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SODIUM AND BISMUTH LIQUID METAL FUEL SYSTEMS;
A LITERATURE SEARCH TO JUNE 30, 1957

by

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ABSTRACT

The literature on sodium, NaK, and bismuth liquid metal reactor fuel systems is reviewed to June 30, 1957. The various criteria which have been used for the selection of liquid metal fuel carriers are discussed. Corrosion information on each fuel carrier is summarized and some discussion of the fabricability of components from possible materials of construction is included. Work done on the testing of various fuel concepts for each carrier is indicated.

I. INTRODUCTION

A. Statement of Problem and Method of Attack

Fluid fuel systems for reactors have a number of advantages which suggest exploitation. One of the most important advantages of a fluid fuel system is the opportunity for high burn-up without the physical deterioration that thereby accompanies the use of solid fuel elements. The simplicity of fuel preparation, as compared to the fabrication of solid fuel elements, is also important.

In comparison with the aqueous homogeneous reactor schemes, liquid metal systems have several advantages. Among these are the following:

- (a) higher temperatures of operation - the homogeneous aqueous reactor systems are generally considered to be limited to the temperature of the critical point of water, 374 C, while few liquid metals boil below 800 C;
- (b) lower pressure of operation - the pressures in liquid metal-fueled reactors are in general limited to the hydrostatic head of the liquid metal which, for heavy metals, can be as high as 200 to 300 psi, which is small compared with the 2000 to 3000 psi of the aqueous homogeneous reactor systems;* and

*However, at high temperatures and in large pipe sizes the heavy metals impose a substantial structural problem. Thus, a 10-inch bore pipe carries a bismuth load of about 330 lb/ft at 540 C. According to C. D. Boadle⁽¹⁾ much of the advantage of the low pressure of the reactor is lost in the high structural loads which must be supported in the piping if the heavier liquids are employed.

- (c) lack of appreciable gas evolution - in the aqueous homogeneous reactor deuterium and oxygen are formed, due to radiolytic decomposition of D_2O .

Since a research program directed at the development of fluid fuels for nuclear reactors might have important results, a literature search was undertaken. This search covers the following general categories: sodium, sodium-potassium alloys, bismuth and its pertinent alloys, slurries in liquid metals, and liquid metal-fueled reactor concepts. A more extensive literature search would also have considered other possible liquid metal systems. Time limitations, however, dictated that consideration be restricted to sodium and bismuth systems. The literature was searched through June 30, 1957. Since that time, there has been a considerable volume of literature which is not covered in this report. Aqueous homogeneous and fused salt reactors were, in general, excluded from consideration.

The plan which will be used in presenting this information is the following. The various criteria that have been used by other investigators for selection of liquid metal fuel carriers will be reviewed. The liquid metal carriers for the fuel will be used as a primary basis of dividing the information rather than considering, for example, slurries of uranium dioxide in all liquid metals. The reason for this is that the corrosion problem in handling liquid metal fuels is of great, if not controlling, importance, and this problem is largely a function of the carrier.

In the discussion of the results, the corrosion information available for the particular liquid metal fuel carrier will be summarized. Then the work done on the various fuel concepts using a given liquid metal will be presented. For example, the information on plutonium solutions in bismuth, uranium solutions in bismuth, and uranium dioxide slurries in bismuth will be given.

B. Liquid Metal-Fueled Reactors Previously Considered

1. General Types of Reactor Core Systems

Several reactor core systems based on fluid fuels have been proposed. For example, the fluid fuel might be held in a calandria through which a coolant is circulated. This coolant might be either a liquid metal or a gas. Falkenberry⁽²⁾ has, for example, described a reactor in which a liquid metal fuel is held in a graphite core structure cooled by helium. The helium might be used directly to run a gas turbine power plant. The reactor system might also consist of a vessel and an external boiler-heat exchanger through which the fluid fuel might be pumped. A related type of liquid metal-fueled reactor (with gas-cooled heat exchanger) has been considered in detail by Raytheon.⁽³⁾ The fluid fuel could also be

completely sealed in small cans, each having a void at the top for the accumulation of fission product gases.⁽⁴⁾ This system has been described by Finniston.⁽⁵⁾ Another possibility might be to place the fluid fuel in cans to which charging and discharging pipes are fitted. The plumbing on this type of system could, of course, become quite complicated.

Several more novel designs have been proposed which are aimed at solving the materials problems for the heat exchanger. These include a centrifugal fluid fuel reactor⁽⁶⁾ and a concept⁽⁷⁾ in which it is proposed that the cooling of the liquid metal fuel be accomplished by boiling a liquid metal contained in the fuel. Liquid metals have large heats of vaporization and therefore could be quite effective.

2. Specific Fluid Fuels

a. Uranium Dissolved in Bismuth

Brookhaven National Laboratory in many publications has discussed the feasibility of using a solution of uranium dissolved in bismuth.⁽⁸⁻¹³⁾ This concept was considered by the MIT Reactor Technology group in 1952 for plutonium production.⁽¹⁴⁻¹⁶⁾ A group of industrial concerns assigned personnel to Brookhaven for a study of this reactor. Their efforts were summarized⁽¹⁷⁾ in 1955. More recently Babcock and Wilcox has assumed the responsibility for the construction of a small liquid metal-fueled reactor of this type. Babcock and Wilcox feels that there are still a rather large number of problems to be solved.⁽¹⁸⁾ The British also have a program based on liquid metal-fueled reactors using uranium dissolved in bismuth as a fuel.^(19,20) In most of the above concepts the reactor fuel itself is pumped through a heat exchanger. Another liquid metal is in turn used to transfer the heat to steam. However, in some versions of the British concept⁽²⁰⁾ the liquid metal core is internally cooled. This fluid fuel system has the disadvantage of rather limited solubility of uranium in bismuth.

b. Plutonium Dissolved in Bismuth

A fluid fuel of the true solution type which has been considered is a solution of plutonium in bismuth.⁽²¹⁾ This reactor would consist of a fixed fluid fuel in a calandria through which a liquid metal coolant, probably also bismuth, is circulated. The solubility of plutonium in bismuth is apparently high enough to make a fast reactor possible.

c. Iron-Plutonium Eutectic

The fast reactor group at Los Alamos have been designing a fast fluid fuel reactor.⁽²²⁾ This reactor is different from those previously mentioned in that the concentration of fissionable material is

considerably higher. Eutectic alloys of plutonium with iron, nickel, and cobalt all have melting temperatures in the vicinity of 400 to 450 C. Other alloys which the Los Alamos group mentions are the magnesium-plutonium and the bismuth-plutonium systems. Their compilation of interesting fuel alloys is given in Table 1. The alloy they are most seriously considering is the iron-plutonium eutectic. The coolant, which may be sodium, will be circulated through the core.

Table 1

POSSIBLE FLUID FUEL ALLOYS^a

Alloy	Eutectic Composition, atom per cent	Melting Point, C	Density, g/cc
Pu-Fe	9.5 Fe	410	16.8
Pu-Co	10 Co	405	16
Pu-Ni	12.5 Ni	465	16
Pu-Mg	85 Mg	552	3.4
Pu-Bi	non-eutectic	271-900	

^a"Lampre - A Molten Fuel Reactor Concept," LA-2112 (May 1957).

d. Uranium in Iron, Nickel, or Cobalt

The use of uranium dissolved in iron, nickel, cobalt, or manganese has been mentioned as a possible fast reactor fuel.^(14,23,24) The eutectics all melt between 700 and 750 C and thus are not particularly attractive.

e. Uranium Dioxide Slurries in Sodium

Slurries of uranium dioxide in sodium or sodium-potassium alloy have been considered as possible fluid fuels for reactors.^(25,26,27,48-56) These are in the laboratory stage of development. The reactor concept using these slurries is not yet definite. In Frost's opinion⁽¹⁹⁾ it is unlikely that a slurry would ever be considered seriously for a fast reactor system unless it were canned, since it is very important that the fissile material be homogeneously dispersed throughout the core.

f. Other Slurries

A number of other slurries have been considered^(5,28,29) for example, USn_3 in tin, and UPb_3 in lead. However, these have not been brought to a firm stage of development.

II. CRITERIA FOR SELECTION OF LIQUID METAL FUEL CARRIERS

Although this literature search has been restricted to bismuth and sodium-base fuel carriers, it is appropriate to re-examine the criteria for selection of liquid metal fuel carriers.

A. Operating Temperature Range

In a nuclear power plant costs may be an optimum at some lower operating temperature than those considered necessary in a conventional plant. For example, a study by North American Aviation, Incorporated⁽³⁰⁾ indicates that neither extremely high temperature systems nor extremely low temperature systems are desirable. These writers feel that the optimum fluid fuel for power recovery may be one that permits operation in the medium temperature range from 500 to 800 F.

B. Nuclear Criteria

In thermal systems the solvent must have a low thermal capture cross section. According to Frost⁽¹⁹⁾ the cross section for sodium of 0.45 barn is about the maximum acceptable. According to Addons⁽¹⁴⁾ the proper criterion for cross section should be one barn for a thermal reactor. It is, of course, difficult to set a cross-section requirement, since it is also necessary to consider how much of the particular element will have to be introduced into the reactor. Semi-quantitative limits on the amount of carrier material of a particular cross section which can be added to the fuel may be estimated by a procedure suggested by Teitel.⁽³¹⁾

For fast reactor systems, the fuel carrier is less restricted by cross-sectional requirements than for thermal reactors. Addons, et al.,⁽¹⁴⁾ felt that for fast reactors the neutron cross section of the fuel carrier for 1-Mev neutrons should be less than 0.01 barn. He states that this criterion excludes all elements heavier than cobalt, except such elements as rubidium, strontium, barium, lead, and bismuth.

Moderating materials should also be absent in a fast reactor. A criterion which has been used is that the atomic weight should be over 20 to avoid undue moderation.⁽¹⁴⁾

If degradation of the neutron spectrum is undesirable, due to the presence of materials of high thermal capture cross section, the fuel carrier also should have a low inelastic scattering cross section. Boadle⁽¹⁾ points out that both lead and bismuth have inelastic scattering cross sections which may lead to appreciable neutron degradation. However, in a recent paper⁽²¹⁾ calculations indicate that a plutonium solution in bismuth is feasible as a fast reactor fuel. These authors specifically state that "Recent experiments in Zephyr with lead and bismuth envelopes show that

the neutron spectrum in the envelope is appreciably harder than in the uranium envelope and we may conclude that inelastic scattering is not so important in the mechanism of neutron energy degradation."

In view of the rather vague nuclear criteria for fast reactors it seems best to place emphasis on physical criteria, such as melting point, and on the feasibility of developing a compatible fuel system for a particular liquid metal carrier rather than to eliminate it through nuclear consideration alone.

C. Criteria for Physical Properties

1. Melting and Boiling Points

For all types of liquid metal-fueled reactors Frost⁽¹⁹⁾ suggests that the fluid media should have a melting point of less than 400 C for ease of start-up. He also suggests a boiling point of over 800 C to minimize evaporation or distillation troubles in the circuit. Acceptance of both of these criteria should be qualified. If one must externally heat the reactor at start-up it is difficult to set an upper limit. The limit of 400 C seems a practical one. However, it is undesirable to omit systems which might possibly have other extraordinarily good properties. This limit should therefore be quite flexible.

The lower limit of 800 C for the boiling point of the liquid metal fuel carrier which Frost selects should also be used with care. It is possible that a reactor might be cooled by boiling metal. Because of the rather large heats of vaporization of metals it is estimated by Addons, et al.,⁽¹⁴⁾ that the volume of cooling fluid required would be considerably less than that for liquid cooling. A heat exchanger of the tubular or other thin-walled type would be avoided. A condenser would be required, but it would not be in contact with the fuel itself. It therefore seems appropriate to ignore the boiling point criterion proposed by Frost since it is conceivable that a low boiling material might be advantageously used. In Table 2 are presented possible metals with melting points of less than 850 C. This high melting point is selected so that metals forming a low melting binary or ternary system will not be excluded. All systems composed of one or more of these elements should be seriously considered as liquid metal fuel carriers. The metals with high thermal cross sections might possibly be useful in fast reactors and are therefore included.

2. Other Physical Properties

There are other questions concerning the physical properties of a liquid metal fuel carrier which must be asked before it is seriously considered. If this reactor is cooled by circulation of the fuel through a

heat exchanger, the heat capacity and the viscosity of the liquid metal fuel are important. Most liquid metals have relatively low viscosities. Therefore, this property should not exclude any liquid metal fuel carrier in the early phase of consideration.

Table 2

METALS MELTING BELOW 850 C WHICH MIGHT
FORM LIQUID METAL FUEL CARRIERS

Element	Melting Point, C	Cross Section for Thermal Absorption, barns
Lithium-7 ^a	186	0.033
Sodium	98	0.45
Magnesium	651	0.06
Aluminum	660	0.21
Phosphorus	44	0.20
Sulfur	119	0.49
Potassium	62	2.0
Calcium	810 (850)	0.43
Zinc	420	1.1
Gallium	30	2.7
Arsenic	500	4.1
Rubidium	39	0.70
Strontium	750-800	1.2
Cadmium	321	2400
Indium	155	190
Tin	232	0.65
Antimony	630	5.5
Cesium	285	29
Barium	830 (850)	1.2
Lanthanum	826	8.9
Cerium	640 (600)	0.70
Mercury	-39	380
Thallium	304	3.3
Lead	327	0.17
Bismuth	271	0.032
Plutonium	640	-

^aThe high thermal neutron absorption of natural lithium is due to the lithium-6. Lithium-7 has a sufficiently light nucleus to be useful as a moderator.

D. Containment Criteria

In spite of the fact that it is rather obvious to indicate that a fluid fuel must be containable, the containment of fluid fuels is one of the very serious problems. The container material must not suffer appreciable corrosion even under conditions of thermal gradient, high flow rates, and, in the case of slurry fuels, erosion due to particulate matter. The container should also not react with the fissionable material dissolved or suspended in the liquid metal fuel carrier. It is desirable that fission products of high specific activity or high cross section not be removed from the fuel by the container material. In a thermal reactor the container material must be of reasonably low cross section. The material selected should also be reasonably cheap, available and fabricable into reactor components.

During the course of reviewing the corrosion work, several valuable references of a general nature were found. Antone D. S. Brasunas^(32,33) has outlined some of the general principles which should be observed in conducting corrosion studies in liquid metal systems. In particular, he points out that simple weight loss observations can be misleading. He suggests that crude bend tests may be quite valuable for guidance. Eldred⁽³⁴⁾ presents work carried out at Cambridge between 1950 and 1953 on the interactions between solids and liquid metals. He discusses various mechanisms of liquid metal corrosion and points out interesting and unusual specific corrosion cases. These investigators screened eight liquid metals against 23 solid metals. Taylor⁽³⁵⁾ discusses mechanism of inhibition of liquid metal corrosion in a general way. Gurinsky⁽³⁶⁾ has discussed the problems in finding a container material for the uranium-bismuth system in general terms.

Corrosion data on specific systems will be discussed later.

III. SODIUM AND SODIUM-POTASSIUM ALLOYS

A. General Information

There are good summaries available describing the properties of sodium. There is, for example, an American Chemical Society Monograph by M. Sittig (American Chemical Society Monograph on Sodium). It will, therefore, be necessary to mention only a few of the properties of particular significance to our purpose.

Sodium melts at 97.8 C and boils at 881 C. The vapor is partly dimeric. Sodium burns readily in a normal atmosphere to form dense fumes of oxide. The action of sodium on contact with the atmosphere is

important in that the end product is Na_2O , which results in a considerably increased attack on metal containers. Sodium contracts on freezing in a normal manner, as contrasted to bismuth which expands on freezing.

Potassium melts at 63.7 C and boils at 753.8 C. The sodium-potassium phase diagram may be found on Page 33 of the Liquid Metals Handbook Supplement. A reasonable range of composition is liquid at or near room temperature, while the eutectic composition freezes at -12.3 C. The sodium-potassium alloy reacts similarly to sodium with the exception that it is generally more reactive. When exposed to oxygen, potassium oxidizes finally to the superoxide, KO_2 , which is the stable oxide at room temperature and one atmosphere pressure. However, the oxide which precipitates from solution in sodium-potassium alloy at 200 C is entirely sodium monoxide. Explosions in handling potassium may be attributed to the formation of KO_2 and the subsequent reaction of the superoxide with the hydrocarbon under which the potassium has been stored. An explosive carbonyl is formed when potassium reacts directly with carbon monoxide.

Sodium and sodium-potassium alloys, although similar in many respects, have some distinctly different characteristics. Except for the higher melting point the physical properties of sodium are more advantageous for reactor work than those of the alloy. A comparison of the physical properties is given in Table 3.⁽³⁷⁾ Sodium has a higher specific heat, higher thermal and electrical conductivities, and a lower thermal-neutron absorption cross section. The higher melting point of sodium creates problems of preheating but has utility in providing frozen seals. Sodium-potassium alloy is easier to use than sodium within a piping system, primarily because of its lower melting point, which eliminates the tendency of sodium to freeze and plug. Sodium is easier to handle in air because it is less reactive and, being solid at room temperature, it forms a protective coating of oxide.

Table 3

COMPARISON OF PHYSICAL PROPERTIES OF Na, K, and NaK^a

	Heat Capacity, $\frac{\text{cal}}{(\text{g})(\text{C})}$ at 600 C	Thermal Conductivity, $\frac{\text{cal}}{(\text{sec})(\text{cm})(\text{C})}$ at 500 C	Thermal Neutron Absorption Cross Section at 2200 m/sec, barns
Sodium	0.2998	0.1596	0.45
Sodium-potassium (56% Na)	0.248	0.0675	1.1
Potassium	0.1825	0.0898	2.5

^aHurst, R. and McLain, S., Progress in Nuclear Energy, Series IV, Trocki, T., et al., Sodium and Sodium Potassium Alloy for Reactor Cooling and Steam Generation.

B. Containment

Kelman, Wilkinson, and Yaggee(38) and Epstein and Weber(39) have summarized the early available static and dynamic corrosion data pertaining to the corrosion of metals by liquid sodium and sodium-potassium alloys.

Several experimental heat transfer systems using sodium and NaK have been operated for extended periods at temperatures up to 540 C. There is also some experience in dynamic systems at temperatures as high as 815 C.(40)

In Table 4 are presented materials that, according to the Liquid Metals Handbook Supplement, are sufficiently good as container materials to be considered for long-term use for sodium and sodium-potassium alloys. The Liquid Metals Handbook Supplement in an expanded table of this type indicates many other materials which are borderline in performance.

Table 4

RESISTANCES OF MATERIALS TO LIQUID SODIUM AND SODIUM-POTASSIUM ALLOYS

G = Good - Consider for long term use
L = Limited - short time use only
U = Unknown

	Temp C:	500	600	700	800	900
Ferrous Metals						
Armco Iron		G	G	G	G	G
18-8 Stainless Steels		G	G	G	G	G
Type 310 SS		G	G	G	G	G
Ferritic SS (27 Cr)		G	G	G	G	G
Fernico (28 Ni, 18 Co)		G	G	U	U	U
Nickel and Nickel Alloys						
Nickel		G	G	G	G	G
Inconel (13 Cr, 6.5 Fe)		G	G	G	G	G
Nichrome (15 Cr, 25 Fe)		G	G	G	G	G
Hastelloy A B C		G	G	G	G	G
Monel (30 Cu)		G	G	L	L	L
Refractory Metals						
Niobium		G	G	G	G	G
Molybdenum		G	G	G	G	G
Tantalum		G	G	G	G	G
Titanium		G	G	L	L	L
Tungsten		G	G	G	G	G
Zirconium		G	G	U	U	U
Chromium		G	G	G	G	G
Other Metals						
Co and High Co Alloys		G	G	G	G	G

According to the Liquid Metals Handbook Supplement most early workers selected type 347 stainless steel. Thus, most of the sodium systems which have been built and operated for any length of time have been made principally from this material. However, in later work type 304 stainless steel has proved to be as resistant to corrosion as type 347. At the present time, it is believed that for long time service at temperatures about 500 C stainless steel 304 is to be recommended.

A number of other materials have been exposed to static screening tests. In general, they seem to be as resistant to corrosion in sodium as the austenitic stainless steels. Inconel, Inconel X, and pure nickel all give every indication of satisfactory performance in sodium up to 540 C.

The most significant operating experience with sodium and sodium-potassium alloys has been accumulated in two experimental systems - a large-scale heat-transfer system operated at KAPL, and EBR-I. The heat-transfer system at KAPL used sodium in the primary circuit and sodium-potassium alloy in the secondary loop. Steam was then generated by the sodium-potassium alloy. The piping circuits for the liquid metal were constructed of type 347 stainless steel. L-nickel was used in the heat-exchanger tubes. The rated heat throughput of this system was 2.35 megawatts, with a design maximum sodium temperature of 510 C at the heater exit. The rated temperature difference was 150 C. The system operated very satisfactorily for more than 8000 hours, which included 500 hours at temperatures of 560 to 650 C. In later tests the secondary circuit for sodium-potassium alloy was eliminated.

The EBR-I represented the first use of alkali metals in reactor cooling. The maximum operating temperature was around 300 C. Two coolant circuits in series were used. Both the primary or reactor circuit and the secondary or steam-generation circuit use the sodium-potassium alloy (78 weight per cent potassium). Nickel and stainless steel are the materials of construction used. Although EBR-I operates at a relatively low power level, it has successfully operated for a rather long period of time.

It was recognized early in laboratory investigations that oxygen accelerated the corrosion of metals by the alkali metals. Oxygen in sodium above 500 C accelerates the attack on ferrous alloys and, on metals such as zirconium, forms brittle surface layers of absorbed oxide in solid solution. In high concentrations (above 0.1 per cent) sodium oxide will attack stainless steel intergranularly, producing an embrittled surface layer which cracks upon deformation. The oxygen content can be minimized by a cold-trap method since the oxide is less soluble at lower temperatures. For example, the solubility at 149 C is about 0.001 weight per cent oxygen;

at 204 C, 0.003; at 315 C, about 0.015 weight per cent. The precipitation can take place in a crystallizing tank filled with steel wool fiber to facilitate growth of oxide crystals. With the use of this type of oxygen control, it has been possible to operate large-scale systems at a level of 50 ppm oxygen.⁽³⁷⁾ Operation at oxide levels in this region results in extremely low corrosion rates.

Carbon is an important impurity in sodium if the austenitic stainless steels are being used. These carburize in the presence of excess carbon. This hard brittle layer of carburized material reduces the ability of the material to deform plastically.

According to Trocki, et al.,⁽³⁷⁾ the oxygen control has satisfactorily solved the corrosion problem and little further work is going on at the present time. However, R. A. Baus, et al.,⁽⁴¹⁾ have done some work on the redistribution of radioactive stainless steel constituents in sodium. The rate of transfer is seriously accelerated by increases in oxygen level and temperature.

C. Status of Sodium and Sodium-Potassium Alloy Containment Problem

Boadle⁽¹⁾ summarizes the containment problem for sodium and NaK by stating that it is now possible to select structural materials and equipment for service up to 500 C. For temperatures over 600 C much of the data relating to liquid sodium is more fragmentary, and it is probably not safe to extrapolate existing data up to temperatures of 700 to 750 C without further confirmation. Further information is offered by those working on SIR.⁽⁴²⁾ They report that leakage occurred in the heat exchangers of the sodium reactor plant. Leaks were originally confined to one superheater and its piping. Subsequent investigation revealed leakage also in the associated steam generator. The British at Harwell contracted with Foster Wheeler, Ltd. to construct and run a steam generating loop with sodium.⁽⁴³⁾ This loop developed a leak after 348 hours. It is thought that this leak was caused by chloride-induced stress corrosion from the steam side. This corrosion problem was aggravated by the alkaline solution then formed by the sodium leaking into the water side of the loop.

D. Fluid Fuel Systems Using Sodium or Sodium-Potassium Alloy as a Carrier

1. UO₂

The sodium-UO₂ system is of the comparatively non-reactive slurry type.⁽¹⁹⁾ This means, according to Frost's definition, that in a reactor fuel system difficulty might be expected in getting the

liquid metal carrier to wet the dispersed phase, but that less difficulty should be experienced due to particle growth because of the low solubility. Teitel^(29,44,45) did some of the early work on dispersions of uranium tetrafluoride and uranium dioxide in sodium and found these compounds to be wetted. Livey and Murray⁽⁴⁶⁾ have carried out a general study of wetting of uranium dioxide, uranium carbide, and other materials by sodium and other materials of interest. Their work is an excellent general reference.

B. Abraham and H. E. Flotow have recently been working with dispersions of uranium dioxide in sodium-potassium alloy. In 1955 they⁽²⁷⁾ discussed some of the general aspects of slurry fuels. The selection of sodium and sodium-potassium alloys through nuclear and containment considerations limits the compounds to be considered because of the reactivity of the carrier. Since these investigators feel that the operating temperature may be as high as 700 C (higher than suggested in Section II), the thermodynamically stable compounds are limited to the dioxides, and possibly the silicides, nitrides, or carbides of uranium and plutonium. Abraham suggests that plutonium dioxide will be reduced to a lower oxide.

Settling experiments were carried out, using irradiated uranium dioxide. In the early experiments the material settled out at 500 C before the tube could be scanned. If the particles have settled according to Stokes' Law, at least half would have remained suspended for 2.5 minutes. This clearly indicated that the solid was agglomerated. The difficulty was caused by using uranium dioxide with a slight excess of oxygen, i.e., $\text{UO}_{2.03}$. Much better results were obtained using $\text{UO}_{2.00}$.

Abraham built a small pump circulation loop designed to operate at room temperature. This was operated on $\text{UO}_{2.04}$ at a concentration of 5 volume per cent. A flow rate of 5.2 feet per second was required to give a uniform composition in the sump of the loop. Ten minutes after the pump was turned off, the composition in the sump was uniform and corresponded to 23 volume per cent. It was reported that the pumping characteristics of the 5 volume per cent slurry were essentially indistinguishable from those of the pure carrier. However, the pressure drop and pump power consumption rose sharply when the uranium dioxide concentration was increased to 10 volume per cent. A flow rate of 7.4 ft/sec was then required to maintain a uniform concentration in the sump.

A high-temperature loop was next built by Abraham. The circulating volume was 133 ml. The contents were circulated by means of an electromagnetic pump. During the course of the experiment, it was observed that as the temperature in the slurry exceeded 500 C, the flow rate dropped from any fixed value in the range of 3 to 8 ft/sec to as low as 1.3 ft/sec in a matter of minutes. Scanning of the system by a counter indicated none of the irradiated uranium dioxide in suspension. However,

as soon as the temperature was reduced to 480 to 490 C the flow rate returned to the value commensurate with the pump power, and the uranium dioxide was completely suspended in a matter of seconds. This effect was reversible. These experiments were carried out for 300 hours at room temperature and for 400 hours between 400 and 600 C. In a particle-size distribution determined outside the system, the amount of 2- to 3-micron particles increased at the expense of the 0- to 2-micron particles. Similar behavior was observed when uranium dioxide was heated in vacuum, so no significance was attached to the change by Abraham.

Abraham built another loop to clarify the questions of high-temperature settling. The uranium dioxide was very carefully prepared to be close to $\text{UO}_{2.00}$. The high-temperature settling phenomenon was again observed. Powdered uranium in the micron range (0.1 volume per cent) was added to the loop. This slurry had a uranium dioxide concentration of 4.0 volume per cent. It was circulated for 40 hours at temperatures varying between 500 and 600 C with no evidence of settling. Davidson⁽⁴⁷⁾ also observed that uranium dioxide was not wet by bismuth but that, when uranium was added, the uranium dioxide was wet.

Some corrosion information on the behavior of the above system is offered⁽²⁶⁾ by Abraham. He analyzed the sodium-potassium alloy and found essentially no detectable quantity of stainless steel components in either the loop washings or the uranium dioxide. Examination of the Mark I loop (first high-temperature loop) showed only the enhancement of grain boundaries, a characteristic of heat-treated stainless steel. Measurements across the tube walls also indicated no change in thickness. It should be emphasized, however, that these were short-time corrosion tests.

A program on uranium dioxide slurries was also carried out at Knolls Atomic Power Laboratory under isothermal conditions and also with a temperature gradient. At the time of the termination of the program an in-pile loop was being designed.⁽⁴⁸⁻⁵⁷⁾

Laboratory experiments were carried out on various methods of preparing uranium dioxide slurries in NaK. Furman⁽⁵⁵⁾ developed a method of preparing a very voluminous uranium dioxide. The material had a bulk density of about 0.1 gram/cc. Furman observed the settling behavior of uranium dioxide in sodium-potassium alloy for compositions from 3.5 to 30 weight per cent. If the uranium dioxide had been freshly prepared and exposed to only a clean inert atmosphere, the wetting of the uranium dioxide by sodium-potassium alloy was easily obtained. Wetting by pure sodium did not occur rapidly below 200 C. Livey and Murray⁽⁴⁶⁾ found that uranium dioxide (not the voluminous type) was readily wetted above 400 C. However, Furman found that as little as one per cent potassium promoted wetting of the voluminous oxide at a

temperature just above the melting point (100 C) of the sodium-potassium alloy he was using. The settling rate of the uranium dioxide in sodium-potassium alloy was found to be dependent on the concentration of dioxide in suspension. Hindered settling became very prominent in settling phases having about 15 weight per cent dioxide. The settled bed had a composition of about 25 weight per cent. Suspensions containing about 18 weight per cent dioxide were rather stable when heated at 625 C for several hundred hours in a capsule. A different result was found when the suspension was heated at 775 C. The UO_2 lost its voluminous character after 100 hours. X-ray diffraction examination showed that the dioxide heated at 775 C had experienced crystallite growth.

Furman suspected that an oxygen impurity present in the suspension was influencing the behavior. A study was made of the effect of additives on the stability of voluminous uranium dioxide. The additives used were barium, strontium, magnesium, calcium, and uranium. It was found that each additive when present in approximately 15-mole per cent amounts was effective in preserving the hindered settling property of the dioxide under conditions that for non-gettered systems resulted in rapid settling material. Crystallite growth was also discouraged. X-ray diffraction studies showed that strontium, magnesium, and calcium formed uranium metal by reduction of the uranium oxide, particularly when stoichiometric amounts of these elements were used. In the case of barium, $\text{BaO} \cdot \text{UO}_2$ was found. When higher than stoichiometric amounts of barium were added, uranium metal was formed.

The beneficial effect of an additive in stabilizing the voluminous dioxide was observed in rotating capsule experiments. Suspensions containing barium retained the hindered settling property after 467 hours at 600 C. Non-gettered suspensions settled rapidly after 150 hours under the same conditions. When the suspensions which contained barium were rotated at 800 C, however, the property of hindered settling was not retained.

In agreement with Abraham's observations, workers at KAPL observed⁽⁴⁹⁾ that, if the uranium dioxide were prepared with a composition of $\text{UO}_{2.01}$, the material was not wetted by sodium-potassium alloy at room temperature. However, when the material had a composition of $\text{UO}_{2.003}$, it was wetted rapidly and completely by sodium-potassium alloy. Experiments were also carried out^(52,53) to determine the effects of large amounts of oxygen and nitrogen on fuel suspension.

The KAPL workers have used an experimental technique which somewhat simulates loop conditions.⁽⁵³⁾ Capsules were rotated in a long horizontal tube at a speed such that the slurry did not turn with the capsule. Thus, the liquid velocity relative to and near the wall was equal to the linear velocity of the capsule wall. In this type of equipment with a linear velocity of 0.75 ft/sec at the capsule wall, the following experiments were carried out.

(1) A capsule containing only the dioxide was rotated for 120 hours at 700 C. Previous to this treatment the capsule had been statically heated at 700 C for 600 hours and had a particle size of 6 microns. After the dynamic treatment, the particle size decreased to 3.5 microns. Apparently, the particles were broken up by the agitation at high temperature.

(2) A capsule containing the dioxide and uranium with an over-all oxygen uranium ratio of 1.66 was rotated at 700 C for 120 hours. It had a particle size of 9 microns after static heating at 700 C for 200 hours. After the dynamic treatment the particle size increased to 17 microns. This particle size was identical with that obtained by the KAPL workers in isothermal loops with uranium dioxide-uranium-sodium potassium alloy slurries.

(3) A capsule containing uranium and the dioxide of the same composition as experiment 2 was rotated and heated at 800 C for 113 hours after a static treatment of 233 hours at 800 C. After the static treatment, the particle size was 6.5 microns, and after the dynamic treatment it was 17 microns.

From the experiments cited above, it can be suggested that particle growth will be a problem only in the presence of uranium. It should be mentioned that the temperatures used in these experiments may be somewhat higher than those needed in reactor operation.

In isothermal loop studies⁽⁵³⁾ a uranium charge was prepared from 85 per cent ball-milled dioxide and 15 per cent uranium hydride. This was added to eutectic sodium-potassium alloy to give a suspension of 24.8 weight per cent dioxide. Essentially all the dioxide remained in suspension when the slurry was cycled at 4 ft/sec for 90 hours at 600 C and 500 hours at 700 C. The fuel would readily resuspend at moderate flow rates after the flow was terminated. Less than 2 weight per cent of the charged fuel adhered to the loop surface. X-ray examinations of the 304 stainless steel corrosion specimens indicated that

- (1) the deposition on the surfaces was largely UO_2 ; and
- (2) alloys of uranium and iron were not detected in the remaining deposit.

A second isothermal loop,⁽⁵⁴⁾ run similar to the one cited above, ran for 390 hours at 700 C. Mechanical difficulties terminated this run but it was quite successful. Substantially all of the charged solids, 24 weight per cent, remained in suspension throughout the run.

In an isothermal loop run using voluminous dioxide and barium getter, essentially all of the fuel (20 to 25 weight per cent) remained suspended at 3 ft/sec. At 600 C the suspended concentration decreased by 1 to 3 weight per cent per day. At 700 C the suspended concentration usually decreased rapidly and erratically over 800 hours to a low value.

One of the last loop experiments which the KAPL group did before the program was terminated was a Δt loop test. The charge was similar to that used in the successful isothermal runs; except that part of the dioxide had been irradiated in order that the settled out material might be located in the loop. Of the 25 weight per cent of the uranium dioxide, about 20 weight per cent was suspended when the flow was started or temporarily increased beyond the usual flow rates. This 20 weight per cent remained suspended at the lower temperatures, but at higher temperatures the amount suspended decreased gradually and somewhat erratically by about 5 weight per cent per day. This settling out was observed at 700 C with a Δt of 150 C, and at 590 C with a Δt of 140 C. During the course of the run the apparent Stokes' diameter of the solid as measured in the loop increased from 14 to 15 microns near the beginning of the run to 24 to 30 microns near the end. Thus, the Δt appears to have effected an increase in particle or agglomerate size. Following the extended periods of operation during which the suspended concentration decreased, the activity of the fuel was found to be concentrated in the upper horizontal leg of the loop. The investigators conclude that the velocity of 2.2 ft/sec was not high enough to suspend the material under the higher temperature conditions.

The KAPL investigators obtained some preliminary corrosion data. These are presented in Table 5.

Table 5

CORROSION OF STAINLESS STEEL 304 AND 316
BY UO_2 SUSPENSIONS IN NaK

Type of Stainless Steel	Temp. C	Time at Temp, hr	Flow Rate, ft/sec	Slurry Composition	Corrosion Rate, mils/yr
304	450	90	5	6 wt % UO_2	0.055
304	680	40			
304	660	850	4.3	5.5 wt % UO_2	0.028
304	780 ^a	900	Static		0.042
316	800	400	0.75		0.7
316	800	400	0.75		1.0
316	800	400	0.75	$\text{UO}_{2.41}$	1.7
316	800	400	0.75	$\text{UO}_{3.13}$	1.7
316	800	400	0.75	$\text{UO}_{4.38}$	6

^aX-ray fluorescence analysis of the surface of this sample showed no uranium to a depth of 1 mil, no change in the iron, chromium, and nickel content, but a decrease of about 20 per cent of the manganese in the surface of the stainless steel.

A paper of general interest to the experimentalist working with slurries has been published by Gould⁽⁵⁸⁾ on gamma-ray attenuation as applied to slurry fuel investigations.

The conclusions which can be drawn from both the ANL and the KAPL experiments, bearing in mind that these conclusions need to be substantiated by more experiments, are:

- (1) $\text{UO}_{2.00}$ can be suspended in NaK at temperatures below about 500 C, but above this temperature the material is not a practical reactor fuel due to settling;
- (2) additions of uranium will stabilize the uranium dioxide prepared by ball milling at higher temperatures of, perhaps, 700 C;
- (3) fuels consisting of uranium dioxide with uranium added have been successfully circulated in isothermal loops;
- (4) in the one Δt loop experiment tried, the fuel was not sufficiently stable at 700 C with a temperature difference of 150 C to be a satisfactory reactor fuel; and
- (5) although the corrosion data are preliminary it appears that there are no serious problems.

2. Uranium

Greenwood and Sharpe⁽⁵⁹⁾ have investigated the effects of thermal gradients on metallic slurries. It was found that for thermal gradients of about 200 C per cm a complete transfer of particles to the cold end of a stainless steel can was observed for UPb_3 in liquid lead and for UBi_2 in liquid bismuth. The results were quite different for the uranium-sodium system. Fine uranium powder of a mean particle diameter of about 1 micron was used. A radiograph of the uranium-sodium slurry after 10 days in the thermal gradient showed the particles distributed along the bottom of the can. This indicates that gravitational forces played the chief role. Greenwood and Sharpe suggest that the reason for the difference in the behavior of uranium in sodium compared to the other systems is in the extremely low solubility of uranium in sodium. At 600 C the solubility of uranium is less than 10^{-6} gram/ml, whereas at 400 C the solubility of UBi_2 is about 0.02, and at 500 C the solubility of UPb_3 is about 0.001 gram/ml.

Williams in 1954⁽⁶⁰⁾ did a few experiments on the sintering of uranium in sodium. The uranium powder used had a particle size of less than 60 microns. There were oxide films on this powder. After a week at

600 C the uranium sintered to form a strong cake. Williams then did a few experiments on the effect of additives. Lead, gold, and tin were tried. It appeared that tin prevented some of the sintering.

Somewhat in contradiction to the work of Williams,⁽⁶⁰⁾ Greenwood and Sharpe⁽⁴⁾ carried out experiments in which no sintering of uranium suspended in sodium was noted. Three grams of uranium powder, with a maximum particle diameter of less than 60 microns, were used with 15 grams of sodium. The mixture was placed in a stainless steel can and welded shut. After seven days at 630 C the sodium had wetted and penetrated the bed of uranium particles. Microscopic examination showed the uranium powder to be unchanged. The investigators, in order to eliminate the possibility of oxide coating on the uranium, carried out other experiments in which the uranium powder was prepared by hydriding and dehydriding. Heat treatments were carried out for one week at 400, 600, 700, and 800 C, respectively. On cooling, wetting and complete liquid penetration of the powders had occurred in each case. No sintering was observed. Greenwood and Sharpe suggest that the sintering which Williams observed may have been caused by small amounts of iron or nickel in the sodium which reacted with the uranium to form an intermetallic compound of low melting point, which aided sintering. An interesting aspect of the Greenwood and Sharpe paper is that it presents a theoretical analysis of slurry particle growth.

In conclusion of this section it might be mentioned that the Los Alamos fast reactor group is considering a uranium-sodium paste as a blanket material for LAMPRE.^(61,62) Also, one phase of the Australian program⁽⁶³⁾ involves the study of slurries of uranium in sodium.

IV. BISMUTH AND ITS ALLOYS AS LIQUID METAL FUEL CARRIERS

Bismuth is being seriously considered as a fuel carrier by groups at Brookhaven National Laboratory and Harwell. This choice is a natural one. Bismuth has a very low capture cross section for thermal neutrons. Also, the solubility of uranium in bismuth, although not high, is great enough to make a homogeneous fuel system possible. The problems of containment of bismuth, although not completely solved, are at least not so severe as to be completely discouraging. Bismuth is also a possible fuel carrier for plutonium in a fast reactor. Alloys of bismuth with tin and lead have also been considered as fuel carriers.

In this section the status of bismuth as a liquid fuel carrier will be considered.

A. General Information on Bismuth

Bismuth melts at 271 C. The following are the approximate vapor pressures of bismuth:

<u>Temp, C</u>	<u>Vapor Pressure, atm</u>
600	10^{-6}
917	10^{-3}
1315	10^{-1}

Upon freezing bismuth expands about 3.5 per cent. The liquid has a maximum density of 10.06 at 270 C in the supercooled condition. The effects of additives upon this expansion have been studied.⁽⁶⁴⁾ It appears that rather high concentrations are necessary to overcome the expansion on solidification. The specific electrical conductivity of bismuth is low, about 1.4 per cent of that of silver. Antimony and bismuth are the only metals whose conductivity is less in the solid state than in the liquid state. The ratio of conductivity just after fusion to conductivity just before fusion of most metals is about 0.5, whereas the ratios for antimony and bismuth are 1.33 and 2.08, respectively. The behavior of bismuth indicates the existence of polyatomic molecules in the liquid and probably in the solid state. Solid bismuth has the lowest thermal conductivity of any metallic element except mercury. The thermal conductivity of liquid bismuth at 400 C is 0.037 cal/(sec)(sq cm)(C/cm). The thermal conductivity is about 1.8 per cent that of silver.

Bismuth is diamagnetic and its electrical conductivity is greatly affected by the magnetic field⁽⁶⁵⁾ far more than any other known metal. Bismuth vapor at all temperatures examined is a mixture of monomer and dimer. The percentage of monomer is 40 at 850 C, 50 at 1650 C, and 90 at 2070 C. Studies have been made of zone refining of bismuth.^(66,67)

Further information can be found through a number of literature surveys on the physical and chemical properties of bismuth.⁽⁶⁸⁻⁷³⁾

B. Containment

In the following paragraphs is surveyed the corrosion work for liquid bismuth on most materials, with the exception of ceramics. Coultas⁽⁷⁴⁾ and Reed⁽⁷⁵⁾ have studied the use of ceramics to contain bismuth, but these materials are not included; although they will contain liquid bismuth, they would probably make poor materials of construction.

1. Graphite

There are several aspects to the use of graphite as a container material for molten bismuth. One is the penetration of the bismuth into graphite as a function of temperature, pressure, and graphite properties. Another is the interpretation of graphite behavior in the usual corrosion terms (wall thinning). A third is the possible reaction of solutes dissolved in bismuth with graphite. Rather old data (1919) indicate⁽⁶⁸⁾ that the solubility of carbon in bismuth is 0.01 weight per cent at 1400 C and 0.02 at 1500 C. It is reported that the carbon crystallizes out as graphite on cooling.

a. Corrosion of Graphite by Bismuth

A number of investigations have shown that graphite is a good material for containing molten bismuth.^(74,76,77) No investigator has ever reported serious penetration in the sense of wall-thinning of graphite by liquid bismuth in a static system.

Static corrosion tests at 1400 C on types AWG and AUF graphite were carried out for 168 hours, and corrosion was not detectable.⁽⁷⁵⁾

W. J. Hallett⁽⁷⁷⁾ carried out experiments to determine the effects of corrosion and mass transfer of graphite by liquid bismuth using a thermal convection loop. The loop was built of a single piece of National Carbon Company Type AWG graphite and mounted on a ball jar plate made of metal. The experiment was carried out under an argon atmosphere. The loop was operated for 279 hours at maximum temperature of 1400 C and minimum temperature of 875 C. No measurable corrosion occurred. The velocity of flow in the loop was estimated to be about 0.6 feet per second. Metallographic examination of the bismuth indicated no detectable solubility of graphite in bismuth but chemical analysis of the bismuth showed 0.2 per cent free carbon.

Experiments have been carried out at Brookhaven⁽⁷⁸⁾ to see if erosion would take place when a thorium-bismuth dispersion was circulated. A graphitar sample did not erode but an AGWT graphite sample did. The graphite pot in which the experiment was done also eroded.

b. Penetration of Graphite by Bismuth

In most reactor concepts using a bismuth-base fuel and graphite as a moderator, the graphite is subjected to considerable pressure. For example, in the British LMFR, Frost points out that the pressure may be as high as 200 to 300 psi.⁽²⁰⁾ Frost mentions that there is some tendency for penetration into the graphite. In very early work (1944)⁽⁷⁹⁾ using the lead-bismuth eutectic, absorption in graphite was of

the order of 1 gram/sq cm at 300 C and 90 psi. Investigators at Brookhaven National Laboratory⁽⁸⁰⁾ recently carried out some experiments at 450 C and 125 psi. Bismuth was picked up by Type P, but not the Type A, National Carbon graphite. A sample of fine-grain electrode stock made by Great Lakes Carbon Company did not take on bismuth after 160 hours submersion. Work is continuing on this problem. The Babcock and Wilcox group does not feel that the problem of penetration of bismuth into graphite has been completely solved.^(81,82)

c. Reaction of Graphite with Uranium, Zirconium, and Rare Earths Dissolved in Bismuth

At Brookhaven National Laboratory a number of experiments, which define the conditions for reaction between graphite and uranium dissolved in bismuth, have been carried out. As a result of these it was concluded that zirconium prevents the formation of uranium carbide from molten uranium-bismuth and uranium-bismuth-lead alloys under conditions that would normally result in the formation of uranium carbide. The zirconium reacts to form a thin adherent layer of zirconium carbide-zirconium nitride on the graphite surface. The amount of zirconium required is less than one-quarter of the uranium concentration in the liquid metal.⁽⁸³⁾ In the following paragraphs these experiments will be described in more detail.

Experiments performed at 500 C in which uranium in bismuth was contacted with graphite for 60 hours showed no detectable reaction. It is thought that a uranium carbide film was formed in these experiments, but that it was about one Angstrom thick. Thus, it was not detected microscopically or by X-ray diffraction. Also, when uranium was added to bismuth in contact with graphite in concentrations of one per cent or less, no uranium carbide was detected at temperatures up to 1200 C. However, when the uranium addition was increased to 4.7 per cent, surface deposits of carbide were noted at 1100 C. The addition of zirconium to the liquid bismuth in all samples at temperatures of 1000 C or higher produced surface deposits of a solid solution of zirconium carbide and nitride, identifiable by X-ray diffraction.

The use of lead-bismuth eutectic rather than bismuth as a solvent produced a marked increase in the amount of uranium carbide but not of the zirconium carbide formed. However, the addition of 0.36 weight per cent zirconium to a solution containing 4.2 weight per cent uranium in lead-bismuth will prevent the formation of uranium carbide in 100 hours at 1100 C.

The effect of different types of graphite surfaces on the formation of uranium carbide from lead bismuth eutectic was also investigated. Rods of graphite grade G, graphitar and AGHT graphite were exposed. The thicknesses of the deposits were essentially the same on all four types of samples.

In another type of experiment done under a helium pressure of 100 psi to force the bismuth into the graphite (AGHT) pores,⁽⁸⁴⁾ the conclusions were not essentially different from those cited above. The investigator also observed the different behaviors of bismuth and the lead-bismuth eutectic. It was pointed out that the reason was not certain, but that the effect may be due to a difference in wetting of the two systems. However, somewhat in contradiction with this opinion is the fact that zirconium from bismuth solutions will react with a graphite surface as well as from lead-bismuth solutions.

Brookhaven has carried out experiments in which AGHT graphite cylinders were exposed in Croloy $2\frac{1}{4}$ convection pots.^(80,85) Uranium, zirconium and magnesium solutions in bismuth were held in the pots for extended periods at 550 C. The concentrations of the various components were followed. The results in general can be summarized by saying that the uranium concentration does remain constant at reasonable fuel concentrations. The test period has been as long as a year in certain experiments. The magnesium concentration also remains constant, but the zirconium concentration slowly drops in almost all experiments.

W. E. Miller and J. R. Weeks⁽⁸⁴⁾ considered the possibility that some of the fission products dissolved in bismuth might react with graphite. The formation of rare earth carbides would be particularly detrimental, since graphite surfaces contaminated with a layer of these would have a very large cross section for thermal neutron capture. In a preliminary experiment carried out at 1400 C for 100 hours zirconium in the bismuth prevented the formation of neodymium carbides.

d. Fabrication of Graphite Components⁽⁸⁶⁾

From the standpoint of electrical and thermal conductivities graphite is metallic. From the mechanical standpoint, it is ceramic, showing high crushing to tensile strength ratios, lack of ductility and malleability, and a practical coincidence of yield point and fracture. It increases in strength with increase in temperature. Graphite is available in sizes up to 75 cubic feet in volume and its machinability makes it a versatile engineering material.

In the building of large structures design generally follows masonry principles with stresses taken under compression wherever possible. Selection of mortars and cements is important. When practical for the chemical and temperature conditions, resinous cements are preferred because of the excellent bond to carbon and graphite. Other cements, such as litharge and glycerin, silicates, and portland, and molten sulfur cements, are used where bond strength is not of paramount importance. For high-temperature applications and those conditions where a 100 per cent

carbon structure is desired, carbonaceous cements and pastes which are carbonized by baking to temperatures ranging from 575 F up are used. The latter are available in a wide range of compositions ranging from cements which are applied cold to hot-applied pastes of varying degrees of plasticity.

2. Steels and Croloys

Various types of steels have been the materials of construction most seriously considered for molten bismuth. This is due to the easy availability and fabricability. In early work summarized in the Liquid Metals Handbook (1952) it is pointed out that ferritic iron, low carbon steel, and the low alloy steels have good resistance to bismuth at temperatures below their transformation temperatures.

Table 6

SOLUBILITY OF COMPONENTS OF STEELS IN BISMUTH

Temp C: Species	ppm			
	400	500	600	725
Fe	2	13	40	200
Cr	8	40	130	500
Mo	--- less than 1 ppm ---			
Ni	---- quite soluble ----			

The solubilities of some of the components of the various steels are given in Table 6, and the approximate compositions of the alloys of interest are given in Table 7. A survey of solubility data for bismuth at 400 C has been made.⁽⁸⁷⁾

Table 7

APPROXIMATE COMPOSITIONS OF STEELS AND CROLOYS

Material	Weight Per Cent							
	C	Mn	Si	Cr	Mo	Ni	Fe	O ₂ N ₂
Pure Fe	0.003							0.012 0.00018
Armco							99+	
Croloy 2 $\frac{1}{4}$	0.15	0.3 to 0.6	0.5	2.0 to 2.5	0.9 to 1.1		Bal	
Croloy 5	0.15	0.3 to 0.6	0.5	4.0 to 6.0	0.45 to 0.65		Bal	
Croloy 5 Silicon	0.15	0.3 to 0.6	1.0 to 2.0	4.0 to 6.0	0.45 to 0.65		Bal	
410 SS	0.15	1.00	1.00	11.5 to 13.0		0.5	Bal	
304 SS	0.08	2.00	0.75	18.0 to 20.0		8.00 to 11.00	Bal	
347 SS	0.08	2.00	0.75	17.0 to 20.0		9.00 to 13.00	Bal	

Static tests have been used to select those materials worthy of further consideration. Experiments have been done by Cordovi,⁽⁸⁸⁾ Atherton^(89,90) Prey, et al.,⁽⁹¹⁾ and Elgert.⁽⁹²⁾ A summary of the results of Cordovi and Atherton as prepared by Weeks⁽⁸³⁾ and somewhat expanded from the original work is presented in Table 8.

Table 8

TYPICAL RESULTS OF STATIC CORROSION TESTS ON
VARIOUS MATERIALS IN LIQUID BISMUTH, 1000 HOURS
AT 550 C

	Additive to Bismuth, Weight Per Cent			Maximum Penetration, mils
	U	Mg	Zr	
Armco	-	-	-	0.71
Armco	0.1	-	-	0.55
Armco		0.1	-	0.78
Armco			0.1	0
Armco		0.1	0.1	0
2½% chromium	-	-	-	0.59
2½% chromium	0.4	-	-	0.78
2½% chromium	0.1	0.05	0.05	0
Croloy 5	-	-	-	1.36
Croloy 5	0.4	0.1	0.1	0.34
Croloy 5 silicon	-	-	-	1.2
Croloy 5 silicon	0.4	0.1	0.1	0
304 SS	0.4	-	-	2.1
347 SS	-	-	-	9.7
410 SS	-	-	-	1.2
Molybdenum	-	-	-	0

The results indicate that in static isothermal tests the corrosion of Armco iron and Croloy 2½ is greatly reduced by the presence of zirconium in the bismuth. In an attempt to explain corrosion inhibition of bismuth by zirconium, it has been postulated that the zirconium reacts with nitrogen or carbon present in the steel. Zirconium nitride was found on the surface of Croloy 2½, supporting this suggestion.^(84,85,90-93,95) In a typical experiment to establish this point a group of Croloy 2½ samples were placed in graphite crucibles and exposed to different bismuth solutions for 3000 hours.⁽⁹⁶⁾ The conditions and results are the following:

Additives	Temp C	Zirconium Nitride Layer
U, Bi, Mg, Zr	750	Yes
U, Bi	750	No
U, Bi, Mg, Zr	550	No
U, Bi	550	No

The mass-transfer problems are of great importance in a study of corrosion of steels. Klamut in 1955⁽⁹⁷⁾ carried out an investigation of this phenomenon using pure iron. The results of his work have been summarized by Weeks⁽⁸³⁾ and are presented in Table 9.

Table 9

RELATIVE RATES OF MASS TRANSFER OF
PURE IRON IN BISMUTH IN GRAPHITE
THERMAL CONVECTION POT

Run No.	Additives (ppm)			Max Temp (C)	Δt (C)	Transfer Rate (mg/hr $\times 10^{-5}$)
	Mg	U	Zr			
3 ^a	-	-	-	467	32	430
4 ^a	-	-	-	475	31	645
18	-	-	-	438	23	13
17	100	-	-	466	25	2
8 ^a	130	800	-	484	48	1.2
12	400	2000	-	484	20	4.6
5 ^a	100	700	200	472	28	0.8
6 ^a	100	400	140	468	22	0.06
7 ^a	100	600	200	457	31	0.2
9 ^a	-	500	175	476	32	0.15
13	100	-	150	495	35	0.1
14	125	-	75	501	32	0.07
15	100	-	35	477	22	0.2
16	100	-	5	465	30	0.2

^aTank argon atmosphere; other runs in purified helium atmosphere.

It can be seen that the change from an argon atmosphere of questionable purity (runs 3 and 4) to a purified helium atmosphere produced a considerable drop in the amount of activity transferred. The addition of magnesium (run 17) and magnesium plus uranium (runs 8 and 12) further reduced the mass transfer rate. The addition of zirconium plus magnesium or zirconium plus uranium plus magnesium "all but

eliminated transfer under these conditions." For example, in run 14, the analytical method was insufficiently sensitive to measure the mass transfer. This investigation indicated the very beneficial effect of having zirconium present in the bismuth in reducing mass transfer corrosion in certain instances.

Elgert and Egan in 1953(98) investigated the resistance of steels to dynamic corrosion and mass transfer by liquid bismuth. They attempted to control the process by using small amounts of titanium plus magnesium as inhibitors. They found a greater than 100-fold reduction in the corrosion rate of 5 per cent chromium steel by adding 50 ppm titanium and 350 ppm magnesium to a thermal convection loop with a temperature differential of 700 to 615 C. All runs with chromium-alloyed steels without additives to the liquid metal gave excessive corrosion rates.

Brookhaven National Laboratory is carrying out an extensive program on the corrosion of various steels by bismuth. Most of the recent experimental work has been carried out in loops. The following few paragraphs attempt to present the recent data on various materials.

Croloy 2 $\frac{1}{4}$ (See Table 7 for Composition)

Weeks in 1956(83) briefly summarized the results of loop experiments using Croloy 2 $\frac{1}{4}$. The results of some 25 loops indicated that the time required to plug completely a 1/2-inch IPS Croloy 2 $\frac{1}{4}$ loop was about 300 hours when the circulating liquid was bismuth with uranium and the temperature gradient was 40 C. When Weeks wrote his summary, a Croloy 2 $\frac{1}{4}$ loop had operated under the above conditions with 250 ppm zirconium added to the liquid bismuth-uranium solution for 13,000 hours.

When the temperature gradient was increased to 150 C for loops containing 250 ppm zirconium, 300 ppm magnesium and 1000 ppm uranium in the bismuth, Weeks indicated that transferred material appeared in the cold leg soon after the loop was started. However, the amount was quite modest and at the time Weeks wrote his summary they had been in operation for 1800 hours.

In Table 10 is presented a summary of the most recent thermal loop data available (as of December 1957). These data suggest that the corrosion behavior of Croloy 2 $\frac{1}{4}$ still needs further investigation.

To test further the erosion behavior of bismuth on Croloy 2 $\frac{1}{4}$ Brookhaven has built several high-velocity test loops. In 1000-hour runs under a temperature gradient of 125 C and with a velocity of 8 ft/sec no serious corrosion was observed.(99) These experiments are continuing.

Table 10

CORROSION RESULTS ON LOOPS MADE OF CROLOY 2 $\frac{1}{4}$
LOOPS IN OPERATION OCTOBER AND DECEMBER 1957

Brookhaven National Laboratory Data

Data presented are generalized for simplicity of presentation.

Solution circulated is bismuth containing uranium (1000 ppm), zirconium (250 to 400 ppm) and magnesium (350 ppm,) unless otherwise indicated.

Time at isothermal operation not indicated.

Loop No.	Approx Max Temp, C	Approx Δt	Total Operation Time, hr	Radiography Inspection		Remarks
				Hot Leg	Cold Leg	
33	550	90	16,000	Pitting in Pipe and welds	ppt	Pitting and ppt increasing
40	550	40	650	No corrosion	Slight ppt	ppt increase
	550	100	1,000	No corrosion	Slight ppt	
	600	50	5,000	No corrosion	Slight ppt	
	600	75	2,700	No corrosion	Slight ppt	
	600	100	2,600	No corrosion	ppt	
42	550	40	800	No corrosion	no ppt	
	550	100	10,100	Weld corrosion	ppt	
41	525	40	1,100	No corrosion	no ppt	
	575	170	9,400	Slight pipe corr.	Slight ppt	
43	500	40	900	No corrosion	no ppt	
	500	100	9,300	No corrosion	no ppt	
45	525	40	500	No corrosion	no ppt	
	525	125	9,100	Weld corrosion	ppt	
46 (nitrided)	550	40	500	No corrosion	no ppt	Zr conc falling
	550	135	8,900	No corrosion	Slight ppt	
48	525	40	1,000	No corrosion	no ppt	
	525	50	8,300	No corrosion	Slight ppt	
44	575	40	1,400	No corrosion	no ppt	
	575	160	7,300	Slight weld corrosion	Slight ppt	
53 (normalized)	550	40	2,300	Pipe corr.	no ppt	
	500	100	3,700	Pipe corr.	Slight ppt	
55 (normalized)	550	40	2,100	No corrosion	no ppt	
	525	95	2,300	No corrosion	Slight ppt	
56 (w/Be insert no uranium)	550	40	2,700	No corrosion	Slight ppt	
	500	100	50	No corrosion	Slight ppt	

A recent British publication⁽¹⁰⁰⁾ indicates somewhat higher corrosion rates of 2 $\frac{1}{4}$ per cent chromium - one per cent molybdenum steel by liquid bismuth than that observed by the Brookhaven group. The conditions are somewhat different, however. The results of seven laboratory-scale thermal convection loops are reported. The corrosion was studied at flow rates of 0.12 in/sec or slightly higher. A

somewhat higher temperature, 625 C, was used instead of 550. The low temperature varied with the condition of the loop. One loop without zirconium inhibitor began to show signs of plugging after 160 hours. On sectioning the loop it was found that the steel had been intergranularly attacked along the entire length of the hot limb. There was no sign of pitting corrosion. The corrosion rate at the highest temperature section was 650 mils/year.

A second loop was run with 500 ppm calcium and 250 ppm zirconium. Plugging occurred after 2146 hours. Examination of the loop revealed that the hot limb was very badly pitted and that the steel had been attacked intergranularly at the base of the pits. Analysis of the bismuth for zirconium showed that its concentration had decreased to less than 20 ppm.

A third loop experiment was carried out under the same conditions as the second, except that the loop was inserted in BEPO in an undisturbed thermal flux of 10^{12} neutrons/(sq cm)(sec), the fast to thermal neutron ratio being of the order of 1. The loop plugged after 850 hours, unplugged in 40 more hours and finally plugged after 1200 hours. Pitting corrosion had occurred. The authors indicated that they could not draw definite conclusions from a single experiment, but they did feel that there was no beneficial effect due to irradiation and that perhaps irradiation may accelerate the corrosion.

Since the second loop suggested that the protection afforded the steel by 250 ppm of zirconium was not satisfactory, the fourth loop was run under identical conditions, but with 500 ppm of zirconium and 500 ppm calcium. A gammagraph indicated a corrosion of 170 mils/year.

The fifth loop was run by replenishing the zirconium periodically. In spite of consuming 950 ppm of zirconium the loop plugged after 2130 hours.

In an interesting experiment the sixth loop was run in an atmosphere (outside) of dry ammonia. After 2800 hours a slight precipitate was observed. The loop was shut down after 2930 hours. Microscopic examination of the hot limb showed some pitting corrosion, but the pits had been sealed off by the growth of a new film. Intergranular attack was prevented and the maximum corrosion rate was about 10 mils/year. The film on the inside of the loop was identified as zirconium nitride.

Horsley and Maskrey⁽¹⁰⁰⁾ concluded that the higher corrosion rate compared to that observed at Brookhaven might be due to the 75 C higher temperature used.

Croloy 5 Silicon (See Table 7)

In static tests presented earlier Croloy 5 silicon appeared to be worthy of consideration for bismuth in the presence of zirconium. Weeks⁽⁸³⁾ points out that a 1.7-inch ID loop made of 5 per cent chromium silicon steel running with a 40 C temperature gradient required 2440 hours to plug. However, with 250 ppm of zirconium a similar loop was circulating for more than 19,000 hours without plugging. Subsequently the temperature gradient was increased to 150 C in a loop containing 250 ppm zirconium, 300 ppm magnesium, and 1000 ppm uranium in the bismuth. After 1060 hours this loop was shut down and metallographically examined. The corrosion rate on the hot leg sample was 2 mils/year.

A loop made of Croloy 5 silicon was run with a reduced cold leg size of 0.213-inch ID. The hot leg was 0.622-inch ID. The bismuth contained uranium, magnesium, and zirconium. Complete plugging of this loop took place after 2400 hours, using an initial temperature gradient of 150 C.

A study of the data of several other loops of Croloy 5 silicon indicates that the loops were often stopped by plugging in from 2000 to 4000 hours when temperature gradients were about 100 C. Brookhaven is no longer running loops using Croloy 5 silicon.

Stainless Steel 347

Stainless steel 347 was considered for uranium-bismuth solutions particularly because it is a good material for the fused salt system being developed by Brookhaven for chemical processing. However, it is subject to mass transfer corrosion not mitigated by additions of zirconium. In addition, intergranular corrosion caused by nickel leaching takes place.⁽¹⁰¹⁻¹⁰⁴⁾ For example, Loop E, which operated with a temperature gradient of 165 C with a hot leg at 615 C, developed a plug in seven weeks. The bismuth from the loop was found to contain 900 ppm of nickel and the uranium concentration had dropped from 540 to 65 ppm. The plug in the loop was an iron-chromium alloy. The presence of the nickel in the bismuth decreases the solubility of uranium very markedly.⁽¹⁰¹⁾ Thus, at 500 C, 0.05 per cent nickel reduces the uranium solubility to about 1000 ppm. One per cent nickel reduces it to approximately 200 ppm. Two intermetallic compounds have been found in bismuth solutions containing nickel and uranium.⁽⁸³⁾ These are UNi_2 and UNi_5 . Brookhaven has run a number of loops which demonstrated the statements made above.^(90,101,103)

3. Tantalum

Tantalum is one of the materials which can be seriously considered for bismuth at elevated temperatures. Tantalum, however, has a cross section of 21 barns for thermal neutrons and is difficult to fabricate.

It is under serious consideration as a container material for the Los Alamos fast reactor (plutonium-iron) and has been mentioned as a reasonable fast reactor material by Frost⁽²¹⁾ when the fuel system is plutonium dissolved in bismuth.

a. Corrosion Data

In experiments carried out in 1951⁽¹⁰⁶⁾ at 1000 C for 100 hours, tantalum was exposed to a 2 atomic per cent uranium solution in bismuth. The investigators reported that tantalum was quite stable. The same experiment was repeated later⁽³²⁾ with essentially the same results. E. L. Reed⁽⁷⁵⁾ reports that tantalum showed pronounced intergranular attack after 227 hours at 1000 C. When the bismuth was analyzed it was found to be 0.11 weight per cent in tantalum. Visual examination indicated that the tantalum was wet by the bismuth. Since this investigator is the only one to have observed corrosion of tantalum it may be that his samples were poor. Tantalum quality has a tendency to be erratic.

Recently R. W. Fisher^(107,108,109,110) has been studying the corrosion of tantalum by circulating bismuth in a loop at temperatures approaching 1000 C. The tantalum loops were enclosed in an outer envelope of Inconel, since tantalum is unstable when exposed to air at temperatures above 350 C. Helium was kept in the annulus between the tantalum and the Inconel. The tantalum wall thickness was 30 mils. A 5 weight per cent uranium in bismuth alloy was circulated, using a specially designed electromagnetic pump. The loop was run at 950 C for 5250 hours (219 days) with a Δt of 100 C. At the end of 2000, 4000, and 5000 hours, analyses showed less than 6 ppm of tantalum in the alloy. Upon dissection of the apparatus no corrosion or erosion of the tantalum was noted. However, the tantalum showed pits about 5 mils deep where the Inconel contacted the tantalum under extreme pressure. In the areas of highest and lowest temperatures the tantalum showed signs of attack of less than 1 mil. The material remained shiny and ductile throughout the experiment. Fisher concludes that tantalum is a satisfactory container for 5 weight per cent uranium in bismuth at 950 C. In another loop experiment,⁽¹¹⁰⁾ 0.3 weight per cent manganese was added by Fisher to the above uranium-bismuth alloy and circulated for 4500 hours at 950 C. Slight attack was found. Since the addition of the manganese only reduced the melting point of the system by 30 C, work with the ternary was stopped.

Plans are being made at Ames⁽¹¹⁰⁾ to make an in-pile test of an operating loop of the type described above. It may be a double-pass loop in which uranium-bismuth alloy will pass through a sodium-cooled tantalum heat exchanger. The sodium will also be circulated through a loop, probably constructed of Inconel which has been found satisfactory up to 800 hours at 800 C.

b. Fabrication of Tantalum Components⁽¹¹¹⁾

Tantalum is comparable to mild steel in its ability to be drawn, stamped or otherwise formed into complicated shapes. Annealed tantalum takes a permanent set in stamping or forming and does not spring back from the dies. Tantalum becomes work hardened at a much slower rate than most other metals. Reduction in thickness of 60 per cent or more, without any intermediate anneal, is standard practice.

Tantalum can be machined, but precautions must be taken against its tendency to gall and tear.

Tantalum can be welded to itself and a number of other metals. Welds are made either by resistance welding, or by adaptations of the inert gas arc-welding process. In either case, not only oxygen, but all common gases must be excluded. Spot welding and seam welding are usually done under water, and in arc welding, the inert gas is specially purified and the entire area around the weld region is carefully shielded. Johnson and Burris report^(112,113) that Ames investigators can successfully weld rather complicated tantalum shapes in an inert atmosphere. A GE selenium rectified dc welder is employed.

Rather intricate tantalum-lined equipment has been made, including kettles, condensers, heat exchangers, and coils. Tantalum tubing is available and may be obtained with flanges or flares at one or both ends, or with one end capped.

It is interesting to note that the Los Alamos fast reactor group feels that a satisfactory core cage may possibly be fabricated from tantalum.⁽¹¹⁴⁾ They report⁽¹¹⁵⁾ that the outlook for tantalum shapes and components is very encouraging.

4. Molybdenum

In a number of investigations molybdenum has been shown to contain bismuth quite well at elevated temperatures. It has been suggested⁽²¹⁾ as a possible container material for a bismuth-plutonium fast reactor fuel. The thermal absorption cross section of 2.4 barns is not impossibly high for use in thermal reactors; it is numerically the same absorption cross section as iron. The solubility of molybdenum is very low. In the following paragraphs will be summarized the literature on the behavior of molybdenum exposed to bismuth.

a. Corrosion Data

Parkman and Shepherd⁽¹¹⁶⁾ in some early investigations found that bismuth at 1000 C did not appreciably attack molybdenum in 200 hours. Reed's data⁽⁷⁵⁾ for one week at 1000 C agree. Coultas⁽⁷⁴⁾ also

found at 1000 C and 167 hours that molybdenum was compatible with bismuth. In experiments carried out in 1950 at Oak Ridge^(106,32) it was found that 2 atom per cent uranium in bismuth did not attack molybdenum at 1000 C in four hours. Grassi, et al.,⁽¹¹⁷⁾ found no decrease in strength in stress rupture tests for molybdenum exposed to bismuth at 1000 C for 100 hours. Reed⁽⁷⁵⁾ found no apparent attack at 1430 C in a 2-hour test.

Cordovi⁽⁸⁸⁾ exposed molybdenum to a 0.4 weight per cent uranium in bismuth solution at 500 C. He found a corrosion penetration of 3.3 mils/year. When a lead-bismuth eutectic containing 2 weight per cent uranium, was used, the corrosion rate was 4.3 mils/year. When the lead-bismuth-tin eutectic with 2 weight per cent uranium was used, the corrosion rate was 3.6 mils/year. Cordovi carried out all of these three experiments for about 2000 hours. He feels that a corrosion of 5 mils per year is the highest rate acceptable for a reactor.

b. Fabrication of Molybdenum Components⁽¹¹⁸⁾

The room-temperature hardness of molybdenum and its alloys increases with increasing amounts of mechanical working below the recrystallization temperature. With very fine wire tensile strengths up to 300,000 psi may be obtained. The ductility of molybdenum and its alloys at elevated temperatures is ample for almost all applications. Swaging and hammer forging can be done by conventional methods. In sizes under about 0.02 inch in diameter or thickness, forming, bending, punching and shirring can be carried out at room temperature. Molybdenum sheet in these thicknesses will take a 180° bend without difficulty. Heavier material should be warmed to 200 to 1000 F, depending on size. Molybdenum can be deep drawn without difficulty. Molybdenum can be spun by customary procedures with tools of aluminum, bronze, or other suitable low-friction materials. Molybdenum saws readily with high-speed steel band or hack saws. No difficulty is encountered in turning molybdenum to produce a finish if the proper tools and lubrication are used.

Molybdenum is often joined by brazing or riveting, but less frequently by welding. It can be welded to itself by a number of different processes including arc, electrical resistance, percussion and flash. It can also be welded to those metals and alloys with which it readily alloys. In all cases absolute cleanliness of the molybdenum is essential.

The possibility of coating Croloy steels with molybdenum by a vapor-phase deposition process has been considered by Battelle.⁽¹¹⁹⁾ Recent work⁽¹²⁰⁾ indicates the deposition of molybdenum by decomposition of molybdenum hexacarbonyl gives brittle but uniform coating with a tendency to be nonadherent. It appears that considerable work remains before such a process is generally applicable.

5. Tungsten

Tungsten has an absorption cross section for thermal neutrons of 19 barns, which is rather high for a thermal reactor. Very little work has been done on tungsten as a container material for bismuth. Experiments at Oak Ridge⁽¹⁰⁶⁾ indicated that at 1000 C a 2-atom per cent uranium in bismuth-tin solution did not appreciably attack tungsten in four hours. In later experiments⁽³²⁾ at 1000 C tungsten behaved well in 40-hour tests. Reed⁽⁷⁵⁾ found that tungsten showed essentially no corrosion after a week at 1000 C. When the bismuth was analyzed it was found to contain 0.001 weight per cent tungsten. Parkman and Shepherd⁽¹¹⁶⁾ found that in 100 hours at 1000 C tungsten was not attacked by bismuth. Information is available on the fabrication of tungsten components.⁽¹²¹⁾

6. Vanadium

The solubility of vanadium in bismuth is 100 ppm at 600 C and 750 ppm at 1000 C.⁽¹²²⁾ The absorption cross section for thermal neutrons is 5.1 barns.

Brasunas⁽³²⁾ found that vanadium had good behavior in 40-hour tests at 1000 C. Nuclear Metals, Inc.,^(122,123) demonstrated that vanadium was susceptible to thermal gradient mass-transfer attack. These investigators concluded that commercially pure vanadium is not a suitable container material for molten bismuth.

7. Niobium

Early Oak Ridge data^(32,106) suggest that niobium is quite stable when exposed to 2 atom per cent uranium in bismuth or pure bismuth at 1000 C in 100-hour tests. Grassi⁽¹¹⁷⁾ reports that niobium suffered a severe loss in strength and ductility when exposed to bismuth for 100 hours at 1000 C. Parkman and Shepherd⁽¹¹⁶⁾ found that niobium was attacked in 100 hours at 1000 C. It seems likely from these data that niobium is not a good material for use with bismuth.

8. Beryllium

There are very few data available on the corrosion of beryllium by bismuth. In a 5-hour test at 1000 C reported by Kitzes⁽¹²⁴⁾ beryllium seems to have withstood bismuth. Cordovi⁽⁸⁸⁾ reports that beryllium resists attack by bismuth-lead eutectic containing 2 weight per cent uranium for 1000 hours at 550 C. In a 24-hour test at 700 C it is reported that there was essentially no reaction.

C. Status of Bismuth Containment Problem

In Table 11 is given the status of the various containment materials for molten bismuth. The statements have been generalized for the sake of compactness of the table, and the reader should refer to the earlier sections for detailed information. There is no proved material of which to construct a reactor that will have molten bismuth as a fuel carrier. There are two materials which can be seriously considered; tantalum and Croloy 2 $\frac{1}{4}$ (or some Croloy variation).

Much of the Brookhaven corrosion data has been reviewed. It is evident from recent loop data that some of the loops show at least mild corrosion. The times involved are often up to 10,000 hours (400 days) or more before very much precipitate is observed in a loop. The top loop operating temperature used in recent experiments has been 600 C. One version of the LMFR has a maximum operating temperature of 540 C. This leaves a 60 C margin for error if some part of the reactor suffered overheating for an extended period.

Any corrosion problem which is solved by the addition of a trace of zirconium (350 ppm), whose concentration must be carefully monitored, should be carefully considered. However, the corrosion problem met in the use of mercury in turbines by General Electric was solved in this manner through the use of low concentrations of titanium and magnesium.⁽¹²⁵⁾ Frost⁽²⁰⁾ points out that chloride must be strictly controlled in a modern steam plant and makes the point that the control of zirconium in bismuth may be an analogous problem. However, keeping a constituent below a specified low concentration should be easier than keeping a constituent at a particular concentration in a radioactive system. This is particularly true since the zirconium has been observed to disappear from solution in certain loops and is known to react with graphite. The latter is pertinent in reactors having a graphite moderator exposed to the bismuth.

Taylor in 1956⁽³⁵⁾ pointed out that there may be a number of limitations to the form of corrosion inhibition arising from a zirconium nitride film in Croloy 2 $\frac{1}{4}$. It relies on a constituent in the Croloy 2 $\frac{1}{4}$ whose content is not large and which is not normally specified closely. Taylor stated that it is not yet certain whether this layer is protective at temperatures higher than 550C. He also pointed out that no data are available for the thermal expansion of zirconium nitride; it is thus impossible to say whether spalling of the film is likely at higher temperatures as a result of differential thermal expansion effects. The effects of radiation on this film may be serious. It is possible that it might spall under irradiation. Taylor mentioned that a major limitation might occur due to the restricted supply of nitrogen available for effective operation of the inhibitor over a long period of time.

Table 11

INVESTIGATION STATUS OF VARIOUS PROMISING CONTAINER
MATERIALS FOR MOLTEN BISMUTH

Generalized Statements - Refer to the text for specific information

	Graphite	Tantalum	Molybdenum	Tungsten	Beryllium	Croloy 24
Absorption cross section (thermal), barns	0.003	21	2.4	19	0.01	
Results of Corrosion Studies						
Static Results	Favorable	Favorable	Favorable	Favorable		Favorable
Temp Range	up to 1400 C	up to 1000 C	up to 1000 C (in 100-hr exper) up to 1430 C (2 hr)	up to 1000 C	up to 700 C	~500 to 600
Amount of Data	Modest (generally short term)	Modest (generally short term)	Very modest	Very modest	2 or 3 experiments	Considerable
Non-isothermal loops						
Results	Favorable	Favorable	None	None	None	Some unsolved problems
Temp Range	1400 (Δt of 525)	950 (Δt of 100)				600 C (Δt up to ~150 C)
Amount of Data	Single experiment (279 hours)	Single 219-day experiment				Considerable
Fabricability into Reactor Components	Easily fabricable into a variety of shapes but strength and shock resistance is poor	Probably feasible	Difficult	Probably impossible	Very difficult	Good
Comments	The graphite must be "impermeable" or bismuth will penetrate. Zr prevents formation of UC. Must be protected from atmospheric oxidation.	Must be protected from atmospheric oxidation				Corrosion inhibited in Zr (~350 ppm)
Conclusions	The problem of the penetration of bismuth into graphite and its fabrication problems make its use as a reactor vessel questionable.	With intensive development on fabrication, welding, etc. tantalum may make a good material for a fast reactor. More corrosion data are needed.	Progress in fabricating techniques, may make molybdenum a real possibility.			More work must be done before it is established as a reactor vessel material

All of the data, although rather meager, on tantalum as a container material are favorable to date. However, the one loop-run at Ames was made at a maximum temperature of 350 C higher than the temperature at which the Croloy data are generally obtained. This loop was run for 219 days which is a reasonable length of time for the first experiment. The principal difficulties with tantalum lie in (a) difficulty of fabrication technology, and (b) lack of extensive corrosion data. The cross section is sufficiently high that the most likely application would be to a fast reactor system.

D. Fluid Fuel Systems Using Bismuth as a Carrier

1. The Uranium-Bismuth System

a. Phase Diagram and Solubility

In a recent article published by Teitel⁽¹²⁶⁾ information is presented on the uranium-bismuth phase diagram. There are three intermetallic compounds: UBi_2 which decomposes peritectically at 1010 C, U_3Bi_4 which decomposes peritectically at about 1150 C, and UBi which decomposes to two liquid phases at a temperature between 1400 and 1450 C. The terminal components react eutectically with the nearest compound. Little solid solubility for either component in the other was indicated. The reactions can best be summarized by the following equations, where the subscripts indicate the composition of liquid phases in weight per cent uranium:

Eutectic: 270 C

Peritectic: 1010 C

Peritectic: 1150 C

Syntectic: 1400 to 1450 C

Eutectic: 1130 C

The solubility of uranium in liquid bismuth has received attention from several authors. These are Baries,⁽¹²⁷⁾ Hayes and Gordon,⁽¹²⁸⁾ Ahmann and Baldwin,^(129,130) and Kaufman.⁽¹³¹⁾ Teitel feels that Baries' solubility data are the most dependable and he presents these. The approximate solubilities are 2000 ppm uranium at 400 C, 20,000 at 600 C, and 80,000 at 800 C.

Workers contemplating the use of the uranium-bismuth compounds should be aware that UBi , UBi_2 , and U_3Bi_4 are pyrophoric.^(132,133,45,129)

The influence of a number of factors on the solubility of uranium has been investigated.⁽⁸³⁾ It appears that the solubility of uranium in bismuth is not affected by dissolved iron. Additional experiments were conducted to determine the stability of the uranium-iron intermetallic compounds in liquid bismuth. Micro-examination of the residue obtained from the equilibration of UFe_2 with bismuth at 800 C followed by filtration at 450 C showed that the UFe_2 had decomposed completely, forming U_3Bi_5 and small particles of iron in bismuth. Weeks reports⁽⁸³⁾ that chromium has little or no effect on the solubility of uranium in bismuth.*

It has been found that the presence of nickel causes a large decrease in the solubility of uranium. This has been mentioned in the section on corrosion. Magnesium, however, does not have a large effect on the solubility of uranium at 500 C.⁽¹³⁰⁾

There has been some discussion as to the effect of zirconium on the uranium solubility. This problem is currently being investigated.

The interaction of uranium in bismuth with possible container materials has been covered in the section on corrosion.

b. UBi_2 as a Slurry Fuel

Since the solubility of uranium in bismuth is rather low, it might be possible to circumvent this difficulty by using a slurry of UBi_2 . This slurry is what Frost⁽¹⁹⁾ would call a reactive slurry, that is, a change in temperature produces a change in solubility which can lead to undesirable effects such as particle growth and mass transfer.

Greenwood and Sharpe^(59,135) studied the effects of thermal gradients on metallic slurries. A thermal gradient was applied across the end faces of a cylindrical stainless steel can, 2 cm long and

*A recent summary of fission product solubilities has been published in the LMFR Monthly Progress Report for May, 1957 (Nuclear Engineering Department, Brookhaven National Laboratory).

2 cm in diameter, with a horizontal axis. The heat input was provided by a nickel bar with one end in "perfect" contact with one face of the can. The cold end of the can was brazed to a long air-cooled copper bar. The heat flux across the can was about 100 watts/sq cm, giving a thermal gradient of 200 C per cm. The slurry consisted of UBi_2 in bismuth, with a particle concentration of about 20 per cent by volume. The average particle diameter of the UBi_2 was about 30 microns. It was found that in a period of several days the particles were completely transported to the cold end of the can. The results can be interpreted in terms of convection flow of the slurry and the difference in solubility. In another paper Greenwood and Sharpe⁽⁴⁾ reported that thermal cycling leads to particle growth of UBi_2 . The extent of plate growth appeared to be limited only by the intersection with neighboring plates or by the container walls. Plates up to 2 cm in length were grown in 20 days.

Greenwood and Sharpe point out that in a possible slurry reactor fuel, these phenomena could lead to complications. They further point out that a slurry of USn_3 in a liquid lead-bismuth-tin matrix has been proposed because the particle and liquid densities may be equal. In such a system it was considered that a uniform particle dispersion in the liquid could be obtained and that in consequence the whole slurry could be maintained relatively fluid. The work of Greenwood and Sharpe suggests that particle transfer to the coldest part of the container is likely even if the particle and liquid densities are equalized.

2. The Bismuth-Plutonium System

Frost, Murgatroyd, and Rutherford⁽²¹⁾ have suggested that a solution of plutonium in bismuth might be an attractive fuel for a fast reactor.

The solubility of plutonium in bismuth has been reported by Los Alamos⁽¹³⁶⁾ and confirmed at Harwell.⁽²¹⁾ Approximate solubility figures are 5000 ppm at 400 C, 36,000 ppm at 600 C and 160,000 ppm at 800 C. The solubility of plutonium in bismuth is about 2.5 times that of uranium at 400 C and two times that of uranium at 800 C.

There is relatively little information on the plutonium-bismuth phase diagram available. The compound PuBi_2 (composition not firmly fixed) decomposes peritectically at about 850 C. PuBi has been characterized.

Little information of the type which exists for the bismuth-uranium system, such as the effect of the presence of a third constituent on the plutonium solubility, is available. No corrosion investigations have been carried out with plutonium-bismuth systems. However, it is reported⁽⁶¹⁾ that plutonium-iron compounds (Pu_6Fe and PuFe_2) are decomposed by molten bismuth to PuBi_2 and elemental iron. This suggests that iron in some form may be a suitable container.

3. Non-Reactive Slurry Systems in Bismuth

Frost defines a non-reactive slurry as a system in which the solid and liquid are inert to each other.⁽¹⁹⁾ He points out that the problem of wetting is serious for this type of system, but that the problem of particle growth should not be serious.

In 1951 Brookhaven reported the results of preliminary wetting experiments^(28,29,44,45) for UO_2 , U_3O_8 , USi , UAl_2 , and UF_4 . According to their data bismuth did not wet any of these compounds. However, pure sodium did wet UO_2 and UF_4 . They point out that there were indications that sodium improved the wetting of UO_2 and UF_4 by bismuth. In a report of the information exchanged in a 1953 visit by Finniston of Harwell to Brookhaven⁽¹³⁷⁾ it is mentioned that at Harwell attempts to produce stable dispersions of ionic compounds, such as UO_2 , U_3O_8 , and UF_4 , were unsuccessful because of insufficient wetting. They feel that addition of the sodium to the bismuth did not give adequate improvement. Later experiments indicated that the presence of uranium in bismuth increased the wettability to a degree which might permit the formation of a stable dispersion. Livey and Murray⁽⁴⁶⁾ also indicate that bismuth, tin and lead do not wet uranium dioxide until temperatures well above their melting points have been attained.

In June, 1956, Davidson, Robb, and Salmon⁽⁴⁷⁾ (a revised version of this document is KAPL-1686) published a reactor concept in which UO_2 suspended in bismuth is the fuel. It was proposed that the fuel have particle sizes of 1 to 5 microns. The slurry would contain 10 to 15 volume per cent of UO_2 . Davidson, et al., were led to consideration of this fuel by experiments in which they successfully wetted UO_2 . In a series of seven experiments, 5 atom per cent of magnesium, sodium, titanium, lithium, and tin and 3 atom per cent uranium were added separately in an attempt to find an additive which would promote wetting and dispersal of UO_2 in liquid bismuth. These capsules were heated to 750 C for 2 hours and shaken vigorously every twenty minutes. The capsules were cooled to 25 C and cut open. The capsule walls were thoroughly wetted by the bismuth containing any one of the additives magnesium, sodium, titanium, and uranium; no unwetted UO_2 was observed. For the capsules containing no additive, lithium or tin the UO_2 did not appear to have been dispersed or wet to any appreciable extent, and the capsule wall above the bismuth surface had not been wetted.

Since in the experiment mentioned above enough magnesium was present to reduce all of the UO_2 to uranium, it was repeated with an increased uranium concentration. In this case there was only enough magnesium present to reduce 20 per cent of the UO_2 . The investigators concluded from this experiment that UO_2 can be wet and dispersed under these conditions in liquid bismuth.

A program is under way at Hanford to develop a plutonium dioxide slurry fuel in bismuth.⁽¹³⁸⁻¹⁴²⁾ Uranium dioxide is being used as a stand-in. In early Hanford experiments they confirm the beneficial effects of magnesium found by Davidson. One unusual idea of the Hanford group has been to form the UO_2 in situ by reacting Bi_2O_3 with uranium dispersed in bismuth. They have used a gamma-ray absorption technique for studying the dispersion of UO_2 in bismuth within a stainless steel capsule.

Livey and Murray⁽⁴⁶⁾ have studied the wetting of uranium carbide by bismuth. Bismuth does not wet at 300, 500, or 700 C in a vacuum. However, if 0.3 weight per cent nickel is dissolved in the bismuth, the uranium carbide is wet at 650 but not at 550 C. Work at KAPL⁽⁵²⁾ indicates however, that in sodium-potassium alloy, uranium carbide at 775 C for 774 hours suffered crystallite growth.

V. SUMMARY

This report has covered the two general systems which have had the most work: UO_2 or uranium in sodium or NaK, and the uranium-bismuth system. It would be highly desirable to extend the survey to other possible systems.

Several experimental heat transfer systems using sodium and NaK have been operated for extended periods at temperatures up to 540 C. Most of the sodium systems which have been built and operated for any length of time have been made principally of 347 stainless steel. Up to temperatures of about 500 C, 304 stainless steel is believed to be satisfactory.

A number of other materials have been exposed to static screening tests. In general they seem to be as resistant to corrosion in sodium as the austenitic stainless steels. Inconel, Inconel X, and pure nickel all give every indication of satisfactory performance in sodium up to 540 C.

There has also been significant operating experience with sodium and sodium-potassium alloys in two experimental systems: a large-scale heat transfer system operated at KAPL, and in EBR-I. The KAPL loop was made of 347 stainless steel and L nickel. The maximum design sodium temperature was 510 C at the heater exit with a rated temperature differential of 150 C. The system operated very satisfactorily for more than 8000 hours which included 500 hours at temperatures of 560 to 650 C. The maximum operating temperature for EBR-I was around 300 C. The materials of construction used were stainless steel and nickel, and the material circulated was sodium-potassium alloy (78 weight per cent potassium).

It now seems possible to select structural materials and equipment for service with sodium and sodium-potassium alloy up to 500 C. For temperatures over 600 C much of the data relating to liquid sodium is

more fragmentary, and it is probably not safe to extrapolate existing data up to temperatures of 700 to 750 C without further confirmation.

Fluid fuel systems using sodium or sodium-potassium alloy as a carrier which have been studied include UO_2 slurries and others.

Bismuth is being seriously considered as a fuel carrier by groups at Brookhaven National Laboratory and at Harwell. Although the solubility of uranium in bismuth is not high, it is great enough to make a homogeneous fuel system possible. The problems of containment of bismuth have not been completely solved, but work is continuing.

Materials which have been considered for containing the bismuth systems include graphite, tantalum, molybdenum, tungsten, beryllium, and the croloy steels. Bismuth is chemically compatible with graphite, but the penetration problem has not been completely solved. Tantalum and molybdenum are possible materials if suitable fabricating techniques can be worked out for all of the necessary components. More work must be done before the croloy steels are proved acceptable as a reactor vessel material.

Fluid fuel systems using bismuth as a carrier which have been studied include solutions of uranium in bismuth, slurries of UBi_2 , bismuth-plutonium solutions, and slurries of compounds such as UO_2 in bismuth.

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