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Mass Transfer and Oxygen Analysis in the SNAP 5 KWe
Ground Test Reactor

AUTHOR

R. L. Eichelberger

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ABSTRACT Mass transfer in the SNAP 5KWe Ground Test Reactor System is discussed. It is shown that because the primary system consists of several different alloys, it is predisposed to be subject to mass transfer processes. For a given combination of materials, the rate at which mass transfer will occur depends upon the maximum temperature and the temperature difference in the loop, and upon the oxygen concentration of the NaK. In order that the system produce its rated power, the maximum temperature and the specified temperature difference must be obtained in operation, so that the only controllable factor affecting mass transfer is the oxygen impurity concentration in the NaK. Because the system does not include a cold trap, it is necessary to effect the control of the oxygen concentration during the NaK charging and clean-up operation. The clean-up operation should involve cold trapping with an auxiliary, removable unit, and it should be operated until the oxygen concentration is no more than 5 wppm, with the system at at least 600° F, and preferably at 800° F. Then the loading and clean-up unit can be removed, and the reactor system sealed off.

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TABLE OF CONTENTS

	Page
INTRODUCTION	3
SNAP 5KWe SYSTEM	6
Stainless Steel	6
Hastelloy-X	7
Inconel-718	7
Ta-10W	7
Chemical Potential Mass Transfer	7
CONTROL OF MASS TRANSFER IN SNAP 5KWe PRIMARY NaK SYSTEM	8
RECOMMENDATIONS FOR FILLING AND START-UP OPERATIONS	8
RECOMMENDATIONS FOR SAMPLING AND ANALYSIS OF THE PRIMARY NaK SYSTEM	9
REFERENCES	10

INTRODUCTION

The 5KWe SNAP reactor contains a primary NaK circuit and a secondary NaK circuit. Temperatures in the secondary circuit will not be appreciably above 600°F, with only a small temperature differential. Therefore, this system should have no problems associated with corrosion or material transfer over the projected five-year life. Even if the final design includes more than one containment material, at 600°F the rate of chemical potential mass transfer will be negligibly small.

Temperatures in the primary NaK system, however, will be as high as 1200°F, with a temperature differential of 100°, and the materials in contact with the NaK include austenitic stainless steel, Hastelloy-X, Inconel-718, and Ta-10W. These circumstances generate the possibility of mass transfer.

Mass transfer deposits have been found in NaK systems under two general sets of conditions: 1) when a temperature gradient is present regardless of the materials of loop construction, and 2) when different construction materials are present in the system, whether or not the system is isothermal. In general, in a system with a ΔT , the material transfer is from the hot region to the colder region. The driving force for such transfer is considered to be the difference in the "solubility" of the construction materials at the extremes of temperature. If only one material is present in the system, i.e., in an all-nickel loop, the rate of transfer depends on the mechanisms of solution and deposition, and may be controlled by the rate of solution or deposition, or by diffusion through a liquid boundary layer. If there are several materials in the system, or if the material is an alloy of several metals, the transfer rate may change with time, as some components are depleted in the hot region, or their availability to the liquid metal is controlled by solid state diffusion. The driving force for the transfer is still the difference in "solubility" at the higher and lower temperatures.

"Solubility" is put in quotes above to indicate that the actual physico-chemical process involved may not be simple solution (although it may be) but may include oxygen- or carbon-related mechanisms.

In an isothermal system which contains only one solid metal, there is no driving force for mass transfer and none occurs. The same is true if the metal is an alloy of constant composition, since in this case the equilibrium in the system is the same at all points, the equilibrium being only a function of temperature in a system of constant composition. The amount of each constituent of an alloy which is in solution at any temperature is determined by the chemical potential of the constituent in the alloy. The concentration of a metal in a solution in equilibrium with a pure metal at a given temperature is the solubility of that metal, but if the solid metal is not pure, i.e., an alloy, the concentration of the metal in solution at equilibrium is less than the saturation value. In many systems the concentration in the liquid solution is proportional to the mole fraction of the metal in the solid alloy.

chemical potential be the same in each phase.

If there are different alloys in an isothermal system, mass transfer will occur as the system attempts to re-arrange itself so that the solution "sees" the same chemical potential (i.e., same composition) of the various constituents at all points in the system. For example, in an isothermal NaK system containing stainless steel and Hastelloy, the chemical potential of iron in the steel is greater than that of iron in the Hastelloy, and a driving force for transfer of iron from one alloy to the other is present. If the rate of transfer is sufficiently great, the system can approach equilibrium with regard to iron. If the mechanism of transfer involves the formation of a stable solid solution or intermetallic compound, transfer may continue indefinitely.

Chemical potential-driven mass transfer often occurs rapidly in liquid metal systems. This phenomenon is the basis for the AI "Difcoat" process, in which substrates are rapidly coated with metals in a liquid sodium or liquid lithium bath. A coating of Fe, Ni, and Cr on fuel elements in S8DR, which were clad with Hastelloy-N, apparently formed in less than 100 hours to a thickness of up to 0.0002".^(7, 8) The reactor was not critical at the time, and was heated by electrical heaters, remaining nearly isothermal. Similar coatings have been observed in equally short exposures in NaK loop systems containing Incoloy-800 as the material on which the iron-rich deposit formed.

The literature on the corrosion and mass transfer of containment materials in Na and NaK is extensive, with work on sodium systems constituting by far the greatest part. At least to a close approximation, the corrosion behavior of the materials which have been studied in both Na and NaK has been the same in both liquid metals. Therefore, in the following discussion no special effort is made to separate the results reported for the two media.

A careful look at the literature shows that the status of world knowledge has been shared comparatively recently at a specialists' meeting on the subject of corrosion product behavior in LMFBR primary systems⁽¹⁾. The systems for which information is reported are made of austenitic stainless steel, for the most part. Information on nickel alloys was presented rather completely at the IAEA Vienna meeting in 1966, in articles by Thorley and Tyzack from the UK⁽²⁾, and DeVan from the USA⁽³⁾. The latter work had been carried out a number of years earlier for use in developing aircraft and space power systems, but had been classified. Very little work has been reported more recently on nickel-NaK or Na interactions, although a small effort involving nickel-base alloys in Na was undertaken at ANL⁽⁴⁾. Several groups are building stainless steel loops to simulate LMFBR sodium systems, but no definitive results of corrosion or mass transfer tests have yet been reported from these new facilities.

The most recent experimental work, and interpretation and analysis of earlier reports, was done at BNL by Weeks and Isaacs⁽⁵⁾. An attempt to formalize mathematically the mass transfer in the sodium-Inconel system was presented by Evans and Nelson⁽⁶⁾. Although this latter work is interesting and innovative, the authors state that their analytical results fail to describe satisfactorily the corrosion mechanism in the sodium-Inconel system.

The following discussion is based on the results presented in the references cited above (and the work they reference) and the less formally published observations at AI from S8ER and S8DR experience, as well as associated corrosion loop data.

SNAP 5 KWE SYSTEM

The secondary NaK system was brushed off rather quickly above. There is no reason to treat it in more detail here, except to note that the oxygen level in the NaK must be kept under about 100 wppm to prevent the precipitation of Na_2O , which could plug the lines.

The primary system, however, does have the potential for transfer of material, both through temperature differential mass transfer and chemical potential mass transfer. The four metals in the system will be discussed individually as sources for such transfer.

Stainless Steel. The corrosion of stainless steel in NaK is a strong function of the temperature of the steel, with the rate doubling in about 100°F . Similarly, the oxygen level of the NaK strongly affects the corrosion rate, with an increase of about a factor of 10 at 25 wppm oxygen compared to 5 wppm oxygen. All the corrosion rate expressions which have been proposed would predict a rate of less than 1 mil per year at 1200° if the oxygen level were maintained below 10 wppm. The equations generally also consider a "downstream effect," which reduces the corrosion rate as a function of the distance from the heated region. The effect of a temperature differential in the system is not as well defined, and in fact has not been seen in general. That is, the metal removal rate at the highest temperature is at most a weak function of the temperature difference in the system. The corrosion rate is dependent on the velocity (Reynolds number) to a marked extent, showing that the mechanism of metal removal is related to the thickness of the liquid boundary layer. However, the effect of velocity levels off at about 10 to 15 ft/sec, and the corrosion rate of less than 1 mil per year suggested above for the present SNAP system corresponds to the high velocity experimental work.

The deposition of the corrosion products from the stainless steel in the SNAP system will be general, with somewhat greater deposition in high flow areas (orifices) and at flow disturbance regions such as elbows.

Taken by itself in the primary NaK circuit, stainless steel would not be expected to corrode or deposit to a marked degree at the temperature levels, the 100° temperature differential, and the low oxygen level planned. The probability of chemical potential mass transfer will be discussed later.

Hastelloy-X. This alloy is nearly 50% nickel. Corrosion experiments on high nickel alloys have shown about one-half the attack experienced on stainless steel at SNAP reactor temperatures, at about 10 wppm oxygen. There is a greater dependence on temperature differential than with steel, but at the modest differential (100°) in the 5 KWe reactor and the not extreme temperature (experiments reported were run at 1500°), chemical attack corrosion will not be significant. The oxygen level in the NaK does not have an important effect on the corrosion rate of nickel and high-nickel alloys. Chemical potential mass transfer is discussed below.

Inconel-718. No experiments on this alloy have been reported, but it is expected to behave similarly to other high-nickel materials, in that its corrosion will not be oxygen sensitive.

Ta-10W. This alloy is not noticeably attacked in several thousand hours at 1300° in low oxygen sodium. The possibility of reaction with hydrogen is more serious, but will not be discussed here. At high oxygen levels, this alloy will be a getter, removing oxygen from the NaK.

Chemical Potential Mass Transfer. It can be unequivocally stated that chemical potential mass transfer will occur in the SNAP 5KWe primary system. The degree to which it will take place can be controlled to some extent. In a system containing steel and high nickel alloys, the potential for transfer is present for all the materials to redistribute so that the surfaces seen by the NaK in all regions exhibit the same chemical potential. In an isothermal system, this would mean that the surfaces would eventually all have the same apparent composition. The relatively small temperature difference seen in the SNAP primary system will perturb this to a small extent, and superimpose the possibility of some temperature gradient transfer, but the major transport mechanism is expected to be that associated with the chemical potential (composition) differences in different parts of the system.

If the oxygen concentration of the system is high, the mechanisms for the transport of Fe and Cr (and Mn, although present only in small concentration in the steel) are favored, since the evidence is that oxygenated species participate strongly in the corrosion and alkali metal transport of these metals. Operation at 1200° at high oxygen in the NaK, say over 50 wppm, would result in rapid deposition of Fe and Cr on the nickel alloys in the system,

reaching a quasi-equilibrium in, at most, a few hundred hours. At low oxygen levels, say, under 5 wppm, the rate of Fe and Cr transfer is lower, but the rate of Ni transfer is relatively unchanged. There is no experimental evidence from which to predict a rate of nickel transfer in a low oxygen system containing steel and a high nickel alloy, but it is expected that the direction of transfer would be from the nickel alloy to the steel. In systems with appreciable oxygen, the movement of Fe and Cr is from the steel to the nickel alloy, and it is not really possible to determine from the surface composition in which direction the nickel moves. From examination of the deposits, however, it seems probable that the Ni moves with the other constituents of the steel.

CONTROL OF MASS TRANSFER IN SNAP 5KWe PRIMARY NaK SYSTEM

There seem to be two means of minimizing the mass transfer in this system: keep the temperature low and keep the oxygen level in the NaK low. Keeping the temperature low is of course not a reasonable measure to be used except in preliminary operation of the system, since the temperatures needed for power production are pre-determined. The transfer which might occur during the life of the reactor must be controlled by the proper control of temperature and oxygen level during filling and pre-power generation operation. Recommendations for this are given below.

The recommendations given are based on the assumption that material transfer in the primary system is bad, and must be minimized. Although it is not proved, for example, in the case of S8DR that mass transfer coating on the fuel rods led to cladding failure, this conservative point of view must be taken here.

RECOMMENDATIONS FOR FILLING AND START-UP OPERATIONS

It is assumed that the components are properly cleaned before assembly, and that adequate precautions are observed to prevent the inclusion of oxides, water, solvents, or extraneous solid materials in the system during fabrication.

The filling cart has not yet been designed. It should include an effective cold trap, and a sampling station for flow-through samplers. The reactor system should not be filled until the oxygen level of the NaK is less

than 5 wppm (see below for remarks on sampling and analysis). Filling should be through a sintered stainless steel filter with a pore size no greater than 10 microns.

After filling, system clean-up should be carried out at 600°-800° until the oxygen level is again below 5 wppm. This clean-up may either be carried out with the primary system still attached to the loading cart, using its cold trap, or it may be carried out with a cold trap as an appendage to the primary system. Sampling and analysis devices must of course be employed in either case.

After clean-up of the system, the cart should be detached and/or the cold trap cut or valved out of the system. The temperature can then be raised in whatever manner is desired. Chemical potential mass transfer will occur to whatever extent it will, but no further control measures are feasible. Monitoring of the system for oxygen (and hydrogen) would be desirable during subsequent operation, but this may not be feasible, as discussed below.

RECOMMENDATIONS FOR SAMPLING AND ANALYSIS OF THE PRIMARY NaK SYSTEM

Continuous monitoring of the oxygen level in the NaK by use of an electrochemical oxygen meter would be the ideal method of analysis, since it requires no entry into the system for sampling and gives nearly instantaneous readout. For the relatively short-term demands of the filling and system cleaning operations, the oxygen meter would be dependable and practical, and is recommended if it can be effectively engineered into the system. For post-cleanup use, however, when the system temperature is raised above 800°, the temperature limitation of the oxygen meter makes it unacceptable without extensive re-engineering of the system, an impractical alternative.

Flow-through chemical samplers for oxygen analysis are acceptable, provided the sampling system is standardized properly. This means that rigorous cleaning procedures must be routinely employed on the sample tubes, and analytical tubing blanks must be determined and applied to the analyses. The removal and replacement of sampling tubes must be done in a manner which excludes contamination. This could effectively be done by having the sampling station in an inert atmosphere enclosure.

The use of replaceable samplers is not feasible on the primary system after the loading cart is removed. A knowledge of the oxygen level at several times during operation would be very useful in post-test evaluation of the operation, however. This could be achieved by having three to six sample tubes in parallel on the system in a manner in which they could be valved off and removed without subsequently adding anything to the system. This recommendation may be impractical from the points of view of radiation accessibility or maintaining maximum system integrity. The desirability of knowing the oxygen level in the NaK at known times after nuclear operation suggests that it should at least be considered, however.

The vanadium wire equilibration method of analysis for oxygen in sodium is the RDT Standard method. This method has not been used for NaK, however, nor has any experience with it been developed at AI. It is therefore not recommended here.

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