additional information on the physical appearance of the cold trap deposition as a function of oxide accumulation, short time experiments with a double screen packing were conducted. Inspections of the cold trap were made after a transfer of 30 grams of sodium oxide (50 hours of operation) and after transferring an additional 300 grams of oxide (corresponding to 120 hours of operation).

B. Description of Test Facility

The sodium test facility, shown schematically in Figure IV-1, consisted of a forced circulation loop constructed of type 304 austentic stainless steel. Primary components of the sodium loop included a test cold trap, dump tank, surge tank, plugging indicator and electromagnetic pump. Interconnecting lines were principally one half inch piping with larger pipe sizes used in regions more susceptible to oxide plugging. One inch pipe was used for the cold trap outlet and for the oxide supply line preceding the dump tank; two inch piping was used for the main heater line at the dump tank outlet. Figure IV-2 shows a picture of the completed loop with insulation. The dump tank served as a storage vessel for about 140 lb of sodium use during test and an oxide supply vessel in normal test operation. A flanged opening was provided on top to facilitate periodic batch additions of oxide to the system. A weir plate near the discharge end of the tank served to minimize transfer of undissolved oxide into the outlet, dip line.
FIGURE IV-1, SODIUM PURIFICATION LOOP FLOWSHEET
FIGURE IV-2, SODIUM PURIFICATION TEST LOOP
Plugging Indicator

A plugging indicator was included to permit rapid measurements of sodium oxide concentration in the circulating sodium. This assembly, located in a bypass leg of the main loop, consisted of a regenerative heat exchanger, a sodium-to-air cooler and a temperature-monitored orifice plugging plate on the cooler outlet. The indicator was arranged to permit plugging measurements of the cold trap inlet and outlet lines during test operation. Rate of cooling during plugging runs was regulated to about 10°F/min. by manual adjustment of removable insulation jacket on the sodium-to-air cooler.

Cover Gas and Level Control

Argon, supplied through separate valved lines to the dump and surge tanks, was used as an inert cover gas for the sodium.

The loop contained a three gallon surge tank to allow for thermal expansion and to provide a reservoir for minimizing level variation during operation. During normal operation with sodium flow through the dump tank the desired sodium level was maintained by a manually adjusting the pressure of the gas supplied to the dump tank and surge tank. A pressure equalizer line between these two vessels was fitted with a solenoid valve which opened when de-energized; this control permitted rapid dumping of the loop upon power failure or malfunction. Spark plug probes located at low, normal and high level points in the surge tank were used for sodium level detection.

System Heating

All sodium lines were traced with nichrome heating cable or electrical tubular heaters for preheating and for maintaining system temperatures during operation. The major heat source during test consisted of 4 KW supplied at the dump tank and 2 KW at the dump tank outlet line. Variacs and multiple 110/220 volt switches were used for controlling heat input to the system during startup and operation.

Cold Trap and Packing

The cold trap, shown in cross-section on Figure IV-3, served as the test device for the experiments. The cold trap was constructed of six inch schedule 40 pipe, about 21 inches in overall length and jacketed with a 12 inch length of eight inch pipe to provide an annular space in which cooling oil was circulated to remove heat from the sodium. For reference design conditions a sodium flow of 1/4 gpm coincided with an initial residence time of five minutes in the cold trap. Various types of packings that were tested in the cold trap are shown in Figure IV-4. Pertinent data on the packings are summarized in the following section of this report. A standard, knitted wire mesh packing with a bulk density of 7.9 lb/cu ft was used in run 1; the stainless steel mesh wire was 6 mils in diameter. One half inch diameter, steel Raschig rings with a wall thickness of 1/32 inch were used for run 2. For run 3 the knitted wire packing described above was rerolled to provide greater clearance between adjacent layers.
THREADED STUD

6" O.D. LINER (REMOVABLE)

COOLING OIL OUTLET

SODIUM OUTLET

OIL INLET

SODIUM INLET

PACKED SECTION

18"

12"

2 1/4"

2"

THIS LINE USED AS ZERO REFERENCE LEVEL IN FIGURES IV-7, 8, 9, 10.

FIGURE IV-3, COLD TRAP SECTION
FIGURE IV-4, COLD TRAP PACKINGS

RUN NO.1 (KNITTED WIRE)

RUN NO.2 (RASCHIG RINGS)

RUN NO.3 (KNITTED WIRE)

RUN NO.5 (1/4" MESH SCREEN)
Bulk density of this packing was reduced to about 1/3 or 2.6 lb/cu ft. No packing was used in run 4. Packing for run 5 was composed of 26 layers of 1/4" mesh, stainless steel screen; 3/8" vertical spacing between adjacent layers were obtained with "V" shaped metal strip spacers. The packing was contained in a liner, or basket, to facilitate removal of the cold trap deposit after the test was completed. Access to the deposit and liner was provided by a Marman Conoseal joint located on the upper end of the cold trap.

Cooling Oil

"Mobiltherm 600" high temperature heat transfer oil was used as the cold trap coolant. The oil was circulated by a Corley "Magnaflow" canned rotor, centrifugal pump capable of operating with fluids up to 450°F. Heat received by the oil in the cold trap was dissipated outside of the building to the air in a 4 foot length of finned one inch pipe. Globe valves indicated on Figure IV-1 were manually adjusted to provide the desired temperature regulation.

Control and Shutdown System

Manual control was used for startup and normal operation of the test facility and an automatic dump system was provided to facilitate rapid shutdown. The electrical shutdown system was designed to trip the power and thereby, through use of a normally open solenoid valve in the equalizer line, drain the sodium by gravity to the dump tank when any of the following abnormal conditions were reached:

a. Surge tank sodium contacted high level probe.
b. Surge tank sodium dropped below low level probe.
c. Excessively high temperature level at the main heater (Set point manually adjusted at pyrometer).
d. Cold trap outlet temperature reached 250°F.
e. Cold trap flow dropped below predetermined value (Set point manually adjusted at flow recorder).

The system was dumped automatically upon power interruption to prevent abnormal conditions with subsequent availability of power.

Fire Prevention

Conventional safety and fire protection practices were employed in the design and operation of the facility. A galvanized sheet metal drip pan was provided beneath the loop so as to contain possible sodium spillage resulting from equipment failure or during withdrawal of the cold trap test deposit. Ansul Met-L-X powder was provided in readily available containers located in accessible regions near the test loop.
Design Conditions

To satisfy the experimental program the sodium purification facility was designed for the following conditions:

- Cold trap sodium flow, maximum - 1/2 gpm
- Cold trap residence time, minimum - 2-1/2 minutes
- Cold trap inlet temperature - 700 °F
- Cold trap outlet temperature - 300 °F
- Maximum system temperature - 1000 °F
- Maximum system pressure - 100 psi
- Material of construction - 304 stainless steel

C. Test Procedures and Results

Loop Shakedown Operation

140 lbs of commercial grade sodium were charged into the dump tank and circulated isothermally through the loop up to 500°F and 1 gpm to check out the system operability. After the addition of one pound of powdered Na₂O₂ (analytical reagent grade), operation with the dump tank at 500°F and the cold trap at 350°F resulted in a continuous flow drop, apparently due to plugging in or near the cold trap region which contained no packing. When the addition of more heat to the cold trap outlet line failed to improve flow, the loop was shutdown and the cold trap packed with knitted stainless steel wire mesh equivalent to that shown for test run 1 in Figure IV-3. After adding two more pounds of Na₂O₂ to provide sufficient oxide so as to obtain a complete capacity run, flow difficulties were again encountered when plugging occurred at the dump tank inlet line. Modifications incorporated to overcome this difficulty included enlargement of line size from 1/8-inch to one-inch pipe and increased heat input. After 24 hours of continuous operation with the cold trap inlet at 500°F, cold trap outlet at 380°F and flow at 1/3 gpm, flow through the cold trap suddenly dropped. Upon removal of the cold trap packing with 270 grams of entrapped sodium and sodium oxide, a plug was noted in the cold trap outlet line in the bottom of the vessel. Two modifications were incorporated to prevent recurrence of problems: the outlet line was enlarged from one-half inch to one inch pipe size and was relocated on the side of the lower plenum of the cold trap one inch from the bottom of the vessel.

During subsequent testing with the dump tank at 500°F and the cold trap flow at 1/4 gpm plugging determinations showed that both the cold trap inlet and outlet sodium was saturated at 280°F. Since it appeared that the cold trap was capable of removing the oxide at a much faster rate than the apparent rate of oxide solution in the dump tank, data were obtained to determine how rapidly the system oxide concentration increased when the cold trap was by-passed. At a flow of 1/4 gpm with the dump tank at 480°F, the oxygen apparently went into solution at an initial rate of 0.09 g/hr. With the flow rate of 1/2 gpm, the rate increased to 0.15 g/hr. In an attempt to take advantage of the velocity effect, the one-inch pipe section at the dump tank inlet was adapted for inserting a one-inch diameter, 12-inch long, 60 mesh screen cylinder filled with powdered Na₂O₂ (170 g maximum capacity of cylinder).
With the dump tank and oxide line at 510°F and a flow of 1/2 gpm, the initial rate of oxide buildup was 0.45 g/hr. Increasing the temperature at the oxide sources to 640°F produced a significant improvement in the apparent rate of solution of the oxide. Figure IV-17 shows a plot of the data for temperature and flow effects on the rate of system oxide buildup with and without the additional oxide source.

Normal Test Operation

The normal operating procedure for a typical test run is summarized below:

1. The cold trap packing unit was installed in the cold trap after obtaining a tare weight.

2. With the system temperature less than 300°F, 100-150 grams of Na₂O were inserted in the oxide addition line and 500-1000 grams of Na₂O into the dump tank. The Na₂O was replenished upon completion of a test run or when the oxygen transfer rate fell below 1/2 g/hr.

   (Na₂O₂ instead of Na₂O was used in initial runs before oxide inventory checks, tabulated below, indicated less than 80% recovery of the available oxygen in the Na₂O₂).

   Run No. | Oxide Addition | Available oxygen, g | Cold Trap Deposit oxygen, g
   --------|----------------|---------------------|---------------------
   1       | 1858           | 762                 | 512                 |
   2       | 535            | 219                 | 119                 |
   3*      | 664            | 272                 | 352                 |
   TOTALS  | 1253**         | 983                 |

   *Before run 3 was completed all of the available added oxide was apparently depleted in obtaining an oxygen inventory check. With 650°F-700°F sodium bypassing the cold trap for 16 hours no increase in system oxide content above 400°F saturation was detected.
   **Of the 1253 grams of oxygen available from the Na₂O₂ only 983 grams, or 78% of the added oxygen, was recovered.

3. Total system flow was established at 1/4 gpm with about 50% passing through the cold trap.

   The by-pass flow provided higher dump tank temperature and thereby promoted solution of the excess oxide. This required cold trap sodium flows less than the reference design condition of 1/4 gpm and resulted in corresponding residence times greater than 5 minutes.

4. The dump tank temperature was maintained in the region 600°F to 700°F and the cold trap outlet temperature at approximately 300°F.
WITH ADDITIONAL OXIDE SOURCE

FLOW = 1/2 GPM, T = 640°F

FLOW = 1/2 GPM, T = 510°F

FLOW = 1/2 GPM, T = 480°F

FLOW = 1/4 GPM, T = 480°F

FIGURE IV-17, SYSTEM OXIDE CONCENTRATION VS TIME
5. Plugging determinations were performed twice daily at cold trap inlet.
   After oxide was added to the system the cold trap inlet oxide concentration continuously decreased with time.
   Plugging determinations at the cold trap outlet were obtained at less frequent intervals because of the relatively constant and low oxide concentration at the cold trap outlet. The long residence time (about 10 minutes) in the cold trap tended to yield outlet oxide concentrations which in nearly all determinations were equal to or approached saturation at the minimum cold trap temperature.

6. The amount of oxide transferred to cold trap was determined by integration of cold trap flow times concentration gradient vs time.
   The concentration gradient was obtained by subtracting the oxide solubility at the cold trap outlet from the solubility at the inlet saturation temperature. Plugging data were used to obtain points for time, saturation temperature and flow. Table III-5 was used to convert saturation temperatures to oxygen content.

7. Each test run was continued until rated flow through cold trap could not be maintained without frequent voltage increases and revised valve settings.
   Near the end of a test run flow decreased up to 50%/day if pump voltage was not increased every few hours. During normal operation flow drop was less than 10%/day.

8. The oxide deposit was removed from the cold trap following the completion of a test run.
   Figure IV-5 illustrates this operation in which a plexiglass container flooded with argon surrounds the cold trap deposit as it is removed from the cold trap and cooled to room temperature. For most of the runs it was found necessary to heat the cold trap to between 300°F and 400°F to facilitate removal.

   For run number 1 a basket constructed of 12 gage (BWG) wire was provided around the cold trap packing to assist in removing the deposit at the completion of the test run. Due to the adherent bonding between the packed section and the cold trap cylinder the wire basket did not prove satisfactory; it was necessary to use a hammer and chisel to break the surrounding bond and allow removal of the deposit. For subsequent runs a removable liner was used to contain the cold trap deposit. Threaded studs and nuts provided at the top of the cylinder permitted the use of a jacking action against
FIGURE IV-5, COLD TRAP DEPOSIT DURING REMOVAL OPERATION
the top of the cold trap and thereby facilitated in lifting the cold trap liner. No difficulty was encountered in the removal operation when a 1/16 inch thick liner was used. However, in run number 3 the liner was made of 30 mil stock in an effort to simplify installation. In attempting to remove the liner after the test the upper stud sheared off the thin liner and it was again necessary to resort to a chiseling operation to break the deposit loose. The resulting formation of the cylinder is evident in Figure IV-6 for run 3.

9. After removal from the loop each cold trap deposit was weighed and X-rayed, then samples along the length and diameter were taken for analysis to determine oxide concentration distribution.

Results

A summary of the cold trap packing, operating and deposit data is presented in Table IV-1. X-ray photographs of the cold trap deposit sections are shown in Figure IV-6. Noticeable density variations can be observed for runs 1, 4 and 5. For run 1 the metal basket is evident around the knitted wire mesh packing. The photograph for run 3 shows the thin gage steel liner which was wrinkled during removal from the cold trap. Also, wire spacers for the re-rolled knitted wire packing are visible. The run 4 deposit was sectioned and sampled prior to X-raying; only the lower portion of the deposit was X-rayed and the plan view photograph clearly shows where sodium samples were removed. (The method of obtaining most samples consisted of using a sharpened 3/4 inch OD tube, similar to a laboratory cork borer, to bore out a cylindrical sample about one inch long). In the X-ray view for run 5 the long vertical gaps in the liner represent where the liner was cut then tack welded to facilitate removal of the inner deposit after withdrawal from cold trap.

Results of the chemical analysis for oxide are plotted in Figures IV-7, 8, 9, and 10 for runs 2 through 5. Oxide results from run 1 are not shown because the analytical method employed for these original samples did not yield a satisfactory check of the oxide content in commercial Na2O. A review of the data indicates a general decrease in oxide concentration from the inlet to the outlet of the cold trap. Oxide concentration across the cold trap diameter does not show a consistent trend but usually is lower in the center.

No packing was employed for run 4 yet, surprisingly, the cold trap deposit filled the entire section. Figure IV-11 shows a piece of the porous, brittle deposit broken away from the section within the liner. A freshly broken sample shown in the closeup view in Figure IV-12 indicates the sharp, needle like crystals representative of the structure of the cold trap deposits. Because the samples were handled in air the surfaces rapidly lost the silvery luster and sharp definition as the crystals oxidized.
### TABLE IV-1

**SUMMARY OF COLD TRAP PACKING, OPERATING AND DEPOSIT DATA**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PACKING DATA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>knitted wire</td>
<td>1/32 in. wall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density</td>
<td>7.9 lb/ft³</td>
<td>83 lb/ft³</td>
<td>2.6 lb/ft³</td>
<td>-</td>
<td>16.5 lb/ft³</td>
</tr>
<tr>
<td>Surface/volume</td>
<td>128 ft²/ft³</td>
<td>128 ft²/ft³</td>
<td>42.9 ft²/ft³</td>
<td>-</td>
<td>34.0 ft²/ft³</td>
</tr>
<tr>
<td>Void fraction (initial)</td>
<td>0.983</td>
<td>0.84</td>
<td>0.993</td>
<td>1.00</td>
<td>0.967</td>
</tr>
<tr>
<td>Average flow-path clearance</td>
<td>0.05 in.</td>
<td>0.40 in.</td>
<td>0.15 in.</td>
<td>5.8 in.</td>
<td>0.20 in.</td>
</tr>
</tbody>
</table>

| **OPERATING DATA** | | | | | |
| Run length | 52 days | 11 days | 51 days | 44 days | 21 days |
| Dump tank temp. | 600°F | 580°F | 650°F | 500°F-700°F | 700°F |
| Flow | 0.15 gpm | 0.15 gpm | 0.18 gpm | 0.10 gpm | 0.11 gpm |
| Inlet saturation temp. | 320°F-560°F | 300°F-530°F | 300°F-570°F | 300°F-610°F | 375°F-575°F |
| Outlet temp. | 310°F | 300°F | 320°F | 300°F-350°F | 320°F |
| Residence time | 9.5 min. | 7.5 min. | 7.9 min | 13.5 min. | 11.8 min. |
| Operational difficulties | negligible | (a) | negligible | (b) | negligible |

| **DEPOSIT DATA** | | | | | |
| Cold trap volume | 0.192 ft³ | 0.150 ft³ | 0.190 ft³ | 0.210 ft³ | 0.219 ft³ |
| Na₂O+Na | 9.86 lb | 2.15 lb | 14.25 lb | 12.00 lb | 6.41 lb |
| Na₂O (calculated) | 4.36 lb | 1.01 lb | 5.42 lb | 4.78 lb | 3.08 lb |
| Na₂O capacity | 16.2 vol % | 4.8 vol % | 20.3 vol % | 16.2 vol % | 10.0 vol % |
| Void fraction (e) | 0.353 | 0.825 | 0.097 | 0.255 | 0.551 |

**NOTES:**

a. Throughout most of run 2, cold trap flow could not be maintained without periodic decrease of inlet saturation temperature and pump voltage adjustments.

b. During first ten days of run 4, difficulties described under note 1 were encountered.

c. Includes 0.030 ft³ additional volume below normal packed section.

d. Includes 0.045 ft³ additional volume above normal packed section.

e. Voids determined from data above by subtracting volume of Na₂O+Na from cold trap volume.
The deposit from run 5 is clearly shown in Figure IV-13. It is evident from this picture that most all the deposition occurred in the top portion of the cold trap including the upper three layers of screen packing. Of all the test runs this was the only one where a significant fraction of the oxide was obtained above the packed region. This cold trap deposit was comprised of a porous structure as shown in Figure IV-12.

Figure IV-14 is a photograph of the run 5 deposit located in the upper part of the packed section between the first and second screens. Most of the screen is covered with a brittle, porous structure. The steel strip in the upper part of the picture is a spacer used to separate adjacent screens.

The relatively short test time, available at the completion of the planned program for packing investigations was used to obtain additional information on oxide deposition. In an attempt to observe how the oxide deposits grow, the cold trap was fitted with two 1/2 inch mesh screens spaced at 4-inch and 8-inch intervals from the top of the cooler sections; each screen was supported on a steel block and two rods attached to the liner wall. Figure IV-15 shows some of the results; the views in both photographs represent the same location at different times. A view of the underside of the lower screen from the 50 hour run is shown in Figure IV-16, it can be seen that the oxide deposit on the upper screen after 120 hours is appreciable yet there is little evidence of crystal growth at the visible screen elements. Note that nearly all the deposit is on top of the screen.

Approximate hardness measurements were obtained for the top, middle and bottom sections of the cold trap deposit from run 1. The ball impression technique was employed using a 2.613 gm load with a spherical head 19.15 mm diameter. The sodium deposit was prepared by cutting off the outer layer to provide a freshly exposed surface which was smooth and relatively flat.

Hardness was calculated as Brinell Hardness (9) given by:

\[
\text{Hardness No.} = \frac{P}{\pi D \left( D - D_1 \right) / 2}
\]

where \( P = \text{load} = 2.613 \text{ gm} \)

\( D = \text{ball dia.} = 19.15 \text{ mm} \)

\( D_1 = \text{diameter of impression, mm} \)

Impression diameters (average of two readings) and calculated hardness numbers for the three cold trap sections are summarized below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D_1, \text{ mm} )</th>
<th>Hardness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top section</td>
<td>4.63</td>
<td>0.153</td>
</tr>
<tr>
<td>Middle section</td>
<td>4.47</td>
<td>0.164</td>
</tr>
<tr>
<td>Bottom section</td>
<td>4.51</td>
<td>0.161</td>
</tr>
<tr>
<td>Commercial sodium</td>
<td>7.40</td>
<td>0.057</td>
</tr>
</tbody>
</table>
From plugging indicator measurements the sodium stream leaving the cold trap in runs 1, 2 and 3 was found to be saturated with oxide at the minimum cold trap temperature. In test runs 4 and 5, however, the outlet oxygen concentration ranged up to several parts per million higher than the minimum temperature saturation values. If the efficiency of the cold trap in removing oxide from the sodium stream is defined by

\[ E = \frac{(C_i - C_o)}{(C_i - C_s)} \times 100 \]

where:
- \( E \) = cold trap efficiency
- \( C_i \) = oxide concentration measured at cold trap inlet
- \( C_o \) = oxide concentration measured at cold trap outlet
- \( C_s \) = oxide saturation concentration at minimum cold trap temperature

From the definition the plugging data for the first three runs resulted in cold trap efficiencies of 100%. Calculated efficiencies for runs 4 and 5, tabulated below, ranged from 75 to 100%.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>ppm Oxygen</th>
<th>Accumulated Na(_2)O in Cold Trap, lb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>20 12 10</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>20 10 10</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>92 12 9</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>100 33 11</td>
<td>75</td>
</tr>
</tbody>
</table>

Both the cold trap inlet concentration, \( C_i \), and the outlet concentration, \( C_o \), were obtained from plugging determinations; \( C_s \) was based upon cold trap temperature measurements. Due to operational difficulties imposed by normal bypass flow around the cold trap, \( C_o \) could not be determined readily nor accurately. Note from the efficiency equation that small errors in oxide measurement can cause significant errors in calculated efficiency values, especially at low inlet concentrations.
FIGURE IV-6, X-RAY VIEWS OF COLD TRAP DEPOSITS
FIGURE IV-7, OXIDE DISTRIBUTION IN COLD TRAP
RUN NO. 2 (RASHIG-RING PACKING)
**Figure IV-8, Oxide Distribution in Cold Trap**

Run No. 3 (Knitted Wire Packing)
Figure IV-9, Oxide Distribution in Cold Trap Run No. 4 (No Packing)
FIGURE IV-10, OXIDE DISTRIBUTION IN COLD TRAP
RUN NO. 5 (SCREEN PACKING)
FIGURE IV-11, COLD TRAP DEPOSIT FROM RUN NO. 4
FIGURE IV-12, TYPICAL STRUCTURE OF DEPOSIT FROM RUN NO. 4
FIGURE IV-13, COLD TRAP DEPOSIT FROM RUN NO. 5
AFTER 50 HOURS OPERATION
AND DEPOSITION OF 30 GM \( \text{Na}_2\text{O} \)

AFTER 120 HOURS OPERATION
AND DEPOSITION OF 300 GM \( \text{Na}_2\text{O} \)

**FIGURE IV-15, COLD TRAP (DOUBLE SCREEN PACKING)**

SHOWING OXIDE GROWTH WITH TIME ON LOWER SCREENS
FIGURE IV-16, COLD TRAP (DOUBLE SCREEN PACKING)
SHOWING OXIDE DEPOSITS
D. Discussion

The experimental work discussed in this section provides additional information toward defining the mechanism of oxide (deposit) behavior, the physical and chemical characteristics of such deposits and the purification of sodium by the cold trap method.

Capacity

The greatest capacity for oxide deposit retention - 20% of cold trap volume - was obtained with a low density, knitted wire packing while a capacity of only 5 volume per cent was achieved with a packing of metallic Raschig rings. In comparing the capacity data of the two knitted wire packings it is possible that the additional clearance in the flow passages of the lower density mesh may be a contributing factor in the slightly greater capacity observed. It is also interesting to note that the packings which exhibited the smallest capacity values - Raschig rings and 1/4 inch mesh screen - had the largest packing clearances and were the only packings, of those tested, that did not have relatively uniform deposition throughout the cold trap.

The data for each type of packing was based upon a single test in which inlet oxide concentration varied to some extent due to exhausting excess oxide. Inlet oxide concentration should influence the location at which precipitation was initiated and hence the deposition pattern. The extent to which this variable affects capacity is not apparent; if the effect is not significant for the range of conditions investigated, then the capacity data can be compared on a quantitative basis. It had been expected that with no packing the cold trap outlet region would plug before appreciable crystal growth existed on the cooling wall. This might occur when flow and gravity effects of the sodium stream dislodge deposits. The relatively high capacity results, therefore, were surprising. Apparently crystal growth at the cold wall was relatively uniform so that the deposit had sufficient strength to resist the gravity and low velocity flow forces.

Efficiency

The runs with knitted wire packing and Raschig rings resulted in slightly higher efficiency values than the runs with no packing or 1/4 inch mesh screen. The generally effective oxide removal in all runs is probably due to the long residence times in the cold trap. From the data in Table IV-1 it can be seen that initial residence times range from about 8 to 14 minutes. To measure the effects of various packings on the efficiency of oxide removal, shorter cold trap residence times are necessary; to improve the accuracy of measurements of the efficiency and minimize the effect of errors from plugging determinations, higher inlet oxide concentrations are desirable.
Density Variations

Cold trap deposits obtained during this program exhibited considerable variations in density as evidenced by the deposit x-rays, Figure IV-6, visual observations, and void data listed on Table IV-1. The high density, or dark, regions in the x-ray prints are probably due to high concentration of oxide and/or less void space in the deposit. At room temperature the density of sodium is 60 lb/ft³ and sodium oxide is 141 lb/ft³ so a change in the sodium oxide concentration in the deposit should produce a corresponding change in density. All of the deposits appeared to have layers of porous, brittle growths interspersed with metallic deposits of predominantly sodium. Voids, associated with the porous structure of the deposits and unfilled regions in the cold trap (such as for runs 2 and 5) accounted for deposit volumes ranging from about 10 per cent to 82 per cent of the geometric volume. Apparently the voids resulted from partial draining of the liquid phase in the deposit during post-test system draining.

The density variation for run 2 is largely attributed to the pattern of the Raschig ring packing; the fact that the deposit filled only 18 per cent of the available space and which was largely in the upper two to three inches is not visible in the x-ray. The deposit from run 3 contained less than 10 per cent void space so the variations in density observed in the photograph are due primarily to variations in oxide concentration. The photograph for run 5, Figure IV-13, shows the screen packing with the cold trap deposit essentially confined to the region of the top three screens and above. The lower screens, which do not appear to be uniformly spaced as they originally were, did not retain enough sodium or oxide to maintain the screen positions upon removal from the cold trap.

Oxide Distribution

The variation of sodium oxide concentrations within the cold trap was established by chemical analysis of samples from locations selected to provide both axial and radial distribution. It should be pointed out that oxide mass distribution throughout the deposit is not available due to lack of quantitative data on density distribution and the oxide concentration results for run 1 were discarded due to uncertainties in the chemical analysis. The analytical results for subsequent runs were presented in the previous section.

The oxide concentration for run 2 ranged from about 60 per cent on top to about 10 per cent on bottom with a nearly linear decrease from the inlet sodium level to the outlet. It is interesting to note that this deposit with Raschig ring packing contained most of the deposit near the top so that region of highest oxide concentration and largest quantity of deposit coincided. The bulk concentration of Na₂O in the deposit was 46.8 per cent based upon use of plugging and flow data for the Na₂O value, indicating a general agreement with the range of oxide values obtained chemically.
Since the cold trap deposit for run 3 contained less than 10 per cent voids, the observed oxide concentration should be generally representative of the oxide mass distribution. From the curves on Figure IV-8 oxide concentrations noted at the cold trap wall are higher than in the center, indicating deposit growth initiation at the cooler surfaces. As in run 2 the Na₂O concentration generally decreased from the cold trap inlet to the outlet.

Similar to run 3, the oxide concentration from run 4 was higher at the wall which is indicative of crystal growth initiated at the cool wall surface. The reversal of the oxide pattern in the bottom level appears inconsistent but may be due to redistribution from reheater effects since the oxide deposit filled the bottom plenum. The Na₂O concentration generally decreased from the cold trap inlet to outlet. Since no packing was used, in this run it appears that deposition occurred initially at the wall, then grew until a porous, oxide structure spanned the diameter. From the above observations it appears that packing, when used, helps support and retain the oxide. Some of the difficulties during initial operation of this run also indicate the desirability of having packing in the cold trap. Although the cold trap deposit for run 5 was principally in the region above the packing, the measured oxide concentrations appeared to decrease from inlet to outlet. Oxide analyses for the lower part of the cold trap are not available because there was insufficient deposit for samples.

Appearance of Deposit Structure

The appearance of all the deposits recovered from the cold trap operation can be categorized by two types: porous crystalline structure and relatively solid structure. At room temperature, the crystalline structure was comparatively brittle and easy to break; the solid structure was relatively soft, and prior to exposure to the air, silvery-resembling metallic sodium; apparently these regions contained entrapped sodium which could or did not drain from the deposit prior to removal. Photographs on Figures IV-11 through 16 and recorded visual observations were used in defining the appearance of the deposit structure. The typical crystalline structure representative of the major portion of the run 4 deposit shown in Figure IV-12, was very porous indicating that much of the free sodium drained from the deposit prior to removal.

The deposit from run 5 shows evidence of crystal growths at the surface of the cooling wall. In the opened liner, locations where the oxide deposit had adhered to the wall were clearly visible. For comparison, the deposition on the lower screens does not appear to be adhering to the screen; rather, it appears to be the result of inward growth from the wall with the screens acting as supports for the deposit. Deposition above the packing implies that the inlet sodium stream was nearer the saturation temperature than in other runs. The porous structure representative of the run 5 deposit is very similar to that observed in run 4. Sharp, needle like crystals were evident when the sample was initially broken away from the upper screen but rapid surface oxidation caused the silvery needles to discolor and enlarge.
The last test that was conducted permitted observation of oxide deposition and growth at two arbitrary time intervals. For this run the cold trap liner was "packed" with two, 1/4 inch mesh screens (identical to those used in run 5) which were spaced four and eight inches below the top of the packed section. Pictures of the deposit on the screen after 50 and 120 hours of operation are shown in Figures IV-15 and 16. A comparison of the two views in Figure IV-15 gives definite evidence of growth with time at the liner wall and on top of the screen. It appears that the screen may be trapping by filter action portions of the oxide which initiated growth in the upper part of the cooler zone. After retention on the screen, continued growth by crystallization and possibly by filter action is likely. The upper screen after transfer of 30 grams of Na₂O into the cold trap (50 hours), contained negligible holdup of sodium and/or oxide. The upper screen after transfer of 300 grams of Na₂O into the cold trap (120 hours), shown in Figure IV-16, indicates no crystal growth from the visible wires in the screen. The lack of wetting apparent at the screen, attributed to the low temperature and possibly to the high oxide concentration, may explain the absence of crystal growth. However, the definite evidence of growth from the liner wall region tends to substantiate the mechanism of nucleation and crystal growth at the colder surfaces. Deposition on this upper screen after 120 hours operation and the lower screen after 50 hours operation indicate the probability that mechanical filter action also contributes to oxide retention in the cold trap.

**Oxide Solution Rate**

The oxide solution rate data presented in Figure IV-17 were obtained by measuring the rate of increase of oxide concentration in the system with no flow through the cold trap. Specific solution rates were not obtained because the exposed surface area of the excess oxide was unknown. Some oxide (surface) may have been deposited on the tank walls during previous operation and some, recently added in powdered form, could be in a heap under the access port.

For both of the 480°F curves the loop contained excess oxide only in the low velocity, flow through dump tank. For the higher temperature data, additional excess oxide was provided in a higher velocity region in the one inch pipe section preceding the dump tank. Prior to obtaining the data shown on these curves for 480°F and 510°F, the system had been cold trapped to establish the initial saturation temperature below 280°F giving a concentration at time zero of less than 10 ppm oxygen. Initial oxide level for the 640°F run was not determined; the dump tank sodium had been maintained at 350°F overnight, and approximately one hour was required to increase the system temperature to 640°F. Therefore, concentration at zero time for the 640°F curve was estimated to be about 20 ppm. From a review of the data it can be seen that while increases in both temperature and flow improve the apparent solution rate of the oxide, the temperature effect is predominant.
If the sodium oxide precipitates out of solution more rapidly than it dissolves, it is conceivable that undissolved sodium oxide may be carried along with the sodium stream as it leaves the cold trap. However, in this set of tests it is doubtful that the undissolved oxide was carried beyond the dump tank for the following reasons: the velocity was much lower than elsewhere in the system thus contributing to settling out of solution or redissolving in this higher temperature region, and the weir plate construction preceding the outlet pipe acts as a barrier to transport of solid particles. Furthermore, plugging indicator measurements have established that the oxide concentration at the cold trap outlet corresponded to saturation at the cold trap temperature thereby indicating no evidence of supersaturation in the effluent stream. Bulk transfer of undissolved oxide from the dump (source) tank into the cold trap is doubtful due to the relatively large temperature differences between inlet sodium and the saturation temperature, i.e., the sodium was not saturated with oxygen.

**Plant Application**

Results of this experimental program have direct application to large sodium systems including those in sodium cooled nuclear power plants. During refueling, system maintenance operations or accidental introduction of secondary coolants, sufficient quantities of oxygen or other impurities may be introduced into the sodium to cause deposit formation. For example, the plug growth experiments illustrated that under certain conditions deposits on cooler surfaces can occur. This information supports the established practice of maintaining system sodium temperatures above oxygen saturation levels in all regions where deposition, or potential plug formation, is not desirable. The results of the cold trap test without any packing indicate that under deposit forming conditions, pipe lines and/or vessels with flow paths as large as six inches across, and probably larger, can become completely plugged.

The observation during this program that sodium oxide dissolves at a slower rate than the cold trap should aid in establishing operating procedures for relieving plugged systems and for system purification. Provided that the plant system oxide solution and removal rate characteristics are similar to those of the test loop, it is possible, after the addition of excess oxide, to readily reduce the oxide concentration to normal levels. However, if the purification unit is then stopped the oxide level may increase with time.
V. CONCLUSIONS

1. The formation of plug forming deposits in liquid sodium resulting from sodium oxide as the principal sodium impurity is dependent on oxygen concentration, deposition surface temperature, agitation, and time.

2. Deposits on the cold finger surface and in the cold trap appeared silver in color with regions of metallic sodium interspersed through porous crystalline structures. Ball impression measurements showed that these deposits had Brinell hardness numbers approximately three times that of commercial sodium.

3. The addition of calcium to a sodium system caused a significant decrease in the rate of plug growth.

4. The removal and retention of oxide by a cold trap appears to be due primarily to the mechanism of crystal growth at cooled surfaces rather than by mechanical filtration.

5. The cold trap was effective in removing oxide from the sodium stream regardless of the type of packing tested.

6. Forced circulation cold traps packed with knitted wire mesh are capable of containing up to 20 volume per cent sodium monoxide before significant flow restriction is evident. Packings of metal Raschig rings or 1/4 inch mesh screens are not as effective as the knitted mesh.

7. The rate of solution of sodium oxide in the test loop was much slower than the rate of removal in the cold trap. The solution rate was more dependent upon temperature than upon flow velocity.
VI. REFERENCES


