MATERIALS FOR LIQUID METAL SYSTEMS

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MATERIALS FOR LIQUID METAL SYSTEMS

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By: William Holman

Approved by:

Charles M. Rice, Manager
Reactor Engineering Department

A M E R I C A N - S T A N D A R D
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INTRODUCTION

Liquid metals are of interest to the nuclear power industry because of their excellent heat transfer characteristics, low vapor pressure, and because they are monatomic, and, therefore, cannot dissociate under irradiation. In heat transfer applications where high specific powers are required, the high boiling points of liquid metals make it possible to handle large heat fluxes at high temperatures in essentially unpressurized systems.

Research and development work in this field really started about ten years ago as part of the military reactor programs. Prior to this time, liquid metals had been used as heat transfer fluids in a few chemical engineering processes, the General Electric Company had developed the mercury vapor turbine, and there was experience in containing and handling liquid metals in the smelting and refining industry. In the metals industry, the properties of liquid metals and the interactions between liquid and solid metals had been studied for years in connection with casting, welding, brazing, soldering, galvanizing, and other metallurgical processes. The equilibrium diagrams for hundreds of alloy systems had been determined, and the physical properties of many liquid metals and alloys had been measured. There was clearly considerable practical and theoretical background in the liquid metals field. Experience in the use of liquid metals as heat transfer fluids was extremely limited, however, and even today our liquid metal technology is still in its infancy. We have a small amount of operating experience with sodium and NaK systems, and some laboratory experience with bismuth systems. Other potentially useful liquid metals have received some attention, but a great amount of additional research will have to precede any serious attempt to use them in reactors.

The materials problems peculiar to liquid metal systems are due primarily to corrosion and related phenomena. In any given system, the choice of liquid metals and container materials, and the operating conditions are often limited by corrosion.

Research and development work has produced considerable qualitative information on the corrosion characteristics of many liquid metal systems. The data, however, were frequently gathered from rough tests which were designed primarily to survey available materials. The tests were seldom carried out under controlled dynamic conditions similar to those encountered in reactor applications, and the data can rarely be used to predict corrosion results under service conditions.

Sodium and NaK are exceptions to the above statements since they have been chosen as the coolant for a number of reactors, and their corrosion characteristics have been rather intensively studied. There is still much to be learned about sodium, however, particularly at temperatures above 1000° F.

In the discussions which follow, a number of liquid metals will be compared, and the general problems of selecting container materials will be taken up. This will be followed by a discussion of the types and mechanisms of corrosion and the corrosion testing methods commonly employed. The balance of the lecture will be devoted to a brief review of the principal corrosion problems encountered with several of the liquid metals of greatest interest.

SELECTION OF LIQUID METALS

Liquid metals are used primarily as reactor coolants, as liquid metal fuels, and as heat transfer fluids in fuel elements. They have also been considered for use in shielding, control rods, fuel reprocessing, and other nuclear applications. In power conversion equipment, mercury or other metal vapor turbines could be employed.

The choice of a liquid metal for any of these applications obviously depends on a large number of factors. An ideal reactor coolant, for example, should have a low melting point, low-neutron absorption cross sections, low vapor pressures, and low cost. The pumping power required should be low, the heat transfer coefficient should be high, it should be noncorrosive, produce no induced radioactivity, and have low chemical activity. Since no one metal can meet all these specifications, a compromise must be made which best suits the requirements of the particular reactor design under consideration.

Table I, taken from a paper by William E. Parkins,⁽¹⁾ lists all of the elements with melting points below 1250° F and boiling points above 400° F. Most of these elements can be eliminated from consideration as coolants for economic power reactors because of their melting points, corrosiveness, cross section, or cost. The crosses placed in the columns of Table I indicate the elements eliminated on the basis of each of these factors. The seven remaining elements and four promising binary alloys are compared on a relative performance basis in Table II where the engineering difficulties associated with each of nine factors are estimated on a basis of 1 to 5. Circled numbers indicate that the difficulties associated with that factor are major obstacles to the use of the coolant concerned.

A more quantitative method for the comparison of reactor coolant efficiencies was given at the Geneva Conference by Max Hoyant⁽²⁾ of Belgium, who derived an expression for the calories removed from a reactor per neutron absorbed in the coolant. The thermal power of the reactor, pumping power,

TABLE I

ELEMENTS AND CERTAIN PROPERTIES WHICH ARE EXCESSIVELY HIGH TO PERMIT PRACTICAL APPLICATION AS POWER REACTOR COOLANTS. ELEMENTS ARE LISTED BY INCREASING ATOMIC NUMBER AND INCLUDE ONLY THOSE WITH MELTING POINTS BELOW 1250° F AND BOILING POINTS ABOVE 400° F (WHERE KNOWN)

ELEMENT	MELTING POINT	CORROSION	NEUTRON ABSORPTION	COST
Li			X	
Li ⁷				X
Na				
Mg	X			
Al	X	X		
P				
S				
K				
Zn	X	X		
Ga		X		X
Se			X	X
Rb				X
Cd			X	
In			X	X
Sn				
Sb	X	X		
Te	X			X
Cs			X	X
Ce	X			X
Hg			X	X
Tl				X
Pb				
Bi				

Reference: William E. Parkins
 Proceedings 1953 Conference on Nuclear Engineering
 University of California, Berkeley
 September 9-11, 1953, page F-67

TABLE II

APPROXIMATE RELATIVE PERFORMANCE OF LIQUIDS AS POWER REACTOR COOLANTS. RATINGS ARE FROM 1 TO 5 BASED ON INCREASING ENGINEERING DIFFICULTY ASSOCIATED WITH EACH FACTOR

LIQUID	MELTING POINT	VAPOR PRESSURE	CORROSION	CHEMICAL ACTIVITY	HEAT TRANSFER COEFFICIENT	PUMPING POWER	NEUTRON ABSORPTION	RADIOACTIVITY PRODUCED	COST	TOTAL
Na	3	1	1	3	1	1	3	3	1	17
P	2	5	3	4	4	2	2	1	2	(25)
S	3	3	3	2	(5)	5	3	1	1	(26)
K	2	2	1	3	1	4	5	3	3	24
Sn	4	1	(5)	1	1	2	3	4	4	(25)
Pb	5	1	3	1	2	4	2	1	2	21
Bi	4	1	3	1	2	4	1	(5)	4	(25)
56% Na- 44% K	1	1	1	3	2	2	4	3	2	19
97.5% Pb- 2.5% Mg	4	1	4	1	2	4	2	2	2	22
38.1% Pb- 61.9% Sn	4	1	(5)	1	2	3	3	4	3	(26)
44.5% Pb- 55.5% Bi	3	1	3	1	2	4	2	(5)	3	(24)

Reference: William E. Parkins
 Proceedings 1953 Conference on Nuclear Engineering
 University of California, Berkeley
 September 9-11, 1953, page F-69

TABLE III
COMPARISON OF COOLANT EFFICIENCY

Coolant	Isotop. abund.	k	P	$\mu (10^{-2})$	C	M	σ_a	$\frac{k^{2.5}}{\mu^2} \frac{CM \left(\frac{C\mu}{k} \right)^{0.4}}{a}$	T _{melt}	T _{boil}
Hg		0.019	13.7	1.0	0.032	200.6	380	0.022	-39	357
Hg ²⁰²	29.6%	0.019	13.8	1.0	0.032	202	2.4	3.6	-39	357
Hg ²⁰⁴	6.7%	0.019	13.9	1.0	0.032	204	0.34	26	-39	357
H ₂ O		0.00154	1.00	0.18	1.05	6	0.22	0.91	0	(100)
D ₂ O	0.015%	0.00154	1.11	0.18	0.95	6.7	0.00037	570	3	(102)
56Na/44K		0.066	0.89	0.4	0.26	30.1	0.96	100	19	825
P		0.0005	1.7	1.2	0.2	31	0.19	0.004	44	280
K		0.09	0.82	0.35	0.19	39	1.97	87	62	760
Na		0.17	0.93	0.5	0.30	23	0.49	950	98	880
S		0.0003	1.6	>7	0.35	32	0.49	<7x10 ⁻⁵	115	445
44Pb/56Bi		0.025	10.2	1.5	0.035	208	0.094	74	125	1,700
44Pb ²⁰⁸ +56Bi	50%))	0.025	10.2	1.5	0.035	208.5	0.018	390	125	1,700
38Pb/62Sn		0.05	8.5	1.0	0.05	152	0.53	108	183	
38Pb ²⁰⁸ +62Sn ¹¹⁸	50%) 24%)	0.05	8.5	1.0	0.05	152	0.012	4,800	183	
Li		0.1	0.51	0.8	1.374	6.94	67	1.5	186	1,317
Li ⁷	92.6%	0.1	0.52	0.8	1.37	7	0.033	3,100	186	1,317
Sn		0.08	6.7	1.5	0.065	118.7	0.65	110	232	2,260
Sn ¹¹⁸	24%	0.08	6.7	1.5	0.065	118	0.02	3,600	232	2,260
98Pb/2Mg		0.04	10	2	0.04	207	0.17	82	250	
Pb ²⁰⁸ +2Mg	50%))	0.04	10	2	0.04	208	0.002	6,900	250	
Bi		0.037	10	1.5	0.038	209	0.032	550	271	1,477
Pb		0.037	10.4	2	0.037	207.2	0.17	65	327	1,717
Pb ²⁰⁸	50%	0.037	10.4	2	0.037	208	0.00045	2,400	327	1,717
Mg		0.32	1.5	1	0.32	24.3	0.059	18,000	651	1,103
Al		0.22	2.37	1	0.26	27	0.22	2,900	660	2,057

Reference: Max Hoyaux
International conference on the peaceful use of atomic energy
Volume 9 Page 303

neutron flux, total length of pipes, and temperature differences (inlet to outlet and pipe wall to coolant) were maintained constant. Coolant velocity and tubing diameter were assumed to be such that the above conditions were satisfied for each coolant. Table III, taken from this paper, summarizes the results of these calculations. The term

$$\frac{k^{2.5} \rho^{0.75} CM}{u^2 \sigma_a} \frac{C\mu^{0.4}}{k}$$

combines the coolant parameters into one number which is proportional to the calories removed per neutron absorbed. In this expression, k is the thermal conductivity, ρ is the density, C is the specific heat, M is the atomic mass, u is the viscosity, and σ_a is the absorption cross section.

It should be noted that in this method of comparison only three of the nine factors weighed by Parkins (heat transfer, pumping power, and cross section) are considered. The engineering difficulties associated with melting point, vapor pressure, corrosion, chemical activity, radioactivity produced, and cost are not taken into account. These factors must be included in the final analysis since they are often the primary or limiting consideration. Their relative importance will vary with each reactor concept, however, and as our technology improves, we may find that the magnitude of some of the difficulties will decrease.

At present, there are three liquid metal cooled power reactors in operation and several in the planning and construction phase. As might be expected from the above comparisons, sodium or NaK are used as the coolant in all of these reactors.

For applications other than cooling, sodium and NaK are not always the obvious choices. Liquid lead, for example, could conceivably be used as a combination shield and coolant. Bismuth will be used in a combination liquid metal fuel and coolant. High cross section liquid metals could be used for

reactor control, and a low boiling liquid metal such as mercury would probably be chosen if a metal vapor turbine-generator were employed.

SELECTION OF CONTAINER MATERIALS

Materials which will contain or be in contact with liquid metals must resist corrosion and other interactions with the liquid metal. This requirement limits the number of liquid metals which can be considered for many applications and narrows the choice of container materials to a relatively few metals and alloys. The number of available materials is further reduced by structural requirements. Liquid metal systems generally operate at rather high temperatures, and the container materials are often subject to large temperature gradients and thermal shock conditions. Oxidation resistance, aqueous corrosion in heat exchangers, fabricability, weldability, and all the problems encountered in high-temperature equipment are extremely important.

To date, there are only a few container alloys which have been tested sufficiently to warrant their use in reactors. These are all commercially available standard alloys which have proven successful in non-nuclear, elevated temperature service. Several other metals are known to have excellent resistance to attack by one or more liquid metals, but they have not been used because of fabrication difficulties, welding problems, oxidation rates, or other factors not connected with the liquid metal environment. In special applications, zirconium, beryllium, and other metals have been used in contact with liquid metals but not as containers.

There have been no recent reports of attempts to develop new or improved alloys specifically for liquid metal service. Several special alloys were prepared and tested during the early work on mercury,⁽³⁾ and Manly and Cathcart⁽⁴⁾ have studied the behavior of a few highly alloyed materials in lead. With these exceptions, however, all of the work has been confined to standard alloys.

LIQUID METAL CORROSION

Liquid metals are not electrolytes, and, therefore, do not contain positive and negative ions which can enter into chemical or electrochemical reactions. Transfer of electrons, the basic mechanism in most corrosion processes, does not usually occur when liquid and solid metals interact, and the knowledge and experience which has accumulated on electrolytic corrosion cannot be applied when the corrosive agent is a liquid metal.

Manly⁽⁵⁾ has listed six types of liquid metal attack and nine variables affecting the corrosion process.

Types of liquid metal attack are:

- (A) Simple solution
- (B) Alloying between liquid metal and solid metal
- (C) Intergranular penetration
- (D) Impurity reactions
- (E) Temperature gradient mass transfer
- (F) Concentration gradient mass transfer, or dissimilar metal mass transfer

Variables effecting the corrosion processes are:

- (1) Temperature
- (2) Temperature gradient
- (3) Cyclic temperature fluctuations
- (4) Surface area to volume ratio
- (5) Purity of liquid metal
- (6) Flow velocity or Reynold's number
- (7) Surface condition of the container material
- (8) Number (and type) of materials in contact with the same liquid metal
- (9) Condition of the container material (the presence of a grain boundary precipitate, the presence of a second phase, the state of stress of the metal and the grain size)

Simple solution (Type A) results from the fact that all solid metals have a finite solubility in all liquid metals. In the liquid-solid metal systems of practical interest, the equilibrium solubility is extremely small (ppm). It increases exponentially with temperature, however, and under dynamic conditions, serious corrosion problems (temperature gradient mass transfer) can occur.

Under static, isothermal conditions, the solution rate is generally a function of time, surface-to-volume ratio, and temperature. As the solution approaches saturation, the solution rate decreases, and at equilibrium no further attack takes place. If the surface-to-volume ratio is large, the total penetration (or weight loss per unit area) will be smaller than that of a smaller surface area exposed to the same volume of liquid.

Alloying between liquid metal and solid metal (Type B) takes place when there is some solubility of the liquid in the solid. Solid state diffusion of the liquid metal into the bulk solid, or preferentially into grain boundaries, results in the formation of diffusion zones or intermetallic compound layers which can alter the heat transfer characteristics of the system, change the properties of the container and/or restrict the flow of coolant. Sometimes a metal which will alloy with the container is deliberately added in small amounts to the liquid metal. The resulting diffusion zone may act as a self-healing barrier or coating which reduces the corrosion rate.

Intergranular penetration (Type C) is perhaps the most insidious and least understood type of attack found in liquid metal systems. It can result from preferential attack on impurities or second phases which have segregated into or been precipitated in the grain boundaries of the solid metal. It can also occur when one of the components is selectively removed or leached from a container alloy. Higher grain boundary diffusion rates may cause a reduction in the concentration of the leached component in the vicinity of the boundaries, and this may in turn open up the boundary to penetration by the liquid.

Vacancies left by the outward diffusing atoms may precipitate as holes along the grain boundary and contribute to the opening up process. Surface tension or surface free energy effects, impurities in the liquid alloy, and stress may also play a part in intergranular penetration.

Reactions between solid metals and impurities in liquid metals (Type E) are responsible for most of the corrosion problems encountered in sodium and NaK systems. The mechanism of attack is not clearly understood but over the range of temperatures usually employed, oxygen content appears to be the principal variable affecting corrosion rates. Actually, the rates are so low that the effects of variables other than oxygen content are difficult to determine experimentally. The mechanisms of impurity reactions and the methods of dealing with this type of corrosion will be discussed in detail later.

Temperature gradient mass transfer (Type E) may occur when a temperature gradient exists in the system. The equilibrium concentration of container metal will be higher in the hotter regions than in the cooler regions, and the resulting concentration gradient will cause diffusion to occur. When the concentration of solute exceeds the equilibrium solubility in the cold region, precipitation will take place. The net result is a continual transport of container metal from hot to cooler regions. If the liquid metal is acting as a heat transfer fluid, a temperature gradient must exist and observable corrosion of this type may occur. In a dynamic system, where the liquid metal is circulated through a temperature differential, the concentration of container metal will approach saturation in the hot zone, and the solution will become supersaturated when cooled in the cold zone. Precipitated metal accumulating in cold regions will restrict the flow and may plug the system.

Concentration gradient or dissimilar metal mass transfer (Type F) may occur when two or more different solid metals are in contact with the same liquid metal. Any solid solubility of one metal in the other(s) will result in the transfer of some of that metal from the solution to the other metal and

the formation of a diffusion zone at the surface. While the solid diffusion zone builds up, the concentration of the diffusing element in the liquid at the solid-liquid interface is lower than the concentration of that element at the interface from which it originated. There is, therefore, a concentration gradient in the liquid which furnishes the driving force for this type of mass transfer. It is interesting to note that corrosion can occur by this mechanism in the absence of temperature gradients or circulation of the liquid.

The nine variables influencing the corrosion processes are briefly discussed below:

- (1) Temperature: Generally, the rate of corrosion increases exponentially with increasing temperature, because solubilities, diffusivities, and the rates of impurity reactions are all exponential functions of temperature.
- (2) Temperature gradient: If temperature gradient mass transfer occurs, the rate will increase (approximately linearly) with increasing ΔT .
- (3) Cyclic temperature fluctuations: Temperature fluctuations may produce alternate solution and precipitation of the container metal. If precipitation takes place in the bulk liquid (rather than on the wall), the particles may settle or float away. During the next temperature rise, additional solution of the wall will take place.
- (4) Surface area to volume ratio: In static isothermal systems, the amount of attack is proportional to the surface-to-volume ratio as discussed earlier.
- (5) Purity of liquid metal: This is obviously a very important variable if impurity reactions take place.
- (6) Flow velocity or Reynold's number: The thickness of the lamellar boundary layer at the liquid-solid interface is influenced by velocity. If diffusion through the boundary layer is the rate controlling step in the corrosion process, the rate of attack will be a function of velocity.
- (7) Surface condition of the container material: The rate of attack during the initial stages of corrosion may be influenced by surface

condition if the surface is roughened, cold worked, or has a different composition than the underlying bulk metal

(8) Number (and type) of materials in contact with the same liquid metal:

If two or more materials are in contact with the liquid metal, concentration gradient mass transfer may occur and the rates of other corrosion processes may be affected.

(9) Condition of the container material: The corrosion rate may be influenced by the condition of the container material, particularly if there is a precipitate in the grain boundary. Stress, the formation of a second phase, grain size, orientation, amount of cold work, and other variables all influence the rate of attack.

It is apparent from the above discussion that it is not possible to pick a corrosion rate from the literature and expect it to apply to a different system, even though the materials and operating conditions are similar. The few corrosion rates which have been reported can seldom be applied to systems other than those in which they were measured, and there is a high probability that if the measurements were repeated, the results would differ by several hundred per cent or by an order of magnitude. Even if a reliable corrosion rate is determined under conditions very similar to those anticipated in service, considerable interpretation is required before it can be used in the design of reactor components or systems. If intergranular penetration occurs, for example, a corrosion rate given in terms of weight loss or gain (per unit area per unit time) is useless and misleading. The same criticism applies to those systems in which impurities diffuse from the liquid metal into the container and change its physical properties. If mass transfer occurs, the rate of weight loss in the hot region may not be so important as the rate and mode of deposition of transported material in the cold region. Other examples could be given, but these should be sufficient to point out the fact that numerical corrosion rates in themselves are not numbers which can be used to design reliable systems or predict with any accuracy the life of components.

The current practice is first to choose materials which appear satisfactory in laboratory tests. Large-scale, long-term tests are then carried out under conditions as close as possible to those which will be encountered in practice. If the designs and materials are satisfactory in these tests, it is assumed they will perform adequately in reactor service. This time consuming and expensive empirical method will have to be used until more operating experience has been gained and until more fundamental information is available on liquid metal corrosion mechanisms and corrosion rates.

There have been a few papers in which theoretical corrosion rate equations have been developed. These equations can seldom be applied to real systems because of the idealized and simplified conditions assumed in their derivation, and because the necessary solubility data and rate constants have not been determined for most systems of interest. The equations are of value, however, since they indicate the functional relationships among the important variables and are of assistance in interpreting experimental results.

Under isothermal conditions most solids have been observed to dissolve at a rate which is proportional to the difference between their concentration in the liquid and their equilibrium solubility at the test temperature. A plot of solute concentration versus time has an initial slope of $\alpha A/V$, where α is the specific rate constant, A is the surface area exposed to the liquid, and V is the volume of liquid. If diffusion through a liquid boundary layer is the rate controlling step $\alpha = \frac{D}{\delta}$ where D is the diffusion coefficient and δ is the thickness of the boundary layer. α is simply a proportionality constant relating the rate of solution to the concentration, when the passage of solute atoms into the liquid, (rather than diffusion through the boundary layer) is the rate controlling step. The concentration versus time curves follow the expression

$$S = S^0 \left(1 - e^{(-\alpha A t/V)} \right)$$

where S is the concentration of the bulk liquid at time t , and S^0 is the equilibrium concentration at the test temperature. The slope decreases with

time as saturation is approached. The variation of the solution rate constant (α) with temperature is of the form, $\alpha = \alpha_0 e^{-\Delta E/RT}$, where ΔE can be taken as the over-all activation energy for the dissolution process. (6)

Epstein (7) has developed two theoretical equations for the rate of mass transfer in dynamic pipe loops where the liquid metal is circulated through a temperature differential. In these equations he assumes a uniform attack with the dissolution step controlling the over-all rate.

For the case where passage of atoms into the liquid (rather than diffusion through the liquid) is the rate controlling step, Epstein's equation can be reduced to the following expression:

$$R_T = \frac{\alpha}{2} \left(\frac{dS^0}{dT} \right) \Delta T$$

where R_T = corrosion rate (gms/cm²/sec), ΔT = temperature differential $T_2 - T_1$, $\frac{dS^0}{dT}$ = average slope of the equilibrium solubility versus temperature curve at temperature $\frac{T_2 + T_1}{2}$. A multiplying term containing the length of the loop,

diameter, and velocity $\left(\left[1 + (2\alpha L/\pi V d^2) \right]^{-1/2} \right)$ has been omitted since it is very nearly one in all practical cases. In this case the rate is directly proportional to the temperature difference, to α , and to the slope of the liquidus at the mean test temperature. The variables controlling the thickness of the boundary layer (velocity, diameter, and viscosity) and the diffusion coefficient have no effect on the mass transfer rate when the diffusion step is fast compared with the rate of solution.

When the rate of solution is fast compared with the rate of diffusion through the boundary layer, the liquid at the interface reaches and is maintained at equilibrium with the solid. In this case the rate of mass transfer is determined by the diffusion coefficient and the thickness of the boundary layer. Using the analog between heat transfer and mass transfer, Epstein

developed the following rate equation.

$$R_T = 0.023 (D/d) \left(\frac{Vd}{\nu}\right)^{0.8} (\nu/D)^{0.4} \left(\frac{dS^0}{dT}\right) \Delta T$$

where $\frac{Vd}{\nu}$ = Reynold's number, $\frac{\nu}{D}$ = Schmidt number, D = diffusion coefficient, d = diameter, V = velocity, ν = kinematic viscosity.

It will be noticed that α has been replaced by a series of terms which include Reynold's number and the Schmidt number. The rate is still directly proportional to ΔT and dS^0/dT , but it is now also dependent on velocity, diameter, and the properties of the liquid.

In many liquid metal heat transfer systems, the mass transport process can be broken down into the following steps:

1. Dissolution - transfer of atoms from the surface of the container, across the liquid-solid interface, into the liquid boundary layer.
2. Diffusion of atoms through the boundary layer into the bulk liquid.
3. Transport of dissolved metal (and possibly dislodged grains) from the hot region into colder regions by the flowing liquid.
4. Nucleation and growth of crystals (in the liquid or on the wall) in the colder regions.
5. Transport of nuclei and crystals by the flowing liquid. Some of the crystals may be carried into the hot zone where they will dissolve. Others will become trapped in the boundary layer in the cold zone where they will grow and sinter together.
6. Plug formation by the buildup of crystals in the cold zone.

A solid state diffusion step can be added at the top of the above list in many cases. If an inhibitor has been added or if leaching of one component from the container alloy has resulted in the formation of a barrier film or a new phase at the surface, then diffusion through this film or phase is also a step in the over-all mass transport process.

Many of the above steps could influence or control the over-all rate of mass transport. If Steps 1 or 2 are controlling, then one of the equations developed by Epstein should predict the rate.

TESTING METHODS

Interactions between solid and liquid metals and the suitability of container materials for liquid metal service, have been investigated by four general techniques.

1. Static Capsule or Pot Tests: The solid and liquid metals under investigation are maintained in contact without relative motion. Static tests of this type are frequently carried out by sealing the liquid metal in small containers of the solid metal and submitting the capsules to a predetermined heat treatment. If "inert" materials, such as quartz or vycor (which are not attacked by pure lead or bismuth) are available for encapsulating the liquid metal, it is possible to obtain data with standard corrosion coupons.

Static tests are usually conducted under isothermal conditions. They are relatively cheap tests, and if conducted properly, they are useful for obtaining equilibrium data, solution rate data, and for screening materials. To date, they have been of little value in predicting corrosion results under dynamic, nonisothermal conditions. Basic information obtained from carefully controlled static experiments is of considerable theoretical value, however, since data of this type is necessary for a complete understanding of the mechanisms of corrosion and mass transfer.

2. Dynamic Capsule or Pot Tests: Relative motion between the liquid and solid metals is induced by convection, stirring, rotating the specimen, or by tilting the container. Temperature gradients may be introduced and some measure of the mass transport characteristics of the system may be obtained. The results are seldom quantitative and are used primarily to survey materials.

3. Thermal Convection Loop (or Harp) Tests and Toroid Tests: The liquid metal is induced (by convection or by centrifugal force) to flow through a pipe loop system containing a temperature gradient. Tests of this type are used to screen or compare materials which appear promising in the cheaper

tests (1 and 2 above), and the results are sometimes used to estimate corrosion rates under operating conditions.

4. Pumped Loop Tests: The liquid metal is circulated through a system which simulates in many respects the conditions found in a reactor. Rather high velocities and large temperature gradients are often provided. Pumped loops are expensive since they require pumps, flow meters, surge tanks, sump tanks, cold traps, and many of the other components found in reactors. They are therefore generally reserved for proof testing materials which have proved their compatibility in one or more of the preceding types of tests.

A number of methods are used to determine the results of corrosion tests and to interpret these results in a useful manner. The methods employed will depend on the objectives of the test and the type of test employed. Five common methods are listed below.

- (1) Chemical analysis of the liquid metal
- (2) Weight or dimensional changes
- (3) Plugging time or rate of plugging
- (4) Metallographic analysis
- (5) Change in properties of the container or corrosion specimen
(Creep, stress rupture and fatigue tests are sometimes carried out in the liquid metal)

LIQUID METALS OF CURRENT INTEREST

Mercury

Mercury has found limited application in the nuclear power field. It has been used to fill the annular space in double walled sodium-to-water heat exchanger tubing where it acts as a leak detector and prevents intermixing of the fluids when small leaks develop. It has also been used as the coolant in the Los Alamos research reactor, "Clementine". Its high thermal neutron cross section, however, prevents its consideration as a power reactor coolant.

Mercury may find use as a neutron absorbing control material, and as the working fluid in power conversion equipment. If isotope separation should become economically feasible, the low cross section Hg-204 could be used as a coolant or possibly as the solvent in a liquid mercury-uranium fuel.

Most of the available data on corrosion by mercury was determined about 35 years ago during the development of the mercury vapor turbine.⁽³⁾ Since that time, there have been a few reports of laboratory scale studies^(8,9) but little new information on corrosion has appeared. The early corrosion work was undertaken when it was found that large quantities of iron were transported from the hotter to the cooler regions in mercury boilers. This unexpected phenomenon stimulated an extensive research effort in which hundreds of thermal convection loop (or harp) tests were undertaken. Most of the tests were carried out on low alloy steels at about 1200° F. Austenitic stainless steels were found to have poor resistance at this temperature. Ferritic stainless steels were not tested in dynamic systems, although they were found to have good resistance to attack by static mercury at 1020° F. The best low alloy steel tested contained about 5% Cr, 0.5% Mo, and 1.5% Si (Sicromo 5S or Croloy 5Si).

The effect of additives to the mercury were determined in many of the tests, and it was found that zirconium, titanium, chromium, nickel, and aluminium were effective corrosion inhibitors. Titanium in amounts of about

10 ppm reduced the rate of attack to an inappreciable value. Magnesium was added with the titanium and maintained at a concentration of about 20 ppm. The magnesium promoted wetting by reducing oxides on the steel surfaces, and reacted with any free oxygen, nitrogen, or water vapor which would have reacted with the titanium (in the absence of Mg) and removed it from solution in the mercury.

Development of the titanium-magnesium corrosion inhibitors solved the mass transport problem in mercury boilers and apparently marked the end of research on mercury corrosion. The mechanism of inhibition was never fully understood, although it was postulated that some sort of extremely thin surface barrier or film was formed. This barrier probably changed the corrosion mechanism from one in which the rate was controlled by diffusion through the liquid boundary layer to a much slower process which was controlled by the rate of solution (transfer from wall to liquid through the barrier).

Sodium and NaK

Sodium and NaK are the only liquid metals currently in use as power reactor coolants. As discussed earlier, they have been the outstanding choice for most liquid metal heat transfer applications and have therefore been the subject of a large number of major research and development programs. Most of the liquid metal technology built up during the past ten years has resulted from the intensive effort devoted to the development of reliable sodium and NaK systems.

A comprehensive report of this work can be found in the Liquid Metals Handbook, sodium-NaK supplement⁽¹⁰⁾ where details of several large heat transfer systems are given, together with a number of papers on design, components, properties, heat transfer, and chemical engineering. A good review on corrosion by sodium is given in Reference 11.

The choice of container materials for sodium or NaK at temperatures below 1000°F is rather broad. From a corrosion standpoint any of the

austenitic stainless steels are adequate, although Types 347 and 304 are generally chosen. Ferritic stainless steels and even ordinary carbon and low alloy steels are satisfactory under proper conditions. Nickel or cobalt base alloys, beryllium, the refractory metals (Cb, Mo, Ta, Ti, W, Va, Zr, and Cr), and carbides of tungsten, titanium, or chromium (bonded with either nickel or cobalt) are also resistant to attack by sodium.

There is not a great deal of unclassified information available on corrosion by sodium at temperatures above approximately 1000°F. Temperatures of this magnitude are not contemplated in any of the liquid metal cooled civilian nuclear power plants announced to date, and it can be assumed that this is about the current limit for reliable long-term operation. Higher temperatures may become feasible in the near future, however, since temperatures of 1500°F have been used for short times in several systems such as the recently announced Aircraft Reactor Experiment⁽¹²⁾ and the Mine Safety Appliance Company High Temperature System.⁽¹⁰⁾

Corrosion by sodium and NaK at temperatures below 1000°F is due almost entirely to the presence of trace amounts of oxygen which cannot be completely removed from the system. Stainless steels exhibit weight gains due to the formation of strongly adherent chromium oxides on the surface. Low alloy steels, on the other hand, lose weight, possibly by the formation of a loosely adhering mixed oxide $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$, which spalls off the surface and is in turn reduced by the bulk sodium to regenerate Fe and Na_2O .⁽¹³⁾ The rate of corrosion of iron in oxygen-contaminated sodium is approximately proportional to the oxygen concentration. The process is apparently solution rate controlled with the value of α in Epstein's equation increasing with increasing oxygen concentration.

The discovery that corrosion by sodium is due primarily to oxygen contamination has led to the development of cold trapping techniques for controlling the oxygen content and has emphasized the need for vacuum tight systems.

Fabrication procedures have been modified to insure the complete exclusion of air, and all components are now designed to be as tight as possible. These procedures have reduced corrosion rates to insignificant values and have essentially solved the low temperature corrosion problem.

Oxygen control by cold trapping is based on the fact that the solubility of sodium oxide in sodium is extremely low at low temperatures. Part of the hot sodium stream is continuously bypassed through a regenerative heat exchanger into a cooled chamber or trap where sodium oxide precipitates and is retained. Sodium returned to the main stream has an oxygen content approaching the equilibrium solubility at the trap temperature. Properly designed cold traps can reduce the oxygen content to around 10 ppm.

Hot traps (in which a bypass stream is heated while in contact with zirconium) have recently been developed in an attempt to increase the purity of sodium beyond that attainable with cold traps.⁽¹⁴⁾ Higher purity sodium is needed if zirconium alloys are used in any of the components since oxygen has an appreciable solid solubility in zirconium and the oxides formed at the surface are, in a sense, dissolved by the metal. Even a few parts per million of oxygen in the sodium will in time result in severe embrittlement of zirconium components.

Gross mass transport of container material has not been a serious problem in sodium or NaK systems operating below 1000°F. Oxide plugs will develop in the coldest parts of loops containing oxygen concentrations in excess of the equilibrium solubility (at the lowest temperature in the loop) but there have been no reports of metallic plugs. Minute quantities of material are transported, however, and while there may be no structural degradation, the distribution of radioactivity throughout the system is a serious problem from the accessibility standpoint.

Bismuth and Lead

During the last ten years there have been several relatively small-scale

research programs on the behavior of materials in liquid lead, liquid bismuth, and lower melting point lead-bismuth alloys. The effects of small additions of other alloying elements have also been studied, although most of the work has been focused on pure metals. Bismuth has been investigated because of its low cross section and the fact that it can dissolve enough uranium to act as a liquid fuel. Lead has been of general interest because of its attractive combination of nuclear properties and heat transfer characteristics, but it has not as yet been used as a reactor coolant.

Lead and bismuth have similar corrosion characteristics and both are considered aggressive liquid metals when compared with the alkali metals.⁽¹⁵⁾ Lead is somewhat less corrosive than bismuth but neither is satisfactory as a reactor coolant without the addition of inhibitors. As with mercury, the temperature coefficient of solubility of construction materials is appreciable and considerable mass transport occurs in nonisothermal, dynamic systems.

Additives such as titanium and zirconium have been found to inhibit mass transport by lead and bismuth in much the same manner as they inhibit mass transport by mercury. Details of the mechanism are still under investigation but recent research on bismuth solutions containing zirconium has indicated that a zirconium nitride (ZrN) film is formed on the container surface.^(15, 16) Nitrogen in the steel presumably diffuses to the interface where it reacts with zirconium to form a thin but effective diffusion barrier. Earlier work at Stanford University⁽¹⁷⁾ also suggested the presence of a barrier film.

Lithium

Natural lithium has been of minor interest as a reactor coolant because of its high thermal neutron cross section. A small amount of corrosion work has been reported, but until recently, there has been relatively little activity in the liquid lithium field. In June, it was announced that several companies are separating isotopes of lithium.⁽¹⁸⁾ If lithium-7 should become available, it would be of considerable interest since it is potentially a much better reactor coolant than sodium (Table III).

The corrosion picture is confusing at present, but there appears to be no doubt that lithium is more corrosive than sodium. Most of the early work was carried out with commercial lithium of unknown or poorly controlled purity and the results are questionable. More recent work has indicated that trace amounts of impurities have a great effect. Small additions of lithium nitride, for example, have been shown to produce severe intergranular attack.⁽¹⁹⁾

Hoffman and Manly⁽²⁰⁾ recently reported that pure iron and the austenitic and ferritic stainless steels had good resistance to corrosion by pure lithium at temperature below 1000°F. Nickel and nickel base alloys were severely attacked. The refractory metals (Mo, Nb, Ta, Zr, Ti, W, V) were not tested, but it was predicted that they would resist corrosion at temperatures approaching 1500°F.

SUMMARY

Corrosion has been emphasized throughout this presentation because it is the only liquid metal selection factor (with the exception of cost and isotope concentration) over which we can exert any control (Table I, II, and III), and because, it is really the only new factor which must be considered in the selection of high temperature materials for liquid metal systems.

During the past ten years our liquid metal technology has been developed to the point where sodium and NaK are being used as reactor coolants at temperatures approaching 1000° F. Higher temperatures will be possible in the future, and with additional work, several other liquid metals may find applications in the nuclear power field.

Progress has been slow because of the severe operating conditions, the low corrosion rates required, the dirth of good basic corrosion data, and a lack of experience with large dynamic liquid metal systems. We are fortunate that pure sodium and NaK, with their excellent combination of nuclear and physical properties, are essentially non-corrosive in the temperature range of current interest.

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