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**SURVEY AND SELECTION OF MATERIALS
FOR PROGRAMMATIC EVALUATION
FOR A GAS-COOLED REACTOR EXPERIMENT**

Edited by

Donald L. Keller

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September 20, 1956

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**SURVEY AND SELECTION OF MATERIALS
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INTRODUCTION

On February 1, 1956, Battelle was awarded a contract to determine what materials can be used successfully in building a gas-cooled reactor experiment (GCRE) of 2-megawatt capacity. The objective is to have some of the materials information available by September, 1956, and to provide more detailed information during the succeeding 12-month period. A design contractor can proceed then with the design and engineering of an experimental reactor to be in operation about September, 1958.

To choose a set of materials that are sure to work within the time schedule and to do an economical job from the standpoint of efficient use of time, facilities, and the money available, considerably more than careful planning of a materials testing program is needed. The rather large number of materials that might be used for fuel-element construction, for control rods, for moderators, the various gases that might be used as coolants, together with the performance specifications, total a tremendous number of material-environmental test conditions. These could be studied for many years without producing an answer to the question: How does one go about building a gas-turbine reactor power plant? In order to provide reasonable assurance that all the problems for a given reactor have been recognized and solved, it is necessary to focus attention on one or, at the most, two or three alternate materials for any component.

In order to do this, it has been essential that Battelle do a certain amount of design study in the absence of a design contractor and, with the results of these studies as a guide, determine through related experience and survey work which materials appear promising enough for detailed evaluation.

This report is concerned principally with this survey work, which has been the basis for many of the decisions leading to the initiation of twenty or more research projects now under way at Battelle. The section "Programmatic Studies" is essentially an outline of these programs, many of which have been completed.

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GCRE SPECIFICATIONS, REQUIREMENTS, AND
CHARACTERISTICS

The GCRE program is a part of the over-all Army Package Power Program under the direction of the Army Reactor Branch (APB). At the beginning of the GCRE program, Battelle was concerned with the materials problems associated with three gas-cooled systems, a Core I military system, an advanced military system, and a civilian power system. As the program advanced during the early months, it became apparent that a concentrated effort would be needed to solve the problems which Core I alone presented. Hence, a decision was made early in the program to postpone all attention to advance systems; consequently, they receive no further mention in this report.

The APB specifications for the GCRE, Core I, are as follows:

Power level - 2 megawatts
Gas-inlet temperature - 700 F
Gas-exit temperature - 1150 F
Gas coolant - nitrogen, air, or CO₂
Operating pressure - 200 psi, maximum
Core-pressure drop - 10 psi, maximum
Core lifetime - 10,000 hr
Coolant flow rate - 16.6 lb/sec

Other pertinent characteristics are:

- (1) The core shall be small, a 2-ft right cylinder about 2 ft high, and contain a critical mass not exceeding 15 kg.
- (2) The plant shall be small and capable of transportation on a trailer-truck.
- (3) Permanent shielding will not be complete, a part of the biological shielding being provided from materials available in the field, such as earth.
- (4) Access to the turbine will not be essential.

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SELECTION OF REFERENCE COOLANT

Donald L. Keller

It is the purpose of this section to review the considerations that entered into the selection of nitrogen as the reference coolant for the GCRE. The limitations of time and money made it imperative to select one coolant and to solve the problems of materials that would work with that coolant.

Method of Selecting Reference Coolant

The various operating specifications such as life of core, power level, and temperature and the various desired characteristics of the plant, such as portability, core size, and shielding accessibility during operation are the starting points in selecting the reference coolant. Then without regard to other materials considerations, the coolant gases that can meet the performance specifications are selected. Next, the specification and performance characteristics are applied (with no consideration given to coolants) to the major reactor components, i. e., the moderator and fuel, to eliminate moderator and fuel materials that are incapable of meeting the specifications. Finally, each coolant gas is considered with each of the components to determine the number of problems that must be solved in each combination. The severity of the problems and the chances of success in solving them are estimated.

It should be emphasized that at this stage no serious attempt has been made to determine the magnitude of all the possible problems. Rather, the problems and the possibility of problems have been listed, counted and weighed and judgments made on the basis of presently available information. Undoubtedly, some problems will appear more severe in the future than they do at present, and others will appear less severe.

Coolants. None of the three gases considered as possible coolants (nitrogen, air, CO₂) can be eliminated by the specifications and general requirements. Helium would present almost no material problems, but has been eliminated from further consideration at this time because no gas turbine is available for efficient operation with helium.

Hydrogen would be better in several respects, particularly heat transfer, while the problems of turbine design are only slightly worse. Sonic velocity in helium is 2.9 times that in nitrogen, while in hydrogen it is only 1.34 that in helium. On the other hand, heat-transfer effectiveness

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in hydrogen is 5 times better than in helium while helium is only 2.7 times better than in nitrogen. Thus, one might expect it worthwhile to go all the way in turbine design to use the greatly improved heat transfer offered by hydrogen.

With nitrogen, air, and CO₂, turbine design is not a serious problem.

Induced radioactivity will be slight in CO₂ and nitrogen and very much higher in air. The nitrogen-16 activity produced in all three gases by oxygen-16 (np) or nitrogen-15 (np) reactions will not be serious because of the short (7 sec) half-life. The 1.8-hr argon-41 activity will be much more serious. In commercial high-purity nitrogen containing 50 ppm argon, the equilibrium activity of argon-41 will be of the order of 1 curie. In air, with 10,000 ppm argon, the equilibrium activity is of the order of 200 curies. Since argon-41 has a 1.7-mev gamma, routine servicing of the turbine after shutdown would be difficult. This fact alone is a strong argument against the selection of air as the coolant, but it is not sufficient to eliminate air from further consideration on the basis of present performance specifications. Unless the turbine is shielded against neutrons, remote servicing is necessary anyway.

From a logistics standpoint, air has the advantage in availability and cost if it can be used in the raw state. Over-all operating costs should not be affected greatly by the delivered cost of the coolant because very little make-up gas should be required.

Fuel Elements. The problem of selecting a reference fuel-element material for development is being considered separately. It may be stated, however, that the general specifications and conditions lead to a first-choice selection of a UO_2 dispersion in a metal matrix with a suitable metallic cladding to contain fission products. In particular, the possibility of using an all-ceramic fuel element is ruled out because of several defects in ceramic materials, but particularly because of the lack of adequate means of containing fission products. The time schedule for the first reactor is such that no extensive development of fuel elements, either ceramic or metallic, can be undertaken.

Moderator. The requirement that the power plant be small and portable eliminates graphite, beryllium and beryllium oxide from consideration as a moderator. Hydrides, however, look extremely attractive. The problem of moderator selection, which is being considered separately, is one of extreme importance in the development of materials for the gas-cooled reactor. As will be seen, a decision to use a hydride moderator is the overriding factor in the choice of a coolant.

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Comparison of Coolant Gases

In this section, the problems that may be encountered in utilizing CO₂, nitrogen, and air are considered. The assumption is made that a hydride will be used as a moderator and that the fuel elements will be metal-clad dispersions of UO₂ in a suitable metallic matrix. The general reactor-plant specifications and characteristics are also considered during the comparison of the three gases. Each of the important components of the reactor system are considered in turn with each of the proposed coolant gases.

Moderator. Zirconium and calcium hydrides look promising and should be seriously considered. With these, as with any other likely hydride, loss of hydrogen to the coolant gas by diffusion through the walls of the moderator cans must be expected in 10,000 hr unless a reasonable back pressure of hydrogen can be maintained in the coolant. This means that hydrogen must be present in the coolant gas to a partial pressure of the order of 10² mm mercury. The alternative is an extensive development job to produce hydrogen-impervious metal cans. Even if this problem can be solved, and it is by no means certain that it can, the resulting cans are likely to be very expensive.

With nitrogen as a coolant, it would appear that hydrogen can be added to maintain a back pressure of hydrogen equal to or greater than the decomposition pressure of the hydride moderator. It is believed that the presence of this hydrogen in the nitrogen will not have any serious effect on the other components of the reactor system, although with some metals it may accelerate the nitriding corrosion process. Should there be a rupture, pinhole, or other failure in the moderator can, it seems unlikely that there would be any serious effects. The can itself must be resistant to corrosion by nitrogen at the operating temperature of the reactor.

With CO₂, as with nitrogen, the prevention of the diffusion loss of hydrogen from the moderator can be accomplished by adding hydrogen to the coolant. The resultant gas will be a mixture of CO, CO₂, H₂, and H₂O. Corrosion problems in this mixture are not believed to be serious, although they are not as well defined as in the case of nitrogen and hydrogen.

In the case of air, the only way to retain hydrogen in the moderator is by using a truly impervious can. Such a can is likely to be an expensive multiwalled structure containing a number of different materials, one of which would probably have to be molybdenum. There seems to be no certainty that such a can could be developed with adequate imperviousness to hydrogen for the life of the reactor, even though one could make such a container with a sufficiently low hydrogen diffusion rate to give the

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moderator adequate life. Some hydrogen would probably escape to the coolant with possible complex corrosion effects in a closed-cycle air system. Oxides of nitrogen will be present in the air under irradiation. While nitric acid, formed if hydrogen escapes from the moderator, might be present in any liquid phase, it seems unlikely that it will be a serious problem at the temperatures in the core.

If a rupture or pinhole should develop in the can wall, there is a good possibility that the result would be catastrophic in the case of air and possibly severe in the case of CO_2 .

For use with hydride moderators, nitrogen and CO_2 rate about equal and somewhat better than air.

Fuel Elements, Control Rods, and Brazing and Structural Metals.
The heat transfer and strength properties of these materials are not affected by the various gases except insofar as these properties are affected by corrosion by the coolant gases.

In considering the corrosion problem, it is assumed that hydrogen will be present in the coolant gases. This means that the effect of hydrogen and its compounds must be considered. The most important of these compounds is water vapor in the case of CO_2 and air.

With CO_2 as a coolant, the selection of materials to resist oxidation is not a serious problem. With hydrogen added to maintain appreciable hydrogen pressure, the coolant gas will become a mixture of CO , CO_2 , H_2 , and H_2O . Again, with this mixture, there appears to be no serious corrosion problem.

In the case of nitrogen, the big uncertainty is whether or not there are metals that will resist nitriding sufficiently. Hydrogen in the nitrogen may promote nitriding, although this is not certain.

In the case of air, it is believed that materials can be found that have adequate oxidation resistance. If hydrogen is present from the moderator, the problem becomes more complex. Not only is water vapor present, but its interaction with nitric oxide may produce traces of nitric acid. The latter will probably not be present in the gas phase, however, and therefore will probably not be a problem at operating temperatures.

From the standpoint of corrosion of the fuel and other metallic parts of the reactor core, the problems with CO_2 appear capable of solution. The nitrogen system is the simplest system, and the problem is straightforward: Can a suitable material be found that is capable of resisting

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nitriding? The problem with air is complex, and air must rate third to CO_2 and nitrogen largely because of this complexity.

Insulation. It is believed that there are no serious problems posed by any of the proposed gases.

Pressure Vessels, Piping, Valves, Etc. Corrosion questions much like those considered for metallic materials in the reactor core arise here. Temperatures are generally lower; hence, the problems are less serious, except possibly for the effect of nitric acid in the case of air as a coolant. Otherwise, there appears to be no strong reason to favor any one of the coolant gases.

Turbines. The same corrosion problems discussed above arise again but they are probably not serious.

Conclusion

The problems of corrosion of metallic parts in the reactor by CO_2 , nitrogen, and air in the pure state are real but do not seem insurmountable. However, the requirement that the reactor core be small leads to the choice of a hydride moderator which, in turn, means that hydrogen will be present in the coolant either from diffusion through the walls of moderator cans or because it is deliberately added to prevent diffusion loss of hydrogen from the moderator. With hydrogen present in the coolant, the corrosion problems with an air coolant look somewhat more complex than with nitrogen or CO_2 . This consideration, plus the possibility that there might be a serious or even catastrophic reaction should a moderator can be ruptured in air, supports the choice of nitrogen or CO_2 as the coolant gas. The directness of the problems associated with nitrogen led to its selection over CO_2 as the reference coolant gas.

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EVALUATION OF MODERATOR MATERIALS

J. B. Vetrano

Preliminary Evaluation

Carbon Moderators. Graphite would probably make a very serviceable moderator in a nitrogen-cooled reactor, since no reaction between nitrogen and graphite is expected within the temperature range of 700 to 1500 F. Furthermore, radiation damage would probably not be a problem.

It appears that graphite expansion will not be serious if used in the GCR at 700 to 1500 F.

The thermal-fracture resistance of graphite is good and it will stand about a 20 times greater steady-state temperature gradient than BeO.

The one disadvantage to the use of a graphite moderator, and the one which eliminates its consideration in the GCRE, is the large bulk required. Space is at a premium in the mobile gas-cooled reactor, and, consequently, other moderators which require less bulk than graphite must be considered.

Beryllium Moderators. Two materials were considered, beryllium metal and beryllium oxide.

Permanent effects by neutron bombardment of beryllium are small or absent; thus, there is no significant change in resistivity, elastic modulus, or damping. Beryllium exhibits greater thermal-fracture resistance than even graphite. However, beryllium is very reactive to oxygen, forming the stable oxide, and with nitrogen or ammonia, forming the nitride, Be_3N_2 . The reaction with ammonia occurs appreciably at 1650 F, and probably to a considerable extent at lower temperatures.

Beryllium oxide is somewhat affected by radiation. Beryllium oxide can be heated in nitrogen at 2000 F with no reaction and in air free from water vapor at temperatures above 3000 F.

Beryllium and beryllium oxide, although attractive in some respects, would require fuel loadings in excess of the specified 15 kg for the small system under consideration. For this reason, they have received no further attention.

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Hydrogen-Containing Moderators. Water, the most common hydrogen-containing moderator, is unsuitable for GCRE application. Some of the solid metal hydrides offer considerable promise as moderator materials because of their hydrogen content and stability at 1000 to 1500 F. The initial choice of hydride moderators which would be suitable for the GCRE reduces to metal hydrides which (1) are formed from elements of low neutron cross section, (2) have an insignificant dissociation pressure at 1000 to 1500 F, (3) contain a high concentration of hydrogen per unit volume, (4) are readily available or easily produced, and (5) are not unreasonably costly.

Choice of Moderator Class. Potentially, the metal hydrides would offer many advantages over other moderators. Some are exceptionally stable at high temperatures, they retain hydrogen in extremely high concentration, they are easily fabricated, and are nontoxic. Because of these reasons, and because of the fact that greater moderating action per unit volume could probably be realized with the metal hydrides, the decision was made to concentrate all effort on the use of the solid hydrides as moderators.

It is recognized that the use of metal hydrides as moderators introduces additional problems; these materials in general are reactive to nitrogen and will require protective cladding, the amount of hydrogen they retain is dependent on their temperature, and their use as moderator materials has not been completely proven or developed.

Solid Hydride Moderators

Based on the criterion of low neutron cross section, hydrides of barium, calcium, cerium, magnesium, niobium, rubidium, sodium, strontium, zirconium, and yttrium should be considered. The significant physical properties of these hydrides are tabulated in Table 1.

The literature contains several discrepancies in values for the densities of some of the hydrides, presumably because of the failure of some investigators to use completely hydrided materials. Knowledge of precise values for the densities are of importance for two reasons: (1) calculation of the number of hydrogen atoms per unit volume depends on a knowledge of the density, and (2) if the difference between the densities of the metal and hydride is great, a moderator fabricated from this hydride would have little dimensional stability. The loss of some hydrogen by dissociation would result in either swelling or contracting, bursting the cladding or breaking away from it.

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TABLE 1. PHYSICAL PROPERTIES OF SOME HYDRIDES

Hydride	Cross Section of Metal	Density, g per cm ³		Metal Minus Hydride	N _H ^(a)	Dissociation-Pressure Equation	Dissociation Pressure at 1206 F (925 K), psia
		Metal	Hydride				
NaH	0.505	0.97	1.38	-0.41	3.53	log P (cm) = -5070/T + 9.49 (100% NaH) = -5806/T + 10.32 (90% NaH) = -5958/T + 10.47 (30-80% NaH)	1935
RbH	0.70	1.53	2.59	-1.06	1.80	Decomposes at 300 C	
MgH ₂	0.063	1.74	1.45	+0.29	6.69	log P (psi) = -10,050/T - 20.7 log T + 75.8	2690
CaH ₂	0.43	1.55	1.8	-0.25	5.2	log P (cm) = -7,782/T + 8.070 (100% CaH ₂) log P (cm) = -10,870/T + 10.493 (20-90% CaH ₂)	0.1 (100%) 0.01 (20-90%)
SrH ₂	1.16	2.6	3.27	-0.67	4.43	log P (mm) = -6500/T + 8.66	0.9
BaH ₂	1.17	3.5	4.21	-0.71	3.66	log P (mm) = -4000/T + 6.86 (99% BaH ₂) log P (mm) = -6450/T + 8.20 (93.7% BaH ₂)	6.6 (99%) 0.3 (93.7%)
ZrH ₂	0.18	6.4	5.625	+0.8	7.32	P = 760 mm at 660 F (ZrH _{1.93}) = 760 mm at 1090 F (ZrH _{1.90}) = 760 mm at 1562 F (ZrH _{1.63})	
YH ₃	1.38	5.51	--	--	--		
CeH ₃	0.70	6.5	5.5	+1.0	7.01		
NbH	1.1	8.4	6.0-6.6	+2.1	3.87 to 4.26	N _H = 1.06 ($\frac{H}{M} = 0.2$) at 1000 F (estimated) N _H = 0.3 at 1500 F (actual)	

(a) N_H = 10⁻²² times the number of hydrogen atoms per cm³ of sample.

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In order for an N_H value to be meaningful, the conditions for which it applies must be stated. The N_H values reported here are calculated for the fully hydrided material at room temperature and thus represent maximum values. At higher temperatures, where dissociation becomes measurable, the N_H values become less due to loss of hydrogen.

The dissociation pressures of all these hydrides are composition dependent in some composition ranges, generally being quite a bit less for incompletely hydrided material. The compositions for which the dissociation pressures reported apply are therefore noted. The alkali and alkaline-earth metal hydrides have a range of composition averaging between about 30 to 80 per cent hydride where the dissociation pressure is independent of composition. The dissociation pressures of the interstitial hydrides, on the other hand, are more completely composition dependent over the entire range of composition. In terms of the phase rule, this means that the alkali and alkaline-earth metal hydrides form two condensed phases, a hydride-rich phase and a hydride-poor phase in the composition range of 30 to 80 per cent, whereas, with the interstitial hydrides, two phase regions exist only over narrow composition ranges.

Sodium Hydride. Sodium hydride is one of the least expensive and most readily available hydrides under consideration. Furthermore, it has an attractively low cross section.

However, its N_H value is marginal at even slightly elevated temperatures, and at 1000 to 1500 F and 1 atm, it would be too low for a moderator application. An overpressure of hydrogen of approximately 2000 psi would be required to prevent its dissociation at 1200 F and to maintain an acceptable N_H value.

Rubidium Hydride. In comparison to sodium hydride, rubidium hydride is more costly, less available, has a higher cross section, a lower N_H value, and a higher dissociation pressure at comparative temperatures. It, therefore, has no apparent advantage over sodium hydride as a moderating material from any viewpoint.

Magnesium Hydride. Magnesium hydride should make an excellent moderating material from the standpoint of cross section and N_H . However, it would not be suitable at elevated temperatures because of its high dissociation pressure (2690 psi at 1200 F for example).

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Calcium hydride has one unfavorable property as a moderator, its relatively poor thermal conductivity. Since 5 to 10 per cent of the heat generated in a power reactor originates in the moderator, an effective method of removing this heat must be incorporated in the design.

Zirconium Hydride. The relatively low cross section and high N_H of zirconium hydride make it a potential moderating material. At 1500 F, $ZrH_{1.47}$ has a dissociation pressure of about 1 atm and an N_H value of about 5.7; at 1000 F, $ZrH_{1.94}$ has a dissociation pressure of about 1 atm and an N_H of about 7.2.

Yttrium Hydride. Yttrium hydride has a larger cross section, is less available, and is considerably more expensive than zirconium hydride.

Cerium Hydride. The moderate cross section and high N_H of cerium hydride make it attractive for a moderating material. At a given temperature and pressure, it has an N_H greater than zirconium hydride. From the data available on the densities of cerium and cerium hydrides, it is expected that cerium hydride would exhibit the same type of dimensional instability as zirconium hydride when it loses or absorbs hydrogen.

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Samarium, one of the rare earths in the cerium group, would be an objectionable contaminant to cerium which was to be incorporated into a moderator because of its extremely high cross section (5500 barns per atom).

Niobium Hydride. The limited data on the N_H values for niobium hydride suggest it would not be a suitable moderator at 1000 to 1500 F. An N_H of 0.3 at 1500 F has been reported by Battelle. This is in agreement with a calculated value at this temperature, based on the supposition that a N_H -versus-temperature curve for niobium hydrides would fall between similar curves for vanadium and tantalum hydrides (which are available).

Mixed Interstitial Hydrides. The higher N_H values of yttrium and cerium hydrides and the lower cost and greater availability of zirconium may both be taken to advantage by using mixtures of zirconium and yttrium hydrides or zirconium and cerium hydrides. In this manner a compromise between performance and cost is possible.

Mixed Saline Hydrides. It is known that low-melting eutectics are formed by mixtures of calcium and barium hydrides. For example 50 w/o BaH_2 -50 w/o CaH_2 melts at 1480 F and boils at 1690 F. Such mixtures offer interesting possibilities as moderators for the GCRE. However, because of the higher cross section of barium, and the relatively low hydrogen content of barium hydride, the use of such eutectics adds greatly to the fuel inventory.

Summary. On the basis of this preliminary survey of possible high-temperature hydrogenous moderating materials, it is apparent that only the hydrides of calcium, zirconium, yttrium, cerium, and alloys of zirconium with yttrium or cerium should be given further consideration. Of these it is deemed undesirable to consider yttrium or cerium hydrides on the basis of cost and availability, even though technically they are attractive possibilities. The possibilities, then, are calcium hydride and zirconium hydride. Of these two, zirconium hydride is chosen as the reference, and calcium hydride is chosen as a likely alternate.

Technology of Zirconium Hydride

Preparation. Zirconium hydride may be prepared in the massive form by subjecting zirconium bars at about 1800-2000 F to 5-15 psi of very pure hydrogen. The hydrogen is purified by passing it successively over

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(1) a platinum catalyst to remove oxygen, (2) calcium hydride heated to about 1400 F to remove water and nitrogen, and (3) through heated titanium or zirconium chips to getter out any gases not removed by the previous treatments.

In order to prevent cracking and the formation of voids while hydriding large pieces of zirconium, the metal is first heated in vacuum to a temperature greater than that at which it is desired to carry out the hydriding. This expands the zirconium lattice. Hydrogen is then admitted and the temperature is dropped stepwise. When the sample is no longer taking up hydrogen, it is pulled to the cool zone of the furnace and cooled under a stream of an inert gas. Cooling under hydrogen results in excessive hydrogen pickup.

Zirconium hydride may be prepared in the powder form by reduction of zirconium oxide with calcium hydride.

Physical Properties. Hydrided zirconium with an N_H of 3.4 has a thermal expansion of 6.5×10^{-6} in. / (in.) (F) from room temperature to about 1000 F (comparable to Type 446 stainless steel) but it drops off greatly in the range 1000 to 1100 F.

Tensile strength values for zirconium hydride ($N_H = 3.8$) are tabulated below:

<u>Temperature, F</u>	<u>Ultimate Tensile Strength, psi</u>
800	40,000
1200	12,000
1400	8,000
1600	6,000

The thermal conductivity of zirconium hydride with an N_H of 3.6 is 11.4-15.3 Btu/(hr)(ft)(F) between 500-1600 F. By comparison, zirconium metal has a range of 9.9-13.8 Btu/(hr)(ft)(F) at 500-1600 F.

Figures 1 and 2 show, respectively, a series of isochores and the phase diagram for the system zirconium-hydrogen as presented by Gilbert*.

*Gilbert, Paul T., NAA SR-1399.

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FIGURE 1. P-C-T RELATIONSHIPS IN THE ZIRCONIUM-HYDROGEN SYSTEM

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FIGURE 2. THE CONSTITUTIONAL DIAGRAM OF THE ZIRCONIUM-HYDROGEN SYSTEM

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In order to translate from hydrogen-to-metal ratio (X) to N_H it is necessary to know the density of the material since

$$N_H = \frac{(60.6) (X) (\text{density})}{(\text{molecular weight})} \quad (1)$$

There are available several sources of density-versus-composition data in the system zirconium-hydrogen. For purposes of comparison, the data were reduced to common coordinates and all plotted on the same graph. The result is illustrated in Figure 3. Two points are immediately evident: (1) lack of agreement of the data from each source, in spite of internal consistency, and (2) sparsity of data in the range of X from 1.2 to 2.0.

The assignment of a "most reliable" value of density as a function of composition to these data is purely arbitrary. Lacking any other supporting evidence, however, it becomes necessary to do this, at present, in order to calculate N_H values and to maintain a consistency within the GCRE calculations. A straight line fitting the equation,

$$\text{density} = 6.5 - 0.45X \quad (2)$$

has been superimposed on the data in Figure 3. At the present time, this will be considered to represent the variance of density with composition in the system zirconium-hydrogen. The fact that this equation represents an extrapolation considerably beyond the experimental data should be recognized.

By combining Equations (1) and (2) and substituting an equivalent value for the molecular weight of the hydride, Equation (3) is derived:

$$N_H = \frac{(60.6) (X) (6.5 - 0.45X)}{91.22 + 1.008X} \quad (3)$$

This function is plotted in Figure 4.

Technology of Calcium Hydride

Preparation. Calcium hydride of a commercial purity is a readily available chemical. It is prepared by the direct combination of calcium and hydrogen at 750-950 F, and its purity is determined by the purity of the starting materials used.

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FIGURE 3. DENSITY VERSUS COMPOSITION IN THE ZIRCONIUM-HYDROGEN SYSTEM

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FIGURE 4. THE EFFECT OF X ON N_H

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Physical Properties. Calcium hydride reacts with moisture in the air, releasing hydrogen and forming calcium oxide. The oxide spalls off, exposing a new surface for further reaction. Its rate of reaction with moist air is dependent upon its rate of subdivision. Although it reacts rapidly in contact with gross amounts of water, the release of hydrogen is not explosive.

It is supposed that calcium hydride is a poor thermal conductor, although this property has not been accurately determined.

The dissociation pressure of calcium hydride as a function of temperature is adequately described by the following equation:

$$\log P \text{ (cm)} = -7782/T + 8.070. \quad (4)$$

Although calcium hydride has been known since 1898, many of its properties, such as its ease of compacting, its reaction with various materials of construction, its hardness, and its tensile strength are still unstudied. These properties have not been studied because the interest in calcium hydride has been largely centered in its use as a chemical and not as a material to fabricate and utilize for its physical properties.

Problems in the Use of Solid Hydrides as Moderators

Heat Transfer. Since 5 to 10 per cent of the total heat output of the reactor will be generated in the moderator, it is imperative that a good thermal path be established between the moderator and the coolant-gas stream. This implies that the moderator itself and any cladding materials be good heat conductors. It also implies that the moderator and the cladding be bonded adequately so that gas pockets will not interrupt the heat flow. Alternatively, the moderator could be loosely "canned" and a liquid metal or salt used as a heat conductor between the element and the can.

P-C-T Data and Hydrogen Migration. It is obvious that since the dissociation pressure of zirconium hydride is a function of temperature, the imposition of a temperature gradient on a sample of hydrided zirconium will result in a redistribution of composition until each small isothermal section of the sample is at its equilibrium composition for the particular pressure and temperature at which it is maintained. The situation at equilibrium (in a closed system) will be one of constant hydrogen pressure, with a gradient of hydrogen content in the condensed phase, dependent upon

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the thermal gradient. This redistribution of hydrogen in the solid phase causes local density changes, and results in swelling and cracking. From the P-C-T data of Gilbert it is possible to predict what the gradient of hydrogen content will be in an enclosed sample with a given thermal gradient. This is done simply by replotting the data of Figure 1 as isobars. This has been done in Figure 5 for the 0.1-, 1.0-, and 2.0-atm isobars. For the 0.1-atm isobar there is a very large composition gradient in the 1000 to 1500 F range. This is much less when the pressure is 1.0 atm or greater. The problem of hydrogen migration between 1000 and 1500 F, therefore, can be minimized by using zirconium hydride with an N_H greater than about 5.5, and by maintaining it in about 1 atm partial pressure of hydrogen.

If this approach is not feasible, it may be possible to compartmentalize the moderator with a hydrogen-impermeable layer. If the thermal gradient is not very great throughout the compartment, the hydrogen migration will be insignificant.

Problems Associated With the Nitrogen Coolant. It is recognized that there is the possibility of the nitrogen coolant reaching the solid hydride moderator, either by penetration of the cladding or by diffusion through a pinhole or defect in the cladding. If this is the case, there is the possibility that the nitrogen will replace some or all of the moderator hydrogen by formation of the nitride, since both zirconium and calcium nitrides are known to be quite stable.

Cladding. If a hydride moderator is used in the GCRE, it will be necessary to clad it. A great deal of effort has been expended by other installations on numerous ways to fabricate clad zirconium hydride components. Such techniques as coextrusion, brazing, swaging, roll cladding, and the in situ hydriding method have been used to obtain bonding. In general, Type 316 or 446 stainless steels have been used as the cladding material, while the intermediate bonding layers have been selected from such materials as chromium, copper, molybdenum, or niobium. The emphasis has been on the attainment of the finished element in a predetermined shape.

Radiation Damage. It is hoped that radiation damage will not be a problem with zirconium hydride. Both ambient-temperature and high-temperature (1700-1750 F) radiation-damage studies on unclad zirconium hydride have shown no evidence of damage.

Nothing is known of the radiation damage to calcium hydride.

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FIGURE 5. ISOBARS IN THE ZIRCONIUM-HYDROGEN SYSTEM

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Mechanical Properties. In order for a material to be fabricated easily, it must be fairly ductile. It is known that calcium hydride is very brittle, and if it is used as a moderator material doubtlessly it will have to be compacted with a more ductile binder.

As reported above, the tensile strength of zirconium hydride, with an N_H of 3.8 (approximately $ZrH_{0.94}$) has been measured between 800 and 1600 F. The nature of the breaks indicated that zirconium hydride of this composition was quite ductile. Zirconium hydride (N_H = about 4) becomes quite workable at temperatures greater than about 1300 F. The best temperature for hot working it while still retaining most of the hydrogen is about 1600 F.

In an earlier section it was concluded that the optimum composition of zirconium hydride to be employed, on the basis of hydrogen migration, was about $ZrH_{1.5}$ to $ZrH_{1.9}$ (N_H = about 5.5-7.0). From the constitutional diagram of the zirconium-hydrogen system (Figure 2), it is apparent that in this composition range the stable phases are the delta and epsilon phases. The previously mentioned tensile-strength tests were made on samples of the beta phase. There is no assurance that the delta and epsilon phases will be as ductile as the beta phase. In fact, qualitative observations indicate that these higher compositions may be quite brittle.

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SURVEY OF CONTROL MATERIALS

S. J. Paprocki

This portion of the program is concerned with the selection of a suitable control material for the GCRE. Several factors influence the selection of a material for this application. They are control effectiveness, stability under irradiation, resistance to nitriding, structural strength at 1500 F, fabricability, cost, and availability.

It is certain that no one material will be superior in all of these factors; however, it is the purpose of this investigation to select the material with the best balance of properties. Factors which directly govern the satisfactory operation of the control material, such as control effectiveness, high-temperature strength, dimensional stability under irradiation, and resistance to nitriding, have received the primary consideration.

The initial phase of the work involved a review of elements possessing a sufficiently large thermal-neutron-absorption cross section to consider them as potentially promising control materials. The elements were evaluated on the basis of cost, availability, and physical and mechanical properties. Primary emphasis was placed on properties essential to satisfactory operation in the GCRE. Many of the elements were eliminated on this basis.

Boron

Theoretically, boron is an excellent control material. Its absorption cross section varies inversely with neutron velocity in the thermal range. Natural boron possesses a thermal-neutron-absorption cross section of approximately 755 barns. This cross section is concentrated in the isotope boron-10, which constitutes approximately 19 per cent of natural boron. The boron-10 isotope possesses a cross section of 4,010 barns. Neutrons reacting with this isotope produce an (n, α) reaction with the formation of lithium-7 and helium.

Natural boron metal and compounds are readily available at a low relative cost. Metallic boron enriched to 90 per cent boron-10 is available at a cost of approximately \$6 per g.

Boron can be alloyed with most of the high-temperature steels. The amount that can be alloyed is limited to a maximum of about 2.0 w/o boron. An addition in excess of this amount results in severe embrittlement. Because of this limitation on loading, it is usually necessary to alloy the high-temperature steels with the boron-10 isotope.

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Boron materials have been effectively dispersed in titanium, zirconium, copper, nickel, and stainless steel matrices. These materials include metallic boron and compounds B_4C , B_6C , ZrB_2 , and CrB_2 . The loading in the dispersion-type specimen is governed by fabricability and the reaction rate between the dispersant and matrix materials. Specimens embodying 60 w/o B_4C in copper and up to 30 w/o of other dispersants in titanium and zirconium matrices have been prepared and fabricated. This larger loading permits use of the natural-boron materials.

At the proposed GCRE operating temperature, it will be necessary to use a matrix material possessing good high-temperature structural strength. Boron and many of the compounds are expected to react with the high-temperature steels during fabrication or during the long operational life of the reactor. This will result in embrittlement and may limit the use of such a control system.

Containers filled with boron or compounds have also been utilized as control elements. This allows for a heavy concentration of control material. Use of such a system in a high-temperature reactor would involve the risk of failure of the container. This could be minimized by the use of a compartmentalized control element.

Extensive irradiation tests have been conducted on boron materials. All of these tests have been conducted at the MTR ambient temperature or at temperatures below 650 F. These tests are still in progress; only a cursory observation can be made at this time.

Stainless steel alloys containing additions of approximately 1 w/o boron-10 embrittled severely as a result of irradiation at the MTR ambient temperature and postirradiation heat treatment at 600 F. After heat treatment, the ductility of the specimens was reduced to the point that the specimens possessed less than 1/2 per cent elongation in a tensile test. This embrittlement was also accompanied by a volume change.

Dispersions embodying boron and compounds enriched in the isotope boron-10 have exhibited micro and macro cracking and severe localized damage after irradiation. There is some feeling that this material will be unable to withstand complete burnup of the boron-10 isotope.

Natural-boron materials irradiated at the MTR ambient temperature and heat treated after irradiation to a temperature of 660 F have exhibited a varying resistance to irradiation stability, evaluated on the basis of helium release. Capsules containing powders of boron, boron carbide, and zirconium diboride have been irradiated. Preliminary results indicate that boron is least resistant and zirconium diboride is most resistant. Less than 1 per cent of theoretical amount of contained helium in the zirconium diboride specimens was released after 80 per cent burnup and postirradiation heat treatment at 660 F.

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Dispersions embodying natural-boron materials appear to be relatively stable under irradiation at the MTR ambient temperature. A volume increase and loss of ductility has been observed; however, fracture of the matrix has not been observed.

Rare Earths

Many of the rare-earth elements possess large thermal-neutron absorption cross sections and consequently are potentially promising as control materials. All of these elements capture neutrons by an (n, γ) reaction and are expected to be stable under irradiation. They possess many disadvantages which are mostly related to their scarcity and limited application. The cost of these materials is relatively high, and their availability is limited. Only a limited amount of information is available on their mechanical and physical properties. Alloys of these materials have received only meager attention. Several programs are under way to study alloys of rare-earth elements possessing high cross sections; however, it will probably take several years before alloys can be fully developed for reactor use.

Most of the investigations of control materials embodying rare-earth elements have utilized compound forms. The oxides of the elements have received the most attention. Since the oxides are unreactive with almost all metals and alloys, they can be used as dispersants in almost any metallic or alloy matrix. The only limitation on loading is the fabricability of the resultant dispersion and its corrosion resistance to the reactor coolant. In high-temperature water, the oxides are hydrated.

Dispersion specimens embodying oxides of rare-earth elements have been irradiated. As expected, no structural damage has been observed. A relatively small volume change and loss of ductility has been observed. The slight loss of ductility would probably not be observed after the specimen had been annealed at elevated temperatures.

Fabrication techniques for preparing full-size control elements embodying dispersions of the rare-earth elements have not been fully developed. It should be possible to prepare simple flat plates or rounds with moderate loadings by techniques known now. Complex shapes or cladding will require additional development.

The rare-earth elements, samarium, gadolinium, europium, dysprosium, and erbium, are being considered for use in control systems.

Samarium. The thermal-neutron-absorption cross section of samarium is approximately 5500 barns. The absorption is concentrated in the

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isotope samarium-149 which is present in natural samarium to the extent of about 14 per cent. Since the absorption is concentrated in one isotope, the material will burn out.

The oxide is available in appreciable quantities at a cost of about \$2 per gram. A mixture of Sm_2O_3 and Gd_2O_3 is available at a cost well below \$1 per gram. This mixture is more effective as a control material and being substantially lower in cost is preferred over samarium oxide.

Gadolinium. Gadolinium possesses a thermal cross section of 46,000 barns concentrated in the isotopes gadolinium-155 (14.7 per cent), 70,000 barns, and gadolinium-157 (15.7 per cent), 160,000 barns. Some uncertainty exists concerning the absorption characteristics of this element in the high thermal and epithermal regions. This is true of all the rare-earth elements and many of the other elements. They possess resonance peaks in these regions, and their true effectiveness as control materials is best determined by conducting actual control effectiveness tests.

Gadolinium oxide is available at a cost of about \$1 per gram. Metallic gadolinium is also available in limited quantity at a substantially higher cost.

Europium. This element possesses a cross section of 4,600 barns. All five isotopes are absorbing and extensive resonance peaks are present in the high thermal and epithermal regions.

Europium is least abundant of the rare-earth control elements. The oxide is available in limited quantity at a cost of about \$10 per gram. Aside from the high cost and limited availability, this element is considered to be the most desirable control element of the rare-earth group. Producers of rare-earth materials claim that sufficient quantity of any of the rare-earth control elements can be produced at substantial cost reductions with the existence of a strong demand for these materials.

Dysprosium and Erbium. These elements are not being considered promising control materials. The other rare-earth elements, europium, gadolinium, and samarium, are more effective control materials.

Cobalt

In comparison with other control material, cobalt is not a strong neutron absorber. It has a relatively low cross section of 37 barns with some absorption in the epithermal region.

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Cobalt alloys of approximately 60 w/o cobalt are available commercially at a cost of about \$2.50 per pound. The alloys are designed for high-temperature use and can be cast or fabricated to most desired control shapes.

The element possesses two major drawbacks for use as a control material: it is partially transparent to neutrons and becomes a high-intensity gamma emitter upon irradiation.

Hafnium

This element is an excellent control material. Although its cross section is relatively small, 105 barns, it is an effective absorber in both the thermal and epithermal ranges.

Hafnium metal or alloys are not suited for GCRE application. The metal is plastic at 1500 F, and no high-temperature alloys have been developed. It may be possible to use hafnium compounds as dispersants in high-temperature-steel matrices; however, their use would be limited by the availability of the metal. Hafnium is obtained as a by-product of the zirconium-metal production and at the present time, the demand for this metal far exceeds the supply.

Cadmium

Cadmium metal has a cross section of 2500 barns, with essentially one absorbing isotope cadmium-113 (12.3 per cent), 20,800 barns. The element is a relatively poor absorber in the epithermal region.

The use of cadmium metal or alloys is restricted to temperatures well below those proposed for the GCRE. Apparently, the only possibility is to use compounds of cadmium dispersed in a high-temperature high-strength matrix. Reaction studies conducted at Battelle have shown that CdS did not appear to react with nickel at temperatures up to 2000 F.

Iridium

This element possesses a cross section of 430 barns. It is commercially available in sheet and plate form and has suitable mechanical properties at high temperatures. The metal oxidizes readily, and the oxide is volatile. It also has the disadvantage of high cost, approximately \$1500 per pound.

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Gold

This element does not appear suitable for use as a control material in the GCRE. The metal and alloys are relatively plastic at low temperatures, and the metal is costly.

Rhenium

Rhenium metal is available in sheet and plate form at a cost of about \$1000 per pound. Aside from the disadvantage of high cost, the metal oxidizes extensively above 750 F, and the oxide is readily volatile. However, it does not become embrittled in a hydrogen or nitrogen atmosphere.

Silver

Silver has a thermal-neutron-absorption cross section of 62 barns, with moderate absorption in the epithermal region. Powder dispersions of Ag-CdO are used commercially for electrical contacts; however, silver-base materials are limited to service at low temperatures.

Rhodium

This element has a cross section of 150 barns; however, its high relative cost of \$1800 per pound prohibits its use as a control material.

Conclusions

Of the elements possessing large thermal-neutron-absorption cross section, boron, cobalt, cadmium, and some of the rare earths were selected as potential control materials for the GCRE. Stellite 25, a cobalt-base alloy, was chosen as the reference material. As previously mentioned, cobalt is relatively gray to neutrons, and, consequently, its effectiveness as a control is questionable. It also has the disadvantage that with irradiation it becomes a high-intensity gamma emitter. Although, it was realized that the control effectiveness of cobalt was doubtful, the cobalt alloy was selected as reference material because of its commercial availability, high-temperature strength, and low cost. Of all the potential control materials, it was the only one that could be evaluated immediately without any required development.

Boron is being considered as one of the alternate control materials. The only major drawback to the use of this element is its possible instability under high-temperature irradiation. No data are available on the behavior

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Some rare-earth elements are also being considered as alternate control materials. There is every indication that these materials will be stable under high-temperature irradiation. The oxides of these elements can be dispersed in almost any high-temperature-steel matrix. They possess the disadvantage of a relatively high cost and limited availability. The best choice of material from this standpoint appears to be the $\text{Sm}_2\text{O}_3\text{-Gd}_2\text{O}_3$ mixture. This material is appreciably lower in cost than the other rare-earth control materials.

Aside from the reference cobalt-base alloy, all of the other control alternate materials will require considerable fabrication development. It is not planned to undertake fabrication development studies until a specific selection of a control material is made. It is anticipated that all of the control materials will require cladding to prevent attack by the coolant gas and subsequent fragmentation and spalling. However, the decision regarding the use of cladding will be reserved until after the results of nitridding studies are available.

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FUEL ELEMENT CONSIDERATIONS

A dispersion-type fuel element of the stainless steel- UO_2 type was immediately selected as the reference fuel element for the GCRE. On considering Core I specifications, particularly temperature, coupled with the desirability of selecting as the reference fuel a well developed material, the choice was almost straightforward. Naturally, there were several other types considered, and the most favorable among these are being evaluated as part of the alternate fuel program discussed in a later section.

The directness of the selection of the reference fuel element does not mean that the GCRE will not have fuel-element problems. To the contrary, conditions imposed by this reactor will introduce an impressive set of problems, each of which must be evaluated before a satisfactory performance can be expected from the stainless steel- UO_2 element. Noteworthy among these are radiation-damage resistance, resistance of the fuel element and brazed joints to deformation at elevated temperatures over extended time periods, and the possibility of stringent fabrication conditions being imposed by nuclear design considerations. Each of these problems will, of course, receive attention but to a different degree as the program progresses. For instance, initial nitriding studies have shown that Nichrome V is most resistant to nitriding under severe conditions. These results suggest that a Nichrome V- UO_2 fuel element would be most suitable. However, nuclear considerations force a compromise to a Nichrome V-clad stainless steel- UO_2 system. At this point a series of cursory experiments are planned to evaluate this later system, but until further nitriding results are available an extensive development program is not justified. On the other hand, radiation-damage resistance is recognized as a serious problem with this type of element. A change in cladding or matrix materials between somewhat similar metals is not expected to give significantly different results; hence, a more detailed study is warranted early in the program.

In line with the survey nature of this report the following sections are directed at emphasizing the large amount of development work which has gone into this type of element, and reviewing its radiation-damage resistance, which is expected to be its most marginal property under GCRE conditions.

Development of Reference Fuel Elements

D. L. Keller

The development of dispersion- or cermet-type fuel elements was initiated some years ago when an investigation was made as part of the

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NEPA program to determine the feasibility of fabricating a molybdenum-cored cylindrical element containing fuel particles dispersed uniformly in the molybdenum matrix. Since this time, many sites have contributed to the development of this type of reactor fuel element, with the stainless steel- UO_2 cored element having received the greatest attention.

It has been demonstrated that stainless steel sheet, rod, wire, and various other shapes can be readily fabricated into fuel elements with protective cladding and containing up to 30 volume per cent UO_2 in the core section.

Investigations at ORNL have led to the development of fuel plates for the APPR (17 to 34 w/o UO_2 in Type 304 stainless steel), while work at NEPA and GE-ANP was directed toward obtaining elements (30 w/o UO_2 in Type 310 or Nichrome V) for the direct-cycle aircraft reactor. A similar element (30 w/o UO_2 in Type 347) was developed at Battelle intended for service in the SCW reactor. During the course of these and other studies, a great deal of data have been compiled on the corrosion resistance, and mechanical and physical properties at room and elevated temperatures, as well as resistance to radiation damage of these fuel-element sheets. It has been demonstrated at each of these sites that the method of preparation, particle size, and strength of the UO_2 used as a dispersant have a significant effect on the fabricability and final properties of the fuel element.

For the fabrication of these materials, the methods employed have generally consisted of three steps:

- (1) Mixing the component core powders
- (2) Preparation of a sandwich-type billet
- (3) Fabrication of the billets into fuel sheet.

During hot rolling, it has been observed that the tendency for the oxide particles to align themselves into stringers, resulting in a loss in strength of the core body, can be related to several factors. Among these are the particle size of the UO_2 and the matrix powder, the plasticity of the matrix material, the rolling temperature, and the rate of reduction.

During cold rolling and during some hot-working operations, the UO_2 particles usually fracture, further increasing the tendency to form stringers and perhaps resulting in poorer performance during irradiation.

The fabrication of stainless steel-UO₂ rod or wire-type elements has developed along the same lines as the sheet elements. Work at KAPL and SEP has shown that elements of this shape incorporating high loadings of UO₂ (up to 30 w/o) are readily fabricable by hot extrusion, hot-drawing, or

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hot-swaging methods. A combination of these methods generally yields the best results. Cold extrusion of the mixed metallic and oxide particles has shown very promising results when a small amount of binder is added to the powder blend. These extrusions are sintered to a high density, then bonded by hot swaging to a tubular sheath or clad, a technique which has resulted in a reduced amount of oxide fracturing. One method of reducing this fragmentation, presently being investigated at KAPL, involves the strengthening of UO_2 by alloying it with small additions of other metal oxides.

The fabrication of special shapes (including perforated wafers and tubular bodies) of this basic stainless steel- UO_2 material is also receiving close attention.

Radiation-Effects Survey

G. D. Calkins

A survey of the effects of radiation on UO_2 cermets showed that there was little information available under conditions pertinent to GCRE. The existing data indicated that failure of the UO_2 cermet may be expected under certain conditions as a result of blistering or cracking, probably from fission-gas pressure. It appears that pin-type fuel elements fail by cracking and the plate-type fuel elements fail by blistering. The important factors to be considered are burnup, temperature, fuel loading, particle size and distribution of the UO_2 , time at temperature, and effect of coolant.

Fuel Loading

A few experiments have been conducted on the effect of UO_2 concentration. KAPL studied flat-plate specimens containing 5, 10, 20, and 30 w/o UO_2 . These were evaluated at 1300 F and 1850 F to 20 per cent burnup. All of the specimens were satisfactory at 1300 F, while only the 5 w/o specimen was satisfactory at 1850 F.

There are two schools of thought in regard to UO_2 concentration. One suggests that the better way of improving the stability of UO_2 cermets is to reduce the UO_2 concentration by using highly enriched uranium. This increases the strength of the matrix and makes it more resistant to yielding from fission-gas pressure. The other suggests that the UO_2 concentration be maintained and the enrichment reduced. In this case, the idea is to retain the fission gases in the UO_2 so that the gas pressure will be less. There is not sufficient information to select the better of these two hypotheses.

However, data at 1400 F and 14 per cent burnup suggest that it will be necessary to use a fuel loading (either concentration or enrichment) of less than the

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equivalent of 30 w/o of 93 per cent enriched UO_2 , unless it is possible to operate at a burnup of less than 10 per cent. A study of the data suggests that an element containing 10 w/o of highly enriched UO_2 might take about 20 per cent burnup or perhaps a 15 w/o material a burnup of 15 per cent at 1500 F. Experimental evidence is needed to support this opinion.

UO_2 Density, Particle Size, and Distribution

Existing data on the effect of density of the UO_2 show that it is desirable to use a material having as high density as possible. Experiments by WAPD on the release of fission gases as a function of the density of the UO_2 indicate that the amount of fission gases released decreases markedly with UO_2 having a density of 95 per cent or greater of the theoretical attainable.

KAPL has recently suggested that an over-all core density greater than 97 per cent resulted in the failure of specimens having burnups of 20 and 25 per cent. According to their calculations, an over-all density of 98 per cent of theoretical will allow a burnup of only 10 per cent before failure. This is not contrary to the WAPD results, since the latter were based only on UO_2 density. These data imply that a high UO_2 -particle density in a matrix sufficiently porous to accommodate the radiation damage would be effective.

Theoretical considerations show that the size of the UO_2 particles in a dispersion may be important in determining the radiation life of a UO_2 cermet. The UO_2 particles should be large enough, about 100 μ in diameter, to minimize the number of fission fragments that can leave. With 100- μ particles in a core containing 20 w/o UO_2 , approximately 5 per cent of the volume of the matrix will be reached by fission fragments. This will retain the fission fragment damage in the UO_2 , thus protecting the matrix material. Also, the fission-gas atoms may be retained in the UO_2 , reducing the gas pressure.

This concept has been checked fairly well experimentally. Flat-plate specimens containing UO_2 particles having diameters of less than 3 μ were found to develop serious cracks in their cores during a postirradiation bend test after a burnup of about 5 per cent or greater, while similar specimens containing 15 to 44- μ particles did not. The recently completed irradiation of specimens at 1400 F and 14 per cent burnup showed that specimens containing UO_2 particles of 44 to 105 μ developed less damage than those having 15 to 44- μ particles, which in turn were better than those having particles of less than 3 μ .

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In this regard, it should be mentioned that micrographs of UO_2 cermet containing highly enriched UO_2 before and after irradiation show that the UO_2 particles appear to sinter during irradiation. Several examples of UO_2 particles that were fragmented before irradiation showed no signs of fragmentation after irradiation, and the cracks had healed. In addition, some etched sections of UO_2 cermet at KAPL showed that the UO_2 particles were surrounded by a dark ring of material after 8 per cent burnup. The composition of this material is not known, but it may be oxides of the fission products or matrix materials. It is believed that the sintering observed may have resulted from thermal spikes in the UO_2 and that as a result of the sintering the fission products may be free to move.

This may mean that although there is some advantage in using the larger size of UO_2 in a dispersion the advantage may not be large because of the sintering action that frees the fission products.

It is clear that the UO_2 particles must be evenly distributed in the matrix materials to attain the maximum radiation life. Specimens containing stringers of UO_2 particles have been observed to fail by cracking along the lines of stringers.

Time at Temperature

There are no definitive data available on the effect of time at temperature on the UO_2 cermet. Most of the data available are from irradiations for a few thousand hours. Data for times at temperature of 10,000 hr are nonexistent.

Several factors may be influenced by the effect of time at temperature. Two of the most important are the rupture strength of the fuel element and the amount of fission gases that diffuse from the UO_2 . The rupture strength of the materials in the element will decrease with time at temperature, while the amount of gas diffused from the UO_2 will increase. Both of these factors are affected in a similar fashion by an increase in temperature.

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NITROGEN AS THE GCRE GAS COOLANT

A previous section has dealt with the factors involved in selecting nitrogen as the coolant gas. The following sections deal with the materials problems arising from this choice. The first of these is concerned with the resistance of materials to nitriding and includes a literature survey of this subject as well as results of initial exploratory nitriding tests conducted at Battelle which are considered to be part of the survey work. Subsequent sections review the chemistry of nitrides and discuss some possible radiation effects on nitrogen, nitrogen-hydrogen mixtures, and nitrogen-oxygen mixtures.

Resistance of Materials to Nitriding

H. J. Wagner, C. J. Slunder, and A. M. Hall

The effect of the gaseous environment on various materials which will serve as reactor components is being investigated.

Nitrogen has been chosen as the reference coolant. It is also believed that the hydride moderator to be used in the experiment will require a small percentage of hydrogen to be present in the coolant. Ideally, it would be desirable to know the resistance of materials to an environment corresponding to the actual reactor conditions. This environment was determined to be as follows:

Gas Mixture, volume per cent	
Hydrogen	7-1/2
Nitrogen	82-1/2
Pressure, psi	200
Metal Temperature, F	1500
Type of Force Field	Radiation

It is known that molecular nitrogen in a radiation field will break down into atomic nitrogen, as well as other species. It is expected that materials will react more readily with the more active forms of nitrogen than with molecular nitrogen.

Ammonia gas has been used as a source of nascent nitrogen for the purpose of imparting to certain metals a hard outer case consisting primarily of metal nitrides. Commercially, nitriding is carried on in anhydrous ammonia atmospheres at temperatures of 900 to 1200 F. Ammonia cracking is catalyzed by the surface of the metal to be nitrified, and nascent nitrogen is provided for reaction with the metal.

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It would be expected that materials resistant to an environment wherein nascent nitrogen is available at the metal surface would likewise be resistant to the active forms of nitrogen encountered in the reactor.

Consequently, a program has been aimed at determining the resistance of materials to ammonia at a 1500 F metal temperature.

Literature Survey

A literature survey revealed that investigations had been made along several lines related to the present problem: (1) the effects of molecular nitrogen on metals at elevated temperatures, (2) the effects of mixtures of hydrogen, nitrogen, and ammonia on metals under conditions encountered in commercial nitriding, and (3) the effects on metals of mixtures of hydrogen, nitrogen, and ammonia under conditions encountered in the commercial synthesis of ammonia by the Haber process. The pertinent information is summarized in Tables 2, 3, and 4.

TABLE 2. ABSORPTION OF MOLECULAR NITROGEN BY ALLOYS AT ELEVATED TEMPERATURES

Alloy Composition, w/o	Environment	Temperature, F	Time, hr	Results
Fe-Cr, 0-30 Cr	Argon with access to N ₂	2462	6-1/2	0.02 w/o nitrogen absorbed; original nitrogen was 0.02 w/o
10.4 Cr	Air	1832	1/2	Deep nitrogen absorption to center of 0.30-in. -thick specimen
18-8 stainless steel	Pure N ₂	1700	--	Nitrogen absorbed; inhibited austenite- to-ferrite transformation
18-8-Mo stainless steel	N ₂	1292	10,000	8 to 20-mil depth of nitrogen penetration
304 stainless steel	Air	1600	500	No marked increase in nitrogen content
Ditto	Air	1800	Ditto	250 per cent increase in nitrogen content
Fe-25Cr-12Ni	Air	1000 to 2000	Up to 13,000	Nitrogen content increased 100 to 400 per cent at 1500 F for periods up to 2800 hr
Fe-25Cr-20Ni	Air	Ditto	Ditto	Ditto
Fe-16Cr-13Ni-3Mo	Air	Ditto	Ditto	Ditto

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**TABLE 3. COMMERCIAL NITRIDING OF HIGH-CHROMIUM
AND AUSTENITIC STEELS**

Conditions: Temperature - 1200 to 1220 F

Time - 90 hr

NH₃ in exit gas mixture - 45 to 55 volume per cent

Material Composition, w/o					Depth of Case, mils
C	Cr	Ni	W	Fe	
0.28	13.4	0.35	-	Balance	25
0.16	17.2	1.40	-	Balance	20
0.26	26.30	0.25	-	Balance	17
0.13	18.4	8.75	-	Balance	12
0.4	13.0	12.8	2.2	Balance	9
0.47	13.4	26.5	3.5	Balance	5.5
-	15	65	-	Balance (Nichrome)	Nil

Initial Tests to Evaluate Materials in
Ammonia Atmospheres

The initial experimental program was planned to determine the resistance of materials to an ammonia atmosphere at 1500 F. For these tests, 100 hr was arbitrarily chosen as a suitable time of exposure. It was recognized that the condition wherein both nascent nitrogen and nascent hydrogen were available at the metal surface by dissociation of ammonia would be more severe than the conditions to be expected in the reactor. However, materials found entirely resistant to the ammonia would be expected to resist the environment in the reactor satisfactorily.

Heating of the specimens was carried out in a Hevi-Duty tube furnace. Preliminary tests indicated that a Vycor glass muffle would be more satisfactory than an Inconel (i. e., metallic) muffle because of the greater tendency of the Inconel to catalyze the ammonia dissociation on its surface. It was thought that as much ammonia as possible should be available for cracking on the surface of the test specimens.

The temperature of the furnace was controlled by a Leeds and Northrup recorder-controller, using a Chromel-Alumel thermocouple sensing element. The thermocouple was located in a ceramic protection tube in the center of the furnace.

Anhydrous ammonia was passed through nonindicating Drierite (anhydrous calcium sulfate) to remove water vapor. The entering gas flow

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TABLE 4. THE EFFECTS ON METALS OF EXPOSURE TO HYDROGEN,
NITROGEN, AND AMMONIA AS ENCOUNTERED IN
INDUSTRIAL AMMONIA SYNTHESIS

Material (Compositions given in w/o)	Remarks
Tough-pitch copper	Deteriorated
Boron-deoxidized copper	Ditto
Nickel	Ditto
Monel	Ditto
Ingot iron	Ditto
Low-carbon steel	Ditto
Hydrogen reduced, oxygen-free copper	Appearance unchanged after six months
Invar, Fe-36 Ni	Deteriorated
Fe-16 Cr-15 Ni-3 Si	16-mil penetration in six months
80 Ni-15 Cr (approximately)	Intergranular fissures
Fe-Ni-Al alloy casting	No deterioration, but high initial porosity
Various steels: Cr-W, Cr-V, Ni-Cr, Ni, Cr, plain low C	Deteriorated; 2 w/o Cr most resistant
0.3-0.4 Ti, 2.84-3.24 Ni, 0.15-0.17 C steel	Recommended for use
Various steels: Cr-Mo, Cr-Ni, Cr-V, Ni	Deteriorated 18-8 stainless steel most resistant
AISI 304, AISI 347, 25 Cr-20 Ni-Fe, 12 Cr steel, 2 Cr-0.5 Mo, 5 Cr-0.5 Mo, 12 Cr-60 Ni-2 W-25 Fe, Ni steel	Said to be used in industrial ammonia plants

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Two preliminary 24-hr tests were made on SAE 4150 and SAE 4340 steels, which are commonly nitrided commercially. These tests were made under commercial conditions for the purpose of detecting any flaws in the experimental setup. Microscopic examination and hardness surveys on the specimens indicated that nitriding had indeed occurred.

The first 100-hr test was made for the purpose of screening a large number of materials with respect to resistance to nitriding. An auxiliary purpose was to determine what thermocouple materials would be satisfactory in the reactor so that temperature control can be maintained in future in-pile tests. The surfaces of certain specimens in this first test were covered with a black, sooty powder which was at first thought to be a result of contamination. The relative amounts of black substance on various materials are given in Table 5.

In Test 3 the apparatus was thoroughly checked for leaks, black rubber stoppers were replaced with amber rubber stoppers, and the ends of the muffle were more efficiently cooled. In Tests 2 and 3, however, the black substance was still formed on certain alloys. The fact that this black coating was a natural result of the nitriding action was confirmed by X-ray diffraction analyses of the substance scraped from some of the alloys. Results of these analyses are shown in Table 6.

Results of Metallographic Examination. Having determined that the experimental procedure was reliable, the metallographic structure of the specimens after exposure to the nitriding atmosphere was examined. A

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TABLE 5. SUMMARY OF THE RELATIVE AMOUNTS OF BLACK SUBSTANCE FOUND ON MATERIALS EXPOSED 100 Hr IN AMMONIA AT 1500 F (Test 1)

Material	Composition, w/o				Relative Amount of Black Substance on Specimen Surface
	Ni	Cr	Fe	Other	
Nichrome V	80	20	--	--	High
Nichrome	65	15	Balance	--	High
Inconel	76.5	14	Balance	--	High
Chromel P(a)	90	10	--	--	High
Driver-Harris Alloy 242(a)	Balance	20	--	1Si, 1Nb	High
AISI 330	35.7	16	Balance	--	Some
Incoloy	34	21	Balance	--	Some
AISI 314	19.5	23.5	Balance	Mn + Si	Some
AISI 347	10	18	Balance	--	Some
AISI 310 S	20	25	Balance	--	Nil
Fe-Cr-Al	--	25	Balance	5Al	Nil
AISI 446	--	25	Balance	--	Nil
Alumel(a)	Balance	--	--	1Si, 2Al, 2.5Mn	Nil
Driver-Harris Alloy 33(a)	Balance	--	--	3Si	Nil
Copper (OFHC)	--	--	--	99.96Cu	Nil
"A" Nickel	99.4	--	--	--	Nil

(a) Thermocouple wires.

TABLE 6. RESULTS OF X-RAY DIFFRACTION ANALYSES OF BLACK SUBSTANCE FOUND ON CERTAIN ALLOYS AFTER NITRIDING AT 1500 F

Base Material	Results of X-Ray Analysis			
	Strong	Faint	Medium Faint	Very Faint
Nichrome V	(Ni-Cr)	CrN		
Inconel	(Ni-Cr-Fe)	Fe ₄ N CrN		
Nichrome	Fe ₄ N		CrN	(Ni-Cr-Fe)
Incoloy	Fe ₄ N	CrN		

(a) Parentheses indicate identification not positive.

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detailed description of each structure is given, although many of the materials are clearly unsuited for use in the reactor. It is thought, however, that in the event that an alloy-development program becomes necessary, any information relating to the manner in which nitriding proceeds will be of importance.

Nichrome V. A second phase appeared to a depth of about 0.8 mil. This was presumed to be a chromium nitride. Beyond this zone was a 0.4-mil zone in which the original carbides had expanded in size and number, while a slight color change was apparent (see Figure 6). It is believed that chromium carbonitrides had formed in this region and that the distance from the outer edge of the specimen to the end of the carbonitride zone is the total depth of nitrogen penetration. In Test 2 a peelable lamination was observed on the surface, not the fine powdery black surface observed in other tests. The zone of nitrogen penetration was seen to be somewhat different in character in the two tests. This is shown by comparison of Figure 6 with Figure 7.

Nichrome. The surface of the specimen showed a white, eutectic-like zone about 0.5 mil in thickness. This probably corresponds to the Fe_4N , CrN , and metallic component observed in the X-ray examination of the surface material. Further inward, to a total depth of 2.2 mils, was a complex region thought to be primarily chromium nitrides. The carbonitride transition zone observed in the Nichrome V was also visible to a maximum depth of about 2.8 mils. Knoop hardness indentations shown in Figure 8 clearly indicate the increased hardness in the affected zones, particularly in the chromium nitride region.

Inconel. As shown in Figure 9, the affected region was clearly divided into a white zone at the surface and a dark, eutecticlike zone. Within the dark zone, a second phase appeared in the grain boundaries. Presumably these were nitrides of either iron or chromium or a complex nitride. It is theorized that the white layer at the surface is an iron nitride. A small amount of precipitate was observed for about 0.5 mil beyond the heavily affected zone. Knoop hardness impressions illustrate the relative hardness of the various zones.

AISI 330. Two zones were distinguishable. A dark zone 2.5 mils thick was seen at the surface. In this zone a dispersion of complex nitrides of iron and chromium was thought to be the main phase. In this zone there appeared a yellow phase in the grain boundaries. The second zone, extending to about 5.5 mils below the surface, had more clearly discernible

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FIGURE 6. NICHROME V AFTER EXPOSURE
TO NITRIDING ATMOSPHERE
(Test 1)

500X

Etchant: Glyceregia

N31894

FIGURE 7. NICHROME V AFTER EXPOSURE
TO NITRIDING ATMOSPHERE
(Test 2)

500X

Etchant: Glyceregia

N31916

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FIGURE 8. NICHROME AFTER EXPOSURE TO NITRIDING ATMOSPHERE

FIGURE 9. INCONEL AFTER EXPOSURE TO NITRIDING ATMOSPHERE

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phases, and probably consisted largely of chromium nitrides. The grain-boundary phase appeared gray in this zone, rather than yellow. Evidence of further nitrogen penetration was seen for about 0.5 mil beyond the two zones.

Incoloy. Similar to AISI 330 in composition, the Incoloy behaved in a comparable manner. The relative thickness of the two zones was different, but the structure of the deepest zone indicated that nitriding occurred in a similar manner.

AISI 310S and AISI 314. Three zones were apparent in the microstructures of these alloys. The surface zone was a complex multiphased structure somewhat like the complex zones observed in the other alloys described. The next layer, however, was unlike the others in that it consisted of a lamellar structure; the nitrides possibly formed on certain planes in preference to others.

AISI 347. As in the above-described stainless steels, three distinct zones were apparent: a surface zone showing a complex structure, a middle zone showing clearly two different types of nitrides, and a carbonitride transition zone.

AISI 446. Various layers were observed in the affected zone. Because of great depth of the affected region, an X-ray diffraction study was made on this alloy. The surface layer was found to be CrN and either Fe₂N or Cr₂N. It was not possible to distinguish between the latter two. At a depth of 2 mils was found CrN, Cr₂N, Fe₂N, and, possibly, Fe₄N. Below this the X-ray analysis showed only CrN and base metal. Metallographic examination showed that at a depth of 10 to 16 mils the nitrides were mixed with a dark eutecticlike structure present in relatively large amounts. At the point where the nitrided zone ends, the transition from carbide to nitride was readily observed.

Iron-Chromium-Aluminum Alloy. At least four different zones were present in the microstructure of this material. The deepest zone showed typical aluminum nitride needles, indicating the selective nitriding of aluminum. Following this, a zone consisting of mixed aluminum and chromium nitrides was apparent. The third zone had a eutecticlike appearance, with white grain boundaries. It is possible that in this zone sufficient nitrogen was present in solid solution to convert the matrix from ferrite to austenite. The surface layer had the appearance typical of iron nitride, with no other phases visible.

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Alumel. Attack of the Alumel appeared to proceed in two steps. The first step, corresponding to the deepest zone, showed the formation of a finely dispersed phase. This did not appear to be an aluminum nitride, but may have been composed of complex silicon-aluminum-manganese nitrides. Nearer the surface, it is postulated that, the available aluminum, silicon, and manganese having been consumed, the deterioration proceeded in a similar manner to that observed in the nickel. The rate of deterioration, however, was markedly lower than for the nickel.

Discussion. A summary of the depths of penetration observed in three separate tests is presented in Table 7.

**TABLE 7. MAXIMUM DEPTH OF ATTACK OBSERVED ON
MATERIALS EXPOSED TO AMMONIA FOR
100 Hr AT 1500 F**

Test Conditions: Metal Temperature, F	Test 1	Test 2	Test 5
	1450	1450	1500
NH ₃ in Exit Gas, volume per cent	20-25	35-45	30-40

Material(a)	Maximum Depth of Attack, mils		
	Test 1	Test 2	Test 5
	1	2	5
Nichrome V	1.2	1.2 + 2.0 (lamination)	2.5
Nichrome	2.8	2.8	3.4
Inconel	3.1	5.1	2.0
AISI 330	6.0	-	6.1
Incoloy	6.2	6.8	8.6
AISI 310 S	7.7	-	-
AISI 314	8.5	-	-
AISI 347	12.8	-	-
AISI 446	14.9	-	-
Fe-Cr-Al	19.2	-	-
OFHC Copper	0.6	-	-
"A" Nickel	7.7	-	-
Chromel P(b)	7.7	-	-
Alumel(b)	2.0	-	-
Driver-Harris Alloy 242(b)	1.5	-	-
Driver-Harris Alloy 33(b)	12.5	-	-

(a) See Table 5 for composition.

(b) Thermocouple material.

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Results of this phase of the test indicated about a 30 F drift after the first 50 hr of the test. They showed that the control thermocouple in its ceramic protection tube gave a reading about 75 F higher than the true metal temperature. The control temperature in the second test was deliberately not changed, in order that Test 1 might be duplicated. The true metal temperature for these tests was therefore estimated to be 1450 F. For Test 5, the test temperature was raised to give a metal temperature of 1500 F.

The data of Table 7 suggest that the depth of penetration may be plotted as a function of the percentage of nickel in the alloys tested. A graph of this relationship is shown in Figure 10.

The curves drawn suggest that two different relationships exist between the percentage nickel in the alloy and the depth of nitrogen penetration. It is seen that the depth of penetration was progressively retarded as the percentage of nickel was increased to about 80 w/o. Beyond 80 w/o, the depth of penetration was observed to increase, except in the case of Alume1.

The left leg of the curve in Figure 10, together with the microstructures, suggests that the nickel acts to inhibit the formation of nitrides of elements forming stable nitrides. Nickel itself does not form a stable nitride. Therefore, nickel might be expected to inhibit the formation of nitrides of elements with which it is alloyed.

 

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FIGURE 10. DEPTH OF PENETRATION VERSUS AMOUNT OF NICKEL IN VARIOUS ALLOYS EXPOSED TO AMMONIA AT 1500 F FOR 100 HR

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It is thought, then, that the two curves drawn in Figure 10 represent two separate mechanisms of attack by ammonia. The left leg would seem to represent a situation wherein the attack proceeds by the formation of stable nitrides, and is inhibited by the nonformer of nitrides, namely, nickel. In the right leg of the graph, the attack is thought to proceed by an entirely different mechanism, possibly related to hydrogen penetration, or formation and reduction of unstable nickel nitrides.

The apparently anomalous behavior of Alume1 seems to support the above suggestions. In this alloy a high percentage of nickel is combined with an element forming a very stable nitride, causing the nitride-forming type of attack rather than the type of attack typical of nickel.

If the suggestion is valid that hydrogen penetration is responsible for deterioration of high-nickel alloys, the high partial pressure of hydrogen in the ammonia system would lead to faster deterioration than would activated nitrogen alone. In the reactor, only 1 atm of hydrogen in 13 atm total pressure will probably not have the deleterious effect observed in the ammonia system. Extrapolation of the left leg of the curve of nickel content versus depth of penetration to 100 w/o nickel would suggest very little penetration. Thus, provided that the suggested mechanism is correct and that the nitrogen penetration is the controlling factor, nickel would be expected to show resistance to an activated-nitrogen atmosphere containing little or no hydrogen.

In view of the results thus far obtained, it would seem appropriate to study the behavior of materials in an atmosphere more nearly simulating that to be expected in the reactor than does 100 per cent ammonia.

One way of more closely simulating the conditions to be expected in the reactor would be to provide an atmosphere consisting of a mixture of nitrogen and NH_3 . Locally, at the surface where the ammonia cracks, the hydrogen partial pressure would be higher than in the main body of the gas mixture. However, the reaction would be expected to be tempered somewhat by the presence of the nitrogen.

That the tempering would not be in proportion to the dilution is illustrated by the work of Floe*. He found that ammonia present in amounts as low as 15 volume per cent under conditions of industrial nitriding produced results similar to those obtained in atmospheres containing 85 volume per cent ammonia.

Ammonia present under the equilibrium conditions for the synthesis of ammonia comprises about 10 volume per cent of the atmosphere. As

*Floe, C. F., "A Study of the Nitriding Process", Transactions of the American Society for Metals, Preprint, No. 16 (1943).

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discussed earlier, serious deterioration of various materials was observed under these conditions, but may have been due at least in part, to the high hydrogen concentration in the atmosphere.

Pray, Peoples, and Ericson* investigated the resistance of various materials in precracked ammonia atmospheres containing 1.5 to 2.5 volume per cent residual NH_3 at 1500 F. They concluded that Illium R, AISI 347, Inconel X, and Inconel were not greatly affected by such atmospheres. A variety of other high-temperature materials were tested, and although these materials showed severe loss in room-temperature ductility, no effects were attributed to the gaseous environment.

Thus, the sum total of pertinent information suggests that materials should be studied in atmospheres containing from about 1 to about 10 volume per cent NH_3 , balance nitrogen.

Chemistry of Nitrides

J. B. Vetrano

One approach to the problem of determining the nitriding characteristics of various metals and alloys is the direct experimental method. In this method the metal or alloy under examination is exposed to a nitrogen or ammonia atmosphere at a given temperature and pressure. Following exposure the sample is examined metallographically and the depth of the nitride case determined. In this metallurgical approach to the problem the state of the specimen is a function of its history and treatment. Thermodynamic equilibrium has not usually been established, and such factors as diffusion rates and reaction rates control to a major extent the final composition.

An alternate approach is the physicochemical approach wherein the metallurgical history of the sample is not considered. The state of the specimen is defined only by its temperature, pressure, and composition. It is assumed that equilibrium has been established and that this equilibrium is independent of the path by which it was reached. This approach establishes boundaries of composition as a function of temperature and pressure, but does not take into consideration rate factors or diffusion factors. It is a thermodynamic approach.

It is the object of this section to survey the nitriding characteristics of all the elements in the periodic table, drawing both from the experimental metallurgical work and supplementing this with boundary conditions

*Pray, H. A., Peoples, R. S., and Ericson, G. L., "The Behavior of High-Temperature Alloys in Cracked Ammonia Atmospheres", BMI-269.

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determined by the thermodynamic approach. Because of the fundamental differences between the metallurgical and physicochemical approaches already mentioned, the data at times may appear to be contradictory.

In order that the material can be assembled in some logical order, each group of the periodic table will be considered separately. This approach offers the additional advantage of pointing to trends in the properties of the nitrides due to their relative position in the periodic table, and consequently allows one to predict with relative assurance the characteristics of a nitride for which no data are available.

Classes of Nitrides

It is generally recognized that metals form three distinctive classes of nitrides. These are ionic, covalent, and interstitial (or metallic). These are the same classes used to describe hydrides, and if a metal forms an ionic hydride, for example, its nitride will also be ionic.

Ionic Nitrides. The ionic nitrides are all derived from trinegative nitrogen (N^{-3}), and in this respect are analogous to the ionic hydrides which are derived from the negative hydride ion (H^{-1}). They possess a crystalline structure characterized by ionic bonding (positive metal ion and negative nitride ion).

The ionic nitrides react with water to give ammonia and the corresponding hydroxide. For example:

This behavior is analogous to that of the ionic hydrides which are readily hydrolyzed to hydrogen and the corresponding hydroxide.

Covalent Nitrides. The covalent nitrides, as their name implies, are characterized by covalent bonding, resulting from the sharing of electron pairs. The covalent nitrides of the nonmetallic elements are volatile. Those of the metallic elements are nonvolatile, and have a structure similar to carbon.

Interstitial Nitrides. Structurally the interstitial nitrides maintain the metallic structure of the parent metal with the interstices occupied by nitrogen atoms. This structure is analogous to that of the interstitial hydrides such as zirconium hydride. Because of the nature of their structure,

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the interstitial nitrides are not always stoichiometric compounds, but exhibit a variety of compositions.

The interstitial nitrides are characterized by extremely high melting points, extreme hardness, metallic conductivity, metallic luster, and chemical inertness.

Group Ia Nitrides

The only Group Ia nitride which has been reported is Li_3N . This is an ionic compound. It has a dissociation pressure of about 6.6×10^{-11} atm at 1000 F and 2.3×10^{-6} atm at 1500 F.

It is surprising that the nitrides of sodium, potassium, and rubidium have not been reported. They would be expected to form readily and to be structurally and chemically similar to Li_3N .

Group Ib Nitrides

Of the Group Ib elements copper, silver, and gold, the only nitrides which have been characterized are those of Cu (I) and Cu (II). They are ionic nitrides and are formed only by indirect methods, since elemental copper does not react with nitrogen. Both Cu_3N_2 and Cu_3N are unstable above 300-450 C.

Group IIa Nitrides

All the Group IIa elements form ionic nitrides which are characterized by the general formula M_3N_2 . Their structures are anti-isomorphous with oxides of the type M_2O_3 . Their stability decreases in the order Be_3N_2 , Mg_3N_2 , Ca_3N_2 , Sr_3N_2 , and Ba_3N_2 . The dissociation pressures of these nitrides at 1000 F and at 1500 F, are given in Table 8.

These dissociation pressures were calculated from thermodynamic data and represent the equilibrium condition. Qualitative direct experimental data in the literature indicate the Be_3N_2 is prepared by direct combination of the elements at 1000 C and that the reaction is reversible at 2200 C.

Nitrogen is said to displace hydrogen from calcium hydride to form Ca_3N_2 . This reaction has been utilized in removing traces of nitrogen from inert gas streams. The dissociation pressure of Ca_3N_2 as a function of temperature is reported as 1.7×10^{-17} atm at 1000 F and 8.5×10^{-9} atm at 1500 F. These values are in good agreement with those calculated from thermodynamic data and presented in the following table.

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TABLE 8. DISSOCIATION PRESSURES OF THE ALKALINE-EARTH NITRIDES

Compound	Dissociation Pressure, atm	
	At 1000 F	At 1500 F
Be_3N_2	7.9×10^{-23}	1.3×10^{-18}
Mg_3N_2	7.9×10^{-21}	1.5×10^{-15}
Ca_3N_2	1.4×10^{-17}	1.8×10^{-10}
Sr_3N_2	3.2×10^{-14}	8.9×10^{-11}
Ba_3N_2	2.1×10^{-12}	3.2×10^{-6}

Group IIb Nitrides

The nitrides of the Group IIb metals are ionic, but are difficult to prepare. Their stability decreases in the order Zn_3N_2 , Cd_3N_2 , and Hg_3N_2 .

Zn_3N_2 can be prepared by heating zinc dust to 600 C in a stream of ammonia. Using massive zinc and nitrogen in place of ammonia, it is much more difficult to prepare.

Cd_3N_2 is said to occur but has never been analyzed.

It is doubtful that Hg_3N_2 exists.

Group IIIa Nitrides

The Group IIIa metals scandium, yttrium, lanthanum, and the rare earths form interstitial nitrides. In general they correspond to the formula MN , but nonstoichiometric compounds are also known.

The dissociation pressures of some of the Group IIIa nitrides as calculated from thermodynamic data assembled by Kelley are tabulated as follows:

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<u>Compound</u>	<u>Dissociation Pressure, atm</u>	
	<u>At 1000 F</u>	<u>At 1500 F</u>
ScN	2.0×10^{-13}	7.1×10^{-9}
LaN	9.5×10^{-15}	9.6×10^{-10}
CeN	2.5×10^{-16}	6.3×10^{-11}

LaN is prepared by direct combination at temperatures above 450 C.

Group IIb Nitrides

The Group IIb elements boron, aluminum, gallium, and indium being less metallic, form covalent nitrides. They correspond to the formula MN. Thallium does not form a nitride.

The structure of boron nitride is very similar to that of graphite. It consists of a hexagonal unit of alternating boron and nitrogen atoms. These hexagonal rings are packed directly on top of each other. Crystalline boron nitride is very stable, subliming at 3000 C. It is inert to most reagents even at elevated temperatures, but it can be hydrolyzed by water vapor at red heat, giving ammonia and boric oxide.

Aluminum, gallium, and indium nitrides melt at somewhat lower temperatures than BN. They are readily hydrolyzed by cold water to give ammonia and the corresponding hydrated oxide. They crystallize in a Wurtzite-type lattice. AlN is formed rapidly by direct combination at 800 C.

The dissociation pressures of some of these nitrides as calculated from thermodynamic data are tabulated below:

<u>Compound</u>	<u>Dissociation Pressure, atm</u>	
	<u>At 1000 F</u>	<u>At 1500 F</u>
BN	4.8×10^{-12}	9.6×10^{-8}
AlN	1.15×10^{-20}	1.26×10^{-12}

Group IVa Nitrides

The Group IVa elements titanium, zirconium, and hafnium form interstitial nitrides which are very similar to the nitrides of the Group IIIa

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elements. Zirconium and titanium form two of the most stable nitrides known. Because of this property these metals have been extensively used as getters in gas-purification trains and in vacuum tubes. Both TiN and ZrN have dissociation pressures of about 10^{-34} atm at 1000 F and 10^{22} atm at 1500 F, as calculated from thermodynamic data.

In spite of the thermodynamic stability of these nitrides, it is apparently difficult to completely nitride the massive metal, presumably because of the impermeability of the nitride case to additional nitrogen.

Group IVb Nitrides

The nonmetallic elements of Group IVb, carbon and silicon, form stable covalent nitrides which are volatile. However, the metallic elements of Group IVb form only very unstable nonvolatile nitrides. They are probably also covalent, but their structures are not entirely clear.

The following dissociation pressures of Group IVb nitrides were calculated from thermodynamic data:

Compound	Dissociation Pressure, atm	
	At 1000 F	At 1500 F
Si_3N_4	5.2×10^{-16}	6.8×10^{-10}
Ge_3N_4	2.14×10^9	1.14×10^6

These data require comment in two respects. Firstly, it seems quite surprising that Si_3N_4 is so thermodynamically stable, and Ge_3N_4 is so unstable, since both silicon and germanium are in the same group in the periodic table. It does not seem likely that this great difference can be attributed solely to the fact that silicon is nonmetallic while germanium is metallic, since the nitrides of boron, which is nonmetallic, and aluminum, which is metallic, do not differ to this degree in respect to their stability.

Secondly, it is surprising that the dissociation pressure of Ge_3N_4 is greater at 1000 F than at 1500 F. It is difficult to escape the conclusion that Morey and Johnson are in error in the dissociation data which they report for Ge_3N_4 .

Qualitatively it is reported that Ge_3N_4 begins to evolve nitrogen when it is heated to 840 F but is not completely decomposed below 2550 F.

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Group Va Nitrides

The Group Va elements vanadium, niobium, and tantalum form interstitial nitrides which are in many respects similar to those formed by the metals of Groups IIIa and IVa. These nitrides all have melting points in excess of 2500 F, and a hardness of 8 or greater on the Mohs' scale. TaN is thermodynamically more stable than VN as can be seen from a comparison of their dissociation pressures.

Compound	Dissociation Pressure, atm	
	At 1000 F	At 1500 F
VN	2.7×10^{-7}	1.8×10^{-4}
TaN	2.3×10^{-23}	2.3×10^{-15}

Groups Vb, VIb, and VIIb Nitrides

With few exceptions, the elements in these three groups are non-metallic. Those which form nitrides probably form volatile covalent nitrides, and consequently their properties are of little concern to the GCRE.

Group VIa Nitrides

The structures of the nitrides formed from the Group VIa elements chromium, molybdenum, and tungsten are ill defined.

Chromium is said to absorb nitrogen at 800 C to give Cr₂N (nitrogen-rich phase) and CrN (nitrogen-poor phase). At about 950-1000 C, Cr₂N predominates, and at higher temperatures CrN is formed. Cr₃N, a green powder, has also been described.

It has been reported that molybdenum does not absorb nitrogen below 1000 F, but if it is heated above 1000 C in 1 atm of nitrogen and allowed to cool, it absorbs nitrogen, forming at least three compounds. Two of these are MoN and Mo₂N.

The available information on tungsten nitrides is contradictory. Probably this is so because the rate of attainment of equilibrium is slow and some workers probably never reached an equilibrium state. One source reports that nitrogen is without action on tungsten below 2000 C, at which temperature the metal begins to evaporate. Then WN₂ and possibly W₂N₃ are formed.

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The rate of dissolution of nitrogen in tungsten at 1000 F is 1.6×10^{-40} $\text{cm}^3/(\text{cm}^2)(\text{min})$ and at 1500 F is 2×10^{-27} $\text{cm}^3/(\text{cm}^2)(\text{min})$.

The following data give the solubility of nitrogen in tungsten:

<u>Temperature,</u> <u>C</u>	<u>Mg Nitrogen</u> <u>per 100 G Tungsten</u>
2400	0.38
2000	0.11
1600	0.019
1200	0.0013

The dissociation pressures of the Group VIa nitrides as derived from thermodynamic data are tabulated below:

<u>Compound</u>	<u>Dissociation Pressure, atm</u>	
	<u>At 1000 F</u>	<u>At 1500 F</u>
CrN	2.0×10^{-6}	1.2×10^{-1}
Mo ₂ N	0.4	2.72
W ₂ N	1.31	336

Group VIIa Nitrides

The structures of the Group VIIa nitrides are ill defined.

It is reported that manganese reacts with nitrogen very rapidly at 1210-1220 C, burning with a flame and forming mostly Mn_3N_2 and probably some MnN_2 . The nitrogen-poor phase, Mn_5N_2 has also been reported. This compound does not undergo appreciable decomposition below 2400 F.

It has been reported that rhenium does not form a nitride.

The equilibrium dissociation pressures of nitrogen over various manganese nitrides is tabulated below:

<u>Compound</u>	<u>Dissociation Pressure, atm</u>	
	<u>At 1000 F</u>	<u>At 1500 F</u>
Mn_3N_2	0.28	1.43
Mn_5N_2	6.2×10^{-7}	5.3×10^{-3}

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Group VIII Nitrides

Metals in Group VIII form nitrides with undefined structures.

More than one nitride of iron has been reported. Ammonia reacts rapidly with iron at 400-500 C to form Fe_2N (nitrogen-rich phase). This in turn goes to Fe_4N (nitrogen-poor phase) when heated in vacuum above 440 C. At 800 C and in vacuum, only 0.28 per cent nitrogen is present in the condensed phase. The equilibrium partial pressure of nitrogen above Fe_4N is 7.6×10^3 atm at 1000 F and 4.06×10^4 atm at 1500 F.

Detailed information on cobalt nitrides is lacking. Some sources report that cobalt undergoes reaction with ammonia to form a nitride at 470 C, but that this undergoes complete decomposition at 600 C.

The only nitride of nickel which is reported is Ni_3N , which is made by heating nickel in ammonia at 445 C. No equilibrium data is available on this compound. The solubility of nitrogen in nickel is 0.07 per cent at 450 C.

Data is lacking on the nitrides of the platinum metals, rhenium, rhodium, palladium, osmium, iridium, and platinum. However, the distinguishing characteristic of these metals is their nobility, and it is probable that they are not nitride formers.

Summary

The nitriding characteristics of numerous elements are summarized in the periodic table, Figure 11. The elements are coded as to the ease with which they form nitrides. In general, it can be seen that most of the nonnitride formers are found in Groups Ib, IIb, IVb, and VIII. Chromium, molybdenum, and tungsten in Group VIa are borderline cases.

The physical characteristics of the metals likely to exhibit some nitriding resistance are tabulated in Table 9.

Radiation Effects

W. Diethorn, P. Schall, and G. D. Calkins

Gamma and fast-neutron radiation ionize and excite gas molecules. These ionized and excited molecules often have energies many times greater than chemical-bond energies (~ 3 ev). Chemical reactions may, therefore, occur between these molecules or between a gas molecule and a

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1 H	IIa	Transition elements										IIIb	IVb	Vb	VIb	VIIb	2 He
3 <u>Li</u>	4 <u>Be</u>											5 <u>B</u>	6 C	7 N	8 O	9 F	10 Ne
11 <u>Na</u>	12 <u>Mg</u>	VIII										13 <u>Al</u>	14 <u>Si</u>	15 P	16 S	17 Cl	18 A
		IIIa	IVa	Va	VIa	VIIa				Ib	IIb						
19 <u>K</u>	20 <u>Ca</u>	21 <u>Sc</u>	22 <u>Ti</u>	23 <u>V</u>	24 <u>Cr</u>	25 <u>Mn</u>	26 <u>Fe</u>	27 <u>Co</u>	28 <u>Ni</u>	29 <u>Cu</u>	30 <u>Zn</u>	31 Ga	32 <u>Ge</u>	33 As	34 Se	35 Br	36 Kr
37 <u>Rb</u>	38 <u>Sr</u>	39 <u>Y</u>	40 <u>Zr</u>	41 Nb	42 <u>Mo</u>	43 Tc	44 <u>Ru</u>	45 <u>Rh</u>	46 <u>Pd</u>	47 <u>Ag</u>	48 <u>Cd</u>	49 In	50 <u>Sn</u>	51 Sb	52 Te	53 I	54 Xe
55 <u>Cs</u>	56 <u>Ba</u>	57-71 (Rare earths)	72 <u>Hf</u>	73 <u>Ta</u>	74 <u>W</u>	75 <u>Re</u>	76 <u>Os</u>	77 <u>Ir</u>	78 <u>Pt</u>	79 <u>Au</u>	80 <u>Hg</u>	81 <u>Tl</u>	82 <u>Pb</u>	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-96 Actinide Series															

Key to underscoring:

Key to underscoring:

Resistant to nitriding

Somewhat resistant to nitriding

Nitrides readily

FIGURE 11. PERIODIC CHART OF THE ELEMENTS SHOWING DEGREE OF RESISTANCE TO NITRIDING

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TABLE 9. PHYSICAL PROPERTIES OF SOME METALS
WHICH ARE RESISTANT TO NITRIDING

Element	Cross Section, barns per atom	Density, g per cm ³	Melting Point, C
Cadmium	2550	8.65	321
Cobalt	37.0	8.8	1495
Copper	3.69	8.96	1083
Germanium	2.35	5.36	958
Gold	98.0	19.32	1063
Iridium	430	22.5	2454
Iron	2.53	7.87	1539
Lead	0.17	11.3	327
Mercury	380	13.6	-38.9
Molybdenum	2.5	10.2	2622
Nickel	4.6	8.90	1455
Osmium	14.7	22.5	2700
Palladium	8.0	12.0	1554
Platinum	8.1	21.5	1774
Rhenium	84	20	3170
Rhodium	150	12.4	1966
Ruthenium	2.46	12.2	2500
Silver	62.	10.5	961
Tellurium	3.3	6.24	450
Tin	0.60	7.30	232
Tungsten	19.2	19.2	3395
Zinc	1.06	7.13	419

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solid or liquid material exposed to the gas. Chemical reactions of this nature which occur in reactor-gas coolants are of particular interest because reactions between the gas coolant and the reactor core or coolant-circulating system may seriously effect reactor operation. The following discussion is concerned with the nature and chemical effects of radiation-induced chemical reactions in various selected reactor-gas coolants containing nitrogen gas.

Pure Nitrogen

Atomic nitrogen is believed to be an important nitriding species in nitrogen gas-metal systems. At 1500 F, the atomic nitrogen in chemical equilibrium with molecular nitrogen is equivalent to a partial pressure of less than 10^{-14} atm. Electron-impact studies on pure nitrogen gas have shown that atomic nitrogen as well as other atomic and molecular species can exist at low pressures (<1 atm). These species are N, N* (excited), N^+ , N_2^+ , and N_2 . It may be assumed that these species will be produced in a nitrogen gas coolant by pile radiations. The detailed mechanism of formation of these unstable nitrogen species indicates that the average lifetimes of all of them, except N_2^+ , are highly pressure dependent. In view of the 3×10^{11} collisions made each second by each of these species in the nitrogen coolant at 200 psi and 1500 F, most of them will be deactivated before reaching the walls of the reactor core and coolant system. Since the lifetime of N_2^+ is less pressure dependent than the lifetimes of the other species, N_2^+ is likely to be the main species at the walls of the reactor system. It is known that the N_2^+ species dissociates on a metal surface to form a nitriding species N and an ionized nitrogen atom, N^+ . The nitriding of metal in a nitrogen-cooled reactor may, therefore, be largely the result of the reaction between atomic nitrogen from this source and the metal wall.

Nitrogen and Hydrogen

Ammonia is formed when mixtures of nitrogen and hydrogen are exposed to radiation. The reverse reaction, the radiation-induced decomposition of ammonia into hydrogen and nitrogen, also occurs. At very low gas pressures, some hydrazine is also produced in the radiation-induced decomposition of ammonia, but the yield is negligible at the high gas pressures normally used in the reactor. This discussion deals with the problem of ammonia formation in a nitrogen-hydrogen coolant in which the hydrogen partial pressure is constant and determined by the temperature of a hydride moderator. Only enough hydrogen will be added to the nitrogen coolant to prevent thermal decomposition of the hydride. A hydrogen partial pressure of 1 atm is adequate for this purpose, for the equilibrium hydrogen

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pressure of the more stable hydrides is less than 1.0 atm at the expected maximum reactor core temperature of 1500 F.

At high temperatures, some ammonia will also be produced by the thermally activated reaction between hydrogen and nitrogen. If the hydrogen-nitrogen coolant is in chemical equilibrium with the ammonia produced in the thermal and radiation-induced reactions, the concentration of ammonia at various temperatures can be calculated. Below are the equilibrium ammonia concentrations expressed in mole fraction for three selected coolant temperatures:

<u>Coolant Temperature, F</u>	<u>Mole Fraction of NH₃ at 200- PSI Total Gas Pressure</u>	<u>NH₃ Partial Pressure, psi</u>
1500	2.7×10^{-4}	0.054
1100	7.3×10^{-4}	0.147
500	2.4×10^{-3}	0.48

These values of the mole fraction and partial pressure of ammonia are equilibrium values which apply only to the case in which the hydrogen partial pressure is 1.0 atm and the total gas pressure (hydrogen + nitrogen + ammonia) is 200 psi. If the hydrogen partial pressure required to prevent thermal decomposition of the hydride moderator is less than 1.0 atm, the equilibrium ammonia concentrations will be smaller than these tabulated values. Whenever the total gas pressure is much larger than the hydrogen partial pressure, as is the case here, the equilibrium concentration of ammonia varies almost directly with the square root of the total gas pressure.

The ammonia concentration at chemical equilibrium is, of course, independent of radiation effects. The above ammonia concentrations are, therefore, the maximum values if chemical equilibrium is attained throughout the nitrogen-hydrogen coolant. However, chemical equilibrium may not be rapidly attained in some parts of the coolant system, for chemical equilibrium is approached slowly in the hydrogen-nitrogen-ammonia system below 800 F. An ammonia concentration higher than the chemical equilibrium value might, therefore, be supported in some parts of the coolant if the radiation-induced rate of formation of ammonia is high. The rate of formation of ammonia via a radiation mechanism will be a maximum in the reactor core. Chemical equilibrium will probably be established quickly here, for the coolant temperature is high. The average ammonia concentration of the coolant is, therefore, expected to be about equal to the chemical equilibrium value.

Since metals at high temperatures nitride in the presence of ammonia, the reactor core and coolant system may be nitrified by the ammonia

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in the coolant. Because the temperature of the gas coolant is not uniform, some parts of the coolant system will probably be more heavily nitrified than other parts. If the maximum concentration of ammonia at every part of the coolant system were the chemical-equilibrium value at that point, nitride formation would be a minimum in the reactor core. However, the radiation-induced rate of ammonia formation would be a maximum here; if chemical equilibrium is not attained, nitride formation might be heavy in the reactor core. Clearly, nitride formation would remove nitrogen from the coolant, change the gas-flow and heat-transfer characteristics of the coolant system, and perhaps alter the strength of materials in the reactor core. Of course, a nitride layer may form a protective layer and inhibit further nitride formation. If this is not the case, nitride formation could be a serious problem in reactor design.

It has been shown that the ammonia concentration in a high-temperature hydrogen-nitrogen gas-reactor coolant will be approximately equal to that for a mixture in chemical equilibrium with ammonia. Addition of about 1 atm of hydrogen to the nitrogen coolant before reactor startup will easily support this ammonia concentration.

The mechanism of nitride formation in a pure nitrogen coolant discussed earlier will also operate in a coolant consisting of a mixture of hydrogen and nitrogen. In this case there will be two nitrifying species; namely, ammonia and atomic nitrogen. The relative contribution of each to the over-all nitrifying process in hydrogen-nitrogen mixtures is not known.

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REACTOR-DESIGN CONSIDERATIONS

R. F. Redmond and J. W. Chastain

In pursuing a realistic and considered materials program, it has been found necessary to have a preliminary reactor design available. This is required in order that questions connected with the fabrication of possible moderator and fuel shapes can be answered. In addition, problems associated with radiation damage can be answered only when estimates of weight percentage of uranium in the fuel element and total burnup of uranium are known. Radiation damage is also sensitive to temperature which, in turn, is determined by the heat transfer and fluid-flow aspects of the reactor system.

Accordingly, a limited design study has been carried on to guide the materials work. This study remains subservient to the materials program and attempts only to provide information which is helpful in determining the proper direction for the main program to proceed.

All the design calculations have been carried out with a specified set of constants which characterize the system. These are:

L = D = 2 ft
Power = 2 megawatts
Inlet temperature = 755 F
Outlet temperature = 1150 F
Mass velocity = 16.6 lb per sec
Fuel inventory = 15 kg
Coolant = nitrogen
Pressure drop = 5 to 6 psi

The reference fuel system was chosen to be plates of stainless steel- UO_2 clad with Nichrome. The Nichrome was used as cladding because of its better resistance to nitriding. Stainless steel as the core material is a compromise in order to reduce the fuel inventory.

Initially, calculations were made for a number of variations of flat-plate type fuel subassembly. As envisioned, the fuel element will contain a number of flat fueled plates fitted into slotted side plates. The fuel element will be slipped into a circular hole in the moderator, which will be clad with Nichrome. Another possible system might use square unclad holes in the moderator with the top and bottom plates unfueled. These unfueled plates along with the side plates would protect the moderator from the coolant. In some preliminary calculations, several hydrides were studied as possible moderators. In the more careful analyses reported here, only zirconium hydride was considered.

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Results of calculations showing pressure drop, heat-transfer coefficient, and maximum center-fuel-plate temperature for three of the systems considered are shown in Figures 12, 13, and 14. In these figures, the parameters are plotted against the number of fuel subassemblies. The plate spacing for all cases was 0.100 in.

For the heat-transfer calculations, a standard Colburn relation based on a hydraulic diameter was used. The pressure-drop calculations considered the change in density in an elementary way. The maximum center plate temperatures assumed a flat radial power distribution but a cutoff cosine in the axial direction. The heat transfer coefficient calculated from flow conditions was divided by 1.5 to allow for some "hot channel factor".

For both the 0.040-in. and 0.070-in. core, pressure drop and heat transfer are satisfactory for 80 or more fuel elements. The maximum fuel temperatures are about 1600 F, which is fairly high and will intensify the radiation-damage problem. For a 0.100-in. core, about 110 fuel elements will be required to get the maximum fuel temperature below 1600 F.

The nuclear calculations were made for a number of plate-core thicknesses also. The results for plate-core thicknesses of 0.040, 0.070, and 0.100 in. are shown in Figures 15, 16, and 17. In all cases, the cladding thickness was 0.005 in. and hydrogen concentration was 6×10^{22} atoms per cm^3 . The results are shown as thermal utilization versus number of fuel elements. The solid lines were calculated from the equation

$$f = \frac{\Sigma_u}{\Sigma_t}, \quad (5)$$

where

Σ_u = macroscopic absorption cross section of uranium

Σ_t = total macroscopic absorption cross section.

The dotted lines were calculated from the equation

$$f = \frac{1}{n} (1 + B^2 L^2) (1 + B^2 \tau), \quad (6)$$

where

n = number of neutrons produced per thermal neutron absorbed in uranium

B^2 = buckling

L = thermal-diffusion length

τ = age.

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The thermal utilization calculated from macroscopic cross sections was derived for 15, 20, and 25 w/o of uranium-235 in the core matrix. The thermal utilization calculated from the "critical equation" was obtained for reflector savings of 7, 10, 15, and 20 cm.

The region in which the solid line for a given weight percentage uranium lies above the dotted line of interest is the region where a critical reactor can be obtained. For a very good reflector, such as beryllium, reflector savings of 18 to 20 cm may be possible. With zirconium hydride as reflector, only about 7 to 10 cm can be expected. Assuming a 7 to 10-cm reflector savings, only 20 and 25 w/o can be considered, and even these may be marginal.

So far no flux depression and no reactivity allowances have been made for poisoning and burnup. Estimates show the ratio of the average flux in the moderator to the average flux in the fuel element is about 2.5. This may account for about a 20 per cent lowering of the solid lines. This drop is shown for 75 fuel elements on each of the figures. In addition, to maintain a critical condition at the end of reactor life, it is roughly estimated that a 10 per cent reactivity allowance probably will be required.

Essentially, then, consideration of these two effects make even a thick core with a 25 per cent loading look extremely questionable. The most direct way to remedy this situation would be to go to higher fuel concentrations or lower cross-section cladding materials. Both of these simultaneously would help considerably but at present neither is practical. The high burnups required, 10 to 15 per cent, coupled with the higher fuel concentrations constitute a severe radiation-damage problem. Preliminary tests show that lower cross-section materials tend to nitride heavily.

On the credit side for this fuel system, it must be pointed out that so far the reactor has been considered a thermal reactor. With the compositions indicated in Figures 15, 16, and 17, the reactor is not thermal. A modified two-group analysis that will consider epithermal fissioning is planned. This should give an appreciable lift to the system. Secondly, the fuel has not been loaded into an optimum fuel arrangement. Cutting down the number of fuel plates per subassembly or the size of the subassembly or interposing moderator material advantageously will help. This reduces the ratio of average moderator thermal-neutron flux to the average fuel-element thermal-neutron flux.

In summary, the present system seems marginal nuclearwise. However, both the basis for calculation and the fuel-element geometry can be improved. Redetermination of the characteristics of the reactor on the basis of both these improvements and a low-cross-section material that resists nitriding probably would result in a theoretically sound nuclear system.

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FIGURE 12. DESIGN CALCULATIONS FOR SYSTEMS CONTAINING SIX COOLANT CHANNELS AND 40-MIL-THICK CORES WITH 5-MIL-THICK CLADDING

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FIGURE 13. DESIGN CALCULATIONS FOR SYSTEMS CONTAINING FIVE COOLANT CHANNELS AND 70-MIL-THICK CORES WITH 5-MIL-THICK CLADDING

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FIGURE 14. DESIGN CALCULATIONS FOR SYSTEMS CONTAINING FOUR COOLANT CHANNELS AND 100-MIL-THICK CORES WITH 5-MIL-THICK CLADDING

FIGURE 15. NUCLEAR CALCULATION FOR A 50-MIL-THICK FUEL ELEMENT

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FIGURE 16. NUCLEAR CALCULATIONS FOR A 80-MIL-THICK FUEL ELEMENT

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FIGURE 17. NUCLEAR CALCULATIONS FOR A 100-MIL-THICK FUEL ELEMENT

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ALTERNATE FUELS

S. L. Fawcett

The need for an alternate fuel program arises primarily because there is serious doubt that the reference dispersion-type material can withstand the required burnup (10 to 15 per cent of the uranium-235) at 1500 F without failing. Also, with other fuels some advantages may be realized from the physics and engineering design standpoint.

Based on staff experience and through the process of discussion and rediscussion, the number of alternate fuel types was narrowed to three. The first of these is bulk UO_2 or a UO_2 solid solution enclosed in a suitable clad material. Included in this category will be the PWR-type element, the SIR pin, and a Calrod element. A second alternate is a niobium-15 to 20 w/o uranium alloy, and a third choice is a zirconium-uranium hydride alloy in which maximum dilution of the uranium is obtained by alloying with moderator.

Each of the three systems will be evaluated to some extent for application to the GCRE. In some cases the early objective will be to obtain radiation damage information, while with other systems, fabrication feasibility may be approached first. Each element, however, will be evaluated from the design standpoint to indicate physical sizes, uranium loadings, etc., and thereby permit the elimination of completely unacceptable material early in the program.

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IN-PILE LOOPS

S. L. Fawcett

At the beginning of the materials research program for the GCF² it was recognized that in-pile loop tests for this program would have to be carefully integrated with the materials research. Accordingly, Battelle was assigned the following missions to aid the APB in setting up the overall in-pile loop program:

- (a) Consideration was to be given to the type of in-pile loop tests needed to supplement the materials investigation.
- (b) Recommendations were to be made to the APB concerning the feasibility of possible reactor sites for setting up the required in-pile-loop-test facilities.
- (c) Battelle was to assume the responsibility for the preparation and postirradiation examination of all test specimens for the in-pile test program.

In addition, as a part of the consideration of specific test facilities, Battelle was also requested to propose the phases of design, construction, and operation of the test facilities which it could undertake.

This section of the report presents the basic requirements for in-pile loop tests for the GCRE program and the current status and future plans of the phases of the in-pile loop program assigned to Battelle.

Basic Requirements for GCRE In-Pile Loop Tests

Objectives of In-Pile Loop Experiments

The purpose of running in-pile loop experiments is to study the behavior of reactor-core-component designs and materials under reactor-operating conditions. For the GCRE, the important core components to be evaluated are probably the fuel-element assemblies and the moderator.

The important additional information to be gained from an in-pile loop test over an out-of-pile loop test is the effect of irradiation on all materials in the test and the effect resulting from thermal gradients. Since the behavior of materials of construction and the coolant fluid as well as the

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conditions imposed by the design of the core components are interdependent, a study of these factors independently either in or out of the pile does not suffice to prove that the materials selection and the design are sound. For these reasons, in-pile tests perform a necessary and important function in the development of a reactor core.

In the particular case of the GCRE, the following information is considered to be the most important to be obtained from in-pile loop experiments. Undoubtedly, additional phenomena will be uncovered and require investigation as the tests proceed.

Fuel Element Materials

- (1) Effect of burnup at the design temperature and the design burnup rates
- (2) Effect of the gas on the cladding material (e. g., nitriding, erosion, diffusion into element core)
- (3) Effect of power cycling under irradiation.

Fuel Element Assemblies

- (1) Structural integrity under reactor conditions
- (2) Verification of design performance and fabrication methods
- (3) Corrosion and erosion of the braze material
- (4) Behavior of the braze material under power cycling
- (5) Effects of known defects in materials and construction on over-all performance.

Hydride Moderators

- (1) Structural integrity under reactor conditions
- (2) Decomposition phenomena
 - (a) Will the container material contain sufficient hydrogen overpressure to maintain equilibrium against decomposition?
 - (b) Can equilibrium be obtained if necessary by hydrogen additions to the coolant gas?

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- (c) What effect will this have on fuel elements, etc. ?
- (d) Are solid-phase reactions between hydride and container a problem ?
- (3) Ability of container-hydride interface to conduct heat away under reactor-operating conditions
- (4) Effects of defects in moderator system on over-all performance.

Coolant Gas

- (1) General behavior of gas under long-time recirculation through a reactor flux field
- (2) Effects and stability of impurities and additives under long-time dynamic flow and irradiation.

Structural Materials

- (1) Embrittling effects on structural materials from the gas atmosphere.

Loop Requirements

Considering both the objectives of the in-pile loop experiments and the probable reactor design and operating conditions, a list of basic specifications for an in-pile loop to meet these requirements is given below. The design and operating conditions were derived from the following assumptions:

- (1) The reactor system will meet the conditions given in the Sanderson-Porter Report, "Preliminary Design Study of a Closed Cycle Gas Turbine Nuclear Power Plant", dated November 30, 1955.
- (2) The core length will not be greater than 2 ft.
- (3) The fuel will be in subassembly form, the sub-assemblies will not exceed about 1.5 in. OD and there will not be less than about 40 such assemblies.

The first two assumptions appear valid unless the over-all objectives of the GCRE are drastically changed. The last assumption appears

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reasonable from the consideration of available fuel materials, the pressure drop requirements for the core, and the need to minimize the thermal-flux depression in the center of a subassembly.

In-Pile-Loop Specifications

(1) Coolant Gas

Type - Capable of using nitrogen, air, or CO₂, plus possible additives

Inlet temperature - 750 F max

Outlet temperature - 1250 F max

Flow rate - 0.415 lb/sec max

Available head across test section - 10 psi max

Ambient pressure - 200 psi max

Total heat-removal rate - 50 kw max

(2) Test-Section Size

ID 1.5 in.

Length 24.0 in.

(3) Control Requirements

Capable of steady-state operations from zero to maximum power generation, from room to maximum gas temperatures and over a range of gas flow rates. Also capable of changing from one steady-state condition to another during operation.

Note: These requirements are based on the need to test various types and loadings of fuel elements and the need to perform controlled power-cycling experiments.

(4) Measurements During Operation

Fuel-element surface temperature

Inlet and outlet gas temperature

Gas pressure and flow rate

Sample gas stream for composition

Monitor gas stream for radioactivity.

(5) Flux Requirements

The thermal-neutron flux in the GCORE core will probably be about 5×10^{12} n/(sec)(cm²). It would be

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desirable to perform accelerated tests in the in-pile loops to reduce the testing time for specified burnups. However, owing to the interrelation of several of the operation conditions, accelerated tests cannot be performed without throwing other operating parameters off of specification. Until experience is obtained to indicate unimportant parameters, it does not appear wise to design for more than a factor of two increase in neutron flux over the design requirements. Accordingly, a thermal-flux range from 5×10^{12} to 10^{13} n/(sec)(cm²) within the test section appears acceptable for the test program.

(6) Miscellaneous Requirements

Ratio of total gas volume to fuel-element surface area - $1 \text{ ft}^3/\text{ft}^2$ (order of magnitude).

Proposed Program of In-Pile Tests

Description of Tests. The program of in-pile tests outlined below is an attempt at a compromise between the normal desire to obtain a large amount of information, the time schedule for the GCRE, and the total cost of a loop program. While the detailed program may change as the work proceeds, this program represents a reasonable estimate of the required magnitude of the program. The loops have been designated as numbered facilities.

Loop Facility 1 - Reference Test. This loop would test the fuel sub-assembly and small section of clad moderator that represent the best choice of materials, designs, and fabrication techniques available at the present time. The test would be run at or near design operating conditions. The test would be power cycled by the normal shutdown periods of the reactor and possibly by short-time shutdowns at daily intervals. The test would run until some form of failure developed or to specified burnup.

The primary purpose of the test is to define the limitations of the reference core materials. Reference tests will continue as materials or design are modified.

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Loop Facility 2 - Tests to Study the Effect of Fuel Loading and Gas Additives. This loop would test short sections of fuel assemblies at design operating temperatures but at accelerated burnup rates.

The effects of variations in UO_2 -particle size, fuel loading, core and clad materials, and gas additives would be investigated. The loop test would be used as a preliminary in-pile screening evaluation.

Loop Facility 3 - Tests of Alternate Systems. This loop would be used to test alternate materials and designs and long-range development materials including those of interest to civilian application. It might also be used as a backup for the other loop facilities in case a crash effort on some phase of the program is required.

Specimen Requirements. Since in-pile loop tests are primarily engineering tests, fuel assemblies rather than single-plate specimens are the most desirable type of fuel specimens. Parallel-plate assembly configurations will be used as a reference design until or unless the design contractor's studies indicate another configuration to be preferable.

Canned moderator specimens in tubular shape can probably best simulate reactor conditions in the loop test.

In-Pile Test Loop at the Battelle Research Reactor

In the latter part of June, 1956, Battelle was authorized to proceed with the design, construction, and operation of an in-pile test loop at the Battelle Research Reactor.

The design of this loop facility has been initiated. It is contemplated that this loop will be designed to operate completely submerged in the reactor pool with the test section adjacent to the reactor core. It is planned that this facility will meet the requirements of Loop Facility 1 (The Reference Test). The target time schedule for this loop facility sets the date for commencement of in-pile tests at March 1, 1957.

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Design Studies for Future Loop Facilities

A conceptual design study for a GCRE loop facility in the ETR is in progress. It is expected that a conceptual design will be presented to the APB for consideration early in August, 1956.

It is possible that the loop design for the Battelle Reactor may be suitable, with some modification, for use in one of the graphite through-holes in the MTR. However, both the extent of modification required and the perturbed flux available in this location make the advisability of establishing such a loop facility questionable. When the detailed loop design for the Battelle Reactor is sufficiently firm, this possibility will be considered with MTR operating personnel and arrangements will be made to obtain experimental measurements of the flux level in the proposed MTR through-hole. It is expected that this will be accomplished to the extent that a decision can be reached by November, 1956.

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PROGRAMMATIC STUDIES

Donald L. Keller

Previous sections of this report have dealt with a survey and in some cases the selection of materials which seem most applicable for the GCRE. On the basis of this work and related experience, Battelle has begun a substantial number of research programs which, it is felt, will contribute markedly to the know-how of possible core materials for a small gas-cooled reactor experiment. The purpose of this section is to outline some of the main objectives of these programs.

Several of the programs have been completed, others are progressing, while still others have only recently been initiated. The results of these studies will be reported in Battelle's monthly progress reports and will be the subject of the second report in this series for the GCRE.

Moderator

As a result of the survey of metallic hydrides, zirconium hydride appeared most suited for the GCRE. Further, the delta-epsilon phase material with a composition of $ZrH_{1.6}$ to $ZrH_{1.9}$ appears most desirable, since this alloy is less susceptible to hydrogen migration, and therefore more stable, and contains more hydrogen per unit volume than does the beta-phase material. Some undesirable qualities are present. The most pronounced is its apparent brittleness, which may render it more difficult to fabricate.

The following outline lists some of the objectives of the moderator programs. Calcium hydride is an alternate choice, although not a strong one at the present time.

- (1) Determine the resistance to attack of zirconium and calcium hydride to nitrogen at 1500 F and 200 psi.
- (2) Through compatibility tests, investigate the extent of reaction between calcium and zirconium hydride and potential cladding materials.
- (3) Determine some high-temperature mechanical properties of delta-phase zirconium hydride.

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- (4) Measure the thermal conductivity of calcium and delta-phase zirconium hydride.
- (5) Develop procedures for hydriding massive zirconium to delta hydride without cracking.
- (6) Develop a technique for cladding delta-phase zirconium hydride and determine the quality of the cladding.
- (7) Determine the ability of clad moderator specimens to retain hydrogen over long periods of time under imposed thermal gradients.
- (8) Determine the effect of gap spacing between clad and hydride on the thermal conductivity and central temperatures of hydride bodies of various sizes and shapes.
- (9) Investigate the effects of radiation on delta-phase zirconium hydride.

Control

A high-cobalt alloy, Stellite 21, was selected as the reference control material for the GCRE. The choice is known to be marginal because of the grayness of cobalt, and consequently, other possible control materials are receiving equal attention. Some major objectives of the controls program are as follows:

- (1) Determine the control effectiveness of Stellite alloys and measure their resistance to nitriding.
- (2) Evaluate the effect of radiation on boron and boron compounds both as naked powders and as dispersions in various metal matrices. This is being done at Battelle as part of the Navy's control program. The most promising materials will be evaluated by post-irradiation heat treating at the higher temperatures of interest to the GCRE.
- (3) Evaluate the fabrication, nitriding-hydriding resistance, and control effectiveness of cobalt-base rare-earth oxide dispersions.

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- (4) Survey the literature for cadmium compounds which might possess both high temperature stability and compatibility with high-strength metal alloys.

Reference Fuel Element

The reference fuel element is a stainless steel- UO_2 -type dispersion element. Even though this selection was based on the general success of extensive development work with this type of element, its performance under GCRE environments raises many questions. Research work aimed at answering these questions have the following objectives:

- (1) Determine as soon as possible the radiation-damage resistance of reference fuel-element specimens under GCRE conditions.
- (2) During the interim of establishing reference burnup, fuel loading, dimensions, and materials, plus the time required for specimen fabrication, encapsulation, irradiation, and postirradiation examination, other radiation-effects programs are needed. These have the following objectives:
 - (a) Evaluate, by postirradiation heat treatment, UO_2 -dispersion-type fuel elements which have been irradiated at temperatures lower than 1500 F.
 - (b) Irradiate and evaluate "near-reference" UO_2 -dispersion-type elements previously fabricated for other irradiation programs.
- (3) Develop satisfactory techniques for fabricating fuel elements and subassemblies from at least one set of materials possessing satisfactory resistance to nitriding and establish the limitations of some of the other materials.
- (4) Determine the resistance to deformation of reference fuel elements and subassemblies at temperatures up to 1500 F over extended time periods.
- (5) Fabricate reference fuel-element specimens for radiation studies and full-scale subassemblies for in-pile loop testing.

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Nitriding Studies

Initial tests to find a material completely resistant to nitriding under severe conditions were not successful. Further studies will be directed at testing materials in gas environments that will simulate more closely those experienced in the reactor. These studies will include:

- (1) Testing and evaluating materials in an atmosphere of 1 volume per cent NH_3 -balance nitrogen.
- (2) Determining the effect of reactor radiations on coolant gas-metal reactions.

Alternate Fuels

The development of an alternate fuel for the GCRE is progressing with the following objectives:

- (1) Nuclear calculations will be made on the alternate systems to determine the critical mass for a range of geometries and weight percentages of uranium-235. The heat-transfer characteristics and the pressure drop will be investigated to insure a feasible system. The alternate materials will be considered in the order UO_2 , uranium-niobium, and $(\text{U-Zr}) \text{H}_2$.
- (2) Investigate the fabricability of niobium-15 to 20 w/o uranium alloys. Once a satisfactory technique is developed, specimens will be prepared for irradiation tests.
- (3) Investigate the fabricability of a Calrod-type element with a UO_2 core.

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