A STATE OF THE ART REVIEW
OF DEGRADATION PROCESSES
IN LMFBR MATERIALS

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II CORROSION BEHAVIOR

March 7, 1975

Contributors: J. R. Divine
B. Griggs
R. E. Westerman
G. E. Zima

Compiled By: R. L. Dillon

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PACIFIC NORTHWEST LABORATORIES

Richland, Washington 99352

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RELEVANT DEGRADATION
PROCESSES FOR LMFBF
COMPONENTS

	SMELLING	EFFECT OF IRRADIATION ON TENSILE PROPERTIES	EFFECT OF IRRADIATION ON HIGH STRAIN PROPERTIES	EFFECT OF IRRADIATION ON CREEP RUPTURE PERFORMANCE	FUEL - CLAD INTERACTION ON FATIGUE PROPERTIES	SODIUM - CLAD INTERACTION - MECHANICAL PROPERTIES	EROSION	WEAR AND SELF WELDING	CORROSION (EXTERNAL)	SODIUM-WATER REACTIONS				
FUEL ASSEMBLIES	●	●	●	●	●	●	●	●	●	●	●			
CONTROL ROD SYSTEMS	●	●	●	●	●	●				●	●			
POWER INSTRUMENTATION AND GAS LINES										●				
INSTRUMENT TREE AND IVFH MACHINE											●			
CLOSED LOOPS	●	●	●	●	●	●				●	●	●		●
REACTOR VESSEL, GUARD VESSEL			●	●		●								●
CORE SUPPORT STRUCTURE, RESTRAINT SYS		●	●	●	●	●				●				
REACTOR HEAD		●	●			●				●				
BAFFLE PLATE		●								●	●			
PRIMARY AND SECONDARY PUMPS										●	●	●		
PRIMARY AND SECONDARY PIPING		●	●	●	●	●				●	●	●		●
PRIMARY AND SEC. SODIUM PURIFICATION										●				
DUMP Hx, IHx												●		
STEAM GENERATORS												●	●	
INERT GAS SYSTEMS										●		●	●	

FORWARD

Since April of 1972, Battelle-Northwest has been charged with providing to Licensing - Fast Reactor Project Branch any assistance required in dealing with specific LMFBFR materials problems. In partial fulfillment of these responsibilities, BNW has undertaken the preparation of technical summaries of metal degradation processes which are known to occur in sodium-cooled reactor service. As the LMFBFR materials summaries are presently conceived, a two-phase study will be required. This document comprises the first phase and constitutes a review of degradation processes to metals in sodium reactor service. The degradation processes which will be discussed include those affecting mechanical properties (i.e., neutron irradiation, thermal exposure and sodium- and fuel-clad interaction) as well as environmental effects specific to sodium coolants (mass transfer and corrosion, fretting and wear, erosion, etc.); synergism is not considered here.

The second phase of the review of LMFBFR materials degradation is a component by component consideration of reactor systems. Components will be discussed in the context of the degradation processes to which they are susceptible under expected service conditions. In this way, the component design will be compared with the requirements imposed by the anticipated service conditions--both in normal operation and under upset conditions, power transients and loss of cooling; synergism is considered here.

LMFBFR materials technology is a rapidly changing science with many critical questions awaiting resolution from planned experiments or experiments currently in progress. As a result, some viewpoints now generally accepted on the basis of currently available data may give way to different concepts as more information is obtained. Since the purpose of this state-of-the-art summary is to supply Licensing with reliable materials information

usable in connection with LMFBR license application reviews, it is essential to keep the document current with the new experimental information and improved interpretation. We have, therefore, prepared this LMFBR materials degradation summary in a format compatible with periodic updating. The basic accommodations to updating are these:

- ° The summary is prepared in loose-leaf format to simplify replacement of sections which have required revision.
- ° Each topic is comprised of sections that are complete entities (i.e., tables, figures, references) for ease of replacement.
- ° A list of revisions will be supplied and kept current with textual modifications.
- ° Each page is dated for comparison with the revision list.
- ° Finally a distribution list will be kept current (with Licensing - Fast Reactor Project Branch assistance) so that revisions can be supplied directly to all document holders. Copies are numbered to simplify accountability.

The highly structured outline from which the text is prepared is immediately noticeable. This organized presentation has been adapted to assist the reader in finding the material he wants and to minimize the textual changes when revisions are required. There has been a conscious endeavor to provide all the information the reader will require in considering a materials question. While the sources are always identified, it is intended that reference to them will be necessary only in unusual cases. With self sufficiency of the state-of-the-art document as a major objective, data compilations and figures are freely used. Definitive work of all dates has been referenced, but heavy emphasis has been placed on sources of the last three or four years. There are very good reasons

for this policy--principally that only in the most recent work have experimental conditions been well enough defined to preclude significant but unrecognized variations from the nominal.

In the preparation of this document, all available sources of information on materials degradation have been used. Through the auspices of our sponsor we have had access to certain proprietary information, both domestic and foreign. Usually this proprietary information has been supplied on the basis of a limited and clearly designated circulation. Consequently, this document must be distributed with these restrictions in mind.

The document is published in two volumes:

Volume I - Mechanical Properties

Volume II - Corrosion Behavior

Component Application Guides have been included in the document. These guides, one for each chapter, as well as a Summary Guide for the complete document, are intended to aid the reader in more easily finding materials information relevant to a particular reactor component of interest.

The Summary Guides (one to each volume) are inserted after the Table of Contents for each volume; each chapter guide is inserted after the List of Figures for each chapter.

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TECHNICAL SUMMARY

1.0 SWELLING

This chapter discusses the experimental parameters which affect material swelling in the radiation environment of a fast reactor. The data have been obtained by immersion density measurements, diametral change measurements and transmission electron microscopy. The data presented cover principally 304 and 316 stainless steel which have been irradiated in EBR-II. The principal limitations are the limited data on cold worked 316 stainless steel and the lack of high fluence data. In particular, existing data on cold worked 316 stainless steel extends to $\sim 5 \times 10^{22}$ n/cm², whereas goal exposures for the demonstration LMFBF are greater than 2×10^{23} n/cm². This means that extrapolation must be made from a gathering of all existing lower fluence data. British data have not been used in extrapolation or predictions because compositional and heat treatment differences may lead to different swelling behavior. The data are applicable to the swelling of any component if the experimental conditions for that component are known, in particular the neutron spectrum, temperature and stress state of the component. At present, there is a lack of experimental data on spectral effects and the effects of stress on swelling have yet to be fully resolved. (3/31/73)

2.0 EFFECT OF IRRADIATION ON TENSILE PROPERTIES

The effects on tensile properties of irradiation fluence and temperature, test temperature, reactor variables and material variables are discussed. Tensile data reported in this chapter were from several material sources, only one of which -- the 304 stainless steel tested at HEDL -- is prototypic of material to be used in LMFBF, i.e., produced to RDT specifications. The other materials -- the 304 stainless steel and nickel-base alloys tested at GE, the Ti-modified 316 stainless steel tested at ORNL, and the annealed and 20% cold-worked 316 stainless steel tested at HEDL -- produce properties representative only of nominal

values for these materials. In particular, the cold-work 316 stainless steel is not in its prototypic, tubular form for LMFBR usage, and the Ti-modified 316 stainless steel is a development alloy.

The data are limited to very low fluence levels for the 20% cold-worked 316 stainless steel; fluence levels for 304 stainless steel are generally applicable to LMFBR requirements.

Tensile data are applicable to the pressure vessel and to core components other than fuel pins; design criteria for these components call for 10% residual tensile elongation at end of service life. For the pressure vessel and for components other than portions of the inner and outer shield, these criteria are expected to be met; for the latter it appears the fluence levels are too high to ensure the 10% residual elongation. (3/31/73)

3.0 EFFECT OF IRRADIATION ON HIGH STRAIN-RATE PROPERTIES

The effects on high strain-rate properties of irradiation fluence and temperature, test temperature, strain-rate, reactor variables and material variables are discussed. High strain-rate data reported in this chapter are from several sources; the 304 stainless steel and 20% cold-worked 316 stainless steel represent prototypic FFTF heats and product forms purchased to RDT specifications; the nickel alloys represent nominal ASTM heat specifications.

The data are limited by very low fluence levels, particularly for high strain-rate tensile tests. Since these data indicate no significant increase in uniform elongation with strain-rate, ordinary tensile data may be used to approximate high strain-rate properties at higher fluences. Using this approximation, the 10% residual ductility criteria for 304 stainless steel appears to be met for the pressure vessel and for components other than portions of the inner and outer shield in FFTF, for which the fluence is too high. Simulated transient tests on 20% cold-worked 316 stainless steel tubing indicates that a fuel pin integrity limit of 0.7%, which includes 0.5% strain due to upsets and transients, is probably not conservative. (6/3/74)

4.0 IRRADIATION EFFECTS ON CREEP-RUPTURE PROPERTIES

The effects on creep-rupture properties of irradiation fluence and temperature, test temperature, reactor variables and material variables are discussed. The creep-rupture data reported in this chapter are from several sources, only one of which -- the 20% cold-worked 316 stainless steel tested at HEDL -- represents a prototypic FFTF heat and product form produced to RDT specifications; the data for the annealed 316 stainless steel tested at HEDL and at ORNL and the annealed 304 stainless steel tested at ORNL represent nominal values for these materials procured to ASTM specifications.

The data are limited by very low fluence levels for the cold-worked 316 stainless steel, the only alloy for which creep criteria are established for LMFBRs (for fuel cladding). The current design criteria are $\leq 0.2\%$ steady state strain and $\leq 0.5\%$ added creep and/or high strain-rate tensile strain for transient events. Steady state strains as low as $0.18\% \Delta D/D$ are produced even after low fluences at test temperatures near irradiation temperatures. At test temperatures approximately 200°F higher than the irradiation temperature (i.e., a simulation of a transient event), post-irradiation creep ductilities are usually $\ll 1.0\%$, even at low fluences. Lower ductilities would be expected at reference fluences. The possibility exists that a non-damaging irradiation-creep can occur that will allow greater fuel pin strain during steady state operation; however, the mechanism would not be available to increase strain during transients. (6/3/74)

5.0 IRRADIATION EFFECTS ON FATIGUE

This chapter discusses the nature of fatigue data and the factors that affect fatigue lifetime, where possible, with respect to anticipated LMFBR operating conditions. Practical limitations of the application of fatigue data for structural component evaluation are discussed. Methods of characterizing fatigue lifetimes in specimens under low- and high-cycle fatigue and fatigue crack growth are presented; application to components is

limited by difficulties of applying specimen data to the more complex, loaded components.

Irradiation effects on fatigue properties of austenitic stainless steels are discussed. The data are limited, and in some cases sparse, with respect to anticipated LMFBR operational conditions and thus do not as yet provide a satisfactory basis for fatigue design limits. Data on irradiated specimens are confined mainly to unnotched low-cycle fatigue and selected creep-fatigue test conditions. The principal limitations is the small amount of data on cold-worked material and exposure levels that extend to about 2×10^{22} n/cm², only for a small number of specimens, whereas goal exposures for the demonstration LMFBR may be as high as 2×10^{23} n/cm² or more. A satisfactory base had been developed for unirradiated fatigue crack growth (fcg) including a range of simulated LMFBR environmental conditions and cold work. The effect of irradiation on fcg is limited to one 304 stainless steel specimen and one 316 stainless steel specimen irradiated in EBR-II to $\sim 1.2 \times 10^{22}$ n/cm². More data from different fluence levels, irradiation and test temperatures and environments are necessary to make rational extrapolations to anticipated LMFBR irradiation and operating conditions. (10/25/74)

6.0 EFFECT OF IRRADIATION ON WELD PERFORMANCE

The effects of irradiation and material condition on the tensile and high strain-rate properties of weldments are discussed. Post-irradiation creep data are not yet available. The data reported in this chapter were for materials representing prototypic FFTF 304 stainless steel pipe and vessel forms and both standard and developmental weld metals and processes.

The data are for fluence levels up to 7×10^{21} n/cm², $E > 0.1$ MEV. Irradiation lowers the ductility of welds, and this decrease is most severe at the higher temperatures.

Welds in radial shields in FFTF can be exposed to fluence levels higher than that at which 10% total elongation can be expected. Moreover, for TIG welds of 308 in 304 stainless steel base metal the fluence limits may allow the 10% elongation

criterion but would not allow 10% uniform elongation, which is probably the more relevant criterion for transient considerations.
(6/3/74)

7.0 FUEL CLAD INTERACTION

The steady state requirement for fuel performance is basically an integral pin throughout its lifetime with strain not to exceed 0.3%. Plastic strains for irradiation conditions and claddings somewhat different than current LMFBR prototypes have exceeded 0.5%. Current EBR-II irradiations for FFTF have not shown plastic strains in excess of $\sim 0.2\%$. The strain capability between 0.3 to 0.7% for the prototype cladding under LMFBR transient conditions has not been demonstrated. The clad fluences now being extrapolated to LMFBR applications range from 20 to 30% of EOL fluence. Additionally, a single 304 stainless steel datum indicates zero creep strain at about 75% of the FFTF goal fluence of 2×10^{23} .

Considerable data exist which demonstrate a plastic deformation capability in excess of 0.2% at burnups near LMFBR goals but at $\sim 30\%$ of the fluence. Except for the fluence level, these pins probably experienced the full extent of expected fuel clad interactions.

Fuel clad chemical interactions appear to be within projected limits, ~ 2 mils (EOL) at rated conditions. Data with excess penetrations have been considered inapplicable due to non-prototype clad and pellet chemical conditions. However, additional data are needed to provide full support of the current limit.

Data are currently being obtained as part of the LMFBR fuels test program to demonstrate transient strain limits and fuel clad interaction effects at full fluence and rated conditions. The possibly lowered transient failure ductility of irradiated material may lead to a greater number of fuel failures during accidents. The lowered failure threshold may change accident peak energy due to earlier fuel expulsion and thus may also change the consequences of power excursion accidents.
(6/3/74)

8.0 EFFECT OF SODIUM COOLANT INTERACTIONS ON MECHANICAL PROPERTIES

The effect of flowing sodium under carburizing and non-carburizing conditions on composition, microstructure, and mechanical properties are discussed.

The data are limited to unirradiated conditions for a few alloys; data on 20% cold-worked 316 stainless steel, the FFTF and CRBRP cladding alloy are unavailable.

The available data on 304 stainless steel and annealed 316 stainless steel indicate substantial degradation occurs in stress rupture life and ductility at either high temperature in a non-carburizing environment or at high and low temperatures in a carburizing environment. The combined effects of sodium interaction and neutron irradiation would be expected to be more severe than the effects of either alone.

Some effects on the residual ductility of the 304 stainless steel pressure vessel at the upper temperatures may occur; further data are required. The potential for deleterious effects to fuel cladding and other core components should not be overlooked; further data are also required here. (6/3/74)

9.0 CORROSION AND MASS TRANSFER

The corrosion and deposition of reactor structural materials is important because structural entities can be weakened, pressure barriers can be penetrated, radioactive material from the core can be transferred to relatively unshielded positions and the important function of heat transfer can be impeded. The corrosion of engineering materials in liquid sodium systems is examined by subdivision into the various parameters important in understanding and predicting the magnitude and type of the corrosion. The treatment of data is primarily oriented toward conventional sodium system materials. The data are largely ex-reactor loops of GE, Westinghouse, Argonne, AI, French and British. In-reactor data are just now becoming available in the temperature range, fluence, sodium purity, velocity, etc., to be typical of LMFBR design conditions.

It is frequently desired to know the maximum rate of corrosion, mass transfer, interstitial leaking, or radioactive buildup for a given reactor system. The selected application of the ex-reactor loop data to the expected corrosion in the reactor will probably yield results as accurately as the conditions (temperature, oxygen, etc.) in the system are anticipated. There has been no indications that recent refinements in testing and oxygen measurement have given

rise to unexpected corrosion rates. However, care must be used in considering the low oxygen concentrations that the experimenter did indeed know the correct oxygen concentration.

The rare occurrence of shallow intergranular attack in loop piping has not been satisfactorily explained and must be considered an indistinct possibility yet to be explained. Inasmuch as the large reactor systems will probably operate at very low stable oxygen concentrations accurate estimates of corrosion will have to be based on accurate knowledge of the true oxygen concentration.

(3/31/73)

10. EROSION

Pre-service, quantitative, characterization of the erosion problem for even familiar working environments is not possible on the basis of present knowledge of this damage agency. Where there is the possibility for corrosion-assisted erosion, as in the LMFBR systems, then theoretical assistance is even weaker. Historical review of possibly relevant experience is of very limited value.

Erosion by solid particle impingement is expected to be an insignificant damage factor in LMFBR systems. Conceivably, some solid particle intrusion of the liquid metal circuits could result from various corrosion processes. A quantity of solid particles sufficient to present an erosion hazard should, however, force the earliest possible attention to this problem and corrective action against the initiating corrosion process.

Liquid particle impingement on the containment envelope of the LMFBR heat transfer system is not expected to persist beyond presumably short transients. Persistent-potentially damaging-two phase regimes in the liquid metal circuits would be a derivative of improper design, or selection, of circuit components, or gross inattention to system operating parameters. Such factors are also pertinent to cavitation erosion. The goal of zero, or very low, incidence of cavitation will be more difficult to achieve than will the corresponding goal for liquid particle impingement. With respect to circuit design, there is now a substantial body of guidelines for minimizing the possibility of cavitation erosion, e.g., elimination of abrupt flow section changes, gross roughness, flow obstacles which force rapid acceleration of the fluid. However,

pump design to accommodate a wide spectrum of operating conditions presents more subtle problems. It is expected that the greatest potential for significant erosion from cavitation resides in such circuit elements where high performance goals may force a close approach to the two phase regime under some operating circumstances.

(10/25/74)

11. WEAR AND SELF WELDING

The continuous, intermittent or occasional movement of two objects held in position to each other by a bearing surface is a fundamental necessity for a complex machine like a reactor.

The laboratory studies attempting to identify the parameters of this complex interaction have been reviewed as well as the various operating mechanisms where data are available. The data from reactors that have been or are operational, mechanism testing, and design studies by AI, HEDL, GE, and WARD provide a broad base for the lower temperature reactions. The increased corrosion, mass transport, material softening, etc., that takes place with the higher temperatures contemplated for LMFBRs make the applicability of some of these data questionable. The increased testing taking place in prototypic LMFBR conditions will soon give data which will be more applicable to the severe conditions in and above the core. An optimization of oxygen concentration may well be the result of trying to improve corrosion and mass transport (Section 9) as wear and self welding. The optimized value will probably be quite low and less than 5 ppm to reduce the degree of system activation.

(3/31/73)

12. SODIUM-WATER REACTIONS

Sodium-heated steam generators are designed with the realization that occasional contact of sodium and water are inevitable. The primary design goals are minimization of the possibility of leaks and rapid detection of a leak should one occur.

The potential damage resulting from a given leak situation depends in a complex way on system parameters, such as leak size, tube material, geometry, temperature, sodium flow rate, and pressure differentials. The best appreciation of potential leak-caused damage is therefore obtained by experiment, i.e., using simulated leaks under conditions closely duplicating expected steam generator

service conditions. Some qualitative insight can be gained by an understanding of relevant thermodynamic and solubility data, though these are frequently inconsistent and, of course, strictly applicable only to equilibrium situations, and so cannot bear directly on the analysis of damage from pressure pulses or metal wastage.

The early detection of small leaks remains one of the major problems facing the designers of sodium-steam systems. The ideal detector would have an instant response time, regardless of its location relative to the leak. Acoustic detectors appear to offer a great deal of promise, and development work is proceeding in this area. (6/3/74)

13.0 EXTERNAL CORROSION PROCESSES

The subject of this chapter is the potential corrosion problems associated with sodium excursions beyond the planned containment envelope.

Degradation processes considered in the chapter are:

- a. Corrosion processes in which there is exchange of ambient species-- N_2 , O_2 , H_2O (vapor and liquid)--with the sodium.
- b. Corrosion processes in which there is limited exchange in the above respect because of thermal insulation and various protective envelopes.
- c. Corrosion and mass transfer effects associated with sodium events in which nitrogen is a principal ambient species.

Discussion of corrosion behavior under unstressed and stressed conditions is also presented.

The quality of much of the corrosion data employed in Chapter 13 might be challenged by various students of sodium corrosion. This is a natural consequence of a problem area which does not submit easily to theoretical analysis, and does not enjoy the advantage of clearcut experimental data in many important respects of structural material degradation. A principal conclusion of the chapter is that caustic corrosion processes have not received the attention they merit, and this conclusion is directed primarily toward the low alloy, ferritic, materials.

Probable location and cause of sodium leaks and spills are not likely to be predictable until details of plant design and operation are known. The history of sodium facility operation shows that leaks have been discovered by operators inspecting the system visually rather than by the leak detection system.

At CRFBR operating temperatures and in areas covered by nitrogen plus 1% oxygen atmosphere sodium leaks may be expected to produce corrosion rates of tens to hundreds of mils/year. During shutdown, when the system is maintained at lower temperatures and where stresses equal or exceed yield stress for the material, stress corrosion cracking can occur much more quickly. (3/31/75)

9.0 MASS TRANSPORT AND CORROSION

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9.0 CORROSION AND MASS TRANSFER

[illegible]

9.0 MASS TRANSPORT AND CORROSION

9.1 OPERATIONAL DEFINITION OF MASS TRANSPORT AND CORROSION

In the LMFBR primary coolant substantial differences in sodium temperature exist between the energy generating core and the intermediate heat exchanger. These differences may amount to 400 or 500°F. Where the solubility of structural metals in sodium varies as a function of temperature, a mechanism of transport is established with dissolution in the hot leg and deposition in cooler portions of the sodium circuit.

Where bimetallic sodium circuits are proposed, as for example a secondary sodium system with an austenitic stainless steel IHX (hot leg) and a 2.25% Cr 1% Mo steel heat dump, compositional differences can set up a chemical driving force for mass transport in addition to any effects from thermal differences. Since the chemical activities of alloy constituents are more or less proportional to concentration in the alloy, a redistribution of the elemental constituents of the system is favored. In the absence of temperature differences in the circuit a constant chemical potential and uniform distribution of all elements throughout the system would be eventually achieved.

Corrosion or metal wastage is the generalized reduction in useful metal section. This degradation may occur as the result of mass transfer or as the result of oxide formed and retained on the metal surface, or as intergranular attack.

9.2 REVIEW OF VARIABLES AFFECTING CORROSION AND METAL DISSOLUTION

The following review of recent experimental data will be helpful in discussing the parameters of corrosion, mass transfer and deposition. The variables will be treated individually, however, there is frequently a strong interdependence between them which will be indicated. The nearly exclusive use of chromium-nickel stainless steel and occasionally 2.25% chromium 1% molybdenum carbon steel as construction materials of sodium system will be reflected in the available data as well as the treatment of it. Other materials have been used for special purposes such as bearings, electrical conductors, instruments, wear surfaces, etc., as shown by a list of materials in EBR-II (Table 9.2-1). Information on these materials will be included when available.

Table 9.2-1

MATERIALS EXPOSED DIRECTLY
TO PRIMARY SODIUM IN EBR-II⁽¹⁾

Material	Approximate Service Temperature, °F
Aluminum Bronze--Ampco Grade 18-30	700, 800-850, 900
Aluminum Bronze--Ampco Grade 18-23	700
Borated (1½%) Stainless Steel (Type 304)	700
Carbon Steel--ASTM 325-55T	700
Chromium-plated Stainless Steel Types 304, 410, and 420	700 and 900
Colmonoy 4 and 5	900
Inconel 600	700
Inconel X-750	700
Stainless Steel Types 303, 304, 316, 321, and 347	300 to ~1000
Stainless Steel Types 410 and 420	700 and 900
Steel--SAE 4340	700
Stellite Nos. 3 and 6B	700 and 900
Tantalum	700
Tool Steel Types 18-4-1 or -2 and Rex AA	700 and 900

REFERENCES

1. Sherman Greenberg, The EBR-II Materials-Surveillance Program:
I. Program and Results of SURV-1, ANL-7624, Argonne National
Laboratory, September 1969. p. 8.

9.2.1 MASS TRANSFER AS A FUNCTION OF T AND ΔT

In classical mass transfer mechanisms the rate of metal removed depends on the solubility difference of the transferred material at the hot and cold leg temperatures. Of course, when the system is driven hard, that is when the cycle time is short, the dissolution processes in the hot leg or the deposition process in the cold leg may not go to completion. In the absence of true equilibrium in all parts of the system the mass transfer rates will fail to reach theoretical values.

The general character of iron and nickel alloy corrosion in non-isothermal sodium coolants has long been recognized as a mass transfer process dependent on the differing solubilities of the alloy constituents at different coolant temperatures. It has become increasingly evident the dependence is a highly complex one in which many perturbing factors must be considered. Nevertheless considerable effort has gone into the determination of metal solubilities as a function of temperature. From these studies more or less accepted binary solubilities have been determined for Fe, Cr and Ni as a function of temperature and some appreciation developed of the major perturbing factors, especially oxygen. In Figure 9.2.1-1 recommended solubilities for Fe, Ni, Cr as a function of temperature are shown. Figures 9.2.1-2 -3 and -4 are compilations of data for the separate elements which will indicate the diverse results that have been obtained.

The binary solubilities shown in Figures 9.2.1-1 through -4 are further modified in a reactor system by interaction with each other, oxygen, nitrogen, carbon, etc. The solubilities of any compounds formed may be more or less than the pure element in pure sodium. Most binary solubilities are of the form $\log \text{concentration} = A - \frac{B}{T(^{\circ}\text{K})}$ where A and B are constants depending on the element and the units of concentration. Some investigations of addition of third elements have been made for the oxygen - iron system which have shown some marked effects at low and high oxygen concentrations. Isaacs and Weeks⁽¹⁾ were unable to decide which values for the effects of oxygen on iron solubility were correct, however, most investigators found oxygen increased the solubility of iron substantially, if present at concentration: >0.1 of saturation values.

Figure 9.2.1-1⁽¹⁾

RECOMMENDED SOLUBILITY CURVES FOR Fe, Cr, and Ni
from Figures 9.2.1-2, -3, -4

$$\text{Log}_{10} \text{ ppm Fe} = 9.19 - 4310/T$$

$$\text{Log}_{10} \text{ ppm Cr} = 9.35 - 9010/T$$

$$\text{Log}_{10} \text{ ppm Ni} = 2.34 - 1830/T$$

Figure 9.2.1-2⁽¹⁾
SOLUBILITY OF Fe IN SODIUM
All Data

Figure 9.2.1-3⁽¹⁾

SOLUBILITY OF CHROMIUM IN LOW OXYGEN SODIUM

Figure 9.2.1-4⁽¹⁾

SOLUBILITY OF NICKEL IN SODIUM

ALL DATA

Even though differential solubility between the hot and cold leg has been a cornerstone in understanding sodium corrosion, calculations of corrosion rates from solubility measurements have been orders of magnitude too high, especially for iron alloys. The reason for this disagreement is that one of the steps involved in mass transfer is slow. The slow step might involve the precipitation kinetics, the diffusion through a liquid boundary layer or the formation of a complex species at the dissolving surface. Analytical data from stainless steel loops⁽²⁾ indicates that iron and chromium are usually present well in excess of their solubilities in sodium at maximum temperature while nickel tends to fall between solubility at maximum and minimum loop temperatures. This difference is usually ascribed to circulating particulate matter.

The effect of temperature alone on the corrosion of material is difficult to quantitatively separate from other parameters such as oxygen concentration, flow, etc. The relationship is of the same form as the solubility and increases exponentially with temperature.

The effect of temperature difference in a sodium circuit on corrosion at the maximum temperature depends on the rate controlling mechanism. Where simple solubility is rate controlling, corrosion increases linearly with ΔT . Where precipitation is inefficient, or complex surface effects intervene, corrosion can be substantially increased by a very small ΔT but is insensitive to further increases in ΔT .

REFERENCES

1. John R. Weeks and Hugh S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys in Liquid Sodium, BNL 15731R, October 15, 1971
2. R. M. Singer, A. H. Fleitman, J. R. Weeks, and H. S. Isaacs, "Measurements of the Solubility of Iron and Chromium in Sodium," Corrosion by Liquid Metals, JE Draley and J.R. Weeks (Eds), Plenum Press, NY (1970) pp. 561-576.

9.2.1.1 Stainless Steel Corrosion - Effect of T and ΔT

The effect of temperature on the corrosion of stainless steels is difficult to determine accurately from engineering data. Even though corrosion of stainless steels in sodium has been intensively studied for many years, only recently have the various important parameters been sufficiently under control in test loops to generate reproducible data. A plot of some weight loss *vs* time data in Figure 9.2.1.1-1 shows some disagreements which are probably due to variations of unstated experimental parameters.

The minimum ΔT around a circuit necessary to produce maximum corrosion has not been determined, however Thorley⁽¹⁾ states no increase in corrosion rate is seen at $\Delta T > 50^\circ\text{C}$ in the range $\Delta T, 0$ to 400°C .

Figure 9.2.1.1-1⁽²⁾

COMPARISON OF CORROSION RATES OF
STAINLESS STEELS vs RECIPROCAL TEMPERATURE

3/31/73

REFERENCES

1. A. Thorley, "Fission and Corrosion Product Behavior in Primary Systems of LMFBR's - A Brief Review of Current Status of Work Being Carried Out in U.K.," W.F. Brehm, Trip Report - IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, #ST-164, WADCO/FFTF 714526, October 1971 (Official Use Only)
2. John R. Weeks and Hugh S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys in Liquid Sodium, BNL 15731R, October 15, 1971.

9.2.1.2 Nickel Alloys Corrosion - Effect of T and ΔT

The effect of temperature on nickel alloys not containing iron is more pronounced than on the iron alloys (Figure 9.2.1.2-1). Nickel and chromium are preferentially leached in low oxygen sodium from those alloys containing iron until the surface layer is highly enriched in iron which modifies the apparent corrosion behavior. Intermediate alloys containing substantial amounts of iron have a corrosion behavior intermediate between iron and nickel. Table 9.2.1.2-1 shows the effect of nickel content on corrosion of alloys in a medium oxygen content system. The effect of iron content would be even more pronounced in a low oxygen system.

The effect of system ΔT on high nickel alloys is linear as shown in Figure 9.2.1.2-2. This indicates that nickel corrosion is solubility related, however, the linear response to surface velocity indicates the actual rate control is diffusion across the concentration gradient existing in sodium boundary layer.

Figure 9.2.1.2-1⁽¹⁾

CONSTANTS OF SODIUM CORROSION AS A
FUNCTION OF RECIPROCAL TEMPERATURE

- x pure iron
- + stainless steels
- Inconel 625
- o pure nickel

Table 9.2.1.2-1

CORROSION DATA FOR ASSORTED Ni, Cr, Fe ALLOYS⁽²⁾

Data Obtained From Materials Exposed to
Dynamic Sodium (30-40 ft/s) Containing 25-30 ppm
of Oxygen at 650°C for 8 Weeks

	<u>% Ni</u>	<u>% Fe</u>	<u>Extrapolated Loss in Metal Section (10⁻³/in/yr)</u>
Inconel 600 (soft)	77	6	6.1
Nimonic 80A	75		4.9
Nickel	100		3.9
PE 11 (soft)	38	35	2.9
PE 16 (soft)	43	34	2.8
Nilo 50 (soft)	50	50	2.5
18/8/1 Ti			2.4
PE 16 (opt.props.)	43	34	2.3
316 S.S.	11	68	1.8
PE 11 (opt.props.)	38	35	1.8
Nilo K (soft)	29	53 (16 Co)	0.95

Figure 9.2.1.2-2⁽³⁾
EFFECT OF ΔT ON MASS TRANSFER IN
SODIUM-INCONEL PUMPED LOOPS
at 816°C (1500°F) $T_{\max}$

REFERENCES

1. H.V. Borgstedt, "Analysis of Sodium Corrosion Effects in Stainless Steel Candidate Materials for Fuel Element Cladding, Part II," M. Dalle Donne, K. Kummerer, K. Schroeter, (Eds.), Fast Reactor Fuel and Fuel Elements, Proceedings of International Meeting, ANS, Kernforschungszentrum Karlsruhe, September 28-30, 1970. pp. 630-634.
2. A.W. Thorley and C. Tyzack, "Corrosion Behavior of Steels and Nickel Alloys in High Temperature Sodium" Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 97-118.
3. J.H. Devan, "Corrosion of Iron and Nickel-Base Alloys in High Temperature Sodium and NaK," Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 643-661.

9.2.1.3 Steel Corrosion - Effect of T and ΔT

The selective leaching of nickel, chromium, manganese, silicon and possibly titanium from stainless and nickel alloys leaves a surface layer which approaches an α iron structure, similar to low alloy steels such as 2.25 chromium 1 molybdenum steel. Thus, corrosion of the low alloy steels is very similar to the steady state corrosion of higher alloy, e.g., 300 series stainless steel. The dependence of the corrosion rate of low alloy steels on loop ΔT is similar to that for well leached 300 series stainless steel.

9.2.1.4 Miscellaneous Alloy Corrosion - Effect of T and ΔT

The effect of temperature on the corrosion of zirconium and titanium is primarily to accelerate the reaction with oxygen, carbon, etc., and to increase dissolution rates of oxide, carbon, etc., into the base metal leaving a fresh metal surface to react. Titanium and zirconium are frequently used as "hot trap" getters to remove impurities. Niobium, vanadium, tantalum are also affected by impurities in the sodium whose diffusion and reactions rates increase with temperature. Cobalt alloy corrosion initially depends on temperature in a way similar to 300 series stainless steel because chromium and nickel leaching controls the process leaving a cobalt, iron, tungsten rich surface (see Figures 9.2.1.4-1 and 9.2.1.4-2).

Figure 9.2.1.4-1

EFFECT OF OXYGEN ON THE CORROSION OF
HAYNES 25 AND 304 STAINLESS STEEL
(Na velocity = 22 fps)

Figure 9.2.1.4-2

SURFACE COMPOSITION OF SAMPLES
IN FIGURE 9.2.1.4-1 BY
X-RAY FLUORESCENCE

REFERENCES

1. A.J. Romano, S.J. Wachtel, C.J. Klamut, "Preliminary Corrosion Results of Haynes 25 and Type 304 Stainless Steel with 4 and 12 ppm Oxygen in Sodium at Temperatures up to 760°C," Sodium Technology and Large Fast Reactor Designs, ANL-7520, Part I, pp. 151-152.

9.2.2 MASS TRANSFER AS A FUNCTION OF COMPOSITION - TREATMENT OF ALLOYS

Engineering materials in LMFBR's will be alloys of which austenitic stainless steels are important examples. These are complex materials involving several controlled percentage constituents as well as residual impurities. Table 9.2.2-1 gives the composition of some typical materials.

The chemical activity of individual dissolved constituents in alloys is affected by dilution with the other elements in the alloy. For our purposes it is sufficient to represent the activity as that of the pure metal multiplied by the atomic percent in the alloy. Thus the leaching rate for Ni from a fresh 304 stainless steel surface will be that of pure nickel multiplied by the atomic fraction of nickel in the alloy. An apparent exception to this treatment occurs when very stable compounds are formed between the elements in a structural alloy such as between tungsten and carbon.

As preferential leaching of specific constituents proceeds, their concentrations at sodium-structural alloy surface decrease becoming dependent on the diffusion rates from the bulk metal to the surface. Eventually a steady state situation develops in which the leaching rates of all alloy constituents are constant with time. In the meanwhile, the surface layer composition will have changed radically from its original composition. The degree to which the surface compositions are changed depends on many variables such as temperature, flow, oxygen concentration and ΔT . Diffusion of material in the solid metal is not the only rate determining step because frequently the dissolution into the sodium layer and diffusion through the layer substantially effect the rate of removal of an alloy constituent. The driving force for these reactions is the differential activities of an element in various parts of the loop. Thus, in an isothermal section, all the steels tend toward a common surface layer composition.

In the case of hot leg ($\sim 1200 - 1300^\circ\text{F}$) exposure of 316 stainless steel roughly a 0.7 mil layer of iron-rich ferrite will develop due to the selective leaching of Cr, Ni and Mn (see Figure 9.2.2-1).

Table 9.2.2-1

COMPOSITIONS OF REPRESENTATIVE LMFBR ALLOYS

	<u>304</u>	<u>316</u>	<u>Incoloy 800</u>	<u>Incoloy 625</u>
Fe	balance	balance	balance	5 max
Cr	18-20	16-18	19-23	20-23
Ni	8-11	10-14	30-35	balance
Mn	2 max	2 max	1.5 max	0.5 max
Co	residual	residual	-	1 max
Mo	-	2-3	-	8-10
Si	1 max	1 max	1 max	0.5 max
C	0.08 max	0.10 max	0.10 max	0.10 max
N	residual	residual	residual	residual
Cu	-	-	0.75 max	-
Cb + Ta	-	-	-	3.15 - 4.15
Al	-	-	-	0.4 max
Ti	-	-	-	0.4 max

Figure 9.2.2-1⁽¹⁾

COMPOSITION PROFILE OF SOLUTION-ANNEALED TYPE-316
STAINLESS STEEL AFTER 15,726 HOURS EXPOSURE TO
1300°F FLOWING SODIUM

Ex-reactor studies by Wozadlo, et al.⁽¹⁾ at 1300°F indicated most of the change in alloy surface composition occurred in the first year but small changes were still going on near the end of the second year (see Figures 9.2.2-2 and -3).

Microstructural changes resulting from selective leaching of major and minor alloying elements in stainless steels at 1300°F were the formation of sigma phase in grain boundaries of Type 316, the formation of martensite in a layer beneath the ferrite layer of Type 304, the formation of sigma phase in grain boundaries of Type 347, the formation of subsurface voids in a 5 mil layer beneath the surface of Types 321 and 347 and intergranular dissolution for several mils in Incoloy 800. The ferrite layer formation appeared to stabilize at 0.6 mils thick in Type 316 at 1300°F in 10,000 hours. The substantial losses of strength from high temperature (1300°F) sodium exposure are attributed to the leaching of carbon, boron and nitrogen and the formation of sigma phase.

Selective leaching of carbon, silicon, boron, nitrogen and other minor alloying elements or impurities can substantially effect the properties and microstructures of various alloys. Some elements such as silicon, boron and manganese can be removed from the equilibrium solubility situation by oxidation, while carbon and nitrogen can absorb into downstream alloys. Figure 9.2.2-4 shows the kinetics of nitrogen removal and pickup for various alloys at 1300°F in a G.E. loop. These rates can be substantially altered with different piping layout or operating conditions. In general, the stabilized stainless steels (321 and 347) and other alloys with efficient carbide forming elements do not lose carbon easily and have a tendency to pick it up from nonstabilized material.

The localized corrosion can lead to severe penetration in tantalum and niobium base alloys that have become contaminated with oxygen during melting or welding. Local penetration of these two refractory metals described by Harrison⁽²⁾ and Kluch⁽³⁾ has a parallel in local corrosion of stainless steels by local carbon contamination, see Ruther.⁽⁴⁾

Figure 9.2.2-2⁽¹⁾

SURFACE CONCENTRATION OF ALLOYING ELEMENT AS A
FUNCTION OF EXPOSURE TIME IN 1300°F and 1150°F
FLOWING SODIUM

Figure 9.2.2-3⁽¹⁾

COMPOSITION PROFILE OF SOLUTION-ANNEALED TYPE 347
STAINLESS STEEL AFTER 15,726 HOURS EXPOSURE TO
1300°F FLOWING SODIUM

Figure 9.2.2-4⁽¹⁾

EFFECTS OF EXPOSURE IN FLOWING SODIUM ON THE
 NITROGEN CONTENTS OF STAINLESS STEELS
 (Zone F downstream of Zone E)

REFERENCES

1. Summary Report of the Sodium Mass Transfer Program, Effects of Sodium Exposure on the Corrosion and Strength of Stainless Steels, General Electric Co., GEAP-10394, August 1971.
2. R.W. Harrison, "Corrosion of Oxygen Contaminated Tantalum in NaK," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Eds) Plenum Press, N.Y. (1970) pp. 151-175.
3. R.L. Kluch, "Penetration of Refractory Metals by Alkali Metals," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks, (Eds.) Plenum Press, N.Y. (1970) pp. 177-196.
4. W.E. Ruther, T.D. Claar and S. Matras, The Attack on the Cladding of EBR-II Driver Fuel Element C-249-16, Argonne National Laboratory, ANL-7537. March 1969.

9.2.3 The Effect of Oxygen on the Corrosion Rate

The effect of oxygen concentration in the sodium on the corrosion rate of materials is generally to increase the rate. In its simplest reactions such as the oxidation of zirconium, increased oxygen concentration is simply a greater supply of reactant. In more complex reactions it serves to oxidize and precipitate certain solutes such as chromium, silicon and possibly manganese. The exact mechanism of reactions with iron base structural materials is being actively investigated but no general theory has been completely substantiated.

The sources of oxygen in sodium loops are many. Exposure to air or water even in trace quantities will result in the formation of dissolved Na_2O . Surface oxides on many metals are reduced by sodium with the formation of dissolved Na_2O . The dissolved oxide in sodium is usually removed by precipitation in cold traps either of the flow through or diffusion types. Where very low oxygen concentrations are required the sodium is treated with a "getter" such as zirconium in a hot trap. The solubility of oxygen in sodium is shown in Figure 9.2.3-1 which indicates that the oxygen can be reduced to about 1 ppm at 125°C . Cold traps as well as some precipitated metal oxides such as NaCrO_2 are reversible sinks for oxygen and thus buffer the circulating system at a relatively constant oxygen concentration. Malfunction of a cold trap such as loss of temperature control or flows that carry undissolved particles of oxide back to the system will result in high oxygen concentration in the system. System dead legs that have terminal temperatures less than the cold trap will act as diffusion cold traps and accumulate oxide in the cold region which will give rise to a locally high dissolved oxygen concentration if that portion of the system is heated up.

The importance of oxygen concentration in the corrosion of materials has been recognized for decades, however, only recently have analyses and control mechanisms been applicable to low oxygen levels (<10 ppm). Stainless steel corrosion data for LMFBR application are generally obtained in sodium containing less than 10 ppm. The presence of certain oxygen sensitive materials in high temperature regions such as zirconium vanadium, tantalum, etc. will require even lower oxygen levels.

Figure 9.2.3-1

SOLUBILITY OF OXYGEN IN SODIUM⁽¹⁾

REFERENCES

1. B. Minushkin and G. Kissel, "Solubility and Reactions of Oxygen in Sodium," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks, (Editors) Plenum Press, N.Y. 1970. pp. 515-522.

9.2.3.1 Stainless Steel Corrosion - Effect of Oxygen

The effect of dissolved oxygen on the corrosion rate of stainless steels in sodium has been found to vary between the 1.0 and 1.5 power of the oxygen concentration but does not extrapolate to zero at zero oxygen. Starting at about 25 ppm oxygen there is a tendency to form a chromium oxide on the surface of the corroding steel which has been identified as sodium chromite (NaCrO_2). The primary effect of the oxygen seems to be on the control of the iron dissolution rate. The exact mechanism of oxygen induced iron dissolution is not well understood. The possibility of forming sodium ferrites has been explored but they are apparently unstable at low to medium oxygen concentration. Singer, et al⁽¹⁾ have found that oxygen effects the equilibrium solubility of iron but this has not yet found universal acceptance. Weeks and Isaacs,⁽²⁾ have proposed a surface site activation as a mechanism that explains the complex effect of oxygen on the predominantly α -iron surface of corroding stainless steels. Higher concentrations of oxygen, 25 ppm or greater, have been found to promote an intergranular attack on stainless steels which has been observed at 1100 to 1300°F. Zebroski⁽³⁾ discussed I.G. attack found in early G.E. loops. The exact oxygen concentration and temperature necessary for this localized attack is ill defined, but G.E. did not produce I.G. attack on 316 stainless steel at <10 ppm O_2 at 1300°F⁽⁴⁾ in 4000 hours. Subsequent examination of a 304 stainless steel loop operated at 1300°F for 17,628 hours with <2 ppm O_2 revealed a 1 to 2 mil I.G. attack⁽⁵⁾ in a position similar to previously observed attack. Thus, low oxygen does not completely eliminate this form of corrosion but does substantially effect its rate. Wozadlo established that the attack can start immediately when conditions were right and produced up to 0.4 mils attack in 2500 hours at 1100°F. Previous G.E.⁽³⁾ loop studies had shown as high as 9 mils attack in 28,000 hours at 1200°F in the nearly isothermal region downstream of the hot leg. Hiltz⁽⁶⁾ reports that high oxygen sodium (300 ppm) causes preferential oxidation of chromium on the surface as well as in grain boundaries. Under these severe oxidizing conditions the iron is so rapidly dissolved that the surface can be depleted in iron rather than enriched.

The effect of oxygen concentration in the sodium on several alloys of various iron contents is shown in Figure 9.2.3.1-1. The effect of dissolved oxygen on the high iron alloys is striking and very important to LMFBR technology because small amounts of oxygen will cause substantially higher corrosion rates on the thin fuel cladding. The possibility of initiating an intergranular attack will require that low oxygen conditions be maintained everywhere in the hot sodium system. Until all the parameters affecting intergranular attack are known, it is not possible to predict exactly where, if at all, it will affect an LMFBR. From the data available, a possible area to watch for I.G. attack would be just below the surface of the sodium on all the instrument lines, etc. which emerge from the sodium pool. Although the vessel would be just as subject to attack, its greater thickness would make the attack of less concern. The bellows on valves also appear to be a place that could develop high oxygen concentrations and suffer accelerated attack.

Figure 9.2.3.1-1⁽²⁾

EFFECT OF OXYGEN ON SODIUM CORROSION

Top - Effect of oxygen on the corrosion of several metals in sodium.
 Bottom - Interrelation between oxygen concentration corrosion rate and iron content of alloy.

REFERENCES

1. R.M. Singer, A.H. Flectman, J.R. Weeks, and H.S. Isaacs, "Measurements of the Solubility of Iron and Chromium in Sodium," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Ed.) Plenum Press. N.Y. 1970. pp. 561-575.
2. John R. Weeks and Hugh S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys In Liquid Sodium, BNL 15731R, October 15, 1971.
3. E.L. Zebroski, R.S. Young, F.A. Comprelli and D. Dutina, "Effects of Mass Transfer and of Changes in Properties on Austenitic Steels in Flowing Sodium," Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 195-211.
4. G.P. Wozadlo and C.N. Spalaris, Corrosion of Stainless Steel and Deposition of Particulates in Flowing Sodium Systems, GEAP-13544, General Electric Co. Sunnyvale, CA. Sept. 1969.
5. Summary Report, Sodium Mass Transfer Program, GEAP-10394, General Electric Co. Sunnyvale, CA. August 1971.
6. R.H. Hiltz, "The Corrosion of Stainless Steel in Oxygen-Contaminated Sodium at 1200°F and 1400°F," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Editors). Plenum Press, N.Y. 1970. pp. 63-80.

9.2.3.2 Nickel Alloy Corrosion - Effect of Oxygen

Nickel and high nickel alloys are relatively unaffected by oxygen concentrations in sodium up to several hundred ppm. Alloys containing substantial amounts of iron show effects of oxygen roughly in accordance with their iron concentration. This effect is shown in Figure 9.2.3.1-1.

9.2.3.3 Steel Corrosion - Effect of Oxygen

The low alloy steels are subject to substantial increases in corrosion as the oxygen level is increased. The effect in the low and moderate oxygen levels is similar to the effect on the stainless steels because the stainless steels generate a surface layer depleted in chromium and nickel. Thorley⁽¹⁾ noted the corrosion of iron in an iron loop was more sensitive to oxygen concentration, being nearly proportional to the concentration squared.

REFERENCE

1. W.F. Brehm, Trip Report - IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971. #ST-164, WADC0/FFTF 714526, October 1971, p. 22 (OUO)

9.2.3.4 Miscellaneous Alloy Corrosion - Effect of Oxygen

Materials which react with oxygen and form stable oxides in contact with sodium, such as titanium and zirconium, will initially react with any available oxygen. As a surface layer of ZrO_2 builds up it will reduce the rate of reaction to very low levels. If the temperature is increased to 500 or 600°C, the metal will dissolve its surface oxides and in time present a fresh metal surface for reaction with oxygen. At still higher temperature the oxide is dissolved into the metal more rapidly. Thus, in the lower temperature region, protective films will form which will make the material insensitive to oxygen concentration, at intermediate temperature, the rate of reaction will be controlled by the dissolution of its own oxide films, while at high temperature, its reaction rate will be limited only by the supply of oxygen to the surface and thus highly dependent on oxygen concentration and flow. The absorption of appreciable amounts of oxygen embrittle metals such as zirconium and titanium.

Vanadium alloys have been explored as potential fuel cladding. They have proven to be very sensitive to oxygen concentration. The corrosion of some vanadium alloys at various temperatures in a dynamic stainless steel test loop with oxygen <1.8 ppm and N_2 <1 ppm are shown in Figure 9.2.3.4-1. These alloys tend to react with several interstitials from a stainless system as shown in Table 9.2.3.4-1 from Whitlow, et al⁽¹⁾ for a 6% Fe - 5 Nb - 1.3 Zr - 0.05 C - Bal V alloy (VANSTAR 9). Presumably some of the weight change shown in Figure 9.2.3-1 also represents pickup of C, N, etc.

The cobalt base alloys have been considered as hard facing materials for seals, etc. The effect of oxygen on these alloys at 4 and 12 ppm was examined by Romano, et al and shown in Figure 9.2.1.4-1. The effect of oxygen on the surface composition (from the same work) is shown in Figure 9.2.1.4-2. The noteworthy increase in iron may have been caused by deposition.

Figure 9.2.3.4-1⁽²⁾

DYNAMIC EXPOSURE OF SEVERAL VANADIUM ALLOYS TO SODIUM
(Cold Trap Temperature = 110°C)

Table 9.2.3.4-1⁽¹⁾

INTERSTITIAL CONCENTRATIONS IN 0.001 in.-DEEP SURFACE LAYER
OF A VANSTAR-9 SAMPLE EXPOSED TO FLOWING SODIUM
(5 fps, <10 ppm Oxygen at ~790°C)

<u>Element</u>	<u>Before Exposure (ppm)</u>	<u>After Exposure (ppm)</u>	
		<u>1500 hr</u>	<u>2650 hr</u>
Nitrogen	79	22,000	35,000
Carbon	570	6,500	27,000
Oxygen	640	5,800	6,000

REFERENCES

1. G.A. Whitlow, R.J. Hornak, S.L. Schrock, E.C. Bishop, "The Effect of Exposure to Flowing Sodium on Vanadium Alloys in Stainless Steel Containment Systems," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Editors) Plenum Press, N.Y. 1970. pp. 115-135.
2. W.E. Ruther, "The Corrosion of Vandium-Base Alloys in Sodium," Sodium Technology and Large Fast Reactor Design, ANL-7520 Part I, November 7-9, 1968, pp. 182-191.

9.2.4 THE EFFECT OF VELOCITY ON CORROSION

The surface velocity of sodium flowing past a corroding specimen will affect the thickness of the relatively stagnant layer of sodium at the metal surface. Where diffusion of metal solute to the flowing stream is the rate controlling process, the increase in velocity of sodium past the surface will increase the corrosion rate. Similarly, the diffusion of solutes from the flowing stream to the surface will be increased by high surface velocities. The highest temperature surfaces in a reactor are the heat generating fuel element surfaces which require a high velocity sodium stream to cool them. Thus, the highest corrosion rates are generated on the thinnest material which requires an accurate assessment of all the parameters in the corrosion process.

The separation of all other corrosion variables from the effect of velocity is difficult because there are interactions with oxygen and other solute content, entrance effects and erosion. In the Phase I G.E. corrosion equation,⁽¹⁾ corrosion was shown proportional to the 0.88 power of velocity, but was reduced to the 0.44 power in the Phase II equation.⁽²⁾ Presumably a downward revision was necessary because the velocity effect is averaged over the velocity dependent and independent regions of stainless steel corrosion. In a summary of their corrosion work, Roy, et al state⁽³⁾ that corrosion rates should be related to the thickness of the laminar flow layer instead of velocity. Their correlation of data for stainless steel corrosion indicated that the velocity independent thickness of laminar boundary layer was about 0.0002 inch. The corrosion rate was strongly dependent on layer thickness between 0.0002 inch and 0.0005 inch as shown in Figure 9.2.4-1.

Figure 9.2.4-1⁽³⁾

INFLUENCE OF LAMINAR BOUNDARY LAYER THICKNESS
ON THE CORROSION OF STAINLESS STEELS

REFERENCES

1. E.L. Zebroski, R.S. Young, F.A. Comprelli and D. Dutina, "Effects of Mass Transfer and of Changes in Properties on Austenitic Steels in Flowing Sodium" Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 195-211.
2. G.P. Wozadlo and C.N. Spalaris, Corrosion of Stainless Steel and Deposition of Particulates in Flowing Sodium Systems," GEAP-13544, General Electric Co., Sunnyvale, CA. September 1969.
3. Summary Report, Sodium Mass Transfer Program, GEAP-10394, General Electric Company, Sunnyvale, CA. August 1971.

9.2.4.1 Stainless Steel Corrosion - Effect of Velocity

The effect of velocity on the corrosion of stainless steels is shown in Figure 9.2.4.1-1. The velocity dependence is almost linear up to 15 ft/sec where it rounds off into a velocity independent region which extends at least to 40 ft/sec. The general interpretation of this complex relationship is that the low velocity region represents the corrosion control by diffusion through the sodium boundary layer while the independent region represents a surface chemical control. The interaction of temperature and oxygen concentration can be seen in Thorley's data on Figure 9.2.4.1-2. Figure 9.2.4-1 shows correlation of boundary layer thickness with corrosion rate.

Figure 9.2.4.1-1⁽¹⁾

CORROSION RATE AT 1300°F AS A FUNCTION OF
SODIUM VELOCITY AT AN OXYGEN LEVEL OF LESS THAN 10 ppm

Figure 9.2.4.1-2⁽²⁾

EFFECT OF VELOCITY ON THE RATE OF METAL REMOVAL FROM VARIOUS STAINLESS STEELS OR VARIOUS OXYGEN CONCENTRATIONS

REFERENCES

1. Summary Report, Sodium Mass Transfer Program, GEAP-10394.
General Electric Company, Sunnyvale, CA. August 1971.
2. A.W. Thorley and C. Tyzack, "Corrosion Behavior of Steels and Nickel Alloys in High Temperature Sodium," Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 97-118.

9.2.4.2 Nickel Alloy Corrosion - Effect of Velocity

The corrosion of nickel is more nearly a straight solution mechanism than iron alloy corrosion. The high nickel alloys thus display a linear increase in corrosion with surface velocity. Thorley's data for a high nickel alloy are shown in Figure 9.2.4.2-1.

Figure 9.2.4.2-1⁽¹⁾

EFFECT OF VELOCITY ON THE RATE OF METAL LOSS
FROM NIMONIC 80A at 650°C

REFERENCES

1. A.W. Thorley and C. Tyzack, "Corrosion Behavior of Steels and Nickel Alloys in High Temperature Sodium," Alkali Metal Coolants, IAEA, Vienna, 1967. pp. 97-118.

9.2.4.3 Steel Corrosion - Effect of Velocity

It has been assumed that low alloy steels behave in the same manner as stainless steels because of the ferrite layer formation on the surface. Recently Thorley⁽¹⁾ said that steel corrosion in a steel loop did not show a velocity independent region which raises the question of the effect of dissolved loop materials on the velocity effects previously observed in stainless steel loops. Since most applications of low alloy steels are in cooler parts of the circuit these velocity effects may be only of academic interest.

REFERENCE:

1. W.F. Brehm, Trip Report - IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, #ST-164, WADC0/FFTF 714526, October 1971. p. 22 (OUO)

9.2.4.4 Miscellaneous Alloy Corrosion - Effect of Velocity

The corrosion (interstitial pickup) of the refractory metal alloys is affected by velocity because the supply of reacting species is increased at high velocities. Where the rate control is in the surface or diffusion into the metal, the velocity will have little effect. Vanadium tests by Smith, et al⁽¹⁾ at several levels of oxygen showed a velocity independence to higher speeds in the lower oxygen sodium (Figure 9.2.4.4-1) Whitlow, et al⁽²⁾ found an approximate 20% increase in weight gain for an increase in velocity from 5 to 14 ft/sec in sodium with probably <1 ppm oxygen. He felt even some of this increase could be attributed to increased carbon and nitrogen leaching from the heater section due to higher heat transfer rate at the higher flow.

Figure 9.2.4.4-1⁽¹⁾

EFFECT OF DISK VELOCITY ON THE LINEAR
CORROSION RATE OF VANADIUM IN SODIUM

REFERENCES

1. D.L. Smith and T.F. Kassner, "Application of Thermodynamic and Kinetic Parameters of the V-O-Na System to the Sodium Corrosion of Vanadium-Base Alloys," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Editors) Plenum Press, N.Y. 1970. pp. 137-149.
2. G.A. Whitlow, R.J. Hornak, S.L. Schrock, E.C. Bishop, "The Effect of Exposure to Flowing Sodium on Vanadium Alloys in Stainless Steel Containment Systems," Corrosion by Liquid Metals, J.E. Draley and J.R. Weeks (Editors) Plenum Press, N.Y. 1970. pp. 115-135.
3. W.E. Ruther, Corrosion of Vanadium and Vanadium Base Alloys in Sodium, ANL-7505, Argonne National Laboratories, May 1969.

9.2.5 GEOMETRIC EFFECTS - DOWNSTREAM EFFECTS

There is very little reactor corrosion experience to suggest corrosion rates that will be experienced in relatively high temperature FFTF and demonstration LMFBRs. Consequently principal reliance must be made on data from ex-reactor corrosion loops. By necessity these differ radically in size and shape from reactor systems, although attempts have been made in certain loops to simulate some geometric relationship of a reference reactor design. Factors like surface area to sodium volume ratios, and hot leg to cold leg surface area ratios have been considered in several cases. Design constraints of this kind make it impossible to observe other reactor characteristics without building a full size simulation of the reactor itself. When simulating reactor cycle times for a slug of sodium to circulate through the primary system at prototypical flow rates, it is impossible to preserve surface to volume relationships.

Geometrical factors have been observed to effect corrosion rates. A downstream effect in isothermal hot leg sodium has been identified.

- Sodium out of the heater section is more corrosive to upstream surfaces than those farther downstream. The effect is suggestive of rapid saturation of the circulating sodium, lessening the corrosion driving force downstream.
- Corrosion rates of stainless steel decrease roughly with the square of the distance from the heater outlet.
- The flow velocity at which corrosion becomes velocity independent seems to increase with downstream position.
- The Cr and Ni concentrations in the steady-state corroding surface of stainless steel increases in downstream samples.

In loop heater sections which cover a range of temperature, the dissolution rate in any temperature zone, T , is predictable from

corrosion rates in the upstream isothermal section when it is operating at the same temperature. No heat flux effect as such is observed. If fuel cladding surfaces temperature can be accurately calculated, corrosion rates along the length of a fuel rod can be estimated.

9.2.5.1 Downstream Effects in Stainless Steel Systems

The downstream effect in an isothermal hot leg has been observed by most observers and quantitatively evaluated for inclusion in overall corrosion equations. This downstream effect is usually expressed as a length from the heater divided by the hydraulic diameter of the flow channel (L/D). Figure 9.2.5.1-1 shows this effect on corrosion for several flow velocities at substantial downstream positions which appear to be linear with respect to L/D . Isaacs and Weeks⁽¹⁾ described some evidence that indicate this effect is indeed proportional to $(L/D)^2$ at small distances downstream. More importantly, they propose a mechanism for this effect in terms of the chromium and nickel buildup poisoning the active iron dissolution sites downstream thereby reducing the apparent corrosion. The more common view is that the downstream effect is the result of a decreasing activity of the solid with respect to the same activities of the solute because of the increasing concentration of solutes in the downstream sodium coolant.

Wozadlo, et al⁽²⁾ also described an entrance effect which was defined as the L/D starting at each isovelocity, isothermal region. This effect is harder to explain by a simple mechanism than the original dependence on dissolved material or depletion of a reactant. Presumably, it is related to turbulence generated on entering a test section and disappears rapidly. In application to the highest corrosion rates in a reactor, namely the thin fuel cladding, the sodium has been in an isoveoocity region for some time before becoming isothermal and then the sodium velocity is changed by leaving the fuel region. This complex heating and geometrial arrangement may completely mask any entrance effect.

In a subsequent summary of their corrosion studies, Roy, et al⁽³⁾ found substantial interactions between downstream effects and oxygen concentrations. More complex interactions of temperature, oxygen, downstream and velocity effects were not determined. The simple interaction of downstream and oxygen at 1300°F eliminated the squared L/D term of the Phase II equation (see page 9.2.6.5-3).

Figure 9.2.5.1-1⁽³⁾

THE EFFECT OF DOWNSTREAM (SODIUM SATURATION) ON CORROSION RATE OVER A RANGE OF VELOCITIES IS SHOWN FOR EXPOSURE AT 1300°F TO SODIUM WITH LESS THAN 5 ppm OXYGEN

REFERENCES

1. J. R. Weeks and H.S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys in Liquid Sodium, BNL 15731R, October 15, 1971.
2. G.P. Wozadlo and C.N. Spalaris, Corrosion of Stainless Steel and Deposition of Particulates in Flowing Sodium Systems, GEAP-13544, General Electric Co., Sunnyvale, CA. September 1969.
3. Summary Report of the Sodium Mass Transfer Program, Effects of Sodium Exposure on the Corrosion and Strength of Stainless Steels, GEAP-10394, General Electric Co. Sunnyvale, CA. August 1971.

9.2.5.2 Downstream Effects - Other Materials

The downstream effects for other materials have not been studied as extensively as stainless steels. To the extent that a reactive surface is depleted or a solute concentration increased, other material should display downstream effects in the same manner as stainless steels.

9.2.6 CORROSION RATES IN SODIUM COOLANTS

Many of the previous discussions have been concerned with corrosion rate, primarily in a steady-state condition. The initial corrosion of stainless steels involves leaching chromium, nickel, manganese, silicon, carbon, etc., from the surface which logically could give rise to a slightly different rate than the typical linear steady-state. The loops in which most tests are run, involve a period where the chemistry of the sodium, such as oxygen concentration, is perturbed in the initial part of the test which also could contribute to an altered initial rate of corrosion. As the test proceeds the surface of the samples become slightly rougher providing more surface area and deposition processes produce more surface area in the cold leg which may improve the efficiency of the deposition process. It is usually not possible to evaluate all of these facets of a test from the data presented.

9.2.6.1 Corrosion Rates for Stainless Steels

The corrosion kinetics of many alloys have been examined, however, the variables such as oxygen concentrations have only been under strict enough control in recent time to give reasonably reproducible data. The corrosion kinetics of the 300 series stainless steels are similar but slightly different. Thorley⁽¹⁾ and Wozadlo, et al⁽²⁾ consider the corrosion of specimens to be linear with time from a few weeks to more than a year (see Figure 9.2.6.1-1). A recent summary of Wozadlo, et al⁽³⁾ data indicates they now consider the corrosion to follow an exponential function which is nearly linear for Type 316 at 1300°F as shown in Table 9.2.6.1-1. Schrock (Figure 9.2.6.1-2), Ramano (Figure 9.2.6.1-3), and Champeix (Figure 9.2.6.1-4) among others find an initial rate which is nearly parabolic. The importance of this kinetic difference to an engineering structure is insignificant except where wear, cavitation or other process continually destroys a protective layer. When this happens, the material will always be corroding at the initial rate, which for a linear process is the same as it normally corrodes, but for a parabolic process is much higher than its steady-state corrosion, that is, the tail of the parabola. Normally wear and cavitation also generate other destructive effects such as metal surface working and self welding which could mask any increase in corrosion process. These processes become of import on such structures as wire wraps and grid spacers of fuel elements. In general, no problems are yet apparent, however, the testing of typical fuel geometries under LMFBR condition is just beginning.

Figure 9.2.6.1-1⁽¹⁾

A COMPARISON OF THE BEHAVIOR OF VARIOUS STEELS IN
 FLOWING SODIUM AT 650°C, O₂ LEVEL ~25 ppm CENTRAL
 SPECIMENS TAKEN FOR COMPARISON PURPOSES

Table 9.2.6.1-1⁽³⁾

COMPARATIVE CORROSION EQUATIONS

Zone E-1300°F

$$\text{Corrosion (mg/dm}^2\text{)}^* = A t \text{ (hours)}^B$$

Material	Index of Determination		95% Confidence Limits on Parameters			
	Exponential	Linear	A		B	
316	0.9855	(0.970)	0.0839	+0.1137 -0.0482	0.999	±0.108
304	0.9915	(0.927)	0.5152	+1.1405 -0.3548	0.839	±0.143
347	0.9967	(0.979)	0.9601	+0.9292 -0.4722	0.785	±0.083
1-800	0.9994	(0.985)	2.5537	+0.7618 -0.5829	0.708	±0.032

* Corrosion values in units of (mg/dm²) can be converted to mils by multiplying by $4.96 \times 10^{-4} \left(\frac{\text{mils}}{\text{mg/dm}^2} \right)$

Figure 9.2.6.1-2⁽⁴⁾

COMPARISON OF WEIGHT CHANGE AND CORRECTED
CORROSION RATES

Figure 9.2.6.1-3⁽⁵⁾

EFFECT OF EXPOSURE TIME IN HIGH VELOCITY
SODIUM AT 700°C ON THE CORROSION RATE OF
STAINLESS STEELS

Figure 9.2.6.1-4⁽⁶⁾

MEAN CORROSION RATE OF AN AUSTENITIC STEEL versus TIME

3/31/73

9.2.6.1-6

REFERENCES

1. A.W. Thorley and C. Tyzack, "Corrosion Behavior of Steels and Nickel Alloys In High Temperature Sodium," Alkali Metals Coolants, IAEA, Vienna, 1967. pp. 97-118.

A.W. Thorley, "Fission and Corrosion Product Behavior in Primary Systems of LMFBR's - A Brief Review of Current Status of Work Being Carried out in U.K.," W.F. Brehm, Trip Report - IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, #ST-164, WADCO/FFTF 714526. October 1971 (Official Use Only)
2. G.P. Wozadlo and C.N. Spalaris, Corrosion of Stainless Steel and Deposition of Particulates in Flowing Sodium Systems, GEAP-13455, General Electric Co., Sunnyvale, CA. September 1969.
3. Summary Report, Sodium Mass Transfer Program, GEAP-10394, General Electric Company, Sunnyvale, CA. August 1971.
4. S.L. Schrock, J.N. Baysden, R.L. Miller, D.E. Lohr, "Sodium Corrosion of Westinghouse Liquid Metal Fast Breeder Reactor (LMFBR) Materials," Corrosion by Liquid Metals, Plenum Press, N.Y. (1970) pp. 41-62.
5. J.R. Weeks and H.S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys in Liquid Sodium, BNL 15731R, October 15, 1971.
6. L. Champeix and O. Konovaltschikoff, "Kinetic Aspects of Corrosion of Steels in Flowing Sodium," Sodium Technology and Large Fast Reactor Design, ANL-7520 Part I, Argonne National Laboratory, November 7-9, 1968, pp. 150a-150f.

9.2.6.2 Corrosion Rates for Nickel Base Alloys

The type and amount of alloying elements will effect the kinetics, but where nickel is predominant and no interfering surface films form, the kinetics should be linear. The alloy P.E.-16 in Figure 9.2.6.1-1 is 43% Ni 34% Fe and shows this linear rate. Cheng and Ruther⁽¹⁾ reported a corrosion study of nickel in sodium between 550 and 715°C with velocities between 10 and 100 cm/sec. The corrosion was found to be linear with time and proportional to the velocity raised to 0.76 power.

REFERENCE

1. C.F. Cheng and W.E. Ruther, "Corrosion of Nickel in Sodium," Corrosion 28 (1) 1972. pp 20.22

9.2.6.3 Corrosion Rates for Low Alloy Steels

Initial corrosion rates for low alloy steels were found to be parabolic by Champeix⁽¹⁾ but their longer term behavior is considered to be linear. Figure 9.2.6.1-1 shows the corrosion of a 2.25 Cr 1 Mo steel as linear and similar to the 300 series stainless steels.

REFERENCE

1. L. Champeix and O. Konovaltschikoff, "Kinetic Aspects of Corrosion of Steels in Flowing Sodium," Sodium Technology and Large Fast Reactor Design, ANL-7520 Part I, Argonne National Laboratory, November 7-9, 1968. pp. 150a-150-f.

9.2.6.4 Corrosion Rates for Miscellaneous Alloys

Alloys which do not form protective films should all show a linear relationship of corrosion with time. Where selective attack increases the surface roughness, an apparent increase in corrosion rate could occur with time because of the increasing surface area. In complex situations such as wear, the selective leaching of an alloy could generate surface layers of less stability which could generate a higher apparent combined wear and corrosion rate.

9.2.6.5 Corrosion Correlations - Iron Alloys

The combining of all the variables in sodium corrosion of a material into a single mathematical equation has been a challenge and in ways a useful exercise. An equation which accounts for all fundamental mechanisms in the corrosion process allows one to evaluate the deterioration to be expected in a simple engineering structure and qualitatively to help avoid pitfalls in design. Isaacs and Weeks⁽¹⁾ have recently postulated a corrosion equation based on the available fundamented parameters* and mechanisms of the form:

$$R = \frac{7.93 \cdot 10^{11} T}{X_{Fe}} \left\{ \left(\frac{O}{O_{sat}} \right)^{2X_{Fe}} \exp - \frac{50300}{RT} \right\} \left[1 - E \left(\frac{L}{D} \right)^2 \right]$$

Where

R = corrosion rate (mils/yr)

T = °K

X_{Fe} = atom fraction of Fe

O = oxygen concentration

O_{sat} = oxygen concentration at saturation

E = downstream coefficient (empirically evaluated)

R = gas constant

L = distance downstream from heated section

D = hydraulic diameter of flow channels

The constants of this equation have been evaluated from selected experimental data and certain simplifying assumptions have been made. The downstream coefficient (E) must be empirically evaluated for each flow, oxygen concentration and temperature as it is not independent. If one ignores the downstream effect which serves to reduce the corrosion and consider only corrosion in flow velocities which are fast enough to be independent of velocity, then the maximum corrosion will only be a function of temperature and oxygen activity. This would predict

* ΔT is sufficient to make corrosion independent of ΔT.

a zero corrosion rate at zero oxygen concentration which is considered outside the assumptions of the model because the corrosion would revert to the straight solution type mechanism. There are some indications that very low oxygen systems produce very low corrosion rates. Thorley⁽²⁾ mentions a corrosion rate of less than 0.2 mils/yr in a zirconium hot trapped system at 1200°F (probably less than 0.1 ppm O₂). Borgstedt⁽³⁾ actually observed small weight gains in sodium at less than 0.1 ppm O₂.

Wozadlo, et al⁽⁴⁾ has correlated their corrosion data for stainless steels in a more empirical approach and arrived at the following relationship:

$$\begin{aligned} \ln R = & 14.55 + 0.435 \ln V - 0.000958 (L/D) \\ & - 0.122 \ln (L/D) + 1.445 \left(\frac{1}{t} + 1 \right) + 1.156 \ln O_2 \\ & - \frac{23,827}{T + 460} \end{aligned}$$

Where

R = corrosion rate (mg/dm²/mo) to time t

V = surface velocity (ft/sec)

(L/D)₁ = number of hydraulic diameters downstream in an isothermal region (starting 2/3 of the way through the heater) (downstream effect)

(L/D)₂ = number of hydraulic diameters downstream in an isothermal isovelocity region (entrance effect)

t = time (months)

O₂ = oxygen concentration (ppm)

T = temperature (°F)

In this correlation it will be observed velocity, downstream effect, oxygen concentration and temperature are all independent variables, which is an engineering approximation. The velocity covers a range from approximately a linear dependence to independent and cannot be accurate for all velocities.

9.2.6.5-3

In a subsequent review of their corrosion work, Roy, et al⁽⁵⁾ looked at some interactions of oxygen concentrations and downstream effects and found interdependence of the form:

$$CR = -0.33 - 0.119(X_0) + 1.7 \cdot 10^{-4}(L/D) + 1.98 \cdot 10^{-4}(X_0)(L/D)$$

at velocity >22 ft/sec, temperature 1300°F and low oxygen concentrations

where

X_0 = O_2 concentration ppm

L/D = number of hydraulic diameters downstream from heaters

CR = corrosion rate mils/year

Further complex interactions between velocity, oxygen, temperature and time have not yet been studied so an overall corrosion equation was not developed. As mentioned previously, (Table 9.2.6-1), they found a time dependence at 1300°F of the form $\text{Corrosion} = At^B$ where A and B varied according to the 300 series stainless steel alloy used. The equation was essentially linear for 316 stainless steel, ($B = 0.999$).

Westinghouse has also developed similar correlations of observed stainless steel corrosion in sodium. A plot of these correlations as well as other corrosion data are shown in Figure 9.2.6.5-1 for comparison.

Figure 9.2.6.5-1⁽⁶⁾

304-316 STAINLESS STEEL CORROSION RATES AS FUNCTION OF TEMPERATURE

REFERENCES

1. J.R. Weeks and H.S. Isaacs, Corrosion and Deposition of Steels and Nickel-Base Alloys in Liquid Sodium, BNL 15731R, October 15, 1971.
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3. H.V. Borgstedt, "Analysis of Sodium Corrosion Effects in Stainless Steel Candidate Materials for Fuel Element Cladding, Part II," M. Dalle Donne, K. Kummerer, K. Schroeter, (Editors) Fast Reactor Fuel and Fuel Elements, Proceedings of an International Meeting ANS, Kernforschungszentrum Karlsruhe, September 20-30, 1970. pp. 630-634.
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9.2.7 TRANSFER OF MINOR ALLOYING ELEMENTS AND IMPURITIES

The previous discussions concerning the diffusion, leaching, transfer and deposition of major alloying elements will apply in general to the minor elements and impurities if the element chemistry is similar. The reason for treating minor elements separately is because their chemistry is frequently different from the major elements and their effect on the mechanical properties of structural materials can be substantial. Several of the minor alloying elements and impurities such as boron, hydrogen, carbon and nitrogen can diffuse through the metal phase quite rapidly. If the element is tightly bound in a compound in the metal phase, this diffusion and leaching can be slowed or stopped depending on the stability of the compound formed. Thus, the diffusion of carbon out of stainless steel can be mitigated by adding elements such as titanium or niobium which form stable carbides.

9.2.7.1 Stainless Steel - Minor Element Transfer

The minor alloying elements in the 300 Series stainless steels are manganese, silicon, nitrogen, carbon, boron, sulfur, phosphorous, niobium, titanium, and molybdenum, not all of which are present in the same alloy. Wozadlo, et al⁽¹⁾ recently reported data on the leaching of many of these elements from stainless steel at 1300°F and 1150°F.

Manganese is rapidly leached from the surface of stainless steel for the first 3000 hours at 1300°F and 1150°F. After 15,726 hours it is severely depleted in a 1/2 mil surface layer with a slight depletion from the bulk of the Type 316 stainless steel. A substantial depletion to a depth of 5 mils was seen in Type 347 stainless steel. The leached manganese has been reported⁽²⁾ to show up in cold traps and in other lower temperature parts of the system.

Silicon is leached in a manner similar to the manganese with most of the depletion in a 1/2 mil surface layer in 316 stainless steel. Type 347 shows a more gradual depletion for about 5 mils below the surface. The leached silicon is found in the colder parts of the system as sodium silicate.

Molybdenum in the 316 alloy is not preferentially leached from the surface in low oxygen sodium at 1300°F. Bogers⁽³⁾ found molybdenum in deposits at 650°C in about the concentrations of the original alloy in a loop operated from 25 to 7 ppm O₂ with a maximum temperature of 700°C. However, Ray⁽¹⁰⁾ found only 0.01 to 0.03% Mo in deposits under similar temperature conditions, but at 5 ppm O₂ which suggest the transport of Mo is sensitive to oxygen concentration in the sodium. In low oxygen systems, there have been some data^(4,5) that indicate the surface concentration of Mo will increase in a 1 to 2 micron surface layer.

Niobium and titanium are added to Type 347 and 321 stainless steels respectively to precipitate the carbon and prevent heat sensitization of the alloys. The leaching and redeposition characteristics of these elements are not well established even though Type 321 has been extensively used in reactor construction. It has generally been established that Type 321 and 347 corrode more rapidly than Types 304 and 316

in low oxygen sodium. Wozadlo, et al⁽¹⁾ found that depletion of chromium, manganese and silicon penetrated further into Type 347 alloy than 316 (5 mils instead of 0.5 mils) under the same conditions and that subsurface voids were formed in the 347 and 321 alloys. This change in behavior was not mechanistically related to the titanium or niobium concentration of the 347 or 321 alloys by the investigators, however, this is the principal difference between Types 304 and 321 or 347.

Wozadlo, et al⁽¹⁾ investigated the leaching of phosphorous and sulfur from the stainless steels tested. In general no preferential leaching was observed at either 1150°F or 1300°F in low oxygen sodium.

The boron concentration in stainless steels is usually quite small (<20 ppm) however it was rapidly leached from the General Electric⁽¹⁾ specimens and those of other investigators.⁽⁶⁾ This element is considered to have substantial effect on the high temperature strength and stress rupture properties of austenitic stainless steels.⁽¹⁾ An initial concentration of about 2 ppm B was depleted to about 0.6 ppm in 10,000 hours at 1300°F and 0.07 ppm in 15,000 hours in 316 stainless steel specimens. A similar leaching of boron from Type 321 stainless steel was observed. No information on the deposition of boron in the system was found, however, but probably exists as an oxide.

Nitrogen can be leached or added to stainless steels in sodium depending on the activity of the nitrogen in the sodium and steel. Nitrogen is practically insoluble in pure high temperature sodium⁽⁷⁾ and its mechanism of transport has not been completely explained. A nitrogen blanket over sodium in the range of 900°F to 1300°F has frequently caused nitriding of stainless steel surfaces near the sodium-gas interface, and, to a lesser extent, in other parts of the systems.⁽⁸⁾ The spasmodic occurrence of nitriding has suggested an impurity in the sodium is promoting the nitrogen absorption by the sodium. Substantial amounts of cyanide have been found in cold traps which suggest this may be a mechanism for nitrogen transport. Nitrogen compounds are also found in cold leg deposits^(9,10) usually metallic nitrides.

The presence of carbon stabilizing elements such as niobium and titanium in 300 Series stainless steels tends to hold nitrogen as well as carbon in the steels. In certain G.E. tests⁽¹⁾ the Types 321 and 347 increased in nitrogen while Types 304 and 316 were stable; or the 321 and 347 were stable while 304 and 316 decreased in nitrogen. In 10 to 15 thousand hours at 1300°F in an upstream position 304 and 316 stainless steels lost 80% of their nitrogen content while slightly downstream at the same temperature most of the specimen gained a small amount of nitrogen. (See Figure 9.2.2-4)

The movement of carbon in stainless steels is analogous to the previously discussed nitrogen. Carbon can be leached from the stainless alloys and deposited on cold legs as metallic carbide, in cold traps as carbide, cyanide, carbonate and carbon,⁽¹¹⁾ or absorbed in structural alloys.

The kinetics of carbon absorption and leaching in stainless steels has been subjected to a substantial amount of investigation. However, some significant factors are still poorly understood because the data can scatter widely in nearly identical tests. One of the areas of uncertainty is the identity of the carbon species in the sodium and its activity. A second area is the complex diffusion process of carbon in stainless steels where carbides of $M_{23}C_6$, M_7C_3 and M_3C type precipitate with the chromium, molybdenum and iron, depending on the amount of carbon present. Thorely⁽¹²⁾ has discussed the diffusion of carbon into stainless steels in addition to presenting experimental data on carburizing rates from several types of carbon impurities. He found carbon steel, oil and sodium carbonate to be the most efficient carburizers at 650°C. Wozadlo, et al⁽¹⁾ examined carbon leaching from stainless steels in 1300°F sodium and found about half of the carbon in a 35 mil wall of 304 or 316 S/S tubing was removed in about seven month. The driving force for removal of carbon from the hot leg of a non-isothermal monometallic loop is the differential activity of carbon between the sodium and the structural surface. The rate controlling factor is generally considered to be the diffusion of carbon through the structural material to the surface. Roy⁽¹³⁾ hypothesized that the corrosion products in the sodium stream lower the activity of the carbon coming

into solution and promote its removal. As the sodium stream is cooled, these corrosion products will precipitate with part of the carbon and the remaining carbon will agglomerate and become inactive. Active carbon is measured in sodium systems by an equilibration with iron-8% nickel alloys. A modification of this principle has been employed in a carbon meter design.⁽¹⁴⁾

The absorption and leaching of carbon from stainless steels can be localized. Wozadlo, et al⁽¹⁾ as well as others have found the carbon in unstabilized stainless steels is preferentially lost from the grain boundary area at 1300°F which promotes a network of brittle sigma phase. Ruther⁽¹⁵⁾ found that carbon is preferentially absorbed at grain boundaries of 304L stainless steel in 550°C sodium with a carbon source. This selective carburization led to a selective sodium corrosion of the carburized grain boundaries. Valibus⁽¹⁶⁾ also examined grain boundary carburization of a titanium stabilized 316 stainless steel and concluded carbon preferentially diffused into places with high free energy such as grain boundaries. It has been reported⁽¹⁷⁾ that certain surface defects such as scratches can lead to selective carburization and localized embrittlement. Thus, carburizing conditions can lead to localized attack or embrittlement which could be important to thin section material.

The program to measure carburization and decarburization rates continues. Argonne⁽¹⁸⁾ is developing an overall equation to describe carbon leaching, absorption and deposition. G.E.⁽¹⁷⁾ is looking at carbon transport and means to control it in secondary systems that contain ferritic alloys. Westinghouse has an active interest in carbon leaching from its fuel development programs for FFTF.

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9.2.7.2 Nickel Alloys - Minor Element Transfer

The absorption and leaching of minor alloying elements and interstitials from nickel alloys has not been as thoroughly investigated as they have been for stainless steels. Thorley⁽¹⁾ reported phosphorous and silicon were selectively removed from a nickel brazing alloy in 650°C sodium of ~10 ppm O₂. Wozadlo, et al⁽²⁾ indicated only a slight removal of silicon from Incoloy 800 (a 31% Ni alloy) after 15,000 hours in 1300°F sodium. The leaching or absorption of carbon and nitrogen will probably be governed by alloying elements in the nickel such as titanium, etc.

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9.2.7.3 Steel- Minor Element Transfer

The study of leaching and absorption of minor elements and interstitials from ferritic steels has largely been limited to the behavior of carbon. Carbon is rapidly leached from unalloyed steels starting about 400°C. This material is a good source of active carbon for carburizing experiments with austenitic steels. If the material is lightly alloyed with chromium such as the 2.25 Cr - 1 Mo steel, the decarburization is slowed. If a small amount of titanium is added the carbon can be stabilized up to 600°C. Alternatively, the chromium can be increased to 9% to retard the carbon leaching⁽¹⁾ .G.E.⁽²⁾ is actively working on the carbon leaching from the ferritic alloys of interest for steam generator tubing.

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9.2.7.4 Miscellaneous Alloys - Minor Element Transfer

The leaching and absorption of impurities and interstitials from a wide variety of materials is best treated by grouping similar types of materials. The refractory alloys all react readily with oxygen, carbon, nitrogen and some of them with hydrogen, depending on temperature. Hydrogen can be absorbed or leached depending on temperature. Carbon, nitrogen and oxygen are generally strongly bound and not subject to leaching except under unusual circumstances. Absorption of these impurities generally embrittle the metal.

9.3 DEPOSITION OF CORROSION PRODUCTS IN NON-ISOTHERMAL SODIUM CIRCUITS

Significant deposition of stainless steel constituents previously dissolved from hot leg surfaces occurs in the cold leg. The characteristics of the deposition process reported by leading investigators is summarized below. The reference loop material is stainless steel. Reference to any other structural metal will be clearly indicated.

Analysis of circulating sodium coolant from non-isothermal loops usually indicates the concentration of metals leached from hot leg surfaces exceed measured or estimated solubilities at $T_{\max}$ by an order of magnitude.⁽¹⁾ Filtration experiments confirm the fact that a considerable portion of the structural metal content is carried in the sodium as suspended particulates. It must be assumed that the deposition processes apparently do not involve particulates at all, or are relatively slow.

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9.3.1 Effect of Temperature and ΔT on Deposition

Deposition from stainless steel saturated sodium tends to be a sequential process. Chromium-rich compounds are the first to deposit, and include principally chromium carbides, Cr_7C_3 and Cr_{23}C_6 , and lesser amounts of NaCrO_2 .

The next material to deposit is an austenitic material rich in nickel.

In the temperature range of 540°C to 650°C ($1000 - 1200^\circ\text{F}$) the Cr and Ni deposits are highly crystalline, leading Roy⁽¹⁾ to conclude the deposits consist of crystallites formed in the sodium prior to deposition. It is not clear from our review whether the crystalline character of chromium and nickel-rich deposits observed by Roy, et al⁽¹⁾ is related to the composition of the deposits or the temperature of deposition. The deposition process is independent of the nature of the substrate material. Roy, et al,⁽²⁾ take the opposite view, reasoning from apparent growth of particle size with time that particles grow in situ by atom diffusion to the deposit surface. At lower temperatures, $<540^\circ\text{C}$, iron deposits appear as finely divided α -iron particles dispersed in sodium. These deposits occur in areas of disturbed flow (high turbulence) and the magnetic fields associated with EM pumps and flow meters. Roy, et al,⁽¹⁾ believe the α -iron deposits occur by atom diffusion to the substrate surface.

Deposits at minimum circuit temperature are Fe- and Si-rich. Silicon found in cold leg deposits is probably due to solution leaching from hot leg stainless steel surfaces.⁽¹⁾

Maximum deposition occurs in non-isothermal systems at the point where the sodium temperature first begins to drop. A 50°F drop in temperature is usually sufficient to produce deposition.

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9.3.2 Effect of Velocity on Deposition

Deposition rates are velocity and degree of turbulence sensitive. An order of magnitude increase in deposition rate has been observed as flow rates are increased from 2 to 15 fps at 800°F.⁽¹⁾ Roy concludes turbulence increases nucleation rates in the bulk sodium and later precipitation. Ray, et al,⁽²⁾ find their deposition data support the G.E. view.

It has been suggested by Ray⁽²⁾ that limiting thicknesses of deposit must eventually be imposed by flow sheer forces on semi-adherent deposits. Analysis of the Westinghouse data, however, does not indicate lessening of growth rate after 10,000 hours and deposits 10 mils in thickness.

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9.3.3 Effect of System Geometry on Deposition

- Maximum deposition occurs at the point in a non-isothermal sodium circuit where the temperature begins to decrease.
- Preferential deposition occurs in cold leg areas at points of flow disturbance such as flow restrictions, changes in flow direction, etc.
- Particulate deposition occurs in dead legs and other regions of reduced flow.
- Deposition rate decreases with increasing downstream position from hot legs (see Figure 9.3.3-1).

Figure 9.3.3-1⁽¹⁾

DEPOSITION RATE OF MASS TRANSFER PRODUCTS IN PRIMARY AND SECONDARY SODIUM LOOP SYSTEMS.

- (a) and (b) as a Function of Location (L/D)
 (d), (e) and (f) Cold Leg Deposition Rates Versus Time.
 (c) System Temperature - Location Profile

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9.3.4 Effect of Time on Deposition

- Deposit thickness will tend to grow over the design life of the component, limited only by the action of flow shear forces or thermal transient stresses on loosely adherent deposits.⁽¹⁾
- During the period of reactor startup, deposition of chromium, nickel and manganese will predominate until steady-state ferrite surfaces develop on hot leg surfaces.
- Deposition rates decrease for the first few thousand hours and then level out at a steady rate. (See Figure 9.3.3-1)

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9.3.5 Material Balance Between Dissolution and Deposition

No satisfactory analysis of material balances in non-isothermal stainless steel sodium systems have been reported. One question of interest is the ratio of deposition on loop surfaces versus deposition in cold traps for the major stainless steel constituents. Another question is the effect on total sodium contaminant burden of different bypass rates through cold traps or filters. Data of this kind might be helpful in estimating lifetime of particulates in circulating sodium as well as predicting metal contamination of reactor coolants.

9.3.6 Character of Surface Deposits and Interactions With the Substrate

Metallic elements Cr, Ni, Mn, Fe, etc. are observed to deposit in cold leg piping in the temperature related sequence indicated. In addition to these metallic elements, interstitial elements C, Si, N and oxygen are observed to deposit. Carbon up to 2% by weight of specific deposits has been found, usually in the form of Cr_7C_3 and Cr_{23}C_6 .⁽¹⁾ Evidences of carbon transfer from the deposit to the stainless steel substrate have been noted.

Homogenization of mixed metal hot leg surfaces has been noted, for example hot leg, iron, coupons have been observed to pick up substantial nickel and chromium content from the stainless steel loop structure and incorporate these elements in the metal lattice. There have been few evidences that cold leg deposits of Ni, Cr, Mn, Fe, etc. are anything more than loosely adherent. The notable exception of carbon has been noted above. The possibility that after longer periods of time tighter bonding and metal diffusion might occur on cold leg surfaces should be kept in mind. The implications on heat transfer, radioactivity and potential decontamination of out-of-core components are the basis of potential concern.

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9.4 DEPOSITION OF RADIOACTIVE MATERIALS (Corrosion Products)

Mass transfer processes in non-isothermal sodium circuits have been shown to result in metal wastage of hot leg components. Since it is the in-core portions of a reactor primary circuit which constitute the hot leg, activated corrosion products will be included in the mass transfer process. Radioactivity transport processes are entirely analogous to those which have been discussed in terms of general metal wastage and deposition. The isotopes which represent the major sources of radioactivity are, however, minor constituents of stainless steel and have received little attention in most studies of bulk mass transfer, temperature-solubility dependence or compound formation in sodium coolants. Behavior of corrosion product radionuclides has been deduced from sodium reactor experience and the few exposures of irradiated stainless steel thus far reported. In the Table 9.4-1 by Brehm⁽¹⁾ a Corrosion Product Radioactive Inventory has been calculated for a hypothetical LMFBR constructed of 300 Series stainless steel and with stainless steel fuel cladding. The estimate of Table 9.4-1 is based on available information on leaching and deposition of the principal radionuclides. Brehm, et al⁽¹⁾ have a prepared table which identifies the "Preferential Corrosion Factors" which they employ. Table 9.4-2 may be expected to change as additional information is gained, but serves to accommodate source term factors including leaching rate, deposition characteristics, etc. that effect availability to the system. Programs⁽¹⁾ to look specifically at radioactivity buildup in LMFBR heat transport systems have recently been initiated in several countries suggesting that information on this subject will increase rapidly.

Table 9.4-1⁽¹⁾

CALCULATED CORROSION PRODUCT
RADIOACTIVE INVENTORY FOR AN LMFBR

<u>Isotope</u>	<u>Curies of Activity</u>
⁶⁰ Co	137
⁵⁸ Co	286
¹⁸² Ta	11
⁵⁴ Mn	2469
⁵⁹ Fe	80

Table 9.4-2⁽¹⁾

SOURCE TERM FACTORS FOR
CORROSION PRODUCT RADIONUCLIDES

Nuclide	Preferential Corrosion Factor	Basis
⁵⁹ Fe	X 1	Little known about long term behavior
⁶⁰ Co	X 0.2	Low corrosion rate, little reactor experience
⁵⁸ Co	X 0.1	Depletion of Ni parent at surface
¹⁸² Ta	X 0.01	LAMPRE low Ta corrosion rate
⁵⁴ Mn	X 2	Observed preferential leaching

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9.4.1 MASS TRANSPORT OF RADIOACTIVE MANGANESE

Data on release, mass transfer and deposition of ^{54}Mn are very limited from bulk mass transfer experiments. Since ^{54}Mn is likely to be the principal corrosion product contributor (see Table 9.4-1) its movement in the primary system is of considerable interest. The most informative ex-reactor study is the HEDL work reported by Brehm, et al^(1,2) on the transport of ^{54}Mn from a EBR-II irradiated specimen, $T_{\text{max}} 1300^\circ\text{F}$. Reported work can be summarized in the following observations:

- ^{54}Mn was distributed all over the non-isothermal RTL loop. High counting rates were observed in regions immediately downstream of the specimen. Deposition on hot leg surfaces suggests isotopic exchange, but preferential deposition in lower temperatures zones indicates transport by dissolution and subsequent precipitation. Location of ^{54}Mn in the cold trap is interpreted to mean reaction to form a NaMnO_2 analogous to the sodium chromites.
- Deposition of ^{54}Mn was favored in the high velocity sections of the RTL in both hot leg and cold leg situations.
- Studies of the migration of Mn in the RTL after removal of the activity source have indicated a steady reduction of ^{54}Mn activity with time and a corresponding increase of ^{54}Mn activity in the cold trap.
- A general decrease of ^{54}Mn in hot leg regions occurs with time of exposure.
- At LMFBF temperatures some diffusion of ^{54}Mn into pipe walls should be expected. Penetration rates of ^{54}Mn into piping metal substrates are in approximate agreement with diffusion rate theory.
- ^{54}Mn deposition in Rhapsodie was 2 to 5 times greater in the cold leg than in the hot leg.
- ^{54}Mn in the Rhapsodie primary circuit sodium ran at 0.1 to $1\mu\text{ Ci/cm}^2$, ~ 10 to 200 mR/hr.

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9.4.2 MASS TRANSPORT OF RADIOACTIVE COBALT

Since cobalt is present in stainless steel only as a minor contaminant, the only information on cobalt mass transfer comes from RTL,⁽¹⁾ a G.E. Tracer Study,⁽²⁾ or reactor observations. The most important observations are indicated below.

- ^{60}Co released from irradiated specimens in RTL migrated only a short distance downstream from the source. Deposition behavior was similar (in location) to ^{51}Cr .
- ^{60}Co , ^{51}Cr deposited preferentially in high velocity situations.
- Release tendencies: $^{54}\text{Mn} > ^{51}\text{Cr} > ^{60}\text{Co}$
- It is concluded ^{60}Co will be transported only slowly from the core to the hot leg. Due to the long half life of ^{60}Co , a buildup on hot leg surfaces is probable.
- Menken⁽³⁾ has proposed to estimate Co leaching, transport, and deposition from observations of Ni, based on well known chemical similarities. Brehm has disagreed on the very reasonable basis of the differing behavior of Ni and Co alloys in sodium corrosion studies, e.g., corrosion rates of cobalt alloys are lower than nickel base alloys.
- Roy, et al⁽²⁾ found 70% of the released ^{60}Co in the hot leg after 2100 hours at 1200°F but felt the Co would migrate downstream as the surface became saturated at longer times.

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9.5 DEPOSITION OF FISSION PRODUCT AND FUEL FRAGMENTS

9.5.1 DEPOSITION OF FISSION PRODUCTS

Fission products and fuel fragments from defective fuel elements plus U-Pu contamination of fuel pin cladding provide a significant additional source of radiation release to the primary sodium circuit. Some calculations⁽¹⁾ for the German SNR based on 1% fuel pin leakage, surface contamination of the fuel pin cladding at 10^{-7} g/cm² (U-Pu) indicate fission product ¹³⁷Cs would represent the major (non sodium) source of radioactivity in the primary system. Based on EBR-II and Rhapsodie experience it appears the 1% fuel leakers are unnecessarily conservative (high). More realistically the combined corrosion product inventory of ⁶⁰Co, ⁵⁴Mn, ⁵⁸Co, ¹⁸²Ta, ⁵⁷Fe will dominate the radioactive burden in the sodium. Still it is well to bear in mind that fission products can significantly influence the sodium system accessibility.

The principal fission products found in DFR are the following:⁽²⁾

¹⁴⁰Ba-La
¹²⁵Sb
⁹⁵Zr-Nb
¹³²Te
¹³¹I
¹³⁷Cs, ¹³⁴Cs
¹⁴⁴Ce, ¹⁴¹Ce

Regarding the behavior of individual fission products, DFR experience has been that:

- ¹³⁷Cs remains in the sodium rather than deposits.
- Contrary to the DFR and also to EBR-II experience, Cs deposition on surfaces in small loops has been observed. A suggestion proposed by Evans⁽³⁾ is that the ¹³⁷Cs daughter, ^{137m}Ba, may be the absorbing species. It is suspected that ¹³⁷Ba could be cold trapped, (¹³⁷Cs could not).

- Zr and Ba form stable oxides and deposit on the piping.
- ^{131}I forms stable NaI.

A few generalizations are possible regarding the chemical and physical forms that fission products might take in hot sodium coolant environments according to Davies.

- Alkaline earths, rare earths, Zr, Nb and actinide element oxides are more stable than Na_2O and will be present as oxides. These oxides will probably have low solubilities in sodium, be transported as fine suspended particulates to the cold traps or end up in deposits in low flow areas.
- Fission product nuclides forming less stable oxides than Na_2O will be present in elemental form or in other compounds. This class of elements (fission products) will include heavier alkali metals (Rb, Cs), Hg, Ru, Rh, Tc, Mo, and non metals. Rb and Cs are soluble in Na.

REFERENCES

1. A Merkel, "A Survey About Calculation Methods for the Activity Inventory in the Primary System of SNR," in W.F. Brehm, Trip Report IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBFR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, #ST-164, WADCO/FFTF 714526, October 1971. pp. (OUO)
2. R.A. Davies and J.L. Dummond, "The Behavior of Radioactive Impurities in DFR Primary Liquid Metal Coolant," Ibid.
3. H.E. Evans and W.R. Watson, The Behavior of Radioactive Isotopes in Liquid Metal Coolant Fast Reactors, Part II, An Investigation of Cs and Ba Isotopes from Solutions in Liquid Sodium, RD-B-N-1513, Central Electricity Generating Board, January 1970.

9.5.2 TRITIUM REMOVAL

Tritium forms by the nuclear processes:

It is estimated on the basis of 1 ppm B in the stainless steel and 1 ppm Li in the SNR sodium coolant a production rate of 40 Ci³T/day might be expected.⁽¹⁾ Approximately one-half of this production will be cold trapped as sodium tritide. The balance will be carried in the argon cover gas or deposited with sodium frost. Since some leakage of argon and its contaminants around seals is expected, a cover gas clean up step specifically design to remove ³T may be required, e.g.

Kabele⁽²⁾ also estimates 40 Ci/day of tritium production in FFTF however his calculation of distribution is somewhat different because he consider the diffusion of tritium through the stainless steel fuel cladding, IHX tubing and heat transport system piping. The amount of tritium in the secondary system is very much a function of primary and secondary cold trap efficiencies.

Wozadlo, et al⁽³⁾ recently examined the retention of tritium in fuel exposed in EBR-II and found essentially none, indicating it had all diffused to the primary sodium.

REFERENCES

1. A. Merkel, "A Survey About Calculation Methods for the Activity Inventory in the Primary System of SNR," W.F. Brehm, Trip Report IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBFR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, #ST-164, WADCO/FFTF 714526, October 1971. pp. (OUO)
2. T.J. Kabele, Estimates of Tritium Distribution in the FFTF, HEDL-TME-72-19, Hanford Engineering Development Laboratories, March 1972. (OUO)
3. G.P. Wozadlo, B.F. Rubin, and P. Roy, Tritium Analysis of Mixed-Oxide Fuel Rods Irradiated in a Fast Flux, GEAP-13864, General Electric Company, August 1972.

9.5.3 FUEL FRAGMENT BEHAVIOR

In reactors the size of FFTF or SNR the tramp U-Pu inventory, based on the estimate of 10^{-7} g/cm² of cladding surface, will be of the order of a gram or two. The assumed analysis is hypothetical since no technique generally applicable to fuel surface contamination is available at the present time. Fuel release rates from defective fuel or vented fuel concepts are very difficult to generalize upon. It has also proven very difficult to sample sodium coolants reproducibly for U-Pu. The result is that fuel particle inventory estimates for reactors are very approximate.

Davies, et al⁽¹⁾ believe that fuel oxide particles are acted upon by the sodium in a fashion which rapidly reduces oxide particles to very small size favoring suspension in the circulating coolant and eventual deposition in cold traps and low flow regions of the primary coolant circuit. At periods of reactor shutdown (low flow) the U-Pu inventory in the sodium appears to drop.

In connection with the preferential movement of fuel particles to the cold trap, close watch on the U-Pu inventory should be required. Not only is the cold trap geometry relatively favorable to critical mass formation, but the deposition of hydrides at the cold trap is also favored. Hydrogen moderation will considerably reduce critical mass dimension.

REFERENCES

1. R.A. Davies and J.L. Dummond, "The Behavior of Radioactive Impurities in DFR Primary Liquid Metal Coolant," in W.F. Brehm, Trip Report IAEA Specialists Meeting on Fission and Corrosion Product Behavior in Primary Systems of LMFBFR's, and Visit to Karlsruhe Nuclear Center, September 20-24, 1971, ST#164, WADCO/FFTF 714526, October 1971. pp. (OUO)

9.6 CONSEQUENCES OF MASS TRANSPORT AND CORROSION

The purpose of this discussion is to define in a very general way safety related operational and structural problems in LMFBRs that could result from corrosion and mass transfer. The processes that are qualitatively described here, will require quantification in the consideration of a specific reactor design. Some information on the failure rate of specific components can be obtained from a Failure Data Handbook.⁽¹⁾

REFERENCE

1. Failure Data Handbook for Nuclear Power Facilities. A Guide For Design Construction Maintenance, LMEC-Memo-69-7, Rev. 1, Vol. 1 and 2, Atomic International, Canoga Park, CA.

9.6.1 WEAKENED STRUCTURE BY MASS TRANSFER

Mass transfer processes may significantly reduce the effective cross section of critical in-core structures like fuel cladding, and therefore limit the constraint available to fuel swelling. Or again the loss of mechanical properties may be the result of selective leaching of a single alloy constituent such as carbon without apparent reduction in cross section. These two processes will be considered separately, but both are related to loss in properties of critical components due to mass transfer processes in the hot leg regime.

9.6.1.1 Bulk Metal Loss by Mass Transfer

Experience with hot leg components in non-isothermal sodium loops has shown that significant metal losses can be expected at temperatures, ΔT s, velocity and sodium chemistry expected in LMFBRs. The most obvious concerns are for fuel cladding, where limitations on cladding wall thickness imposed by core physics and heat transfer requirements, mean that significant under-estimation of corrosion rates could lead to fuel failure. Sample lines and thermocouple sheathing are thin section, but are not significant heat generating surfaces. For other core components corrosion losses are less significant. This is partly because local sodium temperatures are lower (for non-heat generating surfaces) and partly because core components, other than those noted, have substantially greater cross section and suffer relatively less from the incremental loss of metal.

9.6.1.2 Preferential Leaching of Alloy Constituents

Selective removal of one or more alloy constituents can reduce the mechanical properties of residual metal. Leaching of chromium and nickel from hot zone austenitic stainless steel converts the depleted zone to a ferritic structure with loss in strength. Loss of carbon from hot leg structures which proceeds more rapidly than Cr, Ni, and Mn depletion, also reduces high temperature strength of the residual metal. Thus in calculations of residual cladding properties, wall thickness reduction, the ferritic layer thickness, and the depth of carbon depletion must all be taken into account.

9.6.1.3 Localized Metal Loss, Intergranular Attack

Intergranular attack is periodically reported in sodium systems, but the conditions which produce the attack are still obscure. Available information regarding incidence is cited elsewhere. It is clear, however, that intergranular attack can destroy mechanical integrity, and when associated with thin containment piping can lead to sodium leakage and sodium fires.

9.6.2 IMPAIRED HEAT TRANSFER AND COOLANT FLOW

Deposition processes in non-isothermal sodium circuits have received less quantitative attention than hot leg dissolution processes. Deposits in regenerative heat exchangers observed by Ray, et al,⁽¹⁾ had built up to at least 10 mils in the course of approximately a year's operation. Comparison of heat transfer rates of the fouled heat exchanger against corresponding rates for a similar but clean unit indicated about a 10% loss in efficiency in the unit. In the absence of convincing evidence that a terminal deposit thickness is developed, continuing fouling and further reductions in heat transfer efficiency must be assumed.

Small diameter sodium lines to instruments and sensors of various types are subject to temperature change where they emerge from the pool sodium and would appear to be highly vulnerable to deposition and eventual plugging. We have at hand no specific reference to plugged lines, but propose to look into this potential problem later in greater detail.

Effective methods to reduce deposition related problems chemically or mechanically are simply not at hand for reactor systems. The basic problems are the intense radioactivity which would be associated with access to the deposit, and the absence of criteria to requalify heat exchangers for reactor use after chemical cleaning.

REFERENCES

1. W.E. Ray, R. L. Miller, S.L. Schrock and G.A. Whitlow, The Structure and Properties of Sodium Mass Transfer Deposits, Paper IV-1, Presented at ANS Meeting, Reactor Materials Performance, Richland, WA. April 23-26, 1972.

9.6.3 EMBRITTLEMENT EFFECTS RELATED TO DEPOSITION PROCESSES

Mass transport of interstitial elements carbon and nitrogen in non-isothermal sodium circuits can result in localized deposits considerably enriched in carbon and, presumably nitrogen as well. Ray, et al, report cold leg deposits up to 2% in carbon. In high temperature sodium circuits some or all of the carbon (nitrogen) can diffuse into the substrate metal greatly increasing the carbon content. Decided alteration (embrittlement) of mechanical properties of effected cold leg piping can result.

Non stabilized stainless steels used in this country for sodium containment systems are subject to carbon transport. Since maintainance of carbon concentration within a controlled compositional range is important in both hot and cold leg components, there is clearly an implied problem. Further consideration of carbon transport, of monitoring and alloy selection, is in order.

9.6.4 RADIOACTIVE BUILDUP, OUT-OF-CORE, RELATED TO MASS TRANSFER9.6.4.1 Corrosion Product Radiation Sources

The transport of radioisotopes from irradiated in-core surfaces and their subsequent deposit out-of-core can lead to high radiation fields in working areas. Calculations of anticipated levels in FFTF have been made.^(1,2) Calculations of shielding requirements are handicapped by uncertainties on transport rates and, particularly, identification of probable deposition sites. While shielding is necessary, it is certain to complicate access to components requiring periodic inspection and maintenance.

Looking at the problem from a reactor safety point of view there appears to be the overriding requirement that inspection and maintenance functions can be safely performed under conservative estimates of local radiation fields.

REFERENCES

1. G.P. Wozadlo, C.E. Boardman, M.L. Weiss, Calculated Radio-activity of the FFTF Primary Sodium System Due to Mass Transfer, GEAP-13671, General Electric Company, Sunnyvale, CA. August 1971
2. T.J. Kabele, W.F. Brehm, D.R. Maar, Activated Corrosion Product Radiation Levels Near FFTF Reactor and Closed Loop Primary System Components, HEDL-TME-72-71. Hanford Engineering Development Laboratory, May 1972.

9.6.5 EQUIPMENT MALFUNCTIONS RELATED TO CORROSION AND MASS TRANSFER

The deposition of sodium coolant borne particles or depositable species in solution at wear surface or in critical areas of moving parts could cause malfunction. These subjects will be dealt with later, but require recognition as mass transfer related phenomena.

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CORROSION

[illegible]

10.0 EROSION10.1 INTRODUCTION

Erosion may be defined as the degradation of a solid surface by the mechanical action of solids or liquids. The particulate form of the eroding agent is usually identified in erosion definitions. In the case of liquid agents, however, this definition encounters some difficulty when applying it to the phenomenon of cavitation, where focusing of liquid jets may be involved in a damage process which comes within the purview of erosion.

Erosion is a complex process, involving the physical and mechanical properties of both the agent and the target. Except for the ideal case of a chemically inert target material, the chemical properties of the erosion participants, and the carrier medium, must be added to the list of critical variables. This implies that only rarely is purely mechanical action thought to be involved in the erosion process. Where there is strong involvement of both erosion and corrosion, such as believed possible for the wasting process discussed in another chapter, there can be very serious metal damage in a short time.

To the usual variables determining the erosion process, LMFBR service will add both physical and chemical factors indigenous to this reactor system. Where possible, there will be specific identification of the variables thought to be important to the erosion process in LMFBR systems.

10.2 SCOPE

The very limited data available on liquid metal systems requires an introductory discussion of other erosion studies and experience. Most of the discussion on the basic behavior and characteristics of erosion and erosion-corrosion is described in connection with aqueous systems. Correlation between aqueous and liquid metal systems is discussed.

Experimental results of engineering tests with liquid metals are presented and discussed with respect to their relevance to reactor environments. Sites and conditions within the LMFBF Liquid Metal System where there is thought to be some potential for erosion damage are discussed.

10.3 FUNDAMENTAL PROCESSES

The fundamental aspects of erosion are described in three sub-sections: solid particle impingement, liquid particle impingement, and cavitation.

Originally, liquid particle impingement was handled separately from cavitation. In recent years, however, the similarities between liquid particle impingement and cavitation damage processes have become more apparent. Canavelis⁽¹⁾ discusses these similarities and the parameters thought to be important to the two processes.

Of the three sources of erosion--solid particle impingement, liquid particle impingement, and cavitation, cavitation appears to be the most relevant to LMFBR systems. Most liquid sodium studies have tended to identify cavitation as the principal damage agency.

Some review of solid particle effects is given. Other possible troubles associated with solids are reviewed in another chapter of this report. In a properly operating LMFBR system, liquid particle impingement should be a minor factor. However, some discussion of this mechanism is included.

10.3-2

REFERENCES

1. R. Canavelis, "Jet Impact and Cavitation Damage," J. Basic Eng.
90D, pp. 355-367, 1968.

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10.3.1 SOLID PARTICLE IMPINGEMENT

When a solid particle impacts a surface, damage may consist of removal of material, plastic deformation of the material, or a combination of these effects. Some of the kinetic energy of the particle is dissipated by these functions, and by heat generation in the target material.

The erosion experienced by a variety of metals subjected to solid particle impact has been described by a relation of the form,

$$Q = C(MV^\alpha/2)/p$$

where Q is the volume of metal removed by particles of total mass M , V is the impact velocity, C is an impact 'efficiency' number related to the angle of attack, α is the velocity parameter, and p is the so-called flow stress, often approximated by an indentation hardness number (e.g. VHN number).

With 60 mesh silicon carbide particles (VHN 2400 kg/mm²) in an air carrier medium, and an angle of attack of 20° which gave the maximum erosion effect for his particular test conditions, Finnie⁽¹⁾ used a C value of 0.075. With a variety of metals, spanning a hardness range of about 4-300 (VHN(kg/mm²)/300 g load), he found an α range of about 2.0-2.4. However, α values of 6.5, and higher, have been reported for brittle metals under similar impact conditions.⁽²⁾

Finnie⁽¹⁾ has emphasized the very limited interpretation permitted by the Q - V correlation noted above, both with respect to particular values of the parameters and to the general form of the relationship. He stressed the possible influence of the physical and mechanical properties of both particle and target, as well as corrosion action in any given working situation.

It has been shown⁽³⁾ that abrasion resistance will exhibit a minimum as the hardness of the target material goes from very soft to very hard. For aqueous systems, useful soft surfaces have been made of rubber, or other elastic materials.⁽⁴⁾ Where physical and chemical

10.3.1-2

limitations preclude the use of soft materials, the hard end of the hardness spectrum is the obvious recourse. Stellite is an example of a hard facing material which has exhibited good erosion resistance.⁽⁵⁾

Solid particle erosion is potentially a problem at any location where the entraining fluid experiences abrupt changes in direction of motion, or flow cross section. Pipe bends, converging sections, pump shrouds and impellers, instrument lines subjected to full flow impact, are examples of trouble sites for particle erosion.

REFERENCES

1. I. Finnie, J. Wolak and Y. Kabel, "Erosion of Metals by Solid Particles," J. of Materials, 2 (3), pp. 682-700, 1967.
2. C. E. Smeltzer et al, "Mechanism of Metal Removal by Impacting Dust Particles," J. of Basic Eng., 92D, pp. 639-654, 1970.
3. H. E. Rose and R. M. E. Sullivan, A Treatise on the International Mechanics of Ball, Tube and Rod Mills, Constable, London, p. 258, 1958.
4. L. L. Watkins, "Corrosion and Protection of Steel Piling in Seawater," U. S. Army Corps of Engineers, Tech. Memo. 27, May 1969.
5. M. G. Fontana and N. D. Greene, Corrosion Engineering, McGraw-Hill, NY, 1967.

10.3.2 LIQUID PARTICLE IMPINGEMENT

In studies of liquid particle impingement, Thiruvengadam⁽¹⁾ has noted four basic responses by the target materials:

- a. no permanent deformation,
- b. deformation after some number of impacts,
- c. virtually instantaneous plastic deformation with the first impact, augmented by subsequent impacts,
- d. plastic flow initiated by the first impact and stimulated by subsequent impacts of a high frequency impact situation.

If the term 'deformation' includes material removal as a primary, or secondary, effect, this list of effects is fairly comprehensive. Consideration of the above effects suggests the existence of a threshold for material tolerance of impact, the threshold being expressed in terms of an impact intensity (impact energy per particle per unit time), or an impact energy (total energy imparted over a given time). The various effects also emphasize the importance of the bulk physical and mechanical properties of the erosion participants, the rate at which impact occurs, the total time of impact occurrence, and the nature of the target surface. In a study of generalized erosion relationships for liquid particle impact, Heymann's⁽²⁾ analysis tends to support a fifth power influence of impact velocity. Such a velocity dependence would be included in the span of velocity exponents noted previously for solid particles. Superposition of corrosion action is an additional factor to be considered with liquid metals.

Liquid particle impingement erosion in the sodium systems of the LMFBR is expected to be minor. This type of erosion may be experienced on the water side of the heat transfer complex. In case of a loss of pressure and an overheating of the sodium, some liquid particle erosion on the sodium side is a possibility.

REFERENCES

1. A. Thiruvengadam, "The Concept of Erosion Strength," ASTM-STP-408, pp. 22-41, 1967.
2. F. J. Heymann, "Toward Quantitative Prediction of Liquid Impact Erosion," ASTM-STP-474, pp. 212-248, 1970.

10.3.2.1 Intensity Threshold

The concept of an intensity threshold implies that, up to some limit of impact experience, the target can either resist the action (exhibit no temporary deformation), or it can recover its original shape. Thiruvengadam⁽¹⁾ discusses several concepts relating the strength of the target material to the onset of erosion damage.

From an analysis of the maximum pressure exerted by impacting water drops (the 'water hammer' approach), the following criteria for the onset of erosion damage have resulted:⁽¹⁾

$$\text{(single drop): } \frac{Y_d}{\rho_l c_l V_i} \approx 2 \quad (1)$$

where: Y_d is the yield strength of the material, ρ_l is the liquid density, c_l is the velocity of sound in the liquid, and V_i is the impact velocity.

$$\text{(multiple drops)} \frac{\sigma_e}{\rho_l c_l V_i} \approx 2 \quad (2)$$

where: σ_e is the fatigue endurance limit of the material. Some density and sound velocity data are given in Table 10.3.2.1-1.

Another relationship, due to Engel (see ref. 1), defines a critical impact velocity of a particle as follows:

$$V_i = \frac{\beta Y_d}{\rho_l^{\frac{1}{2}} E_m^{\frac{1}{2}}} \quad (3)$$

where: V_i is the critical impact velocity of a single drop to produce permanent deformation. Y_d and ρ_l are defined above, E_m is Young's modulus of elasticity for the metal, and β is a factor which can be estimated from the expression,

$$2\beta = (E_m/K_l)^{\frac{1}{2}} \quad (3a)$$

10.3.2.1-2

where: K_l is the bulk modulus of the liquid. (As an example: for a water-steel combination, $K_l = 300,000$ psi, $E_m = 30 \times 10^6$ psi; this combination gives a β value of 0.2) In the case of multiple impacts, the endurance limit, σ_e , would be a logical replacement of Y_d in equation (3). Engel's concept of a threshold criterion has been supported by tests with mercury drops against copper, aluminum, lead and steel, and by water drops against copper, aluminum and lead.⁽²⁾

10.3.2.1-3

Table 10.3.2.1-1

VELOCITY OF SOUND AND DENSITY

<u>Material</u>	<u>C_o</u> <u>m/sec</u>	<u>ρ</u> <u>g/cc</u>	<u>T</u> <u>°C</u>	<u>Source</u>
Water (distilled)	1498	0.998	25	3
Mercury	1450	13.5	25	3
Sodium (liquid)	2450	0.89	250	4
Sodium (liquid)	2240	0.79	650	4
347 S/S	5790	7.9	-	3
Iron	5950	7.9	-	3
Titanium	6070	4.5	-	3

C_o is the standard velocity of sound. C₁ is related to C_o by the relation: $C_1/C_o \approx 2V_i/C_o$.⁽⁵⁾

REFERENCES

1. A. Thiruvengadam, "The Concept of Erosion Strength," ASTM-STP-408, p. 22, 1967.
2. O.G. Engel, "Pits in Metals Caused by Collision with Liquid Drops on Soft Metal Spheres," Journal of Research, Nat. Bur. of Standards, Vol. 62, No. 6, p. 3, June 1959.
3. Handbook of Chemistry & Physics, 54th Edition, 1973-1974, CRC Press, Cleveland, Ohio.
4. O.J. Faust (Ed.), Sodium-NaK Handbook, Gordon & Breach Pub., New York, 1972.
5. F.J. Heymann, "On the Shock Wave Velocity and Impact Pressure in High Speed Liquid, Solid, Impact," J. Basic Eng., 90D, p. 400, 1968.

10.3.2.2-1

10.3.2.2 Effects of Target Material Properties

For prediction purposes, it is desirable to have erosion behavior of a material related to its properties and to those of the impacting environment. Some correlations between target material properties and erosion will be discussed.

Hardness: Hardness is known to be an important factor in determining erosion damage, as shown in Figure 10.3.2.2-1 (Ref. 1). It has not been possible to relate hardness to different types of material in one theory. It is clear from the figure that, even within a given family of materials, there can be a strong variation of erosion resistance with hardness. Between families, the hardness-erosion damage characteristics can be markedly different, with respect to slope and absolute values.

Work hardening the surface prior to erosion generally increases the incubation period (defined in Figure 10.3.2.2-2 (Ref. 2)). Thus, it might be expected that impacts on a work hardenable material should delay the onset of damage. Experience has shown, however, that this does not generally occur.⁽²⁾ It is thought that, in this case, work hardening occurs only on a very local scale and leads to localized fatigue cracking, rather than protection.

Other Properties: Garcia and Hammitt⁽³⁾ attempted to correlate erosion data of Hobbs⁽⁴⁾ with several material properties, namely: ultimate resilience (UR), hardness (H), tensile strength (TS), impact strength (IS), and proof resilience (PR). Their correlation, using only the ultimate resilience (UR) parameter is:

$$\text{average MDP rate} = 6.41 + 9.21 \times 10^6 (\text{UR})^{-3}$$

and their expression for a multiple property correlation is:

$$\begin{aligned} \text{average MDP rate} = & -94.9 + 1.39(\text{UR})^{-2} - 6.70 \times 10^{-5}(\text{H})^2 \\ & + 2.64 \times 10^6(\text{TS})^{-1} + 1.69(\text{TS})^{-33} \\ & + 0.27(\text{IS})^{-5} - 3.79 \times 10^3(\text{PR})^{-2} \end{aligned}$$

FIGURE 10.3.2.2-1. EROSION WGT LOSS VS HARDNESS (STEAM TURBINE TEST RIG V_i 1730 ft/sec, 90F, TUNGSTEN TOOL STEEL REFERENCE) (cf REF. 1)

FIGURE 10.3.2.2-2. POSSIBLE REGIMES IN AN EROSION RATE-TIME CHARACTERISTIC (cf REF. 2)

10.3.2.2-4

where: MDP is the mean depth of penetration in mil/hr; UR is $0.5(TS)^2 /$ elastic mod., in psi; PR is $0.5(\text{proof strength})^2 /$ elastic mod., in psi; IS is in ft-lbs; H is apparently expressed in HV-30 numbers; and TS is in psi.

Hobbs⁽⁴⁾ used a magnetostrictive device at 20kc and the tests were conducted in water at 20°C. A number of different alloys were tested (see Ref. 4 for specifications).

These correlation efforts are given only to show current trends in this area and to identify target material properties which have shown some promise with respect to generalized erosion theory. Finnie's warning concerning stretching the interpretation scope of an erosion rate expression (see section 10.3.1) applies equally here.

REFERENCES

1. A. Smith et al, "Erosion of Steam Turbine Blade Shield Materials," ASTM-STP-408, pp. 125-158, 1967.
2. F. J. Heymann, "On the Time Dependence of the Rate of Erosion Due to Impingement or Cavitation," ASTM-STP-408, pp. 70-110, 1967.
3. R. Garcia and F. G. Hammitt, discussion in ASTM-STP-408, p. 180, 1967.
4. J. M. Hobbs, "Experience with a 20kc Cavitation Erosion Test," ASTM-STP-408, pp. 159-185, 1967.

10.3.2.3 Effect of Time

In section 10.3.2.1 the subject of an intensity threshold was discussed. Other observed effects are the variation of the erosion rate with time and the incubation period prior to the appearance of permanent erosion damage. Eisenberg⁽¹⁾ has noted that the incubation period appears to be related to a fatigue mechanism.

Heymann⁽²⁾ has summarized various concepts of erosion attack. Several erosion rate-time characteristics are shown in Figure 10.3.2.2-2 and Figure 10.3.2.3-1. For practical purposes, he suggests that "it is convenient and not too inaccurate to draw a straight line through the general region of maximum steepness, and to specify its slope as a rate parameter and its intercept as an incubation period." Typical cumulative erosion data for the early (non-steady state) phase of the erosion history are shown in Figure 10.3.2.3-2(3).

FIGURE 10.3.2.3-1. AN EROSION RATE-TIME CHARACTERISTIC
(cf REF. 2)

FIGURE 10.3.2.3-2. CUMULATIVE EROSION LOSS VS TIME (cf REF. 3)

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REFERENCES

1. P. Eisenberg, "Cavitation and Impact Erosion--Concepts, Correlations and Controversies," ASTM-STP-474, pp. 3-28, 1970.
2. F. J. Heymann, "On the Time Dependence of the Rate of Erosion Due to Impingement or Cavitation," ASTM-STP-408, pp. 70-110, 1967.
3. W. C. Leith and A. L. Thompson, "Some Corrosion Effects in Accelerated Cavitation Damage," J. of Basic Eng., Transactions ASME, 82D, p. 795, 1960.

10.3.2.4 Surface Effects

Erosion is considered to be affected by two aspects of a surface, namely, the geometrical roughness and certain bulk material properties which affect surface response to impact. It is not known if chemical properties are significant to this phenomenon, other than with respect to surface film formation. In sodium, chemical behavior will be a strong function of impurity levels.

The effects of geometrical roughness are not clearly defined, possibly due to the existence of several erosion mechanisms which react differently to a given surface. One concept, discussed by Heymann⁽¹⁾, considers that when a drop impacts, it spreads radially outward at a high velocity, especially if it is relatively large. Such an effect could exert considerable force on the projections of a rough surface and eventually cause fatigue at the roots of the peaks. Also, cavitation could occur downstream from a projection under high velocity impact. Arndt and Ippen⁽²⁾ have analyzed the effects of isolated and distributed surface irregularities on cavitation inception. They concluded that it is possible for a distribution of surface roughness to actually reduce cavitation, while a single irregularity- such as that caused by a surface mismatch between equipment components comprising a flow channel-can yield a much higher cavitation propensity.

In the case when droplets are small relative to the roughness, they can impact either on the side of a depression, or at the bottom. If a side impact occurs, little energy is absorbed and relatively little damage occurs. With a bottom impact in a dry depression, the impact energy is focused into the base of the pit, causing further deepening of the pit. If the pit contains liquid from previous impacts, the retained liquid may mitigate the impact effect. The degree to which a liquid is retained on the surface is a complex function of shape, position, and relative motion with respect to the flow stream, as well as the rate at which fresh liquid impinges. The amount and distribution of the surface liquid will, in turn, affect the action of subsequent impingement through cushioning, or lubrication of the lateral flow.

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Pouchet⁽³⁾ has analyzed liquid film influence under specific conditions presented by British steam turbine environments. His results, depending on a number of assumptions, are not particularly relevant to this discussion. It is interesting, however, that he deduced a fifth power velocity influence, in support of studies noted earlier in this chapter.

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10.3.3 EFFECTS OF CAVITATION

To date, there is no adequate quantitative description of the cavitation process. Eisenberg⁽¹⁾ has recently presented an excellent, qualitative review of present concepts of the phenomenon. He notes that early calculations showed that if a bubble collapsed, the resulting pressures, due to shock waves, were large enough to damage the surface. However, three factors tend to mitigate this action. First, high pressures are achieved only if the collapse is spherical and experimental observations have indicated that the usual collapse is unsymmetrical. Second, the maximum pressure is reduced by the presence of noncondensable gas, vapor, and heat transfer.⁽²⁾ Third, to be effective, the collapse must occur well within one bubble radius of the wall.⁽¹⁾

These factors tend to minimize the effects of bubble collapse. Eisenberg⁽¹⁾ and Chapman and Plesset⁽³⁾ note, however, that even non-spherical collapse can generate high velocity jets of liquid. Kozirev⁽⁴⁾ compares this jet formation to jets formed with shaped charges. For such jets to damage a surface, they must be directed toward the surface and be sufficiently close. Eisenberg⁽¹⁾ points out that jets directed toward the wall do occur when voids adjacent to the wall collapse. Eisenberg⁽¹⁾ also discusses the phenomenon of 'ultra jets', which are jets with a velocity greater than half the speed of sound in the liquid. The formation of ultra jets is illustrated in Figure 10.3.3-1. The distant shock is too weak to effect damage, but the secondary jet can focus a high velocity impact on the surface, at various angles of attack. Kozirev⁽⁴⁾ notes that descendent jets of this action can have still higher velocities.

In all cases, it is necessary that the void location be on, or near, the surface. Thus, it is necessary to have hydrodynamic conditions which stabilize the bubbles until they can reach a point of collapse near the surface.

Cavitation can be expected at any location where the ambient pressure drops below the partial pressure of the most volatile species in the liquid.

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FIGURE 10.3.3-1. SUGGESTED MECHANISM OF CAVITATION DAMAGE AFTER TULIN (cf REF. 1)

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If voids so formed are subjected to a subsequently greater pressure than the bubble pressure, collapse can occur. Such action is often noted in pumps and where there is sudden expansion of the flow section. Oscillating pressures from unstable operating conditions could also generate the necessary conditions. Cavitation can effect a spectrum of damage very similar to that possible with impingement erosion. Eisenberg⁽¹⁾ discusses these similarities between the two erosion mechanisms.

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10.3.4 INTERACTION OF EROSION AND CORROSION

The relationship between erosion and corrosion is complex. This is intuitively obvious from the fact that there is a superposition of two degradation agencies--both of which are currently enjoying much research attention seeking generally applicable theory useful for prediction and optimization for given service environments.

For most conceivable situations, corrosion would be expected to render a surface more vulnerable to erosion by its many devices for deteriorating the structural quality of a material. Erosion, in turn, would be expected to assist the corrosion process by: (1) removal of reaction products and exposure of a fresh surface to corrosion action; (2) generation of paths into a structure for corrosive agents via inter- and intragranular crack systems caused by the mechanical action of erosion; and (3) creation of micro-stress fields which could, in conjunction with local temperature gradients, make free energy wells favoring corrosion.

The scope for conjoint action between erosion and corrosion is broad and, in most service situations, it might be expected that some such interplay is always operative on either a continuous, or discontinuous, basis. Accordingly, it is reasonable to expect that any general theory of erosion which may evolve will have limited utility without some quantitative cognizance of corrosion.

Some data on erosion-corrosion situations in aqueous systems are given by Thiruvengadam.⁽¹⁾ He notes that in a magnetostrictive test using an 1100-F grade aluminum target at 90F (27C), no differences in the loss of metal occurred whether distilled water, or 1%, 3%, or 9% NaCl solutions were used. On the other hand, 1020 steel eroded three times faster in 3% NaCl than in distilled water at about the same temperature level.

Schulmeister⁽²⁾ also studied erosion-corrosion operation under an extensive range of parameters. He considered three environments: distilled water, artificial hard water (CaCl_2 and CaSO_4 additions), and water with

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additions of proprietary, soluble oil, corrosion inhibitors. He observed that metal loss rates of cast iron were about twice as high in hard water as in distilled. The hard water gave about 20 times higher weight loss than a one percent solution of one of the oils. The same oil, however, increased the metal loss rate, as compared with distilled water, when an aluminum alloy was used. Other oils either increased, or decreased, aluminum loss rates depending on the test temperature. Plesset⁽³⁾ has studied cavitation in non-aqueous systems. He noted that cavitation in organic liquids was less than in distilled water and increased with the amount of water present. One exception was glycerol, which exhibited minimum erosion action when diluted with an equal part of water.

To date, there appears to be very little experimental information pertinent to erosion-corrosion action in LMFBFR systems. It has been noted, however, that 35 ppm and 100 ppm oxygen in sodium at 1000F (538C) and 1500F (876C) had no effect on cavitation resistance of 316 SS.⁽⁴⁾

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10.3.5 GENERATION OF HIGH VELOCITY SOLID AND LIQUID PARTICLES

Solid and liquid impacting agents are discussed. Both droplets and cavitation void collapse are discussed under liquids.

10.3.5.1 Solid Particles

The acceleration of a solid particle by direct coupling, such as being catapulted by an impeller, will not be considered. Except for hopefully rare phenomena, such as wasting, where gas generation from the sodium-water reaction could provide a substantial driving force, direct coupling is probably not of current practical interest.

Acceleration through hydraulic coupling is the prime means of changing a particle's velocity. The coupling occurs because of frictional drag between the fluid and the particle. Levich⁽¹⁾ has noted that, for room temperature water, particles of less than about 0.1 micron in diameter have a greater tendency to be entrained by turbulent eddies than do larger particles. Thus, very small particles tend to follow the fluid and veer from a surface. Larger particles tend to resist changes in flow direction, with a consequent higher probability of impact. The precise 'critical' size for following, or not following, the flow stream lines will depend on the properties of the fluid, and the size, geometry, and surface conditions of the particle.

10.3.5.1-2

REFERENCES

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10.3.5.2 Cavitation Voids

A necessary, though not sufficient condition for the generation of voids is a suitably low pressure. As the pressure on the fluid is reduced, the substance with the highest partial pressure will tend to out-gas. If the fluid is purified so that the partial pressures of dissolved constituents are less than the vapor of the fluid, then the fluid is most likely to vaporize when depressurized.

Although the pressure may be reduced sufficiently low, cavitation will not occur unless the bubbles have nucleation sites. Without nucleation sites, the initial formation of bubbles requires a driving force too large to be achieved under normal conditions. The presence of solid particles (dirt, corrosion products, etc.), or small gas bubbles, provides a low energy site for vapor/gas formation. Generally, a liquid contains sufficient nucleation sites to permit cavitation when the pressure reaches a suitably low level.

Local pressure reductions will occur when the flow cross section is reduced, or, more importantly, suddenly increased. In the case of a reduction in flow cross section, Bernoulli's theorem generally applies-- the sum of the pressure term plus the square of the velocity term is constant. Thus, if the velocity increases, as required in a smaller cross section to maintain the same mass flow rate, the pressure will decrease. On the other hand, when the flow channel suddenly enlarges, the inertial forces tend to keep the fluid in the high velocity, small cross section, configuration. As a result, the region immediately downstream of the enlargement becomes a low pressure zone. Examples are orifices, backsides of impellers, and in certain instances, the front side of the impeller near the tip.

Rayleigh's original calculations showed that a void collapsing to zero radius would generate an infinitely large shock pulse. This effect is mitigated by voids containing non-condensable components. More recently, Florschuetz and Chao⁽¹⁾ examined the mechanics of collapse

10.3.5.2-2

of spherical bubbles to clarify the relative importance of heat transfer and liquid inertia. They defined a collapse number, B_{eff} , which indicates whether void collapse is controlled by heat transfer (low B_{eff}) or inertia (relatively high B_{eff} value). Collapse under heat transfer control is relatively slow and the collapse rate decreases with collapse. Inertia controlled collapse is relatively fast and the rate increases with collapse. A simplified form of the original expression for B_{eff} is given below:

$$B_{eff} \sim \left[\left(\frac{\rho_L c_L}{\rho_V L} \right) \left(\frac{\Delta T}{\Delta P} \right) \right]^2 \times \frac{K_L}{R_0} \times (NPSH)^{3/2}$$

It is seen that high values of B_{eff} , hence inertial control and rapid void collapse, are encouraged by:

- high liquid density (ρ_L)
- high liquid specific heat (c_L)
- a flat temperature-vapor pressure characteristic, i.e.,
a large value of $\Delta T/\Delta P$
- high thermal diffusivity of the liquid (K_L)
- low value of the saturated vapor density (ρ_V)
- low value of the heat of vaporization (L)
- small initial bubble diameter (R_0)
- a large suppression head, i.e., a large differential
between ambient pressure and the saturation vapor
pressure, as reflected by the net positive suction
head (NPSH) term.

The rate at which a void collapses is an important factor in determining the location of possible cavitation damage, and it certainly is directly related to cavitation damage. Using the above expression for B_{eff} , Garcia and Hammitt⁽²⁾ calculated B_{eff} for lead-bismuth and lithium fluids at 500F and 1500F, and mercury at 70F and 500F. For their testing they used an ultrasonic vibrator. Their analysis of cavitation damage

10.3.5.2-3

to 304 SS showed that when a relative damage index was plotted against B_{eff} , the characteristic curve exhibited a rapidly increasing regime they attributed to heat transfer, or 'thermodynamic effects', and a zone of relatively greater erosion damage they attributed to the inertial collapse regime. Data for 304 SS tested in sodium were included in their plot and they corroborated the correlation between B_{eff} and cavitation damage. For their particular test conditions, the transition B_{eff} value was about 1000.

It is possible that both heat transfer and inertia control will be operative during a void's history. The practical utility of a parameter such as B_{eff} is open to question considering the complexity of the cavitation erosion problem. Such analyses, however, are important to the continuing work of identifying critical properties of the erosion participants and system operating characteristics which influence the erosion process.

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10.3.5.3-1

10.3.5.3 Liquid Particles

The acceleration of liquid particles can occur in the same way as described for solid particles, i.e., by entrainment in the flow stream. Liquid particles may also be generated and accelerated during the collapse of cavitation voids, as described briefly in section 10.3.3., above.

10.4 EROSION--LIQUID METAL EXPERIENCE

The results of experiments with liquid metals are described in this section. The discussion is divided into sections on impingement, cavitation and the prediction of erosion action.

Most of the discussion is given to cavitation, because under normal LMFBF operating conditions, liquid particle and solid particle impingement are not expected to occur to a significant extent.

10.4.1 IMPINGEMENT OF SOLID AND LIQUID PARTICLES

Impingement erosion in liquid metal systems is relatively uncommon. Cochran and Collins⁽¹⁾ report that a helical flow electromagnetic pump in a sodium loop failed after 3000 hours due to erosion. The proposed cause of the damage was the entrapment of particles by the magnetic field and subsequent erosion of the containing surfaces. They also noted, however, that 40 similar pumps operated for longer periods without difficulty.

Oakley et al⁽²⁾ studied the flow of sodium at 750F (400C) through the annulus of the FTR fuel nozzle/receptacle assembly. After nearly 3000 hours, with differential pressures up to 140 psi, no erosion was measurable, despite the fact that the sodium contained ferritic iron particles as large as 1/8 inch.

Impingement of liquid particles implies the presence of a vapor phase. In the LMFBR system, no metal liquid/vapor conditions are expected, except for short transients of abnormal operation.

In the case of a vapor system, erosion is worse with low quality vapor (high liquid content) than with higher quality vapor.⁽³⁾ DeVan et al⁽⁴⁾ observed 1 mil erosion on a second stage turbine blade (Nb-1%Zr) with 83% quality potassium vapor. No erosion was observed on the first, or third, stage where the vapor quality was 96%. Phillips⁽³⁾ similarly noted erosion of this alloy in 55-80% quality vapor, but none in 83-96% quality vapor. In the same system, Manson⁽⁵⁾ reports that 96.5% quality potassium vapor produces negligible erosion when exposed to TSM and TZC molybdenum alloys.

Severe degradation of metal structure can occur with sodium leaks into the water side of heat exchangers. This so-called wastage phenomenon is described in some detail in the chapter on sodium-water reactions. The mechanism of wastage is not clear. However, it is probable that both erosion and corrosion are involved. There may be liquid, as well as solid, particles in the vapor phase in the immediate vicinity of the leak. The dynamics of the reaction could generate high impact velocities for such particles. Chamberlain⁽⁶⁾ discusses laboratory tests with sodium and water

10.4.1-2

jets impacted against Cr-Mo steel targets, in which an attempt was made to simulate wastage. There was no success in elucidating the phenomenon of wastage, or in developing damage comparable to what has been attributed to wastage under actual service conditions.

Irrespective of mechanism, there is ample evidence that the damage potential of a wastage event is sufficient to warrant every practicable measure to minimize its occurrence.

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10.4.2 CAVITATION EROSION

Some of the characteristics of cavitation and cavitation erosion have been discussed in previous sections of this chapter. Engineering experience is discussed in this section.

Cerruti et al⁽¹⁾ report that after eight years (32,000 hrs) of operation at 700F (371C), the EBR-II primary sodium pump No. 1 was removed for repair. No sign of erosion was noted. The impeller (304SS) was reported to be in "as-new" condition.

Kulp and Altieri⁽²⁾ report tests of a turbine in liquid potassium and water. Visual monitoring of the turbine impeller (316SS) during testing and post-test inspection showed that cavitation in water caused no damage at suction specific speeds up to 20,000. When tested in potassium at 1400F, at the same suction specific speed ($N=6375$ rpm, $Q=708$ gpm), excessive cavitation damage occurred. The suction specific speed $[N/Q/NPSH]^{3/4}$, where the net positive suction head (NPSH) is the ambient pressure head at the pump inlet minus the vapor pressure head of the liquid at that point] is a useful corresponding state parameter. Penetrations of 50 mils in 350 hours were the most severe noticed. Micro-probe examination failed to show selective leaching of metal components, suggesting that there was no corrosion in conjunction with the erosion. Their conclusions are pertinent to any liquid metal system and are given below as direct quotations.

1. Direct observation and high speed photographs of a test impeller pumping water are enlightening with respect to location and severity of cavitation.

2. A study of the sound emanating from a test pump can be helpful in monitoring the intensity, or degree, of cavitation.

- a. Sound intensity levels may indicate the intensity of cavitation, but must be combined with other knowledge of the variation of cavitation with NPSH.

10.4.2-2

b. The frequency spectrum of the sound of cavitation may be a function of the resonant frequencies of the impeller (or system) rather than an index of cavitation.

3. Cavitation produced on the vane leading edge of an impeller designed for high suction specific speeds can collapse in the liquid stream away from the vane surface and not cause extensive cavitation damage.

4. Streamlining and surface finishing are important in the production of a high suction specific speed impeller which will be required to operate in, or near, cavitation.

5. Cavitation vortex formation produces the most concentrated and extensive damage when it collapses on flow boundaries, such as impeller vanes.

6. Vane tip clearance effects are very important in controlling the extent and intensity of the damage producing cavitation vortices in centrifugal pumps. Experimentally, the least damage observed in the rear flow channels corresponded to the smallest tip clearance.

7. It appears that cavitation damage of a 316SS impeller, tested with potassium at 1400F, is principally due to a mechanical process with little, or no, chemical action involved. (Recrystallization of the impeller material was noted during metallographic examination in both the damaged and undamaged surfaces.)

Young and Johnston⁽³⁾ used the usual magnetostrictive transducer assembly (see Figure 10.4.2-1) to examine the cavitation behavior of L-605 in sodium. The composition of this cobalt base alloy is given in Table 10.4.2-1.

They monitored cavitation at 400, 800, and 1200F (204, 427, 649C) at pressures up to 4 atm. The results are given in Figure 10.4.2-2. They show that cavitation increased with pressure up to the limit of their test and, at constant pressure, was greatest at about 800F (427C).

FIGURE 10.4.2-1. SCHEMATIC DIAGRAM OF CAVITATION TEST APPARATUS (cf REF. 3)

FIGURE 10.4.2-2. EFFECTS OF TEMPERATURE AND PRESSURE ON CAVITATION DAMAGE RATES FOR L-605 ALLOY IN SODIUM (cf REF. 3)

10.4.2-5

Table 10.4.2-1

L-605 Composition

Fe	3%	C	0.1%
Ni	10	Mn	1.5
W	15	Si	1.0 (max)
Cr	20	P	0.04 (max)
Co	Balance	S	0.03 (max)

10.4.2-6

The same authors⁽⁴⁾ also compared 316 SS, Stellite 6B and L-605 at 800F (427C) at various pressures in sodium. The same apparatus was used as for the earlier study.⁽³⁾ The steady state erosion rates of the three alloys versus pressure are given in Figure 10.4.2-3. It may be noted that the best alloy in these tests, Stellite, also exhibited the lowest pressure sensitivity.

Shoudy and Allio⁽⁵⁾ studied the effects of cavitation and quiescent exposure of various alloys in sodium at 550F (288C). They observed that long periods in static sodium effected significant increases in erosion over tests without soaking (Table 10.4.2-2). They also referenced unpublished data from Allis-Chalmers (Table 10.4.2-3) which showed that, at 350F (177C), sodium was about three times more damaging than water at 70F (21C) in vibratory cavitation tests. Similar data are noted in Figure 10.4.3-2. The data in Table 10.4.2-2 suggest a possible, albeit weak, corrosion-erosion interaction.

Smith et al⁽⁶⁾ studied centrifugal pumps in sodium and molten salts (fluorides) at 1500-1400F (565-760C). They found that after 2575 hours (3550 rpm, 500 gpm, 132 ft. total head and suction specific speed of 3200) in sodium, large areas of severe cavitation damage (up to at least 5/16 depth) had occurred on the hub and the trailing edge of the Inconel vanes.

In the first molten salt test (2700 rpm, 645 gpm, 40 ft. total head and suction specific speed of 9300) after 3500 hours, the working faces of the vanes and shroud (Inconel) were in good condition. However, the non-working face of the shroud was damaged. The second molten salt test ran 25,000 hours under the same conditions, but with a suction specific speed of 7000. In this case, there was erosion damage on the leading edges of the vanes and the impeller. Some damage also occurred on the trailing edge of the vanes. The impeller damage nearly penetrated through the 1/8 inch thick blade.

In no cases, however, did the cavitation damage impair the hydrodynamic performance. However, the authors stated that further operation of the second molten salt test impeller would have led to reduced

FIGURE 10.4.2-3. EFFECT OF PRESSURE ON CAVITATION DAMAGE RATE IN 800F SODIUM (cf REF. 4)

Table 10.4.2-2

Vibratory Cavitation Test Results in 550°F Sodium

<u>Material</u>	<u>Percent Weight Loss</u>		
	<u>Cycle 1</u>	<u>Cycle 2</u>	<u>Cycle 3</u>
Annealed 347 SS	0.28	0.50	0.75
Tuffrided (nitrided) 347 SS	0.24	0.30	--
Malcomized 347 SS, 0.0015" Case Ground Off	0.05	0.08	0.16
Inconel X - Double Aged	0.04	0.06	0.15
Malcomized 347 SS	0.02	0.94	--
Stellite 6B	0.003	0.007	0.02

Cycle 1 - 24 hour sodium soak between 17-minute cavitation periods, total cavitation time - 120 minutes

Cycle 2 - 120-minute cavitation exposure only

Cycle 3 - 168-hour sodium soak prior to 120-minute cavitation period

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Table 10.4.2-3

<u>Material</u>	<u>Weight Loss-Milligrams</u>	
	<u>Water</u>	<u>Sodium</u>
	<u>70°F</u>	<u>350°F</u>
347 SS	25.3	105.0
Inconel X	20.0	~55.0
Stellite	0.4	1.8

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performance. The lower damage rate in the molten salt, relative to that in the sodium, can, in part, be attributed to a lower vapor pressure of the salt. Insufficient data are given to consider other effects, such as impurities which may have influenced the test results.

Thiruvengadam and Preiser⁽⁷⁾ investigated the behavior of five alloys in sodium at 400, 1000, and 1500F (204, 538, 816C), using the usual magnetostrictive technique, with 0.5 inch diameter specimens. Some of their results are shown in Figure 10.4.2-4. The alloys are given in Table 10.4.2-4. At 400F, the most cavitation resistant alloy was Stellite 6B, followed by Nb-132M, T-122, and 316 SS (see Figure 10.4.2-4).

Tests at higher temperatures modified the order of merit of the alloys slightly. At 1000F, Stellite 6B was first, followed by 316 SS, Nb-132M, T-122 and TSM (see Figure 10.4.2-5). The Nb-132M and T-122 alloys showed about the same response to erosion action. At 1500F, the order was Stellite 6B, 316 SS and TZM, followed by Nb-132M and T-122 at about equivalent levels. The two highest temperature tests were performed using specimens which had been previously tested at 400F. This, the authors state, eliminated the so-called incubation period (see Figure 10.3.3-2).

FIGURE 10.4.2-4. RELATIVE CAVITATION DAMAGE RESISTANCE OF FIVE METALS TESTED IN 400° SODIUM (cf REF. 7)

10.4.2-12

FREQUENCY-14 KCS

DOUBLE AMPLITUDE- 1.36×10^{-3} INCH

LEVEL-35 ppm

LEVEL-100 ppm

FIGURE 10.4.2-5. CAVITATION DAMAGE RESISTANCE OF REFRACTORY ALLOYS IN HIGH TEMPERATURE LIQUID SODIUM (1000° AND 1500°F)(cf REF. 7)

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10.4.2-13

Table 10.4.2-4

Nominal Chemical Compositions of Test Metals⁽⁷⁾

Weight Percent

Material	Cr	Ni	Mo	C	Mn	P	S	Si	Fe
316 SS	16-18	11-14	2-3	0.08	2.0	0.03	0.03	175	Ba1
	Ta	W	Mo	Zr	C	Cb			
Nb-132M	20	15	5	1	0.1	Ba1			
	C	Ti	Zr	Ni	Fe	O ₂	H ₂	N ₂	Mo
TZM	0.016	0.48	0.08	<.001	<.001	<.002	<.0001	.0003	Ba1
	W	Hf	C	O ₂	N ₂	H ₂	Ta		
T-222	9.02	2.72	0.007	.0019	.0037	.00012	Ba1		
	Ni	Si	Fe	Mn	Cr	Mo	W	C	Co
Stellite 6B	3	2	3	2	30	1.5	4.5	1.1	Ba1

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10.4.3 PREDICTION OF CAVITATION DAMAGE

Prediction of cavitation erosion is, at this time, virtually limited to qualitative statements--particularly when there is potential for corrosion aggravation of the erosion phenomenon, as is the case with liquid alkali metals.

Leith⁽¹⁾ developed a relationship to assist in the prediction of the relative erosion potency of various alkali metal liquids with respect to water. Leith's comparison formula is given below:

$$W_a = 0.6 W_w \times (SG_a/SG_w) \left(\frac{P-VP_w}{P-VP_a} \right)^{10} (V_w/V_a) (ST_a/ST_w)$$

where: W is the cavitation erosion damage index

SG is the specific gravity

P is the ambient pressure

VP is the saturated vapor pressure

V is the viscosity

ST is the surface tension

and the subscripts a and w refer to the alkali metal liquid and water, respectively.

Figure 10.4.3-1 shows both experimental and predicted data for NaK, water and gasoline with various (unspecified) target materials as a function of the temperature (expressed as a percent of the melt-boiling range corresponding to the ambient pressure). Based on the above relationship, Leith proposed the erosion comparisons shown in Figure 10.4.3-2.

While Leith's predictions are essentially qualitative, and intuitive, they are based on extensive cavitation erosion experience. Furthermore, they constitute a much needed advance toward identification of properties important to cavitation erosion. His identification of sodium as a prime cavitation erosion agent has been well supported by work already cited.

FIGURE 10.4.3-1. ACTUAL AND PREDICTED CAVITATION DAMAGE IN WATER, NaK EUTECTIC AND GASOLINE (cf REF. 1)

10.4.3-3

FIGURE 10.4.3-2. PREDICTED CAVITATION DAMAGE IN ALKALI METAL LIQUIDS (cf REF. 1)

10/25/74

10.4.3-4

REFERENCES

1. W.C. Leith, "Prediction of Cavitation Damage in the Alkali Metal Liquids," Proceedings, ASTM-65, pp. 789-800.

10.5 APPLICATION TO LMFBR

Pre-service, quantitative, characterization of the erosion problem for even familiar working environments is not possible on the basis of present knowledge of this damage agency. Where there is the possibility for corrosion-assisted erosion, as in the LMFBR systems, then theoretical assistance is even weaker. Historical review of possibly relevant experience is of very limited value.

Erosion by solid particle impingement is expected to be an insignificant damage factor in LMFBR systems. Conceivably, some solid particle intrusion of the liquid metal circuits could result from various corrosion processes. A quantity of solid particles sufficient to present an erosion hazard should, however, force the earliest possible attention to this problem and corrective action against the initiating corrosion process.

Liquid particle impingement on the containment envelope of the LMFBR heat transfer system is not expected to persist beyond presumably short transients. Persistent-potentially damaging-two phase regimes in the liquid metal circuits would be a derivative of improper design, or selection, of circuit components, or gross inattention to system operating parameters. Such factors are also pertinent to cavitation erosion. The goal of zero, or very low, incidence of cavitation will be more difficult to achieve than will the corresponding goal for liquid particle impingement. With respect to circuit design, there is now a substantial body of guide lines for minimizing the possibility of cavitation erosion, e.g., elimination of abrupt flow section changes, gross roughness, flow obstacles which force rapid acceleration of the fluid. However, pump design to accommodate a wide spectrum of operating conditions presents more subtle problems. It is expected that the greatest potential for significant erosion from cavitation resides in such circuit elements where high performance goals may force a close approach to the two phase regime under some operating circumstances.

It is expected that proper management of the damage potential of erosion in the LMFBF environments will require:

- a. Recognition, and maintenance of careful records, of off-normal operating conditions which conceivably could generate solid, or liquid, particles, or encourage cavitation, in the heat transfer fluids.
- b. Continuous, or semi-continuous, monitoring of the heat transfer fluids for constituents which could participate in erosion, erosion-corrosion action.
- c. To the maximum extent permitted by routine shut-down, or other 'opportunities' for inspection, examination of sensitive system components for evidence of structural deterioration.

These are obvious housekeeping chores which have no particular bias toward a specific damage agency. If it is possible to identify a specific action, e.g., erosion, erosion-corrosion, then this will tend to establish corresponding working limits for the resident materials and suggest guidelines for replacement, or second generation, materials.

As has been noted in this chapter, if significant erosion, erosion-corrosion damage occurs in the LMFBF system, it will likely be a concomitant of even more serious and more immediate problems. Accordingly, the corrective response might be expected to have a more powerful motivation than erosion, erosion-corrosion, mitigation, however beneficial it may be in these respects.

LMFBF structural materials will generally be selected on the basis of a fairly broad range of property qualifications. Erosion resistance is only one of the areas of performance which are expected to receive substantial clarification by actual working experience.

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11.0 WEAR AND SELF
WELDING IN
LMFBRs

	11.1 Fundamental Considerations for Sliding Surfaces	11.1.1 Sliding Surfaces	11.1.2 Material Considerations for Sliding Surfaces	11.2 Environmental Considerations for Sliding Surfaces	11.2.1 Fundamental Considerations Rolling Contact	11.2.2 Material Considerations for Rolling Contact	11.3.1 Environmental Considerations for Periodically Moving Surfaces	11.3.2 Material Considerations for Periodically Moving Contacts	11.4.1 Environmental Considerations for Wear and Self Welding	11.4.2 Basic Laboratory Testing of Mechanism and Wear	11.4.3 Plant Experience with Friction and Wear Testing of Friction	
FUEL ASSEMBLIES	●			●	●	●			●	●	●	●
CONTROL ROD SYSTEMS	●			●	●	●			●	●	●	●
POWER INSTRUMENTATION AND GAS LINES												
INSTRUMENT TREE AND IVFH MACHINE	●	●	●	●	●	●	●	●	●	●	●	●
CLOSED LOOPS	●	●	●	●	●	●	●	●	●	●	●	●
REACTOR VESSEL, GUARD VESSEL												
CORE SUPPORT STRUCTURE, RESTRAINT SYS.									●	●	●	●
REACTOR HEAD							●	●	●	●	●	●
BAFFLE PLATE									●	●		●
PRIMARY AND SECONDARY PUMPS	●			●	●	●					●	●
PRIMARY AND SECONDARY PIPING												
PRIMARY AND SEC. SODIUM PURIFICATION												
DUMP Hx, IHx									●	●		
STEAM GENERATORS												●
INERT GAS SYSTEMS					●			●		●		

11.0 WEAR AND SELF WELDING IN LMFBRs

The operation of a complex machine such as a reactor requires the use of contacting surfaces for the accurate positioning of parts, transmission of motion and as a provision for disassembly. Surfaces may be in static contact for long periods of time before they are required to move, in constant rapid motion such as pump bearings, or any condition in-between. The load on surfaces can vary from nearly zero to several thousand psi, the environment can be inert gas or liquid sodium. The mechanisms dependent on the relative motion of contacting surfaces can fail by adhesion or severe wear.

In most complex mechanisms, adhesion and excessive wear is prevented by introducing a suitable lubricant between the mating surfaces to prevent actual contact of the surfaces with each other. The only lubricant available in an LMFBR Primary System is liquid sodium between 400 and 1300°F. The chemical characteristics and the temperature of the liquid sodium are sufficiently different from conventional lubricants and normal machine temperatures to require careful consideration of the behavior of mating surfaces under operating conditions. Several studies of wear and adhesion in sodium, and experience with many sodium loops and several reactors have generated much useful data which will be reviewed in the following sections.

11.1 FUNDAMENTAL CONSIDERATIONS FOR SLIDING SURFACES

When surfaces are in contact they support the contact pressure on small asperities from the two surfaces. Except under the most rigorous conditions of cleanliness and vacuum, there exists a layer of absorbed gas molecules or oxides of the metals which prevent true metal-to-metal contact. The movement of the surfaces causes the small projections to deform, weld together and break off (adhesive wear). If the material is hard, the projection will break off and gouge or grind the softer bearing material or embed in the surface (abrasive wear). Under absolutely clean, vacuum conditions with sufficient pressure, a "friction weld" would be produced. Interposing an easily sheared film between the two surfaces allows relative motion with only a small number of the minute projections interacting because the film is bearing a portion of the load consistent with its viscosity. If the load is increased, the surfaces are brought into closer contact and more and more of the asperities interact causing higher wear rates.

The general equations that have been semi-empirically developed relate wear to load, movement and hardness in the following manner.

$$V = \frac{KNL}{P_m} \quad \text{or} \quad d = \frac{KWL}{P_m}$$

where

- V = volume of wear
- N = load
- L = sliding distance
- P_m = pressure at which plastic penetration occurs (i.e., hardness)
- d = apparent depth of penetration (assuming even wear over the contact area)
- W = apparent bearing pressure
- K = wear coefficient

These equations are valid only for the mild wear conditions and are not applicable to the unlubricated or poorly lubricated conditions caused by "overload" or insufficient lubricant. The severe wear produced by overload and insufficient lubricant is characterized by severe scratching

and galling. The linearity of wear with time is not observed in the initial "wearing in" period. The length of the rapid initial wear process depends on such variables as the original fit-up of the bearing surface, smoothness, load, etc. When the load is increased on a bearing surface the wear coefficient is steady until at some critical load the wear coefficient increases sharply. This critical load usually coincides with the stress for gross yielding of the bearing material and can be estimated from hardness measurements at the surface temperature of operation.

The application of the above generalities in understanding the behavior of contacting solid materials in a high temperature sodium environment has been qualitatively helpful but not quantitatively useful in picking bearing materials or design.^(1,2) The scatter of data obtained in a large wear testing program at LMEC⁽¹⁾ was rationalized as arising from the sum of about six additive terms where one or another of the terms predominated in a given test. Thus, the designer is apparently left with empirical tests of particular materials, load, temperature, velocity, environment and time, to be reasonably sure of a given wear situation. However, the guidance of friction and wear theory and numerous previous tests will be of qualitative help.

REFERENCES

1. N.J. Hoffman, D.E. Goggin and J.J. Draher, Friction and Wear Screening Tests of Materials in Sodium, LMEC-70-10, July 1970.
2. W.A. Glaeser, "Wear and Friction Characteristics of Structural Materials in Liquid Sodium," Reactor Technology 15 (1) Spring 1972, pp. 1-10.

11.1.1 MATERIAL CONSIDERATIONS FOR SLIDING SURFACES

The primary importance of the contacting surfaces in friction, wear, and galling behavior makes the films that materials form in sodium of great importance. The films that are formed are so thin that the ability of the base metal to support the film under the load applied is also fundamental. In liquid sodium operation, the most important film is that of the sodium which keeps most of the mating structural surfaces from contact. The thin films of adsorbed or reacted impurities on the metal surfaces become of importance in boundary lubrication in high temperature sodium because of the low load bearing ability of the high temperature sodium metal. These factors will be discussed under the environment section.

The properties of materials which are important to wear, friction and self welding are hardness, dimensional stability, melting point, thermal expansivity, thermal conductivity, ductility, impact strength, and corrosion resistance. Hoffman, et al⁽¹⁾ compiled a table of properties of important LMFBR materials which is shown in Table 11.1.1-1. This table gives the composition, thermal expansion coefficient, and the hardness at 1200°F. The importance of these properties is discussed below.

Hardness - A very important property of successful sliding bearings has been hardness at operating temperature. It can be seen in Table 11.1.1-1 that very few materials are very hard at 1200°F. If the temperature were reduced substantially, many more materials like conventional tool steels, etc., would be hard. The load bearing ability of sodium films is low, thus they are thin, which causes the metal asperities to contact each other at relatively low loads and shear off after slight deformation (abrasive wear). The presence of thin films on the hard substrate helps prevent bonding of the asperities to the opposing surface (adhesive wear) and the consequent buildup of smeared metal. The softer material will deform more easily and the thin brittle surface films break, allowing metal-to-metal contact and asperity welding. Although no experimental work on the effect of particles in sodium was encountered; it is well known that many fine iron particles circulate in sodium loops.⁽²⁾ Chromium carbides, silicon oxides and other hard particles are formed in the sodium by mass transfer and also circulate

Table 11.1.1-1

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 1 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
<u>Nickel-Base Alloys:</u> Inconel X-750 (wrought)	Nickel* 70.0 min *Always contains small amount cobalt Chromium 14.0-17.0 Iron 5.0-9.0 Titanium 2.25-2.75 Aluminum 0.40-1.00 Niobium* 0.70-1.20 *Contains small amount tantalum Manganese 1.0 max Silicon 0.5 max Sulfur 0.01 max Copper 0.5 max Carbon 0.08 max	8.4	R _C 28-30
Inconel 718 (wrought)	Nickel 53.0 Chromium 18.5 Iron 18.0 Niobium* 5.1 *Contains small amount tantalum Molybdenum 3.0 Titanium 1.0 Aluminum 0.5 Silicon 0.25 Manganese 0.2	8.6	R _C 37-40

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 2 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) ($\mu\text{in. / in. / }^\circ\text{F}$)	Hardness (at 1200°F)
Inconel 718 (cont)	Copper 0.1 Cobalt 0.1 Carbon 0.05 Sulfur 0.007		
Udimet 718 (wrought) (Equivalent to Inconel 718 but from different supplier)	Nickel 54.2 Chromium 18.0 Iron 18.0 Niobium* 5.2 *Contains small amount tantalum Molybdenum 3.0 Titanium 1.0 Aluminum 0.5 Carbon 0.04-0.06 Boron 0.004	8.6	R _C 37-40
Udimet 630 (wrought)	Nickel 48.3-58.6 Chromium 15-19 Iron 16-19 Molybdenum 2.7-3.4 Niobium* 5.8-6.8 *Contains small amount tantalum Aluminum 0.20-1.00 Carbon 0.04 Titanium 0.7-1.5	8.6	R _C 41-43

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 3 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
Udimet 630 (cont)	Cobalt 1.0 max Boron 0.001-0.007		
Hastelloy C (wrought)	Nickel 54.0 Cobalt 2.5 max Chromium 14.5-16.5 Molybdenum 15.0-17.0 Tungsten 3.0-4.5 Iron 4.0-7.0 Silicon 1.0 max Manganese 1.0 max Carbon 0.08 max Vanadium 0.35 max Phosphorus 0.04 max Silicon 0.03 max	7.3	R _B 87-90
<u>Molybdenum-Base Alloys:</u> TZM (pressed and sintered)	Molybdenum 99.40 Titanium 0.50 Zirconium 0.08 Carbon 0.025 Iron 0.010 max Silicon 0.008 max Nickel 0.002 max Oxygen 0.0025 max	3.1	R _B 95-97

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 4 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
TZM (cont)	Hydrogen 0.0005 max Nitrogen 0.002 max		
Molybdenum (pressed and sintered)	Molybdenum 99.95	3.1	R _B 71-73
<u>Tungsten:</u> Tungsten (pressed and sintered)	Tungsten 99.95	2.4	R _C 43-45
<u>Sintered Carbides:</u> K-95 (pressed and sintered)	Tungsten 91.0 Cobalt 9.0	3.4	R _C 56-58
K-801 (pressed and sintered)	Tungsten carbide 94.0 Nickel binder 6.0	3.1	R _A 87-89
K-162B (pressed and sintered)	Titanium carbide 63.0 Nickel 25.0 Molybdenum 5.0 Niobium* 5.3 *Contains small amount tantalum	4.6	R _C 50-53
<u>Tool Steels:</u> AISI M1 (wrought)	Iron 83.5 Molybdenum 8.5	6.9 (from 75-900°F)	R _C 43-45

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 5 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
AISI M1 (cont)	Chromium 4.0 Tungsten 1.5 Vanadium 1.15 Carbon 0.80 Silicon 0.30 Manganese 0.25		
Rex 49 (wrought)	Iron 76.40 Carbon 1.10 Tungsten 6.75 Manganese 0.45 Molybdenum 3.75 Silicon 0.30 Vanadium 2.00 Chromium 4.25 Cobalt 5.00	6.8	R _C 49-52
AISI M2 (wrought)	Iron 81.8 Tungsten 6.3 Molybdenum 5.05 Chromium 4.15 Vanadium 1.85 Carbon 0.85	6.9 (from 75-900°F)	R _C 40-43
AISI M3 Type 1 (wrought)	Iron 80.5 Tungsten 6.1 Molybdenum 6.0	8.0 (from 70-1000°F)	R _C 40-43

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 6 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
AISI M3 (cont)	Chromium 4.0 Vanadium 2.4 Carbon 1.02		
AISI M3 Type 2 (wrought)	Iron 79.5 Tungsten 6.0 Molybdenum 6.0 Chromium 4.1 Vanadium 3.2 Carbon 1.2	8.0 (from 70-1000°F)	R _C 42-44
AISI M4 (wrought)	Iron 79.7 Tungsten 5.5 Molybdenum 4.5 Chromium 4.5 Vanadium 4.0 Carbon 1.28 Manganese 0.25 Silicon 0.25	8.0 (from 70-1000°F)	R _C 44-46
AISI M43 (wrought)	Iron 74.6 Cobalt 8.2 Molybdenum 8.0 Chromium 3.75 Tungsten 2.70 Vanadium 1.60 Carbon 1.20	8.0 (from 70-1000°F)	R _C 46-48

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 7 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) ($\mu\text{in.}/\text{in.}/^\circ\text{F}$)	Hardness (at 1200°F)
AISI T1 (wrought)	Iron 74.8 Tungsten 18.0 Chromium 4.1 Vanadium 1.1 Carbon 0.75 Molybdenum 0.70 Silicon 0.25 Manganese 0.25	8.0 (from 70-1000°F)	R _C 39-41
AISI T15 (wrought)	Iron 70.7 Tungsten 12.5 Cobalt 5.0 Vanadium 5.0 Chromium 4.75 Carbon 1.57 Molybdenum 0.50	8.0 (from 70-1000°F)	R _C 40-42
AISI M-15	Iron 74.5 Chromium 4.0 Cobalt 5.0 Molybdenum 3.5 Vanadium 5.0 Carbon 1.5 Tungsten 6.5		

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 8 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
Whittaker NM-100	Iron 60.5 Carbon 1.25 Chromium 17.5 Tungsten 10.5 Cobalt 9.5 Vanadium 0.75		R _C 50-53
<u>Nickel Base Hard Facing Alloys:</u> Colmonoy 4 (hard facing)	Nickel 82.8 Chromium 10.0 Iron 2.5 Carbon 0.45 Silicon 2.25 Boron 2.00	8.0	R _C 25-27
Colmonoy 5 (hard facing)	Nickel 77.35 Chromium 11.5 Iron 4.25 Carbon 0.65 Silicon 3.75 Boron 2.50	8.0	R _C 37-39
Colmonoy 6 (hard facing)	Nickel 73.75 Chromium 13.5 Iron 4.75 Carbon 0.75	8.0	R _C 43-45

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 9 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) ($\mu\text{in. / in. / }^\circ\text{F}$)	Hardness (at 1200°F)
Colmonoy 6 (cont)	Silicon 4.25 Boron 3.00		
Colmonoy 70 (hard facing)	Nickel 62.45 Chromium 11.5 Tungsten 16.0 Iron 3.75 Carbon 0.55 Silicon 3.25 Boron 2.50	8.0	R _C 43-45
Colmonoy 75 (hard facing)	Nickel 73 Chromium 13 Iron 4 Carbon 0.7 Silicon 4.2 Boron 3 Tungsten carbide* *Particles	8.0	R _C 43-45
Haynes 273 (hard facing)	Nickel 57.1 Chromium 16.0 Molybdenum 17.0 Tungsten 4.5 Iron 5.3 Carbon 0.1	8.0	R _B 85-87

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 10 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
<u>Cobalt Base Alloys:</u>			
Stellite 1 (hard facing)	Cobalt 55.5	7.3	R_C 40-42
	Chromium 30.0		
	Tungsten 12.0		
	Carbon 2.5		
Stellite 3 (cast)	Cobalt 47.6	7.3	R_C 35-37
	Chromium 30.5		
	Tungsten 12.5		
	Nickel 3.0		
	Iron 3.0		
	Carbon 2.45		
	Silicon 1.0		
Stellite 6B (wrought)	Cobalt 54.9	7.8	R_B 97-100
	Chromium 30.0		
	Tungsten 4.5		
	Nickel 3.0 max		
	Iron 3.0 max		
	Silicon 2.0 max		
	Molybdenum 1.5 max		
	Carbon 1.1		
Stellite 6H (hard facing)	Cobalt 66.9	8.7	R_C 27-30
	Chromium 28.0		
	Tungsten 4.0		
	Carbon 1.1		

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 11 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
Stellite 1016 (hard facing)	Cobalt 48.5 Chromium 32.0 Tungsten 17.0 Carbon 2.5	7.2	R _C 39-41
Stellite Star J (cast)	Cobalt 43.0 Chromium 32.0 Tungsten 17.0 Iron 3.0 Nickel 2.5 max Carbon 2.5	7.2	R _C 39-41
<u>Metal-Ceramic Composites:</u> LT-1B (sintered)	Chromium 59.0 Molybdenum 20.0 Aluminum oxide 19.0 Titanium oxide 2.0	4.7 (from 77-1832°F)	
LT-2 (sintered)	Tungsten 60.0 Chromium 25.0 Aluminum oxide 15.0	4.7 (from 77-1832°F)	

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 12 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
<u>Austenitic Stainless Steels:</u>			
304SS (wrought)	Iron 66.3-71.3 Chromium 18.0-20.0 Nickel 8.0-11.0 Manganese 2.0 Silicon 0.7 Carbon 0.08 max Phosphorus 0.045 max Sulphur 0.03 max	9.7	R _B 40-50
316SS (wrought)	Iron 62.2-69.2 Chromium 16.0-18.0 Nickel 11.0-14.0 Molybdenum 2.0-3.0 Manganese 2.0 Silicon 0.7 Carbon 0.1 Phosphorus 0.045 max Sulphur 0.03 max	9.6	R _B 40-50
<u>Precipitation Hardening Stainless Steels:</u>			
17-4 PH SS (wrought)	Iron 70.2-76.2 Chromium 15.5-17.5 Nickel 3.0-5.0	7.2 (from 700-800°F)	R _C 33-36

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 13 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
17-4 PH SS (cont)	Copper 3.0-5.0 Silicon 1.0 max Manganese 1.0 max Carbon 0.07 max Niobium* 0.30 *Contains small amount tantalum		
17-7 PH SS (wrought)	Iron 72.9 Chromium 17.0 Nickel 7.1 Manganese 1.0 max Silicon 1.0 max Aluminum 1.0 Carbon 0.09 max	6.6 (from 70-800°F)	R _C 27-29
<u>Ceramics:</u> Coors AD-995 (cast)	Alumina 99.9 (Al ₂ O ₃)	4.3 (from 77-1100°F)	R _C 36-40
Lucalox (cast)	Alumina 99.9 (Al ₂ O ₃)	4.3 (from 77-1100°F)	R _C 36-40
<u>Copper-Base Alloy:</u> AMPCO 18-13	Iron 3.4-4.0 Aluminum 10.6-11.2 Copper 86-84.8	~13.8 (from 77-900°F)	

Table 11.1.1-1 (continued)

COMPOSITION, THERMAL EXPANSION, AND HOT HARDNESS OF
CANDIDATE MATERIALS
(Sheet 14 of 14)

Material	Composition (%)	Mean Coefficient of Thermal Expansion (from 70-1200°F) (μin./in./°F)	Hardness (at 1200°F)
<u>Ferritic Stainless Steel:</u>			
METCO 405SS	Iron 85.5 Chromium 11.5-13.5 Aluminum 0.1-0.3 Silicon 1.0 max Manganese 1.0 max Carbon 0.08	7.5	
<u>Chromium Coating:</u>			
Hard Chrome Plate			R _C 42-49

Below T_1 , the lubricative complex is stable in 15 ppm O sodium. If the sodium contained 100 ppm, the lubricative oxide would be stable to T_2 . In sodium saturated with O, the lubricative oxide is stable to T_3 . Conversely, at any temperature below T_3 , the oxygen content of the sodium should adjust itself until it reaches a ppm level with equivalent chemical potential* to that of the oxygen in the polyoxide. For actual values of these curves for certain metals see References 3 through 5. The actual values for the elemental metals are not exactly what the designer needs since the activity of an element in an alloy is not unity and, therefore, the free energy relationships are slightly changed.

*Two solutions are in equilibrium with each other when the "chemical potential" of each component in the two solutions have equal values. The chemical potential includes a term giving the free energy at an assumed standard state and a term that includes the natural log of the "activity" of the component being considered. The activity is roughly equal to the ratio of the actual concentration of the component to its concentration at saturation.

to some extent. Unless the bearing material is harder than these particles, abrasive wear will result when the particles are carried by the sodium between the contacting surfaces.

Wear and friction do not necessarily go hand-in-hand. However, if the friction coefficient is large in a high speed bearing, a problem of heat removal will result. High hardness materials tend to have lower coefficients of friction than softer materials and thus result in less heating. If the surface temperature climbs appreciably the softer materials will get even softer and eventually the two surfaces may melt together in a friction weld. The coefficients of friction in sodium are quite high by normal standards and thus it is desirable to keep the friction coefficients as low as possible on rapidly moving, contacting surfaces.

Dimensional Stability and Thermal Expansivity - The low viscosity of high temperature sodium results in very thin lubricating films in loaded bearings. This very thin film requires a very close tolerance on the fit-up of the bearing to assure the load is applied as uniformly to the bearing surface as possible. Bearings are machined, fit-up and sometimes operated at low temperature and then are heated to normal operating temperature or operated at some intermediate temperature. It is obvious that a mismatch of thermal expansion coefficients will change the operating clearance at each temperature. A designed change in clearance that takes the temperature dependent characteristics of the sodium lubricant into account might be desirable, however, the longitudinal mismatch of circular wear lines caused by differential thermal expansion could cause increased friction and wear. The thermal expansion properties of many of the hard materials are substantially different than the austenitic stainless steels that are used in manufacture of sodium systems. Even though some small bearings can be fabricated of a single hard material, large bearings would require that the hard material be a surface application where the thermal expansion of the whole assembly reflects the base material more than the surfacing material.

The dimensional stability of a bearing through the thermal cycles and long soaking periods at elevated temperature is necessary to preserve clearances except in flat rubbing surfaces. The metallurgical stability of

the bearing material is also important to preserve its mechanical properties and hardness.

Thermal Conductivity and Melting Point - The interaction of the opposing surfaces as they slide past one another generates an extremely local heating effect. The heat generated in the contacting asperities will soften or even melt them, resulting in more welding and friction. The increased friction will produce still more heat and eventually seize or gall the bearing. The extremely local nature of the heating will allow it to flow into the bulk of the bearing if the material has a reasonable thermal conductivity. If an appreciable layer of sodium is present, it will act as an excellent heat transfer media. A reasonable flow of sodium will remove the heat from the bearing area. The higher the melting point of the bearing material the less likely it is to be softened or melted by the frictional heat. The alloying tendencies of materials and diffusion rates are generally increased as the melting point is approached. The use of high melting point materials will reduce these undesirable characteristics at operating temperatures.

Ductility and Impact Strength - Most bearing surfaces are required to absorb shock loadings at some time during their life even if only during manufacture and shipment or accident conditions, so that some degree of impact strength is desired. Many bearing surface materials are applied to structures so the impact loads will only be applied through the base material which has been selected for the proper mechanical characteristics. This should distribute the impact to the whole load bearing surface and lessen its affect. Where the bearing material is utilized for the entire structural entity, its impact properties could become very important.

Ductility in a bearing surface allows hard particles to become embedded and not scar the whole bearing surface, it allows a certain amount of deformation to more evenly distribute the load, promotes deformation and smearing of asperities and allows a surface to become work hardened. Surface deformation may also break up thin surface films which inhibit asperity welding, encourage transfer of material to the opposing surface and encourage galling. Where the material is a surface coating, ductility will allow it to absorb differential thermal expansion and thermal shocks. A little ductility appears to be desirable but too much could promote galling and self welding.

Irradiation Effects - If bearing surfaces are exposed to a substantial neutron fluence, the changes in properties from irradiation will have to be considered. Elements that have high reaction cross sections will be transmuted or activated. Activated elements in the wear products will transfer out of the shielded core region and can produce access problems elsewhere in the system. Transmuted material might change bearing properties or produce dimensional changes. Even bearing materials which produce wear products outside of the reactor core may transfer these particles into or through the core and gradually add to the accessibility problems. The element which has caused the most severe accessibility problems in water cooled reactors has been cobalt. Preliminary estimates of accessibility problems in FFTF still indicate cobalt will be a major contributor to the system activity.^(3,4)

Crystal Structure - A recent review⁽⁵⁾ of sliding surface behavior in sodium has hypothesized that the hexagonal crystal structure performs better than other crystal structures for sliding interaction. The review indicated that the better bearing materials all had at least some constituents in a hexagonal crystal structure.

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11.1.2 ENVIRONMENTAL CONSIDERATIONS FOR SLIDING SURFACES

Bearing surfaces in an LMFBR will be subject to environments which can change their wear, friction and self welding properties. The variables in the liquid sodium environment are temperature, oxygen concentration, particulates, sodium flow, impurities such as nitrogen, carbon, etc., and radiation. Variables in vapor phase exposure include temperature, sodium vapor, impurities in inert gas, radiation and intermittent liquid operation. The environment principally effects the surface which as previously discussed is important in the area of friction and wear.

In liquid phase sliding the temperature will be substantially controlled by the sodium temperature except where large amounts of heat generated by radiation or friction must be diffused away from the bearing. The temperature and oxygen concentration of the sodium-sliding surface interface, interact either to remove or to form surface oxide coatings. In low (<5 ppm) oxygen systems only a few metal oxides are stable, such as tungsten, molybdenum, silicon, manganese, zirconium, chromium, etc. As the temperature is raised from ambient to 1300°F, several of these oxides react with the sodium or are dissolved in the base metal and any lubricating effects are lost. As the temperature is decreased a threshold will be reached where the oxygen in the sodium will react with the metal and reform the surface oxides. At low temperatures the kinetics of these reactions may be too slow to reform damaged oxides or lead to reduction of oxides already formed. The concentration of the reactants at the bearing surface is the fundamental parameter and it could be substantially different than bulk sodium analysis in a long narrow crevice with poor circulation. The temperature of the reacting surface can be substantially hotter than the bulk sodium if generated heat is not carried away by a sodium film. If sodium flow is rapid in the bearing interface, surface changes in composition of the bearing surfaces can take place by selective leaching, corrosion or interaction with impurities such as carbon, nitrogen, etc. The altered surface layer could have better or worse friction and wear characteristics than the original surface. The presence of a pure sodium film between two dissimilar metal surfaces can act as a transport medium between them for any elements whose activity in one material is higher than in the other

material. If temperature is high enough, oxide films can be removed from both surfaces allowing metal-to-metal contact and solid state diffusion of active species such as carbon, nitrogen, etc. This process could result in self welding. Wear debris between two surfaces will have a high surface area and ability to carburize or nitride if these elements are available. Subsequent movement of the surface will now have to shear or plow a harder material and thus require increased force.

11.2 FUNDAMENTAL CONSIDERATIONS FOR ROLLING CONTACT

The use of rolling contact involves certain aspects of the previous discussion such as self welding, when not in motion, and sliding friction and wear on the ball or roller cage. Even though the sliding wear and galling of the cage material has been a serious problem with ball and roller bearings in sodium, only the rolling contact will be treated in this section.

The use of rolling contact bearings in sodium is inviting because of their low friction, accurate positioning of moving elements, and ability to operate well at low speed. A recent program⁽¹⁾ to investigate the use of rolling bearings in sodium under LMFBR conditions reviewed the fundamental characteristics of materials necessary for use in such bearings and reviewed past experience. Most of the previous experience is at low temperature ($<500^{\circ}\text{F}$) with impurities in the sodium which make the data of doubtful value for high temperature LMFBR application. Experiments⁽²⁾ with ordinary rolling bearings in high temperature (400°C) sodium has shown them to be inadequate.

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11.2.1 MATERIAL CONSIDERATIONS FOR ROLLING CONTACT

A rolling contact must theoretically carry the applied load on a line contact which would raise the load/area to very high levels. Slight elastic deformation of the roller and race increase the actual area of contact and reduce the load/area substantially. This slight, cyclic, elastic deformation can produce surface fatigue. Thus, hardness under operating conditions is a requirement for rolling bearings. Erhardt⁽¹⁾ considers an operating hardness of R_C -57 to 58 to be a general rule for normal high temperature service. The high hardness gives increased ability to sustain the high load/area without plastic deformation.

The rolling bearing will experience some sliding friction and wear unless it makes a point or line contact such as a ball on a flat plate or a cylindrical roller. As discussed in section 11.1.1 hardness is a desirable property for sliding wear and thus does not conflict with hardness requirement for rolling contact. Sliding friction is also experienced when the ball or roller contacts the cage material which fixes its position. Any wear products from the cage contact will be carried into the rolling element-race interface and can easily lead to failure of the whole bearing through increased frictional heating.

Other material properties of importance are creep, dimensional stability, impact resistance, corrosion resistance including selective leaching and self welding. Creep and self welding are of importance when the bearing is stationary and the high unit loading is maintained at one point or line for a long time. Dimensional stability through the entire temperature range including thermal expansion differentials is important because of the necessarily close clearances between rolling element and race. Impact resistance must be high enough to insure against shattering the bearing by any shock loadings to which it might be subjected. Corrosion could change the dimensional tolerance, while selective leaching could change the surface hardness and wear characteristics.

The high unit loading of a rolling element and the low viscosity of high temperature sodium promote intimate surface contact between the rolling element and race. The importance of a boundary layer to inhibit self welding of the asperities is obvious. The materials normally considered for high temperature hardness have low self welding properties

because their high chromium, tungsten, titanium and molybdenum contents tend to readily form lubricating oxide films. The necessary high hardness of these materials support their oxide films and avoid their destruction by base metal yielding. Erhardt⁽¹⁾ presented a plot of hardness versus temperature for the groups of materials he considered had potential for rolling bearing application (Figure 11.2.1-1). If one applies the qualitative criteria of hardness R_C -57 at 1200°F to this figure only the cermets appear feasible. However, tests have been conducted at LMEC⁽²⁾ on the in-vessel handling machine for FFTF up to 1100°F in sodium. The machine contains heavily loaded roller bearings which are thought⁽³⁾ to be made of Stellite balls and Inconel 718 races which would only have a hardness of about R_C -45 at 1100°F. These bearings performed well in the extended test.⁽²⁾ Iwai⁽⁴⁾ tested ball bearings at 400°C in sodium with Stellite D6K balls and Stellite 6 on 316 stainless steel races. He found the Stellite races increased in hardness on the wear tracks from R_C -48 before the test to about R_C -55 after the test. He ascribed the surface hardening to the balls rubbing the surface.

Figure 11.2.1-1

Hardness as a Function of Temperature
For Different Classes of Bearing Material*

*Graphic composite made from manufacturer's data on materials.

**A hardness of at least 80 RA (57-58RC) is generally required to provide adequate material fatigue life under normal bearing application conditions. However due to the very narrow range of materials having this hardness at 1200°F, revised bearing designs for manufacture from softer materials may be required.

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11.2.2 Environmental Considerations for Rolling Surfaces

This discussion of rolling surfaces differs from the previous discussion of sliding surfaces in that rolling bearings have very high specific loading and close dimensional tolerances. The high specific loading in the low viscosity, high temperature sodium will remove most of the sodium from the contact area and promote metal-to-metal contact. Thus, the chemistry of the sodium in forming thin oxide layers on the surface of the bearing is very important in preventing asperite welding and adhesive wear. Fortunately, the materials which have the required hardness at high temperature for rolling bearings usually contain elements which form oxide layers in sodium of low oxygen concentrations such as tungsten, chromium, titanium, molybdenum, etc. The concentrations of oxygen in sodium necessary to maintain an oxide film on the bearing surface will be a function of material, temperature, surface velocity, the rapidity that the film is removed by mechanical action and the kinetics of film formation. Droher's⁽¹⁾ simplified figure showing the oxygen concentration temperature relationship to film formation is shown in Figure 11.2.2-1. This figure is based on the formation of $\text{Na}_x\text{Cr}_y\text{O}_z$ type surface film of a chromium alloy. This figure graphically illustrates that one cannot extrapolate the performance of a bearing at one temperature to a different temperature with confidence without a complete understanding of the surface chemistry. Sowa⁽²⁾ explains the wear behavior of molybdenum against Carboloy-78B in sodium as the formation of an oxide layer starting around 700°F and extending through 1200°F.

The rolling bearing usually has only short crevice areas and the bearing surfaces are bathed in lubricant by its own motion. This supply of sodium to all the surfaces will promote equilibrium of the oxide surface layers with the available oxygen in the sodium. The plentiful supply of sodium will serve to remove any generated heat rapidly. However, any particulates in the sodium will also be supplied to the rolling surfaces and could induce wear or dimensional changes from buildup on surfaces.

Bearings which operate in the vapor space over hot sodium will be encrusted with sodium frost. If the bearing is periodically submerged in

Figure 11.2.2-1

Estimation of Friction Regimes as a Function of
Temperature and Oxygen Content in Liquid Sodium

sodium, the frost will probably be removed. Sodium frost is a mixture of sodium, sodium oxide, sodium hydride, sodium carbonate and other sodium compounds. These compounds are generally soft compared to the bearing material and thus may increase the apparent friction in the bearing for the first few revolutions. If sufficient torque can be applied, the frost will probably be extruded and the slight residues will act as a lubricant. The possibility of corrosion of the bearing material is present with the high concentrations of impurities in the frost. Gas phase operation of a bearing will not extract friction heat from the bearing surfaces nearly as well as the liquid sodium environment. If substantial friction coefficients are encountered during rapid motion, the bearing may severely overheat and weld.

The close dimensional tolerance of rolling bearings must be maintained throughout their useful life. The open structure of this type of bearing will promote rapid sodium flow around the bearing surfaces and thus create a potential for corrosion leaching of the bearing material. This leaching process can change the composition and hardness of the surface and thus its wear characteristics and dimension. Most materials considered for rolling bearings are not severely corroded by sodium. Romano⁽³⁾ found the corrosion of Haynes 25 to be similar to stainless steel in low oxygen sodium and better than stainless steel in 12 ppm O₂ sodium at 710 and 760°C. Bodgers, et al⁽⁴⁾ found that Stellite 6B had an increasing wear rate in sodium at 650°C over 858 hours. Part of this wear may have been corrosion.

Whitlow, et al⁽⁵⁾ reported corrosion data for Stellite 6 and Inconel 718 in low and intermediate oxygen sodium at 1200 and 1325°F. Both of these alloys showed surface depletion of elements and a slight surface softening from several thousand hours of sodium exposure at 1325°F. The corrosion rates at 1325°F (<10 ppm O₂) in flowing sodium was about 0.2 and 1.5 mils/year for Stellite 6 and Inconel 718 respectively.

In summary, it appears that a small concentration of oxygen in sodium is beneficial to rolling bearings constructed of materials of suitable hardness at high temperature. Excessive oxygen, carbon or nitrogen in the sodium would be detrimental. The optimum concentration is not clearly defined,

depending on flow, bearing material, rotational velocity, temperature and loading. Presumably impurity concentrations in sodium will be determined by other system requirements and suitable bearing materials will be sought to match these environmental conditions.

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11.3 FUNDAMENTAL CONSIDERATIONS FOR PERIODIC MOVEMENT OF CONTACTS

Some bearings and contacting surfaces will only move relative to each other at intervals of time up to several months. The considerations brought out for sliding and rolling contacts were more concerned with a kinetic situation than a static load. Although many of the considerations are the same for a static or dynamic situation, there are some specific differences. In the case of journal bearings the static situation allows the bearing surface to have most of the sodium squeezed out of the contact area and the impurities in the sodium will not be supplied to the minute crevice. In the case of the rolling bearing there will be a very high specific load contact point which will have to resist creep deformation for substantial time intervals. In both cases the diffusion of alloying elements from one material to its mating material will be enhanced because of the substantial time interval without movement unless oxide or other barriers layers inhibit the diffusion process.

Most of the contacting surfaces in the core region of an LMFB are of the periodic movement variety. The main concern with these contacts is to avoid self welding of the contacting surfaces. Examples of this type of contact are the spacing pads on the fuel assembly, the core restraint to the fuel assembly, the bearings on the instrument tree and fuel handling machine, the inlet nozzle on the fuel to core basket receptical and the absorber assembly to guide duct. These various examples cover a wide range of temperatures, sodium flows, contact pressures, and probable duration of static contact.

11.3.1 MATERIAL CONSIDERATIONS FOR PERIODICALLY MOVING CONTACTS

The temperature, specific loading and surface films are the primary variables in static contacts. The temperature is important because it softens material, increases diffusion rates and can affect the surface films. The temperature will be more important at high specific loadings as are usually present in rolling bearings because long times at high temperature and high specific load will emphasize the creep deformation of the roller and race. Hoffman, et al⁽¹⁾ observed creep deformation on static pin tests in 1200°F sodium which is shown in Tables 11.3.1-1 and -2. However, the writers felt that corrosion product oxide intergrowth had a more important effect on the starting torque required to move the couple after 745 to 1560 hours of static contact than asperity welding or creep. If one compares the starting friction for all their couples in low oxygen sodium and cold trapped sodium there are many more couples that had higher self welding coefficients in low oxygen (<5 ppm) sodium than in the higher oxygen (<30 ppm) test. These data would not support their concept of oxide intergrowth, however, the scatter of this type of data precludes firm conclusions.

Journal bearings have substantial contact areas and thus low specific loadings while rolling bearings have small contact areas and high specific loadings. Creep deformation is thus more of a consideration for rolling bearings than journal bearings or contact pads. Hoffman's data in Tables 11.3.1-1 and -2 give an indication of the high temperature creep resistance of the various couples in the surface contact area measurement. These data were with spherical pins on flat plates, all at the same loading, thus the more yielding a pin and plate combination sustained, the higher the surface area observed after test. It can be seen that the self welding coefficient is generally lower for materials that deform very little, however, there is not a one-to-one correspondence which indicates that alloying elements may be as important as extreme hardness by itself. Even though the high temperature creep indication is useful in choosing material for a rolling bearing, the self welding coefficient is measured in shear and thus not strictly applicable to a rolling contact.

Table 11.3.1-1

STATIC CONTACT RESULTS FROM 1200°F TESTS –
FIRST MATERIAL GROUP

Material Combinations		Pin Contact Area (cm ² x 10 ⁻⁴)	Minimum Pin Surface Pressure (kg/cm ²)	Initial Static Friction Coefficient at Temperature	Average Static Friction Coefficient After >700 hrs at Temperature	Self-Welding Coefficients†			
						Circulating Liquid Sodium			Sodium Vapor Over Cold-Trapped Liquid Na After 792 hr
						Cold-Trapped (< 30 in/in O ₂)		Hot Trapped (< 5 in/in O ₂)	
						After 912 hr	After 1560 hr	After 745 hr	
K-95 (WC)	K-95	27	2740	0.3	0.4	0.5	0.8	0.5	0.4
K-95	K-162B	14	5480	0.3	0.3	1.1	1.2	0.8	0.6
K-95	AISI T1	130	570	0.3	0.8	2.0	3.0	2.1	1.9
K-95	AISI M1	115	650	0.3	0.8	2.4	2.7	3.1	2.1
K-95	AISI M2	168	440	0.3	1.2	2.2	4.1	3.1	2.8
K-95	AISI M3 Type 1	158	470	0.2	0.7	2.0	3.6	2.0	2.1
K-95	Stellite 6B	52	1430	0.3	0.4	0.9	2.0	0.4	0.9
K-95	Colmonoy 4	222	340	0.6	0.3	3.6	4.6	3.6	0.6
K-95	Hastelloy C	68	1000	0.3	0.4	1.3	1.4	1.2	1.5
K-162B (TiC)	K-162B	23	3160	0.3	0.3	0.4	0.8	0.4	0.6
K-162B	AISI T1	106	700	0.3	1.0	1.4	2.0	2.0	2.0
K-162B	AISI M1	120	620	0.3	1.0	0.5	1.4	1.5	1.4
K-162B	AISI M2	112	660	0.2	1.1	2.2	2.3	2.6	2.3
K-162B	AISI M3 Type 1	132	560	0.2	0.6	0.6	1.9	2.2	1.6
K-162B	Stellite 6B	160	460	0.4	0.9	1.3	2.3	1.6	2.0
K-162B	Colmonoy 4	174	430	0.3	0.7	2.2	3.6	2.1	1.3
K-162B	Hastelloy C	120	620	0.3	0.8	1.0	2.4	2.1	0.9
K-162B	Molybdenum	83	890	0.3	0.7	0.6	1.8	1.5	1.0
AISI T1	AISI T1	86	870	0.2	1.2	2.6	2.6	2.6	2.1
AISI T1	AISI M1	129	580	0.2	1.1	1.7	2.4	2.0	2.1
AISI T1	AISI M2	153	490	0.2	1.0	1.0	2.2	2.3	2.0
AISI T1	AISI M3 Type 1	92	810	0.3	1.2	2.0	2.7	2.2	1.5
AISI T1	Stellite 6B	85	870	0.2	1.1	0.6	2.6	2.0	2.0
AISI T1	Colmonoy 4	151	490	0.2	1.1	3.0	5.8	1.8	1.6
AISI T1	Hastelloy C	121	610	0.4	0.6	1.0	2.6	2.5	3.1
AISI M2	AISI M2	108	690	0.3	1.1	1.9	3.1	3.1	2.5
AISI M2	AISI M3 Type 1	143	520	0.2	1.2	2.5	3.1	2.8	2.7
AISI M2	Stellite 6B	134	560	0.2	1.1	0.6	2.2	2.1	2.3
AISI M2	Colmonoy 4	160	460	0.2	0.7	2.5	4.9	1.8	1.7
AISI M2	Hastelloy C	85	880	0.2	0.9	1.8	2.7	2.4	2.0
AISI M3 Type 1	AISI M3 Type 1	149	500	0.3	1.1	2.2	2.3	2.0	2.0
AISI M3 Type 1	Stellite 6B	104	720	0.2	1.0	2.7	3.1	2.4	2.6
AISI M3 Type 1	Colmonoy 4	149	500	0.2	0.9	2.7	5.3	2.0	1.5
AISI M3 Type 1	Hastelloy C	96	770	0.3	1.0	2.1	3.5	2.4	2.2
Stellite 6B	AISI M1	160	470	0.3	0.8	2.1	4.2	3.6	4.9
Stellite 6B	AISI M2	182	410	0.3	0.8	0.5	2.3	2.7	4.0
Stellite 6B	Molybdenum	77	970	0.4	0.4	1.0	1.6	1.4	1.3
Stellite 6B	Stellite 6B	91	820	0.4	0.4	0.9	2.4	1.6	2.0
Stellite 6B	Colmonoy 4	182	410	0.3	0.6	2.2	3.6	2.4	1.4
Stellite 6B	Hastelloy C	49	1510	0.2	0.5	0.4	1.7	1.7	1.0
Hastelloy C	AISI M3 Type 1	246	310	0.4	1.5	1.0	4.4	4.5	4.0
Hastelloy C	Hastelloy C	160	630	0.5	0.4	1.6	2.0	2.0	1.4
Colmonoy 4	Colmonoy 4	165	450	0.3	0.5	3.4	4.5	3.6	1.6
Colmonoy 4	Hastelloy C	165	450	0.3	0.3	2.4	3.6	2.0	1.1
Molybdenum	Stellite 6B	70	1060	0.3	0.5	1.3	2.0	0.6	0.4
Molybdenum	Hastelloy C	72	1040	0.3	0.3	2.3	1.9	1.0	0.4
Molybdenum	Molybdenum	106	700	0.3	0.8	0.9	1.2	1.0	0.9
Tungsten	Tungsten	79	940	0.2	0.5	0.8	1.0	0.7	0.6
Tungsten	Molybdenum	137	540	0.3	0.4	0.6	0.6	0.6	0.6

* Taken on fresh surface

† Static friction coefficient, measured in shear on pin plate combinations that have been under contact pressure during exposure

Table 11.3.1-2

**STATIC CONTACT RESULTS FROM 1200°F TESTS -
SECOND MATERIAL GROUP**

Material Combinations		Pin Contact Area (cm ² × 10 ⁻⁴)	Minimum Pin Surface Pressure (kg/cm ²)	Initial Static Friction Coefficient at Temperature	Average Static Friction Coefficient After 500 hrs at Temperature	Self-Lubricating Coefficient				Surface Change Over Cold Traps (Exposed No. After 702 hr)
						Circulating Oil and Solvent				
						Cold Traps (0.30 ppm O ₂)		Hot Traps (0.50 ppm O ₂)		
						After 720 hr	After 1560 hr	After 702 hr		
K 162R	Star J	71	1046	0.4	0.7	1.0	1.1	0.5	1.3	
Colmonoy 75	Colmonoy 5	142	524	0.2	0.4	0.4	0.9	1.0	0.4	
Colmonoy 75	Colmonoy 70	137	542	0.4	0.7	0.4	1.1	0.7	0.7	
Colmonoy 75	Stellite 1	91	812	0.6	0.7	1.2	1.3	1.5	1.2	
Colmonoy 75	Colmonoy 5	103	721	0.5	0.6	1.3	1.1	1.6	0.9	
Colmonoy 75	Stellite 6H	107	694	0.5	0.8	1.1	1.5	1.3	0.9	
Colmonoy 75	Inconel 718	95	784	0.3	0.8	0.8	0.9	0.9	0.6	
Colmonoy 75	Tungsten	62	1199	0.4	0.7	0.9	1.2	1.4	1.5	
Colmonoy 75	Haynes 273	83	844	0.3	0.8	1.4	1.3	1.2	0.9	
Colmonoy 75	Colmonoy 75	273	772	0.3	0.7	0.4	1.5	0.9	1.5	
Colmonoy 6	Colmonoy 70	159	467	0.3	0.8	0.7	0.7	0.8	0.6	
Colmonoy 6	Stellite 1	81	921	0.4	0.7	0.7	1.3	1.3	1.0	
Colmonoy 6	Colmonoy 5	128	581	0.3	0.7	0.9	1.1	0.5	0.4	
Colmonoy 6	Stellite 6H	131	569	0.7	0.7	0.9	1.0	0.7	0.4	
Colmonoy 6	Inconel 718	108	687	0.3	0.7	0.6	1.2	1.0	1.2	
Colmonoy 6	Tungsten	52	1417	0.7	0.8	0.4	1.4	1.1	1.0	
Colmonoy 6	Haynes 273	85	838	0.7	0.7	1.0	1.1	1.3	1.2	
Colmonoy 6	Colmonoy 6	206	359	0.6	0.6	0.8	0.8	0.8	0.4	
Colmonoy 70	Stellite 1	120	619	0.3	0.9	1.2	1.3	1.1	1.5	
Colmonoy 70	Colmonoy 5	302	746	0.9	0.5	0.9	1.1	0.9	0.5	
Colmonoy 70	Stellite 6H	122	607	1.0	0.8	1.1	1.0	1.3	0.9	
Colmonoy 70	Inconel 718	112	660	0.4	0.6	1.0	1.0	0.8	1.1	
Colmonoy 70	Tungsten	108	683	0.3	0.9	0.9	1.1	0.7	1.1	
Colmonoy 70	Haynes 273	177	420	0.7	0.6	0.9	1.3	1.2	1.2	
Colmonoy 70	Colmonoy 70	151	490	0.3	0.5	1.0	0.7	0.6	0.4	
K 95	Star J	24	3082	0.4	0.4	0.4	0.9	0.9	0.4	
Stellite 1	Colmonoy 5	116	641	0.3	0.6	0.6	1.3	0.3	0.7	
Stellite 1	Stellite 6H	87	856	0.5	0.6	1.2	2.2	0.7	1.6	
Stellite 1	Inconel 718	77	962	0.6	0.6	0.9	1.2	0.4	0.5	
Stellite 1	Tungsten	55	1324	0.5	0.7	1.1	1.2	0.4	0.6	
Stellite 1	Haynes 273	59	1261	0.6	0.7	2.3	2.0	0.5	0.7	
Stellite 1	Stellite 1	37	2018	0.4	0.6	1.0	1.1	0.4	0.8	
Colmonoy 5	Stellite 6H	19	394	0.5	1.1	0.9	1.7	0.8	1.5	
Colmonoy 5	Inconel 718	18	419	0.7	0.7	1.1	1.2	1.5	1.3	
Colmonoy 5	Tungsten	69	836	0.3	0.6	0.6	1.0	1.2	1.1	
Colmonoy 5	Haynes 273	138	538	0.4	0.9	0.8	1.5	1.4	1.7	
Colmonoy 5	Colmonoy 5	474	156	0.8	0.7	1.0	1.3	0.7	0.4	
Stellite 6H	Stellite 6H	81	914	0.3	0.7	1.0	1.4	1.1	1.0	
Stellite 6H	Inconel 718	47	1589	0.4	0.6	0.7	1.2	0.9	0.9	
Stellite 6H	Tungsten	99	752	0.5	0.7	1.3	1.2	0.7	0.6	
Stellite 6H	Haynes 273	50	1486	0.4	0.6	1.1	1.3	0.4	0.5	
Stellite 6H	TZM	56	1330	0.5	0.8	1.2	1.3	1.2	0.7	
Inconel 718	Tungsten	98	758	0.4	0.7	0.7	1.3	1.1	0.5	
Inconel 718	Haynes 273	72	1029	0.4	0.7	1.0	1.3	0.9	1.1	
Inconel 718	Inconel 718	46	1607	0.6	0.7	0.9	1.2	1.2	0.5	
Tungsten	Haynes 273	92	805	0.5	0.9	2.1	2.1	0.6	1.5	
Tungsten	TZM	120	620	0.5	0.7	0.5	0.6	0.7	0.9	
17-4 PH	17-4 PH	150	494	0.6	1.0	2.0	2.0	0.6	2.0	
17-4 PH	304 SS	125	504	0.3	1.0	1.4	2.0	1.5	2.6	
17-4 PH	316 SS	107	692	0.7	1.0	1.6	2.1	1.9	1.5	
304 SS	304 SS	92	806	0.7	1.2	1.4	1.5	2.0	1.6	
316 SS	316 SS	86	866	0.6	0.9	1.2	1.6	1.1	0.7	
Haynes 273	Haynes 273	93	862	0.5	0.6	2.0	2.1	1.0	1.0	
Hex 49	Hex 49	105	702	0.8	1.0	2.0	1.8	1.2	2.4	

*Taken on fresh surface.

†Static friction coefficient, measured in steel, on pin-plate combinations that have been under contact pressure during exposure.

REFERENCES

1. N.J. Hoffman, D.E. Goggin and J.J. Droher, Friction and Wear Screening Tests of Materials in Sodium, LMEC-70-10, July 1970. pp. 110-111.

11.3.2 ENVIRONMENTAL CONSIDERATIONS FOR PERIODICALLY MOVING CONTACTS

The environment a static contact surface actually sees is governed by the contact geometry more than the surrounding medium. In the case of point contacts or multiple point contacts of a rough surface the surrounding medium can penetrate to very near the contact points. This layer of sodium will form a medium for diffusion and equilibration of surface activities but unless an actual flow is established it will not supply bulk sodium impurities to the crevice. In the case of closely mated surfaces, the sodium layer will be largely squeezed out and communication to the surrounding medium nearly eliminated. In this situation any existing oxide layers will stay in place and inhibit metal contact unless pressure is sufficient to break them up because of metal yielding. If no oxide layers exist from previous service, there will be little chance of forming any new layers during the static period and the static metal contact will promote self welding. Examination of Tables 11.3.1-1 and -2 will show that the self welding coefficients tend to be higher in the low oxygen tests than in the higher oxygen tests. Thus, closely mating surfaces should have a higher tendency toward self welding than poorly mated surfaces or point contacts unless the higher specific load of the point contacts breaks up the surface layers.

Some bearings or static contacts may be located in the vapor space and exposed to sodium vapor and inert gas with impurities. Tables 11.3.1-1 and -2 show self welding coefficients for couples exposed to inert gas with sodium vapor. Most of these coefficients are the same or lower than the corresponding ones in liquid sodium of low oxygen content. Some bearings and surfaces will be located such that they must operate in an inert gas without any sodium vapor. Generally these bearings or surfaces can be coated with lubricant films because there is no sodium to remove the films. The friction and wear behavior of metal surfaces in inert gas without any sodium vapor or other lubricant is more severe than in sodium or sodium vapor. Sowa et al,⁽¹⁾ investigated the comparative behavior of several metal combinations in argon and sodium. They still observed oxide formation and removal effects from impurities in the argon, also volatilization and sloughing. The behavior of static contacts in pure inert gas will be controlled by the oxide film on the metals because there is no mechanism for removal except volatilization (e.g., MoO_3) or diffusion into the metal with

metals like zirconium or titanium. To the extent clean metal surfaces are in contact, solid state diffusion and self welding will probably occur.

REFERENCES

1. S.S. Sowa, K.C. Tsao, C. Fiala, and C.J. Divona, Some Observations on Phenomena Affecting Wear of Bearing Materials in Sliding Contact in Sodium and Argon at Temperatures Up to 1200°F, ANL-7580, Argonne National Laboratory, July 1969.

11.4 LABORATORY AND PLANT EXPERIENCE IN WEAR AND SELF WELDING

Wear and self welding of metal contacts in high temperature sodium environments have been of concern since the late 1940's with a number of investigations reported. The importance of temperature and oxygen concentration in the sodium to the friction and wear behavior of surfaces make much of this early work of questionable applicability to the current 1200°F - <5 ppm O₂ LMFBR. Three recent critical surveys of the available earlier data have been made.^(1,2,3) The reviewers generally agreed that more data under closely controlled LMFBR conditions was necessary to accurately evaluate the wear, friction, and self welding problems.

There are three general types of information which will be treated in the following section namely: Basic Testing, Laboratory Simulation Testing, and Operating Plant Data.

REFERENCES

1. J.K. Balkwill, Mechanical Elements Operating in Sodium and Other Alkali Metals, Vol. I, Literature Survey, LMEC-7968, LMEC-68-5 Vol. I. 1969
2. D.J. Kniley, et al., Mechanical Elements Operating in Sodium and Other Alkali Metals, Vol. II, Experience Survey, LMEC 68-5, Vol. II. June 1970.
3. K.E. Erhardt, A Literature Review and Materials Evaluation for Rolling Bearings Operating in Liquid Sodium in The Temperature Range 800°F to 1200°F, NYO-4117-3, SKF Industries, April 1971.

11.4.1 BASIC LABORATORY TESTING IN WEAR AND SELF WELDING

Basic laboratory friction and wear testing generally involves pins rubbed against flat plates. The pins can have flat or spherical ends and can be rubbed periodically or continuously in unidirectional or oscillatory motion. The starting and running torques, pin wear, plate wear, surface micrography, and hardness are the data generally taken. Hoffman, et al,⁽¹⁾ reported a massive amount of data obtained at LMEC under typical LMFBR conditions. Continuation of this testing is reported by Droher,⁽²⁾ Meyers,⁽³⁾ and Hoffman.⁽⁴⁾ Hoffman⁽¹⁾ summarized the wear data in two qualitative tables which are shown in Figures 11.4.1-1 and -2. These tables indicate the best choices based on wear data for contacting surfaces available in 1970. Many other factors such as friction, brittleness, corrosion, thermal expansivity, and fabricability must be taken into consideration in material selection for contacting surfaces.

Subsequent testing of basic parameters has shown the effects of oscillatory motion of 20% cold worked type 316 stainless steel and Inconel 718 materials on themselves. The stainless steel specimens galled⁽²⁾ with high wear coefficients while the Inconel 718 materials⁽⁴⁾ showed a decreased friction coefficient at high loads. Tests⁽²⁾ of Inconel 718 on 316 stainless steel showed intermediate behavior with the stainless steel the more seriously affected material. The basic screening tests have now been largely supplanted by the mechanism oriented testing discussed in the next section.

Pin Material		Plate Material																														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
Tool Steels	AISI-M-1	1	G																													
	AISI-M-41 (Rex 49)	2	G			W																										
	AISI-T-1	3				B																										
	AISI-T-15	4		G																												
Nickel Base	Hastelloy C	5				G	W		2		B							2	B	B	2	B							W		W	
	Inconel 718	6				2	B	B	B										2	2	B	2				B			2		2	
	Inconel 750	7				W	B	B											W			W							W			
	Udimet 630	8				W	B		B										2										2		B	
	Colmonoy 4	9									W								W												W	
	Colmonoy 5	10																													B	
	Colmonoy 6	11																														
	Colmonoy 70	12																														
Cobalt Base	Haynes 273	13				B			2					W		2		2		2									W			
	Star J	14				2	2		2										2				2	2					2			
	Stellite 1	15				W	2												2										2			
	Stellite 3	16				B	W												2	2									2	B	W	
	Stellite 6B	17	G			B	B		2		B					2		2		2									2		2	
	Stellite 6H	18				B	W												B	2									W			
	Stellite 101G	19				B	2							W				B											2			
Mo	TZM	20				2	B		B					B				B			B		W					B		B		
	Molybdenum	21	G			B	G											B					W					B				
W	Tungsten	22				B	W									B		2														
Ceramic	LT-2	23																							1							
	Coors	24																								W						
SS	304	25					W											W		W												
	17-4 PH	26				W							B					W														
Carbides	K-95	27				2			1									2			2								2	B		
	K-162H	28				2																							2			
	K-801	29							B										2										B			
	Colmonoy 75	30				2													2										2			

Code

- 1 = First Choice: $K < 1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb}$
 2 = Second Choice: $1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb} < K < 2.5 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb}$
 2 = Second Choice (Slightly Greater Wear): $1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb} < K < 1 \times 10^{-11} \text{ in.}^3/\text{in.}\cdot\text{lb}$
 W = Wear May Limit Performance: $K > 1 \times 10^{-11} \text{ in.}^3/\text{in.}\cdot\text{lb}$
 G = Galled, Unacceptable
 B = Buildup, Unacceptable

Figure 11.4.1-1

Matrix - Sliding Wear in Liquid Sodium at 1200°F

Pin Material		Plate Material																	
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ni Base	Hastelloy C	1	W	2	2					W		W					2		2
	Inconel 718	2	2	2	W					W		W	2				2		
	Udiraet 630	3	2	W	2					2							2		
	Haynes 273	4		B				B											
Cobalt Base	Star J	5	2		2					2		2		2			2		
	Stellite 1	6								B									
	Stellite 3	7	2							B						2	2		
	Stellite 6B	8		W	B					W									W
	Stellite 6H	9	2																
	Stellite 1016	10	2	B	2	B											2		
Mo	TZM	11	1	B													1		
	Molybdenum	12								B									
W	Tungsten	13	W							B							B		
Carbides	Colmonoy 75	14																	
	K-95	15	1	2	2				B			2					1		
	K-162B	16															2		
	K-801	17	2																

Code

- 1** = First Choice: $K < 1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb}$
2 = Second Choice: $1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb} < K < 2.5 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb}$
2 = Second Choice (Slightly Greater Wear): $1 \times 10^{-12} \text{ in.}^3/\text{in.}\cdot\text{lb} < K < 1 \times 10^{-11} \text{ in.}^3/\text{in.}\cdot\text{lb}$
W = Wear May Limit Performance: $K > 1 \times 10^{-11} \text{ in.}^3/\text{in.}\cdot\text{lb}$
G = Galled, Unacceptable
B = Buildup, Unacceptable

Figure 11.4.1-2

Matrix - Sliding Wear in Sodium Vapor at 1200°F

REFERENCE

1. N.J. Hoffman, D.E. Goggin, and J.J. Droher, Friction and Wear Screening Tests of Materials in Sodium, LMEC-70-10, July 1970.
2. Liquid Metal Engineering Center Semiannual Technical Progress Report, January-June 1971, LMEC-71-7, March 1972, pp. 43-57.
3. Quarterly Technical Progress Report Fuels, Materials, Coolant Chemistry and Fuel Handling Programs, October-December 1971, AI-AEC-13021, Atomic International, February 1972, pp. 33-50.
4. Liquid Metal Engineering Center (LMEC) Annual Technical Progress Report, January-December 1971, LMEC-72-1, Atomic International, March 1972, pp. I-81-124.

11.4.2 MECHANISM TESTING OF FRICTION AND WEAR

The mechanism oriented testing of friction and wear is concerned with three basic types of problems: sliding friction and wear, static friction (self welding), and rolling friction and wear. Most mechanisms involve combinations of at least two of these basic friction and wear problems. Components of major concern for LMFBRs have been the pump bearings, fuel duct contact pads, fuel element-to-spacer wire contacts, fuel nozzle-to-core basket contacts, control rod drives (in argon), in-vessel fuel handling machine bearings, instrument tree bearings, control element-to-guide duct contacts, and various valve facings.

Recent laboratory work concerned with large pump bearings has been reported by Arwas⁽¹⁾ and Jamison.⁽²⁾ Arwas was concerned primarily with the lubricating fluid dynamics in large, high speed hydrostatic journal bearings. The two major concerns with these bearings has been the amount of pump output they consume (up to 7%) to pressurize the sodium flow to the bearing and the slow speed instability and rubbing of the journal when the pressure is low during startup. In practice these bearings have been very good. Jamison⁽²⁾ reported on a continuing effort to develop a large rolling bearing for 1200°F liquid sodium service. The problems of interest in this bearing development are adequate high temperature hardness to withstand the high specific loads on the small contact area and the wear or galling of the cage material by the rolling elements. To date no satisfactory rolling bearing exists for high speed 1200°F sodium service, however, Balkwill⁽³⁾ reported the roller bearings on the In-Vessel Handling Machine test (static at 1100°F and dynamic at 450°F) appeared in excellent condition after several months of testing. The advantages of a satisfactory rolling bearing over a hydrostatic journal bearing in high temperature sodium are: improved low speed performance, more accurate movement, and less parasitic drain on the pump flow. A program recently initiated at G.E.⁽⁴⁾ will examine and develop pumps for the LMFBR. This effort is scheduled to test a prototypic pump at LMEC in 1976.

The fuel ducts must be held in a rigid array during reactor operation but must be removable for refueling. The points of contact between the ducts could be subject to self welding in high temperature sodium

making the ducts difficult to remove singly. Similarly, the inlet nozzle could self weld or gall to the core basket receptacle making removal difficult. Friction, wear and self welding studies of materials and coatings applicable to the fuel duct pads were initiated at LMEC in 1971. The testing⁽⁵⁾ involved complex temperature, pressure and static cycles simulating the FFTF fuel duct environments. One of the coatings that appeared promising was a chromium carbide-15% nichrome binder applied by a proprietary spraying process.⁽⁵⁾ Continued testing of this coating and others was reported by Aungst.⁽⁶⁾ Galling and self welding of the fuel duct inlet nozzle (316 stainless steel, 17-4 PH piston rings) to the core basket receptacle (Inconel 718) are still being examined at HEDL. Galling of the above combination during water testing^(7,8) has indicated a better material combination may be needed.

The individual fuel pins present a potential problem in wear and self welding by interaction with their helically wrapped spacer wires. In this case, the cladding needs to be as thin as possible to promote heat transfer, the material (20% CW type 316 stainless steel) was chosen for its corrosion resistance and other properties. The temperatures and sodium flows will be the highest in the reactor. The motion and contact pressure of the wear points between the wire wrap and fuel element generated by thermal expansion, flow vibration, swelling, bowing, and creep are poorly defined. An ex-reactor test reported by Shively⁽⁹⁾ of a 19-pin bundle clad in 10 to 15% CW-316 stainless steel in flowing (6 fps) 1200°F sodium with 5 ppm O₂ showed numerous points of self welding between the annealed 316 stainless steel wire wraps and fuel pins. Wear testing of a simulated fuel pin and its wire wrap were reported by Hoffman.⁽⁵⁾ In Hoffman's test the wire rubbed on the tube wall in short (0.2 in) strokes at three contact pressures while submerged in 1150°F sodium with <5 ppm oxygen. The 20% CW-316 stainless steel clad and wire transferred material back and forth and finally suffered wear in 10,000 strokes ranging from 0.3 mils for a 1.5 lb load, to 4 mils for a 20 lb load. Despite the concern for fretting corrosion and self welding, wire wrapped elements have generally not suffered seriously from these problems, however, they generally have operated at lower temperatures than those proposed for LMFBs. A recent examination⁽¹⁰⁾ of a prototypical FFTF fuel bundle tested ex-reactor at 1100°F for 9000 hours has indicated no self welding or wear problems.

The fuel handling machines for charging and discharging the reactor require precision movement of several parts relative to the fuel. A prototype mechanism of the FFTF In-Vessel Handling Machine was given a simulated life test which involved more than 25,000 movements in 450°F sodium and a 87-day soak in 1100°F sodium. Balkwill⁽³⁾ reported the roller bearings appeared in excellent condition and turned freely after the test. Measurements indicated the bearings had suffered only minimum wear. Several times during the test an increased force of about 20% was required to move the assembly for unexplained reasons.

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1. E.B. Arwas, et al., Liquid Metal Bearings Technology for Large High Temperature Sodium Rotating Machinery: Part 1 Sodium Bearings Mechanical Technology, NYO-3930-13, July 1971.
2. W.E. Jamison, Development of High Temperature Rolling Bearings for Operation in Liquid Sodium, NYO-4117-8, SKF Industries, March 1972.
3. Liquid Metal Engineering Center (LMEC) Annual Technical Progress Report, January-December 1971, LMEC-72-1, Atomic International, March 1972, pp. I-67-80.
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10. Monthly Technical Progress Report - January 1973, HEDL-TME-73-1, Hanford Engineering Development Laboratory, pp. D-2-8.

11.5 PLANT EXPERIENCE WITH FRICTION AND WEAR AND APPLICATION TO LMFBR

Although there have been five sodium cooled reactors constructed and operated in the U.S. (exclusive of small, military or space systems) and several more in Europe, the conditions under which they have operated are generally less demanding than those currently envisaged for the FFTF and demonstration LMFBRs. All of the U.S. reactors except EBR-II have now been shut down. However, their operating experience with moving contacts is of interest even if not directly applicable to modern LMFBRs. Kniley⁽¹⁾ has surveyed the experience with Hallam (HNPF), Sodium Reactor Experiment (SRE), Experimental Breeder Reactor (EBR), and Enrico Fermi Atomic Power Plant (EFAPP). The summary of his in-depth survey brought out the following points:

- Some mechanisms have operated in hot sodium for as long as 49,000 hours.
- Contact loads and relative velocities have been kept to a minimum except for the pump bearings and oscillator rod shaft supports.
- Austenitic, corrosion resistant steels were used for most fabrication with chrome plate, Colmonoy, Stellite, Haynes Alloy, and Inconel inserts at contact points. EBR-II made extensive use of an aluminum bronze for bearings.
- SRE and HNPF attempted to keep moving mechanisms out of the sodium environment.
- EBR-II and EFAPP made extensive use of in-sodium mechanisms.
- In general, the operation of mechanisms in sodium has been very satisfactory.
- Under certain well defined conditions sodium will act as a satisfactory lubricant, however an adequate design basis does not yet exist.
- Past experience is in the temperature range of 100 to 1000°F. Proposed LMFBR conditions impose more stringent requirements.

- Major problem areas have been binding or clogging and seizure or galling.

Examination of specific equipment malfunctions detailed in the report indicate a substantial number of instances at all reactors where sodium frost caused binding. This occurred on the labyrinth seals of pumps, rotating reactor covers, and other low clearance crevices in the vapor space. Galling, seizure or self welding were relatively uncommon even when stainless steel was in contact with itself.

The early experience with Rapsodie⁽²⁾ produced a primary and a secondary pump bearing seizure. These Colmonoy 5 bearings and Colmonoy 6 journals were replaced with Stellite and the clearance increased from 280 to 400 μ on the 230 mm diameter bearings. These bearing problems were felt to be caused or aggravated by strains imposed by the thermal expansion of connected piping.

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12.0 SODIUM-WATER REACTION

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12.2	Basic Chemistry
12.2.1	Reactions
12.2.2	Thermodynamics
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12.3	Reaction in Steam Generators
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[illegible]

12.0 SODIUM-WATER REACTION

12.1 INTRODUCTION

The economic generation of electrical power using an LMFBR requires the transfer of the heat from the sodium primary coolant to water flowing in the steam generation circuit. In current practice a secondary sodium circuit is interposed between the reactor coolant and the water/steam circuit to provide assurance that radioactive sodium will not contaminate the steam generation circuit. In early designs of sodium heated steam generators (SHSGs), it was felt necessary to minimize the chances of allowing even the non-radioactive secondary sodium contacting the water.⁽¹⁾ Hence, a third fluid compatible with both, such as mercury or an inert gas, acted as an intermediate heat transfer and leak-detection medium. Examples of this type of heat exchanger are shown in Figure 12.1-1.⁽²⁾

The use of a third fluid did not completely prevent sodium-water reactions. This along with controlled sodium-water reaction tests, indicated that the sodium-water reaction could be contained safely.⁽²⁾ With the possibility of safe operation and the incentive of lower fabrication costs, SHSGs were designed in which the secondary sodium and the water were separated only by a single wall. This shifted the emphasis from the leak detection afforded by the third fluid to the improved structural integrity possible with a simpler design.⁽²⁾ Operating experience has shown the decision to switch to the simpler design to be satisfactory, in that leaks and consequent sodium-water reactions have not constituted an unusually serious problem.^(2,3,4,5) Continued use of the simpler systems is expected and because no large heat exchanger can be fabricated with complete assurance that no defects exist, the occasional contact of sodium and water is inevitable.

There are four basic types of sodium-water reactions to consider:

- moist gas injected into sodium;
- sodium injected into moist gas;
- sodium (and sodium vapor) injected into water and steam); and

12.1-2

EBR-I evaporator — schematic

SRE U-tube steam generator — schematic

Figure 12.1-1

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- water (and steam) injected into sodium (and sodium vapor).

The first two types of reaction fall outside the realm of this report. Dumm⁽⁶⁾ and Salmon⁽⁷⁾ provide a brief coverage of these topics. It should be noted that extreme temperature conditions can result. For example, a steam-argon mixture passed over sodium produced temperatures of up to 977°C (1791°F); the temperature might have been still higher had the inert gas been absent.⁽⁷⁾

Of the remaining two types of reactions, emphasis will be placed on the injection of water into sodium, as the water is generally at a significantly higher pressure than the sodium in SHSGs.

The sodium-water reaction when conducted in the presence of oxygen (air) is extremely violent; it produces copious quantities of NaOH smoke and fire (due to the burning of the hydrogen generated with the oxygen in the air). In case of a sodium-water reaction in the absence of oxygen, such as occurs under the surface of the liquid sodium or water, there is no significant secondary reaction such as hydrogen combustion. However, the reaction remains violent due to "thermal explosions" caused by the heat of the reaction raising the sodium to its boiling point causing it to "explosively" disintegrate into small fragments, which, due to a suddenly increased surface area, react rapidly with water to form hydrogen.⁽⁸⁾

The principal adverse effects of the sodium-water reaction are not due to the "explosive" nature of the reaction, however, because the reaction, though fast, is more of a combustion than a true detonation.⁽⁹⁾ The major steam generator problems are caused by the high temperature and corrosive conditions in the vicinity of the reaction and the resulting tube wastage, which can lead to the rapid attack and failure of adjacent tubes. Since there will be large surface areas available, and therefore a high probability to develop leaks in steam generators, the major requirements are to economically minimize the opportunity for leaks and to back the design with a reliable, suitably sensitive leak detector.

REFERENCES

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2. Kurt Goldmann, Experience With Sodium-Heated Steam Generators, presented at the Nuclear Engineering Conference, Palo Alto, CA. March 7-10, 1971. ASME paper #71-NE-15.
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7. M.A. Salmon, Effects of Tube Leaks in Sodium-Heated Steam Generators, NAA-SR-8140, USGPO Cat. #C13.48:37, April 15, 1963.
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9. D.A. Greene, "Steam Generator Vessel Pressures Resulting From a Sodium-Water Reaction -- A Computer Analysis With the SWEAR Code," Nuc. Tech. 14, 1972, pp. 218-231.

12.2 BASIC CHEMISTRY

12.2.1 REACTIONS

The important reactions when sodium and water are mixed have been tabulated by Henry⁽¹⁾ and are shown in Table 12.2.1-1. If the reaction occurs with an excess of water, NaOH and H₂ are the reaction products.⁽²⁾

In the case of excess sodium, the reaction products are NaOH, Na₂O, NaH, and H₂. The exact species present and their quantity will depend on the system temperature and the time elapsed from the start of the reaction. The general opinion is that NaOH or Na₂O, plus H₂, will be the major reaction products, since the formation of NaH appears to be slow.^(1,2,3) Experimentally this has been confirmed; in "NOAH" and "SUPER-NOAH" tests ("NOAH" and "SUPER-NOAH" refer to sodium-water reaction test rigs at Dounreay, Scotland) NaOH, Na₂O and NaH account for about 50%, 40%, and 10% of the solids, respectively.⁽⁴⁾

TABLE 12.2.1-1

REACTION COMBINATIONS

REFERENCES

1. J.L. Henry, A Survey of the Sodium-Water Reaction and Reaction Products, USBM-RC-1469, March 20, 1970.
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3. D.D. Adams, G.J. Barenborg, and W.W. Kendall, "Evaluation of the Sodium-Water Reaction in Heat Transfer Systems" In: Handling and Uses of the Alkali Metals, Advances in Chemistry Series #19, American Chemical Society, 1957.
4. J.A. Bray, "Some notes on Sodium/Water Reaction Work." Summary Report and Papers of the Specialists Meeting on Sodium-Water Reactions, IAEA, Melekes, USSR, May 18-21, 1971. CONF-710548, July 1972.

12.2.2 THERMODYNAMICS

Thermodynamic concepts are of limited value in predicting temperatures, pressures, or reaction products in the immediate vicinity of a sodium-water reaction since thermodynamic principles apply only to equilibrium conditions. However, thermodynamics can be an extremely useful tool in certain near-equilibrium circumstances, such as determining the feasibility of a given reaction, predicting gas-liquid equilibria in the bulk of the liquid sodium coolant, and estimating the overall heat liberation (enthalpy change) associated with various reactions.

Henry⁽¹⁾ has calculated Gibbs free energies for the reactions given in Table 12.2.1-1. These results are presented in Table 12.2.2-1 as a function of temperature and various gas phase pressures. These data are useful in predicting chemical equilibria and reaction feasibility. The data of Table 12.2.2-1 are based on the JANAF⁽²⁾ data, which are presented in Table 12.2.2-2 for compounds relevant to Na/H₂O reactions. These data permit calculation of heat capacities, enthalpies, entropies, Gibb's free energies, and equilibrium constants for the formation of NaH, NaOH, H₂, H₂O, Na, NaO₂, Na₂, Na₂O, and Na₂O₂.

The JANAF data cited are relatively recent, extensive, and probably internally consistent, but are obviously not in agreement with data from all other sources. Comparisons between data are often difficult because the physical state (solid, liquid, or gas) of the reactants or products are frequently not given. Disagreements in physical property data are also common. For example, the boiling point of sodium is given as 880°C,⁽³⁾ 881°C,⁽⁴⁾ 882°C,⁽⁵⁾ 883°C,^(2,6) and 892°C.^(3,7) As another example, Na₂O is reported to boil at 1275°C (2327°F)⁽⁸⁾ or "above 1800°C (3272°F)."⁽⁶⁾

It has been calculated that the maximum theoretical temperature, which can be attained in a constant volume system is 1683°C (3060°F) for an initial reactant temperature of 477°C (890°F).^(1,9) It is clear that if Na₂O boils at 1275°C (2327°F) rather than "above 1800°C (3272°F),"

the calculated maximum temperature will change significantly. Increasing the pressure of the environment will increase the maximum temperature attained. These data are presented here only to point out the necessity of carefully reviewing the available thermochemical data before they are used.

In a true equilibrium situation the temperature could not exceed the saturation temperature of the most volatile substance present in sufficient quantities, e.g., 883°C for sodium and 100°C (212°F) for water at one atmosphere pressure. In practice, of course, heat transfer will be slow and will allow the gas phase temperatures and any surface shielded from the liquid to exceed these values. The degree to which this occurs will depend on reactant input rates, reaction rates, gas phase thermal conductivities and the removal of reaction products.

TABLE 12.2.2-1

FREE ENERGY OF REACTION FOR REACTIONS IN TABLE 12.2.1-1

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2\text{O}, \text{H}_2} = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}$
298	-34.2	-34.2
500	-30.9	-34.1
700	-26.5	-32.8
900	-23.0	-31.2

Correction at 900°K for $P_{\text{H}_2} = 150 \text{ psi}$ is + 2.1 kcal

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2\text{O}} = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}$
298	-42.2	-42.2
500	-34.9	-38.1
700	-26.5	-32.8
900	-19.2	-27.3

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2\text{O}} = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}$
298	-50.0	-50.0
500	-39.6	-42.8
700	-27.1	-33.3
900	-15.2	-23.3

TABLE 12.2.2-1 (continued)

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2\text{O}}, \text{H}_2 = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}$
298	-33.9	-34.0
500	-31.5	-34.7
700	-27.1	-33.3
900	-23.0	-31.1

Correction at 900°K for $P_{\text{H}_2} = 150 \text{ psi}$ is + 4.1 kcal

T, °K	$\Delta G, \text{kcal}$
	0 = 1 atm, 100 atm
298	-7.8
500	-4.7
700	-0.6
900	+4.0

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2} = 1 \text{ atm}$	$P_{\text{H}_2} = 10 \text{ atm}$
298	+0.3	+0.9
500	-0.6	+0.5
700	-0.6	+1.0
900	+0.1	+2.1

T, °K	$\Delta G, \text{kcal}$	$\Delta G, \text{kcal}$
	$P_{\text{H}_2\text{O}}, \text{H}_2 = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}, P_{\text{H}_2} = 10 \text{ atm}$
298	-26.2	-24.8
500	-26.8	-27.3
700	-26.3	-29.3
900	-26.2	-30.2

TABLE 12.2.2-1 (continued)

T, °K	$\Delta G, \text{ kcal}$	$\Delta G, \text{ kcal}$
	$P_{\text{H}_2} = 1 \text{ atm}$	$P_{\text{H}_2} = 10 \text{ atm}$
298	+8.3	+9.6
500	+3.4	+5.7
700	-0.6	+2.6
900	-3.8	+0.3

T, °K	$\Delta G, \text{ kcal}$	$\Delta G, \text{ kcal}$
	$P_{\text{H}_2\text{O}, \text{H}_2} = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}, P_{\text{H}_2} = 10 \text{ atm}$
298	-17.9	-15.2
500	-23.4	-22.0
700	-27.1	-26.9
900	-30.8	-30.7

T, °K	$\Delta G, \text{ kcal}$	$\Delta G, \text{ kcal}$
	$P_{\text{H}_2} = 1 \text{ atm}$	$P_{\text{H}_2} = 10 \text{ atm}$
298	-8.0	-8.7
500	-4.0	-5.2
700	0	-1.6
900	+3.9	+1.8

T, °K	$\Delta G, \text{ kcal}$	$\Delta G, \text{ kcal}$
	$P_{\text{H}_2\text{O}} = 1 \text{ atm}$	$P_{\text{H}_2\text{O}} = 100 \text{ atm}$
298	-34.4	-34.5
500	-30.2	-33.4
700	-26.0	-32.2
900	-23.1	-31.3

Table 12.2.2-2

Sodium hydride (NaH)

(Crystal) Mol. Wt. = 23.999

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	.000	.000	INFINITE	1.496	-12.433	-12.433	INFINITE
100	4.182	2.703	15.013	1.515	-12.992	-11.439	25.000
200	6.748	6.483	10.303	.764	-13.289	-9.789	10.696
298	8.698	9.564	9.564	.000	-13.490	-8.023	5.880
300	8.732	9.618	9.564	.016	-13.492	-7.988	5.810
400	10.150	12.343	8.928	.967	-14.233	-6.066	3.325
500	11.270	14.734	10.653	2.040	-14.250	-4.045	1.768
600	12.120	16.889	11.514	3.212	-14.149	-2.011	.733
700	12.860	18.787	12.410	4.461	-13.957	-.003	.001
800	13.400	20.545	13.327	5.775	-13.691	1.373	-.590
900	13.850	22.150	14.219	7.138	-13.374	3.013	-.950
1000	14.200	23.628	15.087	8.541	-13.020	5.015	-1.271
1100	14.500	24.998	15.927	9.977	-12.643	7.470	-1.526
1200	14.740	26.269	16.734	11.439	-12.159	9.967	-1.815
1300	14.920	27.456	17.515	12.923	-11.573	12.470	-2.108
1400	15.069	28.567	18.266	14.422	-10.888	14.945	-2.373
1500	15.180	29.610	18.987	15.934	-10.100	17.380	-2.616

SODIUM HYDRIDE (NaH)

(CRYSTAL)

MOL. WT. = 23.999

$$\Delta H_f^\circ = -12.43 \pm 0.02 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 9.564 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = -13.49 \pm 0.02 \text{ kcal. mole}^{-1}$$

$$T_d = [700]^\circ\text{K.}$$

Heat of Formation.

$\Delta H_f^\circ 298.15$ was obtained from S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958). The value of $\Delta H_f^\circ 298.15$ reported by C. E. Messer, L. G. Pasolino and C. E. Thalmsayer, J. Am. Chem. Soc. **77**, 4524 (1955) was $-13.60 \pm 0.27 \text{ kcal. mole}^{-1}$ which is in excellent agreement with the value given by S. R. Gunn and L. G. Green, loc. cit. The results of the previous investigations were also reviewed by C. E. Messer, et al., loc. cit.

Heat Capacity and Entropy.

C_p below 350°K were measured by E. F. Westrum, et al., University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. C_p above 350°K were estimated by comparison with those for LiH(c). C_p , 59.94 ~ 91.84°K., were also measured by E. V. Sayre and J. J. Beaver, J. Chem. Phys. **18**, 564 (1950). S° at 100°, 200°, and 298.15° were taken from E. F. Westrum, et al., loc. cit., using $S_{10}^\circ(\text{extrap.}) = 0.008 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.

T_d was estimated from the value of ΔF_f° in the table. The value of T_d given by D. M. Benas, J. J. McSherry and E. A. Sullivan, J. Am. Chem. Soc. **77**, 2007 (1955) was 940°K. It was assumed that NaH would behave similarly to LiH and that decomposition pressures would be purity dependent, and this would produce apparently high T_d 's.

Table 12.2.2-2 (continued)

Sodium Hydride (NaH)

(Ideal Gas) Mol. Wt. = 23.999

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	.000	.000	INFINITE	-2.086	30.166	30.166	INFINITE
100	6.91	37.330	51.288	-1.396	30.158	28.213	-61.657
200	7.011	42.165	45.854	-.698	29.967	26.331	-28.772
298	7.241	45.000	45.000	.000	29.700	24.602	-18.053
300	7.246	45.045	45.001	-.013	29.695	24.571	-17.899
400	7.589	47.176	45.280	.755	28.745	22.959	-12.544
500	7.911	48.605	45.844	1.530	28.430	21.950	-9.418
600	8.172	50.372	46.480	2.335	28.164	20.199	-7.357
700	8.377	51.847	47.129	3.163	27.935	18.690	-5.897
800	8.537	52.777	47.768	4.009	27.733	17.612	-4.811
900	8.664	53.790	48.380	4.869	27.547	16.359	-3.972
1000	8.767	54.708	48.967	5.741	27.370	15.125	-3.305
1100	8.853	55.548	49.528	6.622	27.192	13.907	-2.763
1200	8.926	56.321	50.062	7.511	3.774	13.165	-2.398
1300	8.989	57.038	50.572	8.407	3.601	12.647	-2.145
1400	9.044	57.707	51.058	9.309	3.429	12.126	-1.929
1500	9.094	58.332	51.522	10.215	3.255	11.504	-1.739
1600	9.139	58.921	51.966	11.127	3.081	10.779	-1.574
1700	9.181	59.476	52.392	12.043	2.908	10.054	-1.430
1800	9.220	60.002	52.800	12.963	2.732	9.329	-1.304
1900	9.257	60.501	53.192	13.887	2.556	8.599	-1.193
2000	9.292	60.977	53.570	14.815	2.378	7.868	-1.100
2100	9.325	61.431	53.933	15.748	2.200	7.136	-1.023
2200	9.357	61.866	54.284	16.680	2.020	6.404	-0.957
2300	9.388	62.282	54.623	17.617	1.840	5.672	-0.900
2400	9.418	62.683	54.951	18.557	1.658	4.940	-0.851
2500	9.447	63.068	55.268	19.500	1.474	4.208	-0.808
2600	9.475	63.439	55.575	20.446	1.288	3.476	-0.770
2700	9.503	63.797	55.873	21.395	1.103	2.744	-0.736
2800	9.531	64.143	56.162	22.347	0.914	2.012	-0.705
2900	9.558	64.478	56.443	23.301	0.724	1.280	-0.676
3000	9.584	64.802	56.716	24.259	0.532	0.548	-0.648
3100	9.610	65.117	56.982	25.218	0.337	0.000	-0.620
3200	9.636	65.423	57.241	26.181	0.140	0.000	-0.592
3300	9.662	65.719	57.494	27.146	0.138	0.000	-0.564
3400	9.688	66.008	57.740	28.113	0.134	0.000	-0.536
3500	9.713	66.290	57.980	29.083	0.125	0.000	-0.508
3600	9.738	66.563	58.215	30.056	0.111	0.000	-0.480
3700	9.763	66.831	58.444	31.031	0.091	0.000	-0.452
3800	9.788	67.091	58.668	32.008	0.067	0.000	-0.424
3900	9.813	67.346	58.887	32.988	0.034	0.000	-0.396
4000	9.837	67.595	59.102	33.971	0.004	0.000	-0.368
4100	9.862	67.838	59.312	34.956	0.046	0.000	-0.340
4200	9.886	68.076	59.518	35.943	0.088	0.000	-0.312
4300	9.910	68.309	59.720	36.933	0.129	0.000	-0.284
4400	9.935	68.537	59.917	37.925	0.169	0.000	-0.256
4500	9.959	68.760	60.111	38.920	0.207	0.000	-0.228
4600	9.983	68.979	60.302	39.917	0.243	0.000	-0.200
4700	10.007	69.194	60.489	40.916	0.278	0.000	-0.172
4800	10.031	69.405	60.672	41.918	0.312	0.000	-0.144
4900	10.055	69.612	60.853	42.923	0.345	0.000	-0.116
5000	10.078	69.816	61.030	43.929	0.378	0.000	-0.088
5100	10.102	70.016	61.204	44.938	0.410	0.000	-0.060
5200	10.126	70.212	61.376	45.950	0.442	0.000	-0.032
5300	10.150	70.405	61.544	46.963	0.474	0.000	-0.004
5400	10.173	70.595	61.710	47.978	0.506	0.000	0.024
5500	10.197	70.782	61.873	48.998	0.538	0.000	0.052
5600	10.221	70.966	62.034	50.019	0.570	0.000	0.080
5700	10.244	71.147	62.192	51.042	0.602	0.000	0.108
5800	10.268	71.325	62.348	52.068	0.634	0.000	0.136
5900	10.291	71.501	62.502	53.096	0.666	0.000	0.164
6000	10.315	71.674	62.653	54.126	0.698	0.000	0.192

Dec. 31, 1960; Mar. 31, 1963

SODIUM HYDRIDE (NaH)

(IDEAL GAS)

MOL. WT. = 23.999

Ground State Configuration $1\Sigma^+$ $\Delta H_f^0 = 30.2 \pm 4.6 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = 45.0 \text{ cal. deg}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 = 29.7 \pm 4.6 \text{ kcal. mole}^{-1}$ $\omega_e = 1172.2 \text{ cm}^{-1}$ $\omega_e x_e = 19.72 \text{ cm}^{-1}$ $\sigma = 1$ $B_e = 4.9012 \text{ cm}^{-1}$ $d_e = 0.1553 \text{ cm}^{-1}$ Heat of Formation.

ΔH_f^0 298.15 was calculated from $D_0^0 = 2.05 \pm 0.2 \text{ e.v.}$ reported by S. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., 1953.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., 1950.

HNa

HNa

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Table 12.2.2-2 (continued)

Sodium Hydroxide (NaOH)

(Crystal) Mol. Wt. = 39.99717

T, °K	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
0	∞.000	∞.000	INFINITE	-	2.306	-100.815	-100.815	INFINITE
100	6.631	9.719	26.257	-	2.254	-101.620	-98.127	214.456
200	11.850	10.176	16.855	-	1.282	-101.886	-84.501	103.266
298	14.228	10.400	15.400	-	∞.000	-101.900	-90.867	66.807
300	14.260	15.488	15.400	-	∞.026	-101.899	-90.708	66.147
400	19.320	19.772	15.076	-	1.518	-102.453	-87.060	47.567
500	17.983	23.461	17.109	-	3.176	-102.292	-83.230	34.380
600	20.580	29.710	18.618	-	6.655	-100.721	-79.559	28.979
700	20.560	32.879	20.635	-	8.711	-99.611	-76.164	23.760
800	20.560	35.626	22.166	-	10.767	-99.002	-72.856	19.603
900	20.560	38.046	23.798	-	12.823	-98.199	-69.674	16.007
1000	20.560	40.212	25.333	-	14.879	-97.605	-66.458	14.324
1100	20.560	42.172	26.774	-	16.935	-97.228	-63.394	12.587
1200	20.560	43.961	28.135	-	18.991	-119.903	-59.842	10.800
1300	20.560	45.606	29.416	-	21.047	-119.164	-54.867	9.224
1400	20.560	47.130	30.628	-	23.103	-118.394	-49.951	7.798
1500	20.560	48.549	31.776	-	25.159	-117.654	-45.088	6.569
1600	20.560	49.875	32.866	-	27.215	-116.922	-40.274	5.501
1700	20.560	51.122	33.904	-	29.271	-116.197	-35.505	4.584
1800	20.560	52.297	34.893	-	31.327	-115.481	-30.779	3.737
1900	20.560	53.400	35.839	-	33.383	-114.772	-26.093	3.001
2000	20.560	54.463	36.744	-	35.439	-114.072	-21.444	2.343

SODIUM HYDROXIDE (NaOH)

(CRYSTAL)

MOL. WT. = 39.99717

$$\begin{aligned} S_{298.15}^{\circ} &= 15.400 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ T_m &= 585.95^{\circ}\text{K.} \\ T_m &= 592.25^{\circ}\text{K.} \end{aligned}$$

$$\begin{aligned} \Delta H_f^{\circ} &= -100.82 \pm 0.1 \text{ kcal. mole}^{-1} \\ \Delta H_f^{\circ} 298.15 &= -101.90 \pm 0.1 \text{ kcal. mole}^{-1} \\ \Delta H_f^{\circ} &= 1.519 \text{ kcal. mole}^{-1} \\ \Delta H_m^{\circ} &= 1.519 \text{ kcal. mole}^{-1} \\ \Delta H_f^{\circ} 298.15 (\text{to monomer}) &= [51.5] \text{ kcal. mole}^{-1} \\ \Delta H_f^{\circ} 298.15 (\text{to dimer}) &= [49.0] \text{ kcal. mole}^{-1} \end{aligned}$$

Heat of Formation.

The standard enthalpy of formation, $\Delta H_f^{\circ} 298$ (NaOH, c) = -101.90 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of sodium hydroxide (c) and the heat of sodium metal hydrolysis and the appropriate auxiliary data.

M. A. Peshetnikov¹ has measured the heat of solution NaOH(c) = NaOH(400 H₂O) as -10.445 ± 0.015 kcal. mole⁻¹ at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of sodium hydroxide (c) at infinite dilution is -10.555 kcal. mole⁻¹. Also L. E. Murch and W. F. Glauque³ measured calorimetrically the heat of solution of solid samples of NaOH·nH₂O in the range from n = 0.1 to 1.0. When extrapolated to n = 0 and infinite dilution⁴, this result yields the heat of solution of NaOH(c) at infinite dilution, $\Delta H_f^{\circ} 298 = -10.636$ kcal. mole⁻¹, which is in good agreement with the value selected.

The heat of sodium metal hydrolysis, $\Delta H_f^{\circ} 298$, has been measured in the solution calorimeter by the following investigators. $\text{Na(c)} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH(nH}_2\text{O)} + 1/2 \text{H}_2\text{(g)}$ $\Delta H_f^{\circ} 298$

Source	Number of Moles of H ₂ O	$\Delta H_f^{\circ} 298$ kcal. mole ⁻¹	$\Delta H_f^{\circ} 298$ (NaOH(OH ₂ O)) kcal. mole ⁻¹	$\Delta H_f^{\circ} 298$ (NaOH, c) kcal. mole ⁻¹
Gunn et al. ⁵	1000	-44.047 ± 0.008	-112.448	-101.899
Messer et al. ⁴	∞	-44.215 ± 0.20	-112.530	-101.975
Ketchen et al. ⁵	∞	-44.054 ± 0.20	-112.369	-101.814

The values of $\Delta H_f^{\circ} 298$ (NaOH·OH₂O) were calculated from the heats of reaction $\Delta H_f^{\circ} 298$, using the $\Delta H_f^{\circ} 298$ (H₂O, l) = -68.315 kcal. mole⁻¹.⁶ Combination of the selected heat of solution of NaOH(c) at infinite dilution with the heat of formation of NaOH(OH₂O) gives the heat of formation of NaOH(c) in the last column of the table. A weighted average of these three measurements has been taken for the selected heat of formation of sodium hydroxide (c).

The earlier investigations have been reviewed by P. R. Bichowsky and P. D. Rossini⁹, and C. E. Messer et al.⁴, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

L. E. Murch and W. F. Glauque¹¹ have measured low temperature heat capacities of NaOH·0.04014 H₂O and NaOH·0.97776 H₂O from 15° to 320°K. and calculated the values of C_p for the pure phase of NaOH(c). T. B. Douglas and J. L. Dever⁹ have measured the enthalpy changes from 273° to 973°K. in the drop calorimeter and derived the heat capacities. The low temperature and the high temperature heat capacities were joined smoothly by Murch and Glauque, and the smooth values were adopted in the tabulation. Low temperature heat capacities from 80° to 300°K. have also been measured by J. C. R. Kelly and P. E. Snyder⁷, whose data are in good agreement with those reported by Murch and Glauque. M. M. Popov and D. M. Ginzburg¹⁰ have determined the heat capacities of NaOH(c) in the temperature range from 298° to 577°K. from the enthalpy measurements by drop calorimetry. The reported $H_{500}^{\circ} - H_{298}^{\circ} = 5.112$ kcal. mole⁻¹ is in good agreement with the tabulated value.

Transition and Melting Data.

The adopted heat of transition and the transition temperature, and the adopted heat of melting and the melting point were obtained from Douglas and Dever.⁹ Popov and Ginzburg¹⁰ reported the heat of transition $\Delta H_T^{\circ} = 1.950$ kcal. mole⁻¹ at 576.8°K. and the heat of melting $\Delta H_m^{\circ} = 1.629$ kcal. mole⁻¹ at 595.16°K.

Heat of Sublimation.

See NaOH(g) table for details.

Reference:

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HNHO

Table 12.2.2-2 (continued)

Sodium Hydroxide (NaOH)

HNaO

(Liquid)

Mol. Wt. = 39.99717

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0							
100							
200							
298	20.590	17.727	17.727	.000	- 99.998	- 89.659	65.722
300	20.988	17.857	17.727	.039	- 99.984	- 89.595	65.270
400	20.844	23.875	18.549	2.150	- 99.939	- 86.187	67.090
500	20.710	28.911	20.093	4.208	- 99.917	- 82.820	68.201
600	20.570	32.275	21.821	6.272	- 99.702	- 79.579	28.987
700	20.430	35.435	23.547	8.522	- 98.098	- 76.441	23.866
800	20.290	38.154	25.207	10.958	- 97.509	- 73.587	20.049
900	20.150	40.536	26.780	12.980	- 96.940	- 70.406	17.097
1000	20.010	42.651	28.264	14.388	- 96.395	- 67.487	14.749
1100	19.870	44.552	29.659	16.382	- 95.870	- 64.623	12.830
1200	19.730	46.275	30.973	18.362	- 118.030	- 61.944	11.173
1300	19.590	47.849	32.212	20.328	- 117.962	- 58.600	9.315
1400	19.450	49.295	33.381	22.280	- 117.916	- 51.903	8.102
1500	19.310	50.632	34.487	24.218	- 116.693	- 47.252	6.885
1600	19.170	51.874	35.534	26.142	- 116.094	- 42.643	5.825
1700	19.030	53.032	36.531	28.052	- 115.514	- 38.069	4.894
1800	18.910	54.116	37.478	29.949	- 114.957	- 33.530	4.071
1900	18.795	55.136	38.381	31.834	- 114.419	- 29.021	3.338
2000	18.690	56.097	39.243	33.708	- 113.901	- 24.541	2.682
2100	18.595	57.007	40.067	35.572	- 113.398	- 20.087	2.090
2200	18.515	57.870	40.857	37.428	- 112.913	- 15.654	1.555
2300	18.447	58.691	41.619	39.276	- 112.440	- 11.244	1.068
2400	18.393	59.475	42.343	41.118	- 111.982	- 6.851	.624
2500	18.346	60.225	43.043	42.955	- 111.535	- 2.484	.217
2600	18.310	60.944	43.718	44.787	- 111.100	1.872	-.157
2700	18.287	61.634	44.369	46.617	- 110.674	6.209	-.503
2800	18.265	62.299	44.907	48.445	- 110.259	10.527	-.822
2900	18.250	62.945	45.435	50.270	- 109.851	14.837	-1.118
3000	18.238	63.558	45.953	52.095	- 109.453	19.130	-1.594

Dec. 31, 1960; Mar. 31, 1966

SODIUM HYDROXIDE (NaOH)

(LIQUID)

MOL. WT. = 39.99717

$$S_{298.15}^{\circ} = 17.727 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 592.25^{\circ}\text{K.}$$

$$T_b(\text{monomeric gas}) = 1662.7^{\circ}\text{K.}$$

$$\Delta H_f^{\circ} 298.15 = -99.998 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 1.519 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ}(\text{to monomer}) = 37.9 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The heat of formation of NaOH(l) at 298°K. was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{592.25}^{\circ}$ - $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacities in the temperature range from 592.3° to 1000°K. were obtained from the enthalpy measurements of sodium hydroxide (l) in the drop calorimeter by T. B. Douglas and J. L. Dever¹. The heat capacities below the melting point and above 1000°K. were extrapolated from the selected heat capacity curve.

Douglas and Dever¹ have also compared their heat capacity values with those from W. D. Powers and G. C. Bialock² who have applied the same drop method to determine the heat capacities of NaOH(l). Both results are in reasonable agreement. M. M. Popov and G. M. Ginzburg³ applying the same technique obtained different values of heat capacity. The smoothed enthalpy data reported by Ginzburg⁴ are 200 to 500 cal. mole⁻¹ smaller than the tabulated values at the temperature range from 700° to 1000°K.

The entropy ($S_{298}^{\circ} = 17.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See NaOH(c) table for details.

Vaporization Data.

The boiling point 1662.7°K. was calculated as the temperature at which the free energies of formation (ΔF_f°) for both NaOH(l) and NaOH(g) are equal. The difference in the heats of formation (ΔH_f°) of NaOH(l) and NaOH(g) at the boiling point is the heat of vaporization. If $\text{Na}_2(\text{OH})_2(\text{g})$ is also considered as a minor component in the vapor mixture (approximately 4% of total vapor pressure at the boiling point) the calculated boiling point is 1653°K. (see NaOH(g) table for details).

H. von Wartenberg and F. Albrecht, Z. Elektrochem. **27**, 182 (1921), have studied the vapor pressures of liquid NaOH and reported the boiling point as 1661°K.

References:

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HNaO

Table 12.2.2-2 (continued)

Sodium Hydroxide (NaOH)

(Ideal Gas) Mol. Wt. = 39.99717

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	.000	.000	INFINITE	-2.350	-49.359	-49.359	INFINITE
100	8.095	46.936	64.439	-1.752	-49.618	-50.447	110.292
200	8.888	52.700	57.406	-.903	-49.907	-51.135	55.678
298	9.486	56.456	56.456	.000	-50.400	-51.608	37.636
300	9.496	56.515	56.456	.018	-50.407	-51.615	37.602
400	9.986	59.316	56.835	.992	-51.479	-51.904	28.350
500	10.391	61.589	57.565	2.012	-51.916	-51.958	22.711
600	10.722	63.514	58.400	3.068	-52.306	-51.929	18.015
700	10.998	65.188	59.253	4.154	-52.660	-51.837	14.184
800	11.235	66.672	60.089	5.266	-53.003	-51.696	11.123
900	11.440	68.008	60.804	6.400	-53.322	-51.513	8.500
1000	11.616	69.224	61.409	7.555	-53.620	-51.294	6.1210
1100	11.827	70.343	62.007	8.729	-53.934	-51.048	4.0162
1200	12.065	71.370	62.512	9.920	-54.274	-50.774	2.1653
1300	12.319	72.345	63.084	11.128	-54.646	-50.487	0.5777
1400	12.590	73.251	64.430	12.350	-55.048	-50.174	0.1460
1500	12.818	74.103	65.047	13.585	-55.485	-49.843	0.0337
1600	12.995	74.909	65.638	14.831	-55.955	-49.510	0.0028
1700	13.142	75.672	66.206	16.081	-56.456	-49.180	0.0003
1800	13.278	76.397	66.752	17.341	-56.987	-48.853	0.0000
1900	13.405	77.088	67.278	18.610	-57.548	-48.537	0.0000
2000	13.524	77.748	67.785	19.896	-58.139	-48.232	0.0000
2100	13.636	78.380	68.275	21.200	-58.759	-47.937	0.0000
2200	13.741	78.985	68.748	22.521	-59.400	-47.650	0.0000
2300	13.840	79.566	69.204	23.868	-60.062	-47.370	0.0000
2400	13.934	80.124	69.649	25.240	-60.746	-47.100	0.0000
2500	14.023	80.662	70.079	26.636	-61.453	-46.839	0.0000
2600	14.107	81.181	70.494	28.051	-62.182	-46.587	0.0000
2700	14.186	81.682	70.901	29.486	-62.932	-46.344	0.0000
2800	14.261	82.166	71.295	30.940	-63.702	-46.109	0.0000
2900	14.332	82.634	71.678	32.411	-64.492	-45.882	0.0000
3000	14.399	83.087	72.051	33.900	-65.302	-45.664	0.0000
3100	14.462	83.527	72.414	35.401	-66.132	-45.455	0.0000
3200	14.521	83.953	72.768	36.914	-66.982	-45.254	0.0000
3300	14.577	84.366	73.113	38.440	-67.852	-45.061	0.0000
3400	14.630	84.770	73.450	39.988	-68.742	-44.874	0.0000
3500	14.679	85.162	73.779	41.550	-69.652	-44.694	0.0000
3600	14.725	85.543	74.101	43.121	-70.582	-44.520	0.0000
3700	14.768	85.916	74.415	44.700	-71.532	-44.352	0.0000
3800	14.809	86.279	74.722	46.288	-72.502	-44.189	0.0000
3900	14.848	86.628	75.025	47.890	-73.492	-44.032	0.0000
4000	14.884	86.972	75.317	49.500	-74.502	-43.880	0.0000
4100	14.918	87.308	75.604	51.121	-75.532	-43.732	0.0000
4200	14.950	87.637	75.888	52.760	-76.582	-43.589	0.0000
4300	14.980	87.957	76.165	54.410	-77.652	-43.450	0.0000
4400	15.009	88.271	76.437	56.070	-78.742	-43.314	0.0000
4500	15.036	88.578	76.703	57.750	-79.852	-43.182	0.0000
4600	15.062	88.878	76.965	59.450	-80.982	-43.054	0.0000
4700	15.087	89.173	77.221	61.170	-82.132	-42.930	0.0000
4800	15.111	89.461	77.473	62.910	-83.302	-42.809	0.0000
4900	15.134	89.743	77.721	64.670	-84.492	-42.692	0.0000
5000	15.157	90.020	77.964	66.450	-85.702	-42.579	0.0000
5100	15.179	90.291	78.203	68.260	-86.932	-42.469	0.0000
5200	15.200	90.558	78.438	70.090	-88.182	-42.362	0.0000
5300	15.220	90.819	78.669	71.940	-89.452	-42.258	0.0000
5400	15.239	91.076	78.897	73.810	-90.742	-42.157	0.0000
5500	15.257	91.328	79.120	75.700	-92.052	-42.057	0.0000
5600	15.274	91.576	79.341	77.610	-93.382	-41.959	0.0000
5700	15.290	91.819	79.557	79.540	-94.732	-41.864	0.0000
5800	15.305	92.058	79.771	81.490	-96.102	-41.772	0.0000
5900	15.319	92.293	79.981	83.460	-97.492	-41.682	0.0000
6000	15.332	92.525	80.188	85.450	-98.902	-41.594	0.0000

Dec. 31, 1960; Mar. 31, 1966

SODIUM HYDROXIDE (NaOH)

(IDEAL GAS)

MOL. WT. = 39.99717

Point Group C_sS°_{298.15} = [56.5] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH°_f 0 = -69.4 ± 5 kcal. mole⁻¹ΔH°_f 298.15 = -50.4 ± 5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

437 (1)

[1300](1)

[3700](1)

Bond Distance: Na-O = [1.97] Å O-H = [0.96] Å

Bond Angle: Na-O-H = [110°]

Product of the Moments of Inertia: I_AI_BI_C = [5.3062] X 10⁻¹¹ g.³ cm.³

σ = 1

Heat of Formation.

R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 28, 454 (1958), have found in their mass-spectrometric studies that the NaOH(l) vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. They have also calculated by the slope method the heat of dimerization, ΔH°_d 600 = -54 ± 5 kcal. mole⁻¹, for 2NaOH(g) = Na₂(OH)₂(g) and the heat of sublimation, ΔH°_s 298 = 46.3 ± 3 kcal. mole⁻¹, for NaOH(c) = NaOH(g). The second law values were determined using ion intensity ratios, however, a third law calculation using a single data point converted by the authors to absolute pressure (J. Phys. Chem. 62, 468 (1958)) yields ΔH°_s 298 = -51.8 kcal. mole⁻¹, ΔH°_d 298 (to monomer) = 49.5 kcal. mole⁻¹ and ΔH°_s 298 (to dimer) = 41.1 kcal. mole⁻¹ which are in agreement within the limit of uncertainty. Later, Porter and Schoonmaker, J. Chem. Phys. 31, 630 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container, and the uncertainty in the heat of sublimation might be ±5 kcal. mole⁻¹, but the heat of dimerization should not be seriously affected because it was calculated from slopes of both species. In order to have good agreement between the calculated total pressures of monomer and dimer of sodium hydroxide (g) and the observed vapor pressures by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), the heat of dimerization and the heat of sublimation have been so chosen as ΔH°_d 298 = -54 kcal. mole⁻¹ and ΔH°_s 298 (to monomer) = 51.5 kcal. mole⁻¹, respectively, which are still within the limit of Porter and Schoonmaker's data. The calculated boiling point is 1653°K. which is in good agreement with 1661 ± 20°K. reported by Wartenberg and Albrecht, loc. cit. The heats of formation were calculated from the selected heat of dimerization and heat of sublimation as ΔH°_f 298 (NaOH, g) = -50.4 kcal. mole⁻¹ and ΔH°_f 298 (Na₂(OH)₂, g) = -154.8 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bent molecular configuration with the bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. P. Porter, J. Chem. Phys. 29, 991 (1958). The bond distance O-H was estimated from that in H₂O(g). The bond distance Na-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Na-F(g) (1.92595 Å) which has been accurately measured by R. K. Bauer and H. Lew, Can. J. Phys. 41, 1481 (1963). The Na-O stretching frequency was obtained from L. H. Spiner and J. L. Margrave, Spectrochim. Acta 12, 244 (1956), in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rigid convergence to a constant as a heavier atom is attached. The three principal moments of inertia are I_A = [0.1252] X 10⁻³⁹, I_B = [6.449] X 10⁻³⁹ and I_C = [8.5742] X 10⁻³⁹ g. cm.²

HNaO

12.2.2-10

6/3/74

Table 12.2.2-2 (continued)

Hydrogen (H_2)

(Ideal Gas - Reference State) Mol. Wt. = 2.016

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°	Log K _p
0	5.313	24.367	17.034	-2.024	.000	.000
100	5.383	24.387	17.034	-2.024	.000	.000
200	5.516	24.570	11.831	.662	.000	.000
298	5.692	11.208	11.208	.000	.000	.000
300	5.694	11.251	11.208	.013	.000	.000
400	5.975	13.247	11.480	.707	.000	.000
500	6.193	14.406	11.995	1.408	.000	.000
600	6.364	16.082	12.573	2.104	.000	.000
700	6.516	17.185	13.153	2.808	.000	.000
800	6.647	18.107	13.715	3.514	.000	.000
900	6.764	18.946	14.250	4.226	.000	.000
1000	6.871	19.702	14.759	4.944	.000	.000
1100	6.969	20.394	15.240	5.670	.000	.000
1200	7.059	21.033	15.698	6.404	.000	.000
1300	7.141	21.628	16.130	7.144	.000	.000
1400	7.216	22.187	16.543	7.902	.000	.000
1500	7.284	22.716	16.937	8.668	.000	.000
1600	7.343	23.217	17.314	9.444	.000	.000
1700	7.391	23.695	17.675	10.233	.000	.000
1800	7.430	24.150	18.022	11.030	.000	.000
1900	7.460	24.586	18.358	11.834	.000	.000
2000	7.485	25.004	18.678	12.651	.000	.000
2100	7.506	25.404	18.989	13.475	.000	.000
2200	7.523	25.793	19.290	14.307	.000	.000
2300	7.536	26.166	19.581	15.144	.000	.000
2400	7.546	26.527	19.863	15.983	.000	.000
2500	7.553	26.875	20.136	16.828	.000	.000
2600	7.559	27.213	20.402	17.678	.000	.000
2700	7.560	27.540	20.660	18.535	.000	.000
2800	7.557	27.857	20.912	19.400	.000	.000
2900	7.551	28.166	21.157	20.276	.000	.000
3000	7.544	28.465	21.395	21.160	.000	.000
3100	7.533	28.756	21.626	22.058	.000	.000
3200	7.519	29.040	21.855	22.962	.000	.000
3300	7.502	29.317	22.077	23.881	.000	.000
3400	7.481	29.586	22.294	24.794	.000	.000
3500	7.456	29.850	22.506	25.703	.000	.000
3600	7.428	30.107	22.714	26.616	.000	.000
3700	7.397	30.359	22.917	27.535	.000	.000
3800	7.362	30.605	23.116	28.457	.000	.000
3900	7.324	30.845	23.311	29.385	.000	.000
4000	7.282	31.082	23.502	30.317	.000	.000
4100	7.236	31.313	23.690	31.253	.000	.000
4200	7.187	31.540	23.874	32.194	.000	.000
4300	7.135	31.762	24.055	33.139	.000	.000
4400	7.080	31.980	24.233	34.088	.000	.000
4500	7.025	32.194	24.407	35.042	.000	.000
4600	6.970	32.405	24.579	35.999	.000	.000
4700	6.914	32.614	24.748	36.961	.000	.000
4800	6.857	32.815	24.914	37.926	.000	.000
4900	6.799	33.015	25.077	38.894	.000	.000
5000	6.740	33.211	25.238	39.864	.000	.000
5100	6.680	33.405	25.394	40.835	.000	.000
5200	6.619	33.595	25.547	41.825	.000	.000
5300	6.557	33.783	25.703	42.809	.000	.000
5400	6.495	33.967	25.857	43.797	.000	.000
5500	6.431	34.149	26.008	44.788	.000	.000
5600	6.365	34.328	26.153	45.783	.000	.000
5700	6.298	34.505	26.298	46.781	.000	.000
5800	6.230	34.679	26.441	47.783	.000	.000
5900	6.161	34.851	26.582	48.788	.000	.000
6000	6.091	35.022	26.721	49.796	.000	.000

March 31, 1961

Hydrogen (H_2)

(Ideal Gas - Reference State)

Mol. Wt. = 2.016

$$B_0^\circ = 105.286 \pm 0.15 \text{ kcal. mole}^{-1}$$

Ground State Configuration $1\sigma_g^2$

$$\Delta H_f^\circ 298.15 = 0$$

$$S_{298.15}^\circ = 31.21 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\omega_e = 4405.3 \text{ cm.}^{-1}$$

$$B_e = 60.846 \text{ cm.}^{-1}$$

$$\omega_e x_e = 125.325 \text{ cm.}^{-1}$$

$$\alpha_e = 3.0864 \text{ cm.}^{-1}$$

$$D_e = 0.04644 \text{ cm.}^{-1}$$

$$r_e = 0.7417 \text{ \AA}$$

$$\rho = 2$$

Heat Capacities and Entropy

H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Nat. Bur. Standards* **41**, 379 (1946), calculated the thermodynamic functions by a method of direct summation for normal H_2 (75% ortho and 25% para) using spectroscopic constants derived from an analysis of U. V. band spectra. These constants are more preferable for use in a summation method than those obtained by G. Herzberg, *Can. J. Res. A28*, 144 (1950) from the measured quadrupole transitions in the ground state which accurately describe the lower vibrational levels only. In any case the difference in the functions resulting from the two sets of data are less than 0.2%.

Since the entropies of Woolley et al. contain a contribution from nuclear spin, a correction of $-R \ln 4$ was applied. However, the entropy due to the mixing of ortho and para hydrogen which is a consequence of nuclear spin is included in the total entropy since this results in correct equilibrium constants based upon third law calculations. Differences in the values of R and c_p were found to have a negligible effect upon the functions.

Similar calculations with a different method of estimating the higher rotational levels by M. L. Johnston, L. G. Savedoff, and J. Belzer, Technical Report No. 2, Project R.F-316, Ohio State Univ. (1949), result in functions that are 0.5% lower above 5000°K.

For details concerning the dissociation energy see the monatomic hydrogen sheet.

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12.2.2-11

 H_2

Table 12.2.2-2 (continued)

Water (H_2O)

(Ideal Gas) Mol. Wt. = 18.016

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	0.000	INFINITE	2.367	-57.103	-57.103	INFINITE
100	7.981	36.398	52.302	1.501	-57.433	-58.359	12.500
200	17.997	51.916	41.831	7.781	-57.577	-55.635	40.792
298	26.025	55.106	45.106	10.000	-57.758	-54.438	40.528
300	26.027	55.155	45.106	10.015	-57.803	-54.417	39.786
400	26.196	57.484	45.422	18.25	-58.042	-53.519	29.240
500	26.415	59.334	46.026	1.654	-58.277	-52.361	22.886
600	26.476	60.891	46.710	2.509	-58.500	-51.156	18.633
700	26.496	62.249	47.406	3.390	-58.710	-49.915	15.303
800	26.486	63.464	48.089	4.300	-58.905	-48.646	13.289
900	26.567	64.570	48.749	5.240	-59.084	-47.352	11.499
1000	26.851	65.592	49.382	6.200	-59.246	-46.040	10.062
1100	19.152	56.545	49.991	7.210	-59.391	-44.712	8.883
1200	19.444	57.441	50.575	8.240	-59.519	-43.371	7.899
1300	19.723	58.288	51.136	9.298	-59.634	-42.022	7.064
1400	19.987	59.082	51.675	10.384	-59.734	-40.663	6.367
1500	11.233	59.859	52.196	11.495	-59.824	-39.297	5.725
1600	11.442	60.591	52.698	12.630	-59.906	-37.927	5.180
1700	11.624	61.283	53.183	13.787	-59.977	-36.549	4.699
1800	11.809	61.965	53.652	14.964	-60.047	-35.170	4.270
1900	12.004	62.612	54.107	16.160	-60.099	-33.786	3.886
2000	12.214	63.234	54.548	17.373	-60.150	-32.401	3.540
2100	12.346	63.834	54.976	18.602	-60.198	-31.012	3.227
2200	12.505	64.412	55.392	19.846	-60.242	-29.621	2.942
2300	12.634	64.971	55.796	21.103	-60.282	-28.229	2.682
2400	12.753	65.511	56.190	22.372	-60.321	-26.832	2.443
2500	12.863	66.034	56.573	23.653	-60.359	-25.439	2.224
2600	12.965	66.541	56.947	24.945	-60.393	-24.040	2.021
2700	13.059	67.032	57.311	26.246	-60.428	-22.641	1.833
2800	13.146	67.506	57.667	27.556	-60.462	-21.242	1.658
2900	13.228	67.971	58.014	28.875	-60.494	-19.838	1.495
3000	13.304	68.421	58.354	30.201	-60.520	-18.430	1.343
3100	13.374	68.856	58.685	31.535	-60.542	-17.034	1.201
3200	13.441	69.284	59.010	32.876	-60.598	-15.630	1.067
3300	13.503	69.698	59.328	34.223	-60.631	-14.223	0.942
3400	13.562	70.102	59.639	35.577	-60.664	-12.818	0.824
3500	13.617	70.496	59.943	36.936	-60.703	-11.409	0.712
3600	13.669	70.881	60.242	38.300	-60.741	-10.000	0.607
3700	13.719	71.256	60.534	39.669	-60.782	-8.589	0.507
3800	13.768	71.622	60.821	41.043	-60.822	-7.177	0.413
3900	13.809	71.980	61.103	42.422	-60.865	-5.766	0.323
4000	13.840	72.331	61.379	43.805	-60.910	-4.353	0.238
4100	13.869	72.673	61.651	45.192	-60.957	-2.938	0.157
4200	13.927	73.008	61.917	46.583	-61.006	-1.522	0.079
4300	13.983	73.336	62.179	47.977	-61.056	-0.105	0.005
4400	14.037	73.658	62.436	49.375	-61.109	1.311	-0.065
4500	14.086	73.973	62.689	50.777	-61.164	2.729	-0.133
4600	14.081	74.281	62.938	52.181	-61.220	4.154	-0.197
4700	14.081	74.584	63.182	53.589	-61.279	5.576	-0.259
4800	14.120	74.881	63.423	55.000	-61.339	6.998	-0.319
4900	14.144	75.172	63.660	56.413	-61.401	8.422	-0.376
5000	14.174	75.459	63.893	57.829	-61.465	9.844	-0.430
5100	14.201	75.740	64.122	59.248	-61.532	11.275	-0.483
5200	14.228	76.016	64.348	60.669	-61.600	12.700	-0.534
5300	14.254	76.287	64.571	62.093	-61.669	14.135	-0.583
5400	14.279	76.553	64.791	63.520	-61.741	15.560	-0.630
5500	14.303	76.816	65.007	64.949	-61.813	16.995	-0.675
5600	14.329	77.074	65.220	66.381	-61.889	18.426	-0.719
5700	14.351	77.327	65.430	67.815	-61.965	19.862	-0.762
5800	14.375	77.577	65.637	69.253	-62.043	21.299	-0.803
5900	14.396	77.823	65.842	70.690	-62.122	22.736	-0.842
6000	14.422	78.065	66.044	72.131	-62.203	24.174	-0.880

March 31, 1961

WATER (H_2O)

(IDEAL GAS)

MOL. WT. = 18.016

$$\Delta H_f^\circ = -57.103 \text{ kcal. mole}^{-1}$$

Point Group C_{2v}

$$\Delta H_f^\circ 298.15 = -57.7979 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 45.106 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Vibrational Levels and Multiplicities(g), cm.⁻¹

3657.05 (1)

1594.59 (1)

3755.78 (1)

Bond Length and Angle O-H distance = 0.9584 Å H-O-H angle = 104.45° C_{2v}Product of Moments of Inertia $I_A I_B I_C = 5.7656 \times 10^{-120} \text{ g.}^3 \text{ cm.}^6$ Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. **22**, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, H. M. Classen and J. M. Shaw, J. Research Natl. Bur. Standards **49**, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatz, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p , S , and $H^\circ - H_0^\circ$ at $T = 298.15^\circ\text{K.}$ was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards **55**, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.

 H_2O

12.2.2-12

 H_2O

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Table 12.2.2-2 (continued)

Sodium (Na)

(Liquid) At. Wt. = 22.991

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100							
200							
298	7.817	13.827	13.827	.000	.575	.119	.067
300	7.812	13.875	13.827	.918	.577	.117	.085
400	7.531	16.583	16.750	7.61	.000	.000	.000
500	7.302	17.738	16.693	1.522	.000	.000	.000
600	7.124	19.053	15.314	2.243	.000	.000	.000
700	6.996	20.141	15.928	2.949	.000	.000	.000
800	6.918	21.089	14.514	3.644	.000	.000	.000
900	6.892	21.882	17.066	4.334	.000	.000	.000
1000	6.918	22.609	17.585	5.024	.000	.000	.000
1100	6.993	23.272	18.072	5.719	.001	.000	.000
1200	7.120	23.885	18.531	6.425	21.255	.460	.084
1300	7.293	24.442	18.966	7.145	21.012	2.426	.406
1400	7.493	24.909	19.378	7.884	22.770	4.373	.683
1500	7.693	25.533	19.771	8.644	22.507	6.303	.918
1600	7.893	26.036	20.147	9.423	22.225	8.215	1.122
1700	8.093	26.521	20.506	10.222	21.922	10.109	1.299
1800	8.293	26.989	20.855	11.041	21.600	11.983	1.455
1900	8.493	27.443	21.190	11.881	21.257	13.840	1.592
2000	8.693	27.893	21.513	12.740	20.899	15.677	1.713

June 30, 1962

Na

SODIUM (Na)

(LIQUID)

AT. WT. = 22.991

$$\Delta H^\circ_f 298.15 = 0.575 \text{ kcal. mole}^{-1}$$

$$T_m = 370.98 \pm 0.02^\circ\text{K}$$

$$T_b = 1156^\circ\text{K (Equilibrium mixture)}$$

$$\Delta H_v 1176.9 = 23.285 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 13.827 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m = 0.622 \text{ kcal. mole}^{-1}$$

$$T_b \text{ (Monatomic gas)} = 1176.9^\circ\text{K}$$

Heat of Formation.

Obtained from the heat of fusion by adding $H_{370.98} - H_{298.15}$ for the solid and subtracting $H_{370.98} - H_{298.15}$ for the liquid.

Heat Capacity.

The heat capacity data of T. B. Douglas, A. F. Bell, D. C. Ginnings and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952) were used and were extrapolated below T_m and above 1175°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K .

Vaporization.

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1156°K . The vapor pressure of the monatomic gas reaches 1 atm. at 1176.9°K and the heat of vaporization to monatomic gas is $23.285 \text{ kcal. mole}^{-1}$ [See Na(crystal)].

Na

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Table 12.2.2-2 (continued)

Sodium, Monatomic (Na)

(Ideal Gas) At. Wt. = 22.991

Na

T, °K	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	.000	.000	INFINITE	1.461	25.815	25.815	INFINITE
100	4.968	31.266	41.131	.000	25.822	23.432	51.208
200	4.968	34.730	37.168	.000	25.981	20.960	22.838
298	4.968	36.716	34.716	.000	25.755	18.475	11.542
300	4.968	36.745	34.714	.009	25.752	18.431	13.426
400	4.968	38.174	34.909	.504	24.905	16.070	8.780
500	4.968	39.282	37.277	1.001	24.461	13.890	6.071
600	4.968	40.186	37.489	1.500	24.437	11.757	4.282
700	4.968	40.956	38.182	1.996	24.227	9.460	3.016
800	4.968	41.617	38.501	2.493	24.029	7.593	2.074
900	4.968	42.203	38.880	2.990	23.836	6.350	1.348
1000	4.968	42.726	39.239	3.487	23.643	5.329	.771
1100	4.968	43.200	39.578	3.984	23.448	4.526	.363
1200	4.968	43.632	40.000	4.481	23.253	3.900	.000
1300	4.968	44.030	40.201	4.977	.000	.000	.000
1400	4.968	44.398	40.488	5.474	.000	.000	.000
1500	4.968	44.740	40.760	5.971	.000	.000	.000
1600	4.968	45.061	41.019	6.468	.000	.000	.000
1700	4.968	45.362	41.265	6.965	.000	.000	.000
1800	4.970	45.644	41.501	7.462	.000	.000	.000
1900	4.971	45.915	41.726	7.959	.000	.000	.000
2000	4.973	46.170	41.942	8.456	.000	.000	.000
2100	4.975	46.413	42.149	8.953	.000	.000	.000
2200	4.977	46.644	42.346	9.451	.000	.000	.000
2300	4.980	46.864	42.534	9.948	.000	.000	.000
2400	4.982	47.078	42.725	10.446	.000	.000	.000
2500	4.985	47.282	42.903	10.944	.000	.000	.000
2600	5.013	47.476	43.075	11.442	.000	.000	.000
2700	5.027	47.660	43.242	11.940	.000	.000	.000
2800	5.044	47.831	43.403	12.438	.000	.000	.000
2900	5.065	48.028	43.560	12.936	.000	.000	.000
3000	5.089	48.200	43.711	13.437	.000	.000	.000
3100	5.116	48.360	43.859	13.937	.000	.000	.000
3200	5.148	48.511	44.002	14.430	.000	.000	.000
3300	5.184	48.649	44.142	14.927	.000	.000	.000
3400	5.225	48.785	44.278	15.427	.000	.000	.000
3500	5.272	48.927	44.411	15.929	.000	.000	.000
3600	5.324	49.106	44.540	16.432	.000	.000	.000
3700	5.383	49.293	44.667	16.937	.000	.000	.000
3800	5.449	49.487	44.790	17.446	.000	.000	.000
3900	5.522	49.680	44.911	17.957	.000	.000	.000
4000	5.604	49.871	45.030	18.471	.000	.000	.000
4100	5.694	49.860	45.146	18.989	.000	.000	.000
4200	5.794	49.929	45.260	19.503	.000	.000	.000
4300	5.913	50.136	45.372	20.026	.000	.000	.000
4400	6.043	50.376	45.482	20.550	.000	.000	.000
4500	6.182	50.611	45.590	21.077	.000	.000	.000
4600	6.339	50.849	45.696	21.607	.000	.000	.000
4700	6.513	50.887	45.801	22.140	.000	.000	.000
4800	6.705	50.826	45.904	22.676	.000	.000	.000
4900	6.915	50.666	46.006	23.217	.000	.000	.000
5000	7.147	51.106	46.106	23.764	.000	.000	.000
5100	7.399	51.252	46.206	24.317	.000	.000	.000
5200	7.676	51.399	46.306	24.876	.000	.000	.000
5300	7.972	51.546	46.402	25.442	.000	.000	.000
5400	8.294	51.700	46.498	26.016	.000	.000	.000
5500	8.639	51.855	46.594	26.598	.000	.000	.000
5600	9.009	52.014	46.690	27.184	.000	.000	.000
5700	9.402	52.177	46.785	27.775	.000	.000	.000
5800	9.818	52.344	46.879	28.371	.000	.000	.000
5900	10.256	52.515	46.973	28.973	.000	.000	.000
6000	10.716	52.692	47.067	29.584	.000	.000	.000

June 30, 1962

SODIUM, MONATOMIC (Na)

(IDEAL GAS)

AT. WT. = 22.991

$$\Delta H^\circ_{f, 298.15} = 25.815 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_{f, 298.15} = 25.755 \text{ kcal. mole}^{-1}$$

Ground State Configuration $2s_{1/2}$

$$S^\circ_{298.15} = 36.714 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Multiplicities					
E_1 cm. ⁻¹	g_1	E_2 cm. ⁻¹	g_2	E_3 cm. ⁻¹	g_3
0	2	34,549	10	38,012	2
16,856	2	34,569	14	38,399	46
16,973	4	35,042	6	38,541	2
25,740	2	36,373	2	39,230	34
29,173	10	37,037	10	40,700	94
30,267	2	37,058	14	40,738	100
30,273	4	37,060	18	41,330	258
33,201	2	37,297	6		

Heat of Formation.

Same as the heat of sublimation to the monatomic species; see notes on Na(crystal)

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 467," U. S. Government Printing Office, Washington (1949) p. 89-91. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

12.2.2-14

Na

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Table 12.2.2-2 (continued)

Sodium Dioxide (NaO_2)

(Crystal) Mol. Wt. = 54.991

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	.050	.000	141.415E	4.384	63.070	63.070	INFINITE
100	14.800	7.310	44.380	1.627	61.443	59.654	130.367
200	11.750	18.700	28.385	1.631	62.917	55.425	60.507
298	11.242	27.700	27.700	.000	62.300	52.262	38.322
300	11.240	27.801	27.700	.032	62.293	52.219	38.040
400	10.230	32.905	24.389	1.804	62.574	48.865	26.697
500	10.210	37.078	20.721	3.674	62.174	45.481	19.879
600	20.190	40.667	11.253	5.448	61.680	42.187	15.366
700	21.147	43.852	32.824	7.716	61.096	38.985	12.171
800	22.140	46.782	34.391	9.481	60.828	35.871	9.799
900	23.121	49.407	35.913	12.145	59.864	32.846	7.976
1000	24.170	51.894	37.388	14.506	58.820	29.910	6.536
1100	25.078	54.230	38.814	16.964	57.697	27.065	5.377
1200	26.045	56.462	40.193	19.521	56.128	23.888	4.343
1300	27.011	58.588	41.526	22.176	54.827	19.210	3.229
1400	28.008	60.621	42.818	24.927	53.437	14.076	2.201
1500	29.040	62.569	44.071	27.777	51.955	10.244	1.493
1600	29.957	64.440	45.288	30.724	50.382	5.914	.809
1700	30.935	66.339	46.472	33.768	48.716	1.084	.217
1800	31.913	68.132	47.626	36.911	46.959	2.443	-.207
1900	32.891	69.863	48.751	40.151	45.111	6.472	-.744
2000	33.870	71.595	49.851	43.489	43.171	10.398	-1.136

June 30, 1963

 NaO_2 SODIUM DIOXIDE (NaO_2)

(CRYSTAL)

MOL. WT. = 54.991

$\Delta H^\circ_f 0 = -63.1 \pm 0.7 \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = 27.7 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 196.5^\circ\text{K.}$
 $T_{t1} = 223.5^\circ\text{K.}$
 $T_m = 825^\circ \pm 10^\circ\text{K.}$

$\Delta H^\circ_f 298.15 = -62.3 \pm 0.7 \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_{t1} = 350 \text{ cal. mole}^{-1}$
 $\Delta H^\circ_{t2} = 570 \text{ cal. mole}^{-1}$
 $\Delta H^\circ_m = \text{Unknown}$

Heat of Formation.

$\Delta H^\circ_f 298.15$ was obtained from National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. P. W. Gilles and J. L. Margrave, J. Phys. Chem. **60**, 1353 (1956) measured the heat of decomposition of $\text{NaO}_2(c)$ in H_2O , yielding $\Delta H^\circ_f 298.15 = -62.1 \pm 0.7 \text{ kcal. mole}^{-1}$. From the original experimental data by R. de Forcrand, Compt. rend., **127**, 514 (1898); **158**, 843, 991 (1914), the value of $\Delta H^\circ_f 298.15$ was recalculated to be $-65.0 \text{ kcal. mole}^{-1}$ by P. W. Gilles and J. L. Margrave, loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, $52.13^\circ \sim 296.46^\circ\text{K.}$, were measured by S. S. Todd, J. Am. Chem. Soc., **75**, 1229 (1953). The heat capacities above 298.15°K. were estimated by comparison with those for $\text{Na}_2\text{O}(c)$. $S^\circ_{298.15}$ was given by S. S. Todd, loc. cit., using $S^\circ_{51}(\text{extrap.}) = 2.25 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_{t1} , T_{t2} , ΔH°_{t1} and ΔH°_{t2} were calculated from the data reported by S. S. Todd, loc. cit.

Temperature of Melting.

The melting temperature was obtained from J. L. Margrave, private communication, May 21, 1963.

 Na_2O

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12.2.2-15

Table 12.2.2-2 (continued)

Sodium, Diatomic (Na_2)

(Ideal Gas) Mol. Wt. = 45.982

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	.000	.000	infinit	2.465	33.467	33.467	infinit
100	.0102	45.484	62.848	1.738	33.576	30.166	65.924
200	.016	51.403	55.810	.873	33.285	24.868	29.358
298	.023	54.994	54.994	.000	32.670	23.807	17.450
300	.024	55.050	54.994	.017	32.683	23.752	17.302
400	.033	57.400	55.347	.917	31.075	20.088	11.412
500	.041	59.485	56.015	1.825	30.501	18.409	8.046
600	.049	61.328	56.766	2.737	29.971	16.041	5.043
700	.055	62.742	57.522	3.654	29.476	13.757	4.295
800	.061	63.973	58.253	4.576	29.008	11.545	3.158
900	.067	65.063	58.950	5.502	28.556	9.380	2.280
1000	.071	66.043	59.611	6.432	28.104	7.285	1.592
1100	.075	66.913	60.237	7.364	27.646	5.222	1.038
1200	.078	67.749	60.829	8.303	27.187	4.119	.750
1300	.081	68.503	61.391	9.245	26.729	3.073	1.021
1400	.084	69.204	61.924	10.191	26.271	2.030	1.253
1500	.086	69.859	62.432	11.141	25.813	1.990	1.456
1600	.088	70.474	62.915	12.094	25.355	11.955	1.633
1700	.090	71.055	63.377	13.052	24.916	13.922	1.790
1800	.092	71.604	63.819	14.013	24.487	15.889	1.929
1900	.094	72.124	64.243	14.978	24.058	17.840	2.054
2000	.095	72.621	64.649	15.948	23.629	19.829	2.167
2100	.096	73.098	65.040	16.921	23.200	21.799	2.269
2200	.097	73.552	65.417	17.897	22.771	23.774	2.362
2300	.098	73.988	65.780	18.876	22.342	25.746	2.446
2400	.099	74.407	66.131	19.863	21.913	27.724	2.524
2500	.100	74.811	66.470	20.851	21.483	29.695	2.594
2600	.101	75.200	66.799	21.844	21.052	31.673	2.662
2700	.102	75.576	67.117	22.840	20.620	33.646	2.723
2800	.103	75.940	67.425	23.840	20.188	35.621	2.780
2900	.104	76.292	67.725	24.844	19.754	37.602	2.834
3000	.105	76.634	68.016	25.851	19.323	39.577	2.883
3100	.106	76.965	68.300	26.863	18.891	41.552	2.929
3200	.107	77.288	68.576	27.878	18.458	43.530	2.973
3300	.108	77.601	68.844	28.898	18.025	45.507	3.016
3400	.109	77.907	69.106	29.921	17.591	47.483	3.052
3500	.110	78.204	69.362	30.948	17.156	49.467	3.089
3600	.111	78.495	69.612	31.979	16.725	51.445	3.123
3700	.112	78.778	69.856	33.014	16.290	53.420	3.155
3800	.113	79.055	70.094	34.052	15.854	55.407	3.186
3900	.114	79.326	70.327	35.095	15.419	57.395	3.216
4000	.115	79.591	70.556	36.141	14.983	59.371	3.244
4100	.116	79.850	70.779	37.181	14.548	61.341	3.271
4200	.117	80.104	70.998	38.225	14.113	63.344	3.294
4300	.118	80.343	71.213	39.273	13.678	65.338	3.321
4400	.119	80.597	71.424	40.325	13.243	67.327	3.344
4500	.120	80.837	71.630	41.380	12.808	69.310	3.367
4600	.121	81.072	71.833	42.438	12.373	71.285	3.389
4700	.122	81.303	72.032	43.500	11.938	73.259	3.410
4800	.123	81.529	72.227	44.565	11.503	75.237	3.430
4900	.124	81.752	72.419	45.633	11.068	77.210	3.450
5000	.125	81.971	72.608	46.704	10.633	79.179	3.469
5100	.126	82.187	72.794	47.779	10.198	81.147	3.488
5200	.127	82.399	72.977	48.857	9.763	83.111	3.507
5300	.128	82.608	73.156	49.938	9.328	85.071	3.525
5400	.129	82.814	73.333	51.021	8.893	87.028	3.543
5500	.130	83.016	73.508	52.106	8.458	88.981	3.560
5600	.131	83.216	73.679	53.193	8.023	90.931	3.578
5700	.132	83.413	73.848	54.282	7.588	92.878	3.595
5800	.133	83.607	74.015	55.373	7.153	94.821	3.612
5900	.134	83.798	74.179	56.465	6.718	96.761	3.629
6000	.135	83.987	74.341	57.559	6.283	98.698	3.646

June 30, 1962

 Na_2 SODIUM, DIATOMIC (Na_2)

(IDEAL GAS)

MOL. WT. = 45.982

$$\Delta H^\circ_{f0} = 33.467 \text{ kcal. mole}^{-1}$$

$$\text{Ground State Configuration} = {}^1\Sigma^+$$

$$\Delta H^\circ_{f298.15} = 32.67 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 54.994 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\omega_e = 159.23 \text{ cm.}^{-1}$$

$$B_e = 0.15471 \text{ cm.}^{-1}$$

$$\omega_e x_e = 0.728 \text{ cm.}^{-1}$$

$$\alpha_e = 0.00079 \text{ cm.}^{-1}$$

$$\sigma = 2$$

$$r_e = 3.078(8) \text{ \AA}$$

Heat of Formation.

Same as the heat of sublimation for the diatomic gas; see notes on Na(crystal)

Heat Capacity and Entropy.

Spectroscopic data from G. Herzberg, "Spectre of Diatomic Molecules," 2nd Edn., D. Van Nostrand Co., Inc., New York (1950).

12.2.2-16

 Na_2

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Table 12.2.2-2 (continued)

Disodium Monoxide (Na₂O)

(Crystal)

GFW = 61.979

T, °K	Cp*	gibbs/mol	gibbs/mol	gibbs/mol	kcal/mol	kcal/mol	kcal/mol	Log Kp
		S*	-(G°-H°)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°		
0	.000	.000	INFINITE	-2.966	-98.744	-98.744	INFINITE	
100	7.228	3.979	30.827	-2.685	-99.452	-96.642	211.212	
200	14.233	11.741	19.387	-1.525	-99.815	-93.655	102.341	
298	16.516	17.935	17.935	.000	-99.900	-90.609	64.418	
300	16.550	18.038	17.934	.031	-99.900	-90.550	65.466	
400	18.111	23.617	16.604	1.765	-101.209	-87.329	47.714	
500	19.478	27.217	15.917	3.648	-101.174	-83.658	36.454	
600	20.485	30.056	21.443	5.648	-100.993	-80.410	29.249	
700	21.236	34.073	23.022	7.735	-100.707	-77.003	24.041	
800	21.819	36.948	24.586	9.889	-100.342	-73.640	20.118	
900	22.251	39.546	26.108	12.095	-99.923	-70.327	17.078	
1000	22.628	41.915	27.570	14.345	-99.467	-67.062	14.656	
1100	23.029	44.504	29.004	17.051	-98.572	-63.879	12.692	
1200	23.334	46.521	30.380	19.369	-97.556	-60.832	10.697	
1300	23.611	50.493	31.795	24.547	-96.783	-52.638	8.600	
1400	23.867	52.452	33.209	26.581	-95.835	-46.217	7.215	
1500	24.106	54.107	34.547	29.339	-94.866	-39.564	5.744	
1600	24.334	55.470	35.819	31.742	-93.874	-32.975	4.504	
1700	24.554	57.152	37.031	34.206	-92.864	-26.448	3.400	
1800	24.765	58.541	38.188	36.672	-91.837	-19.983	2.426	
1900	24.969	59.906	39.294	39.159	-90.792	-13.574	1.561	
2000	25.165	61.192	40.355	41.666	-89.731	-7.224	.748	

June 30, 1962; June 30, 1968

DISODIUM MONOXIDE (Na₂O)

(CRYSTAL)

GFW = 61.979

S_{298.15} = 17.935 gibbs/mol

Tt(γ + β) = 1023.2°K

Tt(β + α) = 1243.2°K

Tm = 1405.7°K

ΔHf° = -98.74 ± 1.0 kcal/mol

ΔHf°_{298.15} = -99.90 ± 1.0 kcal/mol

ΔHt°(γ + β) = 0.42 kcal/mol

ΔHt°(β + α) = 2.85 kcal/mol

ΔHm° = 11.4 kcal/mol

Heat of Formation

The enthalpy change of the reaction Na₂O(c) + H₂O(l) = 2NaOH(aq) has been determined by Matsui (1, 2), Roth (3, 4) and Rengade (5). Based on their reported ΔHr° values, the corresponding ΔHf°₂₉₈ for Na₂O(c) are calculated, using ΔHf°₂₉₈(H₂O, l) = -68.315 kcal/mol obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965, and ΔHf°₂₉₈(NaOH, aq) derived from JANAF ΔHf°₂₉₈(NaOH, c) and ΔHsoln and ΔHdil reported by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. The sample employed by Matsui was prepared by the method of Rengade (7) and contains Na₂O₂(c) and Na(c) as impurities. The sample used by Roth also contains 3.96 per cent (by weight) Na₂O₂(c). Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaction 2Na(c) + H₂O(l) = Na₂O(c) + H₂(g) was calculated by Rengade (5) from his measurements (5) incorporating with ΔHr° = -85.2 kcal/mol for the reaction 2Na(c) + 2H₂O(l) = 2NaOH(aq) + H₂(g) determined by Joannis (8). The value ΔHf°₂₉₈ = -94.9 kcal/mol is derived from the data of Forcrand (9) using ΔHf°₂₉₈(Na₂O₂, c) = -122.66 kcal/mol. The results are presented in the table below.

Brewer (11) determined the equilibrium constants, 918-1467°K, for the vaporization of Na₂O(c), using an effusion method. The Na₂O vapor consists predominately of Na(g) and O₂(g) molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na₂O. Based on the reported data, we derive the equilibrium constants for the reaction Na₂O(c) = 2Na(g) + 1/2O₂(g) and evaluate the third law ΔHr°₂₉₈ as 117.1 ± 10 kcal/mol. From this ΔHr°₂₉₈ value, we obtain ΔHf°₂₉₈(Na₂O, c) = -65.6 ± 10 kcal/mol, employing ΔHf°₂₉₈ = 25.76 kcal/mol for Na(g). The value -65.6 kcal/mol is not consistent with the other values described above. This may be caused by an invalid assumption used in the calculation.

The heat of formation at 298°K for Na₂O(c) is tentatively selected as -99.90 ± 1.0 kcal/mol.

Investigator	Reaction	ΔHr°, kcal/mol	ΔHf° ₂₉₈ , kcal/mol
1. Matsui (1929)	Na ₂ O(c) + H ₂ O(l) = 2NaOH(7890 H ₂ O)	-56.81 ± 0.16	-100.08
2. Matsui (1929)	Na ₂ O(c) + H ₂ O(l) = 2NaOH(4600 H ₂ O)	-56.70 ± 0.07	-99.89
3. Roth (1947)	Na ₂ O(c) + H ₂ O(l) = 2NaOH(825 H ₂ O)	-56.03 ± 0.13	-100.55
4. Roth (1948)	Na ₂ O(c) + H ₂ O(l) = 2NaOH(825 H ₂ O)	-55.98 ± 0.13	-100.60
5. Rengade (1907)	Na ₂ O(c) + H ₂ O(l) = 2NaOH(aq)	-56.50	-100.09
	2Na(c) + H ₂ O(l) = Na ₂ O(c) + H ₂ (g)	-28.70	-97.02
6. Forcrand (1900)	Na ₂ O(c) + 1/2O ₂ (g) = Na ₂ O ₂ (c)	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15-380°K, were obtained from Furukawa (9). We make the corrections in the reported Cp values for impurity Na₂CO₃(c) 2.33 per cent (by weight), analyzed by Grimley (10). The effect on heat capacity due to the presence of Na₂O₂(0.91 per cent) impurity is insignificant. Using the smoothed low temperature Cp data the S_{298.15} is calculated, based on S₁₅ = 0.0122 eu.

Grimley (10) measured the high temperature enthalpies, 380.1-1174.6°K, with a copper block drop-type calorimeter. The enthalpies for the γ phase, 380.1-980.4°K, are joined smoothly with the low temperature data and extrapolated to 1023.2°K (the γ + β transition temperature). The enthalpies above 1023.2°K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6°K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz (12) who used a very pure sample. The adopted ΔHt° = 0.42 and 2.85 kcal/mol, are averages of the derived values, 0.36 - 0.48 and 2.7 - 3.0 kcal/mol, respectively.

Melting Data

Tm and ΔHm° were obtained from Bouaziz (12). The adopted ΔHm° is an average of the reported 10.8-12.0 kcal/mol. Tm has been reported as 1193 and 1190 ± 10°K by Bunzel (13) and Brewer (11), respectively, which are not adopted.

References

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Na₂O

12.2.2-17

Na₂O

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Table 12.2.2-2 (continued)

Disodium Monoxide (Na_2O)

(Liquid)

GFW = 61.979

T, °K	C_p	S°	$-(G^\circ - H^\circ)/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Lag Kp
0							
100							
200							
298	25.000	21.895	21.895	.000	- 86.112	- 81.001	59.376
300	25.080	22.050	21.895	.044	- 86.094	- 80.950	58.972
400	25.000	26.242	22.074	7.546	- 80.840	- 76.249	42.753
500	25.000	34.820	24.728	5.046	- 68.987	- 75.476	32.990
600	25.000	39.378	26.861	7.546	- 66.307	- 72.837	26.531
700	25.000	43.239	28.880	10.046	- 67.806	- 70.319	21.954
800	25.000	46.570	30.887	12.546	- 66.897	- 67.893	18.548
900	25.000	49.515	32.797	15.046	- 66.184	- 65.560	15.970
1000	25.000	52.149	34.603	17.546	- 65.677	- 63.306	13.836
1100	25.000	54.532	36.308	20.046	- 64.789	- 61.126	12.145
1200	25.000	56.707	37.918	22.546	- 130.593	- 58.089	10.579
1300	25.000	58.708	39.442	25.046	- 129.515	- 52.090	8.757
1400	25.000	60.581	40.885	27.546	- 128.441	- 46.174	7.206
1500	25.000	62.374	42.255	30.046	- 127.371	- 40.137	5.677
1600	25.000	64.099	43.558	32.546	- 126.303	- 34.569	4.722
1700	25.000	65.415	44.795	35.046	- 125.236	- 28.867	3.711
1800	25.000	66.884	45.985	37.546	- 124.175	- 23.228	2.870
1900	25.000	68.195	47.116	40.046	- 123.110	- 17.449	2.030
2000	25.000	69.478	48.204	42.546	- 122.042	- 12.127	1.325
2100	25.000	70.497	49.247	45.046	- 121.009	- 6.458	.693
2200	25.000	71.860	50.248	47.546	- 119.961	- 1.234	.123
2300	25.000	72.879	51.212	50.046	- 118.915	4.135	.163
2400	25.000	74.036	52.141	52.546	- 117.874	9.466	.662
2500	25.000	75.036	53.038	55.046	- 116.836	14.746	1.269
2600	25.000	76.037	53.903	57.546	- 115.804	19.993	1.681
2700	25.000	76.980	54.741	60.046	- 114.777	25.194	2.030
2800	25.000	77.689	55.551	62.546	- 113.756	30.357	2.369
2900	25.000	78.767	56.337	65.046	- 112.740	35.481	2.675
3000	25.000	79.616	57.099	67.546	- 111.733	40.584	2.957

June 30, 1962; June 30, 1968

 Na_2O

GFW = 61.978

DISODIUM MONOXIDE (Na_2O)

(LIQUID)

 $S^\circ_{298.15} = [21.895] \text{ gibbs/mol}$ $\Delta H^\circ_{298.15} = [-86.112] \text{ kcal/mol}$ $T_m = 1405.2^\circ\text{K}$ $\Delta H_m^\circ = 11.4 \text{ kcal/mol}$ $T_d = 2223^\circ\text{K}$ Heat of Formation

The heat of formation is obtained from $\Delta H^\circ_{298.15}(c)$ by adding ΔH_m° and the difference between $H^\circ_{1405.2} - H^\circ_{298}$ for $\text{Na}_2\text{O}(c)$ and $\text{Na}_2\text{O}(l)$.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $\text{Na}_2\text{SiO}_3(l)$ and $\text{SiO}_2(l)$. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the $\text{Na}_2\text{O}(c)$ table.

Decomposition Temperature

T_d is the temperature at which the Gibbs energy change of the decomposition reaction $\text{Na}_2\text{O}(l) = 2\text{Na}(g) + 1/2\text{O}_2(g)$ approaches zero.

12.2.2-18

6/3/74

 NaO_2

Table 12.2.2-2 (continued)

Disodium Dioxide (Na_2O_2)

(Crystal)

GFW = 77.9784

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	-3.754	-121.257	-121.257	INFINITE
100	9.725	4.491	36.081	-3.409	-122.268	-117.408	296.725
300	18.040	14.767	24.522	-1.951	-122.658	-112.478	122.910
298	21.335	22.658	22.658	.000	-122.660	-107.472	78.779
300	21.369	22.790	22.658	.046	-122.657	-107.370	78.224
400	23.356	26.223	23.522	2.280	-123.016	-102.200	55.839
500	24.801	34.596	25.214	4.691	-123.618	-96.814	42.317
600	25.910	39.719	27.172	7.228	-123.278	-91.483	33.323
700	26.848	43.286	28.185	9.868	-122.826	-86.220	26.919
800	27.150	46.862	31.715	13.657	-120.627	-81.052	22.142
900	27.150	51.860	33.335	16.672	-120.406	-76.098	18.479
1000	27.150	54.770	35.333	19.387	-119.898	-71.202	15.561
1100	27.150	57.308	37.215	22.102	-119.414	-66.359	13.184
1200	27.150	59.670	38.986	24.817	-118.927	-60.642	11.044
1300	27.150	61.843	40.665	27.532	-118.433	-51.944	8.733
1400	27.150	63.655	42.250	30.247	-117.904	-43.315	6.762
1500	27.150	65.729	43.754	32.962	-117.350	-34.745	5.062
1600	27.150	67.481	45.182	35.677	-116.812	-26.231	3.583
1700	27.150	69.127	46.543	38.362	-116.171	-17.768	2.288
1800	27.150	70.679	47.841	41.107	-115.539	-9.358	1.130
1900	27.150	72.147	49.082	43.822	-114.913	-.991	.114
2000	27.150	73.539	50.270	46.537	-114.294	7.326	.001
2100	27.150	74.864	51.410	49.252	-113.678	15.608	1.624
2200	27.150	76.127	52.505	51.967	-113.071	23.851	2.369
2300	27.150	77.334	53.559	54.682	-112.466	32.055	3.046
2400	27.150	78.469	54.574	57.397	-111.873	40.230	3.683
2500	27.150	79.598	55.553	60.112	-111.284	48.383	4.228

June 30, 1963; June 30, 1968

DISODIUM DIOXIDE (Na_2O_2)

(CRYSTAL)

GFW = 77.9784

 Na_2O_2 $\Delta H_f^\circ = -121.28 \pm 1.2 \text{ kcal/mol}$ $S_{298.15}^\circ = 22.66 \pm 0.3 \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = -122.66 \pm 1.2 \text{ kcal/mol}$

Tt = 785 ± 1°K

 $\Delta H_t^\circ = 1.37 \text{ kcal/mol}$

Tm = 948°K

 $\Delta H_m^\circ = \text{Unknown}$

Heat of Formation

The enthalpy change of the reaction $\text{Na}_2\text{O}_2(\text{c}) + \text{H}_2\text{O}(\text{l}) = 2\text{NaOH}(1200 \text{ H}_2\text{O}) + 1/2\text{O}_2(\text{g})$ was measured at 18.5°C by Roth (1). He employed a sample with composition 96.81 per cent Na_2O_2 and 3.43 per cent Na_2O by weight. Using $\Delta H^\circ_{\text{soln}}(\text{Na}_2\text{O}_2, \text{c}) = -58.02 \text{ kcal/mol}$, Roth derived the value $\Delta H^\circ_{\text{soln}}(\text{Na}_2\text{O}_2, \text{c}) = -34.85 \text{ kcal/mol}$. This value was later corrected to be -35.75 kcal/mol (2). From this data we calculate the heat of formation (298°K) of $\text{Na}_2\text{O}_2(\text{c})$ as -121.0 kcal/mol . Forerand obtained $\Delta H_{\text{soln}} = -36.65 \text{ kcal/mol}$ for the same reaction, quoted by Roth (1), yielding $\Delta H_f^\circ(\text{Na}_2\text{O}_2, \text{c}) = -120.0 \text{ kcal/mol}$. The auxiliary data $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -68.315 \text{ kcal/mol}$ is taken from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965; and $\Delta H_f^\circ(\text{NaOH} \cdot 1200 \text{ H}_2\text{O}) = -112.458 \text{ kcal/mol}$ is derived based on $\Delta H_f^\circ(\text{NaOH}, \text{c}) = -101.90 \text{ kcal/mol}$ from JANAF Table and $\Delta H_m^\circ = -10.637 \text{ kcal/mol}$ and $\Delta H_{\text{dil}}(1200 \text{ H}_2\text{O} \rightarrow \infty \text{H}_2\text{O}) = -0.079 \text{ kcal/mol}$ from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.

Gilles (3) determined the enthalpy change of the reaction $\text{Na}_2\text{O}_2(\text{c}) + \text{H}_2\text{O}(\text{l}) = 2\text{NaOH}(3800 \text{ H}_2\text{O}) + 1/2\text{O}_2(\text{g})$, using a purer sample (Na_2O_2 99.2 per cent, Na_2O 0.8 per cent). Based on the reported value $\Delta H_r^\circ_{298} = -34.0 \pm 0.3 \text{ kcal/mol}$ and derived $\Delta H_f^\circ_{298}(\text{NaOH} \cdot 3800 \text{ H}_2\text{O}) = -112.467 \text{ kcal/mol}$, we calculate $\Delta H_f^\circ_{298} = -122.66 \pm 1.2 \text{ kcal/mol}$ for $\text{Na}_2\text{O}_2(\text{c})$.

Leffler (4) studied the oxygen pressure-melt composition for the liquid sodium-oxygen system between 780 and 980°C. These results, together with the thermodynamic data for Na_2O_2 , were used to calculate the heats and free energies of formation of melt compositions between $\text{NaO}_{1.0}$ and $\text{NaO}_{0.5}$. However, there are no numerical results reported. Therefore this data is not used for evaluation.

The heat of formation at 298°K is adopted as $-122.66 \pm 1.2 \text{ kcal/mol}$.

Heat Capacity and Entropy

The low temperature heat capacities, 52.31-296.22°K, were measured by Todd (5). His sample contains (per cent) 94 $\text{Na}_2\text{O}_2(\text{c})$, 3.6 $\text{Na}_2\text{O}(\text{c})$ and 2.4 Na_2CO_3 . Corrections in the reported results have been made for Na_2CO_3 content, but not for Na_2O content which was estimated to be small. The Cp values below 52.31°K are calculated using the equation $C_p = D(\frac{25}{T})^2 + JE(\frac{393}{T})^2$, reported by Todd. S_{298}° is derived from the adopted Cp, based on $S_{30}^\circ = 1.012 \text{ eu}$.

The high temperature enthalpies, 375.4-869.2°K, were determined by Chandrasekharaiah (6), using drop calorimetry. Corrections were made for the contributions from impurities (Na_2CO_3 1.5 and Na_2O 0.2 per cent). A discontinuity was observed in the enthalpies between 773 and 793°K, indicating some kind of transition (see Transition Data). The Cp for $\text{Na}_2\text{O}_2(\text{c})$ at temperatures 298-769.5°K are derived from the enthalpy measurements, 375.4-769.5°K, and joined smoothly with the low temperature data at 298°K, and extrapolated to 785°K(Tt). The Cp for $\text{Na}_2\text{O}_2(\text{p})$ is derived from the enthalpy data, 794-869.2°K, as constant, 27.15 gibbs/mol, and extrapolated to 2500°K.

Vedenev (7) measured the high temperature specific heat of $\text{Na}_2\text{O}_2(\text{c})$ in the temperature interval 292-373°K using adiabatic calorimetry. The reported average value, 21.46 gibbs/mol, is in fair agreement with the adopted ones.

Transition Data

It was reported by Tallman (8), who measured the X-ray power diffraction pattern by a Geiger-counter diffractometer and found that at about 510°C the pattern changes entirely and a new set of peaks indicates a new phase. Separate thermal analysis measurements (9) confirm the transition temperature ($\alpha \rightarrow \beta$) is $512 \pm 1^\circ\text{C}$ or $785 \pm 1^\circ\text{K}$, which is adopted here. Forpl (9) found a thermal anomaly at 485°C in both heating and cooling curves. ΔH_t° is derived from the adopted enthalpy and Cp data on $\text{Na}_2\text{O}_2(\text{c})$ and $\text{Na}_2\text{O}_2(\text{p})$.

Melting Data

Tm is obtained from Benzel (10). Tm = 733 and 783°K were reported by Blumenthal (11) and Rode (12), respectively, which are not adopted.

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 Na_2O_2

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12.2.3 SOLUBILITY

A knowledge of the solubilities of species involved in and resulting from sodium-water reactions is important in determining whether or not line plugging from reaction products can be expected, whether certain types of leak detection are feasible, and in the formulation of thermodynamic relationships involving solutions.

Many of the available solubility data have been summarized by Henry.⁽¹⁾ Data from his report are reproduced in Figures 12.2.3-1 through 12.2.3-9, and describe the following systems:

<u>System</u>	<u>Figure</u>
Na/NaOH	12.2.3-1
NaOH/Na ₂ O	12.2.3-2
H/Na-NaOH	12.2.3-3
NaH/Na ₂ O/NaOH/Na	12.2.3-4
NaOH/Na/Na ₂ O/NaH	12.2.3-5
NaH/Na	12.2.3-6
H ₂ /NaOH-Na	12.2.3-7
NaOH/NaH	12.2.3-8
NaOH/Na ₂ O	12.2.3-9

The equilibrium pressure of hydrogen over hydrogen/sodium solutions is important to the technology of leak detection by hydrogen sensing. Henry⁽¹⁾ and Hayes⁽²⁾ report that the partial pressure of H₂ over NaH is given by:

$$\log P(\text{mm}) = 11.66 - 6100/T$$

$$373^\circ\text{K} < T < 588^\circ\text{K}$$

Meacham⁽³⁾ and Hayes⁽²⁾ note that the solubility of hydrogen in sodium over the same temperature range is given by

$$\log H_2 (\text{ppm})^* = 6.52 - 3180/T \text{ } ^\circ\text{K}$$

The data of Meacham, et al., are valid for systems with less than 25 ppm oxygen and more than 0.5 ppm dissolved hydrogen. Above 1 ppm hydrogen, hydrogen solubility is essentially independent of oxygen content between 7 and 24 ppm.

* ppm = parts per million by weight

Figure 12.2.3-1 Dependence of the Solubility of Sodium in Sodium Hydroxide on Temperature

Figure 12.2.3-2 Solubilities in Sodium of Na₂O Oxygen, NaOH Oxygen, and NaOH - Na₂O Oxygen

Figure 12.2.3-3 Pressure of Hydrogen over the Na-NaOH System. (Na Concentration, mole %)

Figure 12.2.3-4 Equilibrium Diagram of the $2\text{Na} + \text{NaOH} \rightleftharpoons \text{Na}_2\text{O} + \text{NaH}$ Systems at $P = 760 \text{ mm Hg}$.

Curve 2Na-M represents solubility of NaOH in $\text{Na}(\ell)$.

Curve K-D represents the NaOH solubility of NaH and Na_2O .

Figure 12.2.3-5 2Na - NaOH Diagonal Section of the
 2Na + NaOH = Na₂O + NaH System at
 P = 760 mm Hg.

Figure 12.2.3-6 The Solubility of Sodium Hydride in Metallic Sodium.

Figure 12.2.3-7 Pressure-Composition Isotherms for Solutions of Hydrogen in Liquid Sodium.

Figure 12.2.3-8 Fusion Diagram of the NaOH - NaH System

Figure 12.2.3-9 The NaOH - Na₂O System

Vissers, et al.,⁽⁴⁾ have summarized their hydrogen solubility data and the solubility data of others, and find the data to be described by the expression

$$\log H_2(\text{ppm})^* = 6.067 - \frac{2880}{T^\circ\text{K}}$$

$$383^\circ\text{K} < T < 674^\circ\text{K}$$

They give the following expression for the Severt's Law constant, S:

$$\log S = 0.860 - \frac{122.0}{T^\circ\text{K}}$$

$$570^\circ\text{K} < T < 674^\circ\text{K}$$

where

$$S = C_H / P_H^{1/2}$$

C_H = concentration of hydrogen in sodium, ppm by weight;

P_H = pressure of hydrogen, Torr.

* ppm = parts per million by weight

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12.2.4 KINETICS

The initial reaction of sodium and water, either by

or by

is often considered to be "instantaneous."^(1,2,3) Rice, et al., as reported by Henry,⁽¹⁾ state that water reacts with clean sodium in microseconds.

Under very dynamic conditions the rate of reaction depends on how fast the reactants are mixed. Under less rigorous conditions there appears to be a diffusion barrier present. In some cases a NaOH film on the sodium surface is considered to be present. In others, a hydrogen layer in between the water and sodium has been proposed.

Despite the rapidity of the reaction it cannot be called a detonation. According to King and Nelson,⁽⁴⁾ experiments were carried out in which NaK* charges were detonated under water with the aid of explosive boosters. The results were that only about 0.33% of the reaction energy appeared in shock phenomena, whereas with TNT about 25% does. Hence, the sodium water reaction which occurs in an enclosed space will act similarly to gasoline in an internal combustion engine--there will be a smooth increase in pressure, not a true impluse. Consequently, a component structure design is concerned with low strain rates rather than high strain rate consideration.

Some other kinetics data are available. The reaction of H_2 and Na(l) was found to be first order with an Arrhenius law activation coefficient of 16.5 k cal/mol.⁽¹⁾ The rate constant is 0.035 at 280°C (536°F) and 0.050 at 310°C (590°F).

The reaction

has also been studied.⁽⁵⁾ It was concluded that this reaction is the

* NaK = a sodium (Na) - potassium (k) eutectic.

primary relationship between Na and NaOH at 400°C (752°F). The rate of formation of NaH is given by

$$\frac{dc}{dT} = 0.0355 - 0.016 C$$

where

$$C = \text{NaH in mole \%}$$

and

$$\frac{dc}{dT} = \begin{array}{l} \text{moles of NaH formed per hour per cm}^2 \\ \text{of Na/NaOH surface} \end{array}$$

Pelloux and Besson⁽⁶⁾ have studied the reaction of water vapor with sodium over the temperature range of 40 - 240°C (104 - 464°F). They observed that the reaction

always exhibited an initial parabolic rate.

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12.3 REACTION IN STEAM GENERATORS

It must be accepted as inevitable that a few sodium-water leak situations will occur over the life of a steam generator system, even with a design philosophy that aims at completely avoiding all tube failure. The damage resulting from a given leak will depend critically on the size of the leak, the ability to detect the leak (and take corrective action), and the overall design of the heat exchanger system.

12.3.1 LEAK SIZE EFFECTS

On the coarsest scale, leaks are classified as being "large" or "small." More specifically, large leaks are defined as leaks which are the result of tube ruptures⁽¹⁾ and produce high pressure as well as gross movement of the sodium.^(2,3) Ford, et al.,⁽²⁾ suggest that large leaks have a leak rate on the order of 5 to 15 lb/sec of water. Hori, et al.,⁽⁴⁾ considered large leaks to be at least 0.2 lb/sec.

Small leaks are defined as having a reaction zone that more or less remains in one locality^(2,3) and does not effect a gross disturbance of the sodium. Goldmann,⁽³⁾ Hori, et al.,⁽⁴⁾ and Chamberlain, et al.,⁽⁵⁾ indicate that small leaks are generally smaller than 0.1 lb/sec.

In addition to the large/small definition of leak size, there has been some discussion of "microleaks." Microleaks are described by Andreev, et al.,⁽⁶⁾ as being less than about 6×10^{-5} lb/sec and having a tendency to plug spontaneously, either with particles from the water or with reaction products.

That economic and safe operation of sodium heated steam generators is considered feasible is evidence that a damaging large leak is not considered probable.^(7,8,9,10) Maidment⁽⁹⁾ states the most probable cause of steam generator shell failure is fracture due to defects in the header materials and, based on failure data, he does not consider such failure very likely.

Maidment⁽⁹⁾ and Gibbons⁽¹⁰⁾ estimate that the probability of major tube or shell failure due to material defects is small, particularly in the case of materials meeting nuclear code standards. Minor tube or tube sheet failures, leading to small leaks, are considered a certainty.

The large leaks which do occur due to tube failure are expected to have a leak rate of the order of 10 lb/sec.⁽²⁾ This size leak readily trips safety circuits and is easily detected.

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12.3.1.1 Reaction Characteristics

◦ Large Leaks. Large leaks give rise to relatively high pressures and temperatures in the reaction region.

Pressures vary as a function of location in the system, system geometry, initial temperature, and the rate of reactant contact. Salmon⁽¹⁾ has calculated pressure pulses as high as 6000 psi (400 atm) for a constant volume system, with an average peak of about 3000 psi. Maidment⁽²⁾ reports calculations of 3000 atm with experimental values of about 1000 atm. Greene⁽³⁾ reports peak pressure pulse estimates of 33,000 psi (2000 atm). Others generally report average experimental pressures of 1000 psi^(4,5) or less with higher peaks.^(4,5,6) Dumm, et al.⁽⁵⁾ reported test chamber dynamic wall pressures of 104 atm (1500 psi) which correspond to a reaction zone dynamic pressure of 1600 atm (24,000 psi) lasting for less than a millisecond. The short life of the large pulses means there is too little total energy contained in each pulse to cause significant damage.

Calculated maximum temperatures for a constant volume system run to 2730°F (1500°C)⁽⁷⁾ or 3060°F (1680°C).⁽¹⁾ Experimentally, the reaction temperatures are found to reach 900°C (1650°F) to 1200°C (2200°F).^(5,7,8) The lower temperatures may be related to retardation of the reaction due to the necessity of water to diffuse through a hydrogen barrier⁽⁷⁾ or to the melting/boiling point of the materials present.^(5,9)

Large leaks produce reaction products at rates too great to achieve equilibrium.^(7,8,10) Greene⁽¹⁰⁾ points out that under equilibrium conditions less than 1% of the hydrogen generated will appear as gas, whereas in large scale leak conditions around 60% appears in the cover gas.

Bray^(8,11) reports that for every pound of water that reacts, approximately three pounds of solids is obtained. This consists of about 50% NaOH, 40% Na₂O and 10% NaH. The reaction products melt at about 300°C and have a density of about 2 g/cm³. Removal of the solidified reaction products is best achieved chemically. If this is not feasible, a pneumatic drill will probably be required.

◦ Small Leaks. A small leak has been defined as one in which the reaction remains localized.⁽⁴⁾ This type of leak, ranging from a water injection rate of about 0.1 lb/sec or less, is considered to have a probability of occurring approaching unity.^(2,4,9,12)

In many cases the leaks may be classified as micro-leaks; these have a high probability of plugging, reducing the chances of their detection.⁽¹³⁾ Larger leaks are more dangerous, due to the wastage of surrounding tubes, which appears to be a combination of erosion and corrosion. Practical detection of these leaks is on the borderline of effectiveness. Past experience has shown however, that "natural" leaks, i.e., leaks resulting from ordinary material or fabrication defects, generally are too small to cause significant damage before detection.^(10,14)

A small leak by definition will approach a quasi steady state condition. Therefore the pressures involved will be not much different from the sodium system pressure. The overall system temperature will not be greatly affected by the sodium-water reaction resulting from a small leak. Local reaction zone temperatures can attain values of 980°C (1800°F) to 1200°C (2200°F).^(10,15) Both NaOH and Na₂O can be formed directly in Na - H₂O reactions. At temperatures up to 450° (840°F) the rate of the reaction

is slow, requiring hours to equilibrate.^(16,17) The rate will be faster in the reaction zone.⁽¹⁷⁾

The major species present is not clear. The work of Koslov⁽¹⁷⁾ suggests mostly NaOH should be present. Chamberlain, et al.,⁽¹⁸⁾ based on experimental data indicate that the solid deposits consist of about 89% Na₂O, 10% NaOH and 1% NaH. They also note that most of the reaction products remain as solids near the reaction site. The remaining material apparently dissolves in the sodium. Only in cases where sufficient water was injected to saturate the sodium were particulates found in the sodium.

The rate of the reaction

is not known. In some cases the formation of NaH is referred to as slow.⁽¹⁹⁾

12.3.1.1-3

However, some data for slow leaks⁽¹⁰⁾ implies that it is sufficiently fast to consume most of the hydrogen from an approximately 0.0025 lb/sec water leak. Geometry and leak location as well as operating conditions will have a strong influence on the ratio of NaH to H₂.

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12.3.1.2 Component Damage

◦ Large Leaks. In this section it is assumed that the steam generator will be isolated before the effects of the leak can pass the isolation valves on the lines leading to the intermediate heat exchanger. Maidment⁽¹⁾ argues that there is a high probability of such isolation in a suitably short time.

The immediate effects on the steam generator will be dictated by the pressure and temperature attained and their duration. Long term effects will be dictated by shutdown procedures which control how much water enters the sodium (shell) side of the generator and how much sodium manages to get back into the water side leading to contamination of the two sides with Na_2O and NaOH .

Generally little or no corrosive or erosive attack is noted in large leak tests due to the short time that the condition exists.^(2,3) There are exceptions noted, where the ruptured tube suffered attack from reaction products reflected back onto the ruptured tube⁽¹⁾ and where adjacent tubes have suffered wastage.^(2,3)

In test vessels designed to withstand a steady pressure of 300 psi, negligible damage was done to the shell after ten tests;⁽³⁾ different results might exist if the rupture occurred immediately adjacent to the shell wall.

All tests conducted have been for single tube ruptures; a multiple-rupture situation is considered highly improbable.^(1,3) If a subsequent rupture occurs, secondary peak pressures will be less because the sodium will be in motion out of, or already ejected from, the system. Examples of this are from Super-NOAH tests.⁽⁴⁾ In these experiments from 500 to 1000 pounds of sodium were ejected (out of 4000 pounds total) from the rupture of just one tube. Also, pressure tests in which a one-tube leak yielded 600 to 1000 psi produced over 1600 psi in a multiple tube test (with ten times the amount of water).⁽²⁾

The tubes adjacent to the reaction zone are often bowed or distorted.^(2,3) It is possible that tubes in a cross-flow configuration might suffer greater tube bending than for parallel flow cases.

The long term effects must be considered if the steam generator is to be returned to serve. The reaction products must be removed

to bring the impurity levels down to normal operating levels. In the case of the Fermi Reactor, where reaction products entered the secondary system, it took 22 days of cold trapping to lower the impurities to below saturation.⁽²⁾

On the water side, the caustic must be removed to prevent caustic cracking of the steam generator structural materials.

◦ Small Leaks. In the case of small leaks, there are three major effects to consider:

- contamination of the system with impurities, including loss of flow due to plugging of tubes with reaction products,
- accelerated corrosion of regions adjacent to the leak by reaction products,
- wastage of regions adjacent to the leak.

The first two topics, though important, are the province of other sections of this report and will not be discussed here.

Wastage is a phenomenon first noted in the Fermi Reactor in 1962.⁽⁵⁾ It is defined as a rapid attack of the metal in the region surrounding the leak. The general effect of leak size is shown in Figure 12.3.1.2-1.⁽⁶⁾ However, the exact mechanism of wastage is not clear. Lee⁽⁷⁾ concludes that wastage is due to the combined effects of temperature rise and mechanical impingement, that is, erosion. His concept is shown in Figure 12.3.1.2-2. The resemblance to a flame is appropriate since the reaction zone is considered to be a 0.03 inch thick envelope around the jet.⁽⁸⁾

The erosion mechanism proposed by Lee⁽⁷⁾ is based on an examination of test specimens from experiments performed by the Atomic Power Development Associates (APDA). Using a scanning electron microscope he observed no evidence of corrosion, but did find evidence of particle impact and thermal treatment.

Because, as Lee⁽⁷⁾ noted, a jet of water droplets into hot sodium can be accelerated to supersonic speeds, high impact pressures

Figure 12.3.1.2-1 Effect of Orifice Size on Wastage
(constant water pressure)

NOTES:

ALL MATERIAL WASTAGE IS DUE TO IMPINGEMENT. IN REGIONS B, THE WASTAGE IS HIGHER THAN THAT IN REGION A BECAUSE OF THE HIGHER TEMPERATURE IN REGIONS B CAUSED BY SODIUM-WATER/STEAM REACTION.

Figure 12.3.1.2-2 Idealized Configuration of the Droplet Impingement and Sodium-Water Reaction Processes in Rig 10

can be developed. He suggests these pressures, together with temperatures of 1400°F (760°C) to 1800°F (980°C) effect the wastage.

Pugh⁽⁹⁾ has observed that the wastage data scatter are sufficient to include the possibility that the erosion is caused by the collapse of steam bubbles in a superheated water jet.

Cochran and Dhillon⁽¹⁰⁾ on the other hand, go along with the concept of Figure 12.3.1.2-1 but suggest that more of a corrosion mechanism is involved:

The first reaction is the basic sodium-water reaction. The second reaction is the basic corrosion reaction, while the third is a modified thermite reaction which might occur.⁽¹⁰⁾ The reaction products are thought to be swept away from the metal surface by the leak jet, thereby providing a clean surface conducive to rapid corrosion attack. A factor which lends credence to this hypothesis is the influence of the sodium flow rate. Chamberlain⁽⁸⁾ noted that flowing sodium systems would show 0.1 to 0.2 mil/sec wastage rates, whereas stagnant systems showed negligible attack.

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12.3.1.3 Wastage Resistance of Materials

The general types of wastage attack were shown in Figure 12.3.1.2-1. The smoothed basis data for that figure are shown in Figure 12.3.1.3-1.⁽¹⁾ The data for Figure 12.3.1.3-1 are based on 2 1/4 Cr - 1 Mo ferritic steel (Croloy) target tubes. Tests using 304 and 321 stainless steel and Incoloy 800 yielded wastage rates from about 20 to 30 and 30 to 80 times smaller, respectively, than for the Croloy.⁽²⁾ In general, it is found that alloying additions of nickel to iron base alloys reduce wastage rates.

In all cases there is a rapid drop in wastage rates as the water injection rate drops below 0.001 lb/sec. It maximizes at about 0.01 lb/sec and then decreases again beyond about 1 lb/sec, Figure 12.3.1.3-1. Even flow rates of 0.001 lb/sec can be serious, however. Andreev⁽³⁾ reports that for this flow rate, serious damage can be caused in about 100 seconds.

Greene⁽¹⁾ reports another correlation of these data plus some from General Electric, Figure 12.3.1.3-2. Here a conservative correlation between the amount of water injected and the volume of metal removed is presented and results in the relationship

$$\left[\begin{array}{l} \text{quantity of metal} \\ \text{removed (in)} \end{array} \right] = 0.014 \times \left[\begin{array}{l} \text{quantity of water} \\ \text{injected (lb)} \end{array} \right]$$

which can be used to predict the maximum volume wastage for a needle-type jet hitting the target tube under the following conditions:

- water pressures up to 1450 psia,
- sodium velocities in the range of 0 to 4 ft sec,
- tube-to-tube separations of 0.75 in. or greater,
- tube material 2 1/4 Cr - 1 Mo steel,
- sodium bulk temperatures up to 510°C (950°F).

The probability of leaks sufficiently large to cause this type of damage is considered to be small.⁽¹⁾

Figure 12.3.1.3-1 Effect of Leak Rate and Spacing on Tube Wastage Rates

Figure 12.3.1.3-2 Wastage Correlation

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12.3.2 LEAK DETECTION

A large leak has the advantage of being easily and rapidly detected. Within milliseconds after the rupture, pressure becomes noticeable.⁽¹⁻⁶⁾ Fermi Reactor⁽⁷⁾ has used low pressure, 50-60 psig, rupture discs with wires which are broken when the disc ruptures. The broken wires interrupt an electronic circuit and effect system dumping and isolation.

Maidment⁽⁸⁾ has indicated that pressure sensors in the gas space or acoustic detectors give sufficiently fast warning, within one to two seconds after the tube rupture, to isolate the steam generator from the rest of the system. Other detectors, such as for H_2 , O_2 , resistivity (rhometers), and temperature would provide useful signals, but generally have a delay due to slow transport of the product of the reaction to the detector. They can find use, however, as backup systems.

Detection of small leaks is significantly more difficult than that of large ones. The reasons for this are lack of gross effects, such as an abrupt pressure change. Furthermore, small leaks, amounting to several pounds of water per hour, do not effect much change in impurity levels, as is shown in Figure 12.3.2-1⁽⁹⁾ for hydrogen cover gas concentrations.

Several types of detection systems are possible. Those suitable for monitoring the cover gas are:

- Thermal Conductivity Analyzers (TCA)- H_2
- Gas Chromatographs (GC)- H_2

Monitors for the liquid system include:

- Acoustic, reaction noise
- Hydrogen Diffusion Tube (HDT)- H_2
- Rhometer, resistivity changes due to impurities, gas bubbles, particles, solubles
- Hydrogen meter, electrochemical - H_2
- Oxygen meter, electrochemical - O_2
- Plugging meter, impurities, particles, entrained gas, solubles.

Figure 12.3.2-1 Comparison of Hydrogen Release Models with Experimental Data. Data Points from Experiments Indicated by*.

Leak detection based on cover gas monitoring is made difficult by the relatively slow rate of increase of hydrogen in the cover gas during a leak incident (see Figure 12.3.2-1).⁽⁹⁾ There is also a possible loss of signal in the sample lines due to sodium "frost," which could absorb hydrogen or even plug the sample lines completely.

When a water leak occurs in the cover gas region, the water/sodium vapor reaction will liberate large amounts of hydrogen directly into the cover gas. In this case a very rapid response is expected from cover gas hydrogen monitors.

The TCA, though nonspecific for hydrogen, provides continuous monitoring. The GC can indicate whether hydrogen concentrations are varying but only on a periodic basis, approximately every two to five minutes.^(9,10)

For in-sodium detection there are two basic types of detectors: those whose response time is controlled primarily by the geometry and operating conditions of the liquid metal system, and those whose response time is determined primarily by their own operating characteristics.

The rhometer, plugging meter, oxygen and hydrogen meters are examples of the first type. Their response time will largely be a function of how long it takes the reaction products to travel from the leak to the monitor in sufficient quantity to provide an acceptable signal.

The response time of the hydrogen detection tube (HDT), which uses a nickel diffusion membrane, is about 15 seconds for the instrument itself.^(9,10) Overall, Greene⁽⁹⁾ estimates a two minute response time including hydrogen transport from the leak and the operator becoming aware of the indications and taking action.

The oxygen meter as well as the electrochemical hydrogen meter will have a quicker intrinsic response,⁽¹⁰⁾ but will be subject to the same operating delays. These devices suffer from the lack of suitably stable materials of construction and from the unknown effects of other variables on the output potential.⁽⁷⁾ Oxygen meters have also failed because of apparent mechanical defects.⁽¹¹⁾

The rhometer which measures conductivity, provides virtually instantaneous response when the impurities reach the probe.⁽¹⁰⁾ Thus it

too will have a response time determined by operating procedures and geometry. The plugging meter monitors impurity levels by determining the temperature at which a small orifice becomes plugged by the precipitation of soluble impurities. Overall response time ranges from about the same or greater than the other system limited devices.^(10,12)

The acoustic detector has the greatest potential advantages. Because it detects the noise of the reaction via sound transmitted through the liquid metal and the containment system, detection is essentially instantaneous. The basic difficulties are the signal to noise ratio and attenuation of signal between the leak and the detection point.

The passive acoustic detector has to be able to distinguish the noise of the sodium-water reaction from a background of pump noise, the sounds of flowing liquids and the sound of water boiling. Several studies have been made to determine whether the sodium water reaction generates an acoustic spectrum noticeably different than this background.^(12,14) The observed spectra show that a band occurs at about 2KHz due to the heating effects of chemical reaction;^(13,14) this is approximately the same both at room temperature and at 315°C (600°F).⁽¹⁴⁾ Additionally there is a characteristic frequency due to the oscillation of hydrogen bubbles. At room temperature the frequency is about 500 Hz, at 315°C about 800 Hz.⁽¹⁴⁾

A recent survey of acoustic methods for the detection of boiling in LMFBF systems⁽¹⁵⁾ indicates that frequencies as high as 1 MHz would be useful with the best results being obtained above 100 KHz, which was the upper limit of the work described above.^(13,14)

Another advantage of using acoustical devices is the potential ease of locating the leak. The use of three or more detectors can provide sufficient information to calculate the source of the signal, hence the position of the leak.⁽¹⁶⁾

Ford, et al.,⁽¹⁷⁾ proposed a number of criteria for detection systems. The detector should

- be independent of the physical transport of reaction products between the leak and detector, if this is possible.

- be designed to have a detection system transport time close to zero.
- have a response time as close to zero as possible.
- be located such that the detectors are as close as possible to all potential leak locations if they are dependent on the physical transport of products from the leak zone to the detector.
- utilize detectors which are not affected by variations in plant operating conditions or expected changes in background levels of the parameters being measured.
- be developed and tested to the point that operator confidence in the system is such that alarms and/or interlocks can be utilized.
- for detectors dependent upon sodium transport time: have a sufficiently high sensitivity such that it can detect, on the first pass of sodium past the detector, leaks of size which can cause severe damage to the unit in a time period equivalent to approximately two times the sodium cycle time plus the dump time, or shorter.

He states the above requirements are the most important. Other requirements which are less important but which should be pursued are listed below.

The leak detection system shall:

- be in replicate to ensure against adverse effects of instrument or circuit failure, and have provisions for periodic checkout to demonstrate that the detectors are operational and will detect a leak.
- be arranged to provide for maintenance without shutdown of the components.
- have a long and relatively maintenance-free service life, demonstrating a high degree of reliability.
- not be susceptible to degradation of the detector signal or fouling.

12.3.2-6

- be commercially available and of reasonable cost.
- be compatible with the materials of the components and systems in which it is installed and not compromise or reduce their integrity.

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12.3.3 DESIGN REQUIREMENTS

There are a number of items which should be taken into consideration in the design and operation of a sodium heated steam generator.^(1,2)

- Assume that there will be at least one leak of some size during the lifetime of the unit.
- Minimum welding should be done during erection of the apparatus (to minimize the occurrence of leaking welds).
- The design should permit early detection of small leaks.
- The unit should be easily isolated from the rest of the system and the water should be easily dumped.
- Pressure waves from the reaction should be kept away from the primary system.
- Two-phase flow should be assumed for conservative pressure drop calculations.
- Relief systems should prevent accumulation of water and sodium which could initiate further reactions.
- The unit should be easily disassembled and repaired.
- The unit should be easily cleaned.

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12.4 SIGNIFICANCE OF SODIUM-WATER REACTIONS TO LMFBR

12.4.1 INTRODUCTION

Sodium-heated steam generators are generally designed without use of an intermediate heat-transfer fluid, and with the realization that occasional contact of sodium and water is inevitable. Because the steam is at a much higher pressure than the sodium in such a steam generator, the most common failure mode involves the jetting of steam into the liquid sodium, with attendant liberation of heat and reaction products. In the absence of oxygen, the primary sodium-steam reaction products are NaOH, Na₂O, NaH, and H₂.

The most commonly encountered steam generator problem is metal wastage caused by the high temperatures (900° - 1200°C) and corrosive conditions found in the vicinity of the sodium-steam reaction. The metal wastage can be serious enough to cause the failure of adjacent tubes. The primary design goals must be to minimize the opportunity for leaks and to back the design with a reliable, sensitive leak detector.

12.4.2 REACTION RATES, THERMODYNAMICS, AND LEAK CHARACTERISTICS

Thermodynamic principles are extremely useful in certain near-equilibrium circumstances associated with a sodium-steam reaction, such as determining the feasibility of a given reaction, predicting gas-liquid (e.g., H_2 -Na) equilibria in the bulk of the coolant, and estimating the overall heat liberation (enthalpy change) associated with various reaction. The thermodynamic data available show a great deal of inconsistency, and must be used with caution. Selected data are presented in the preceding text, with examples of typical data disagreement.

A knowledge of the solubilities of the chemical species involved in, and resulting from, sodium-water reactions is important in determining whether or not line plugging from reaction products can be expected, whether certain types of leak detection are feasible, and in the formulation of thermodynamic relationships involving solutions. The solubility data are conveniently represented in the form of phase diagrams, which are strictly applicable only under equilibrium conditions and in the absence of extrinsic components. Selected phase diagrams are presented in the text which illustrate approximately the phase relationships which can be expected between the major products/reactants of the sodium-water reaction.

The rate of the sodium-water reaction depends on how fast the reactants are mixed. In the case of relatively quiescent reactants, for example, diffusion barriers composed of NaOH and/or gaseous H_2 , can form. In the case of violently mixed reactants, the rate can become almost instantaneous, though it apparently never assumes the character of a true detonation. The kinetics of the reaction in a steam generator depend on the prevailing circumstances, such as the temperature of the reactants, the system pressure, the size of the leak, the mixing tendency (pressure differential), the reaction volume, the reactant makeup rate, etc.

In a steam generator, leaks are generally classified as being "large" or "small." Large leaks are those which result in high pressures and gross sodium movement, such as would result from a tube rupture; small leaks have a localized reaction zone.

Large leaks produce relatively high temperatures and pressures in the reaction region. Pressure pulses produced by large leaks have been estimated to be capable of reaching 3000 psi. Reaction temperatures to 1200°C have been experimentally measured.

Small leaks will reach a quasi-steady-state condition, so that the pressures involved will approximate the sodium pressure. Local reaction zone temperatures can be as high as 1200°C. The composition of the product formed by the reaction is not known exactly; for example, there is disagreement on whether Na_2O or NaOH is the major constituent.

Generally little or no corrosive attack is noted in the case of large leaks, because of the short time the condition exists. In the case of small leaks the sodium system becomes progressively contaminated, corrosion by reaction products takes place, in the vicinity of the leak, and metal wastage, i.e., metal loss due to the combined effects of temperature rise, erosion, and corrosion, occurs in adjacent tubes.

Alloying additions of nickel to iron base alloys dramatically reduces the wastage associated with small leaks; 300 series stainless steels and Incoloy 800 are reported to be much more resistant to wastage than low alloy steels.

The rate of metal wastage is critically dependent on the leak flow rate. In tests of 2-1/4 Cr - 1 Mo target tubes, the wastage rate was a maximum at about 0.01 lb/sec, and decreased at rates <0.001 lb/sec and >0.1 lb/sec. Because such tests are highly dependent on system conditions and construction materials, they can be considered only qualitative indicators of the response of a system under different test conditions.

12.4.3 DETECTION

A large leak has the advantage of being easily and rapidly detected. Either pressure or acoustic detectors can quickly isolate the steam generator in the event of a large leak. Small leaks are much more difficult to detect. Leak detectors for small leaks take the form of cover gas monitors (H_2 effects), or liquid system monitors (acoustic, H_2 diffusion, rhometer, electrochemical H_2/O_2 meters, and plugging meters). Leak detection by cover gas monitoring is made difficult by the slow rate of increase of H_2 in the cover gas during a leak incident. For in-sodium detection there are two basic types of detectors: those whose response time is controlled primarily by the geometry and operating characteristics of the liquid metal system, and those whose response time is determined primarily by their own operating characteristics. The rhometer, plugging meter, oxygen meter, and hydrogen meter are examples of the first type, in that their response time will largely depend on how long it takes for the reaction product to travel from the leak to the monitor in sufficient quantity to provide a signal. The response time of the hydrogen detection tube, which utilizes a diffusion membrane, is about 15 seconds for the instrument itself.

The acoustic detector has the greatest potential advantages, as detection would be practically instantaneous. An additional advantage of acoustic detectors is the possibility of locating leaks by use of an array of three or more detectors. The basic difficulties are signal-to-noise ratio and attenuation of signal between the leak and the detection point.

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13.0 EXTERNAL CORROSION PROCESSES

FUEL ASSEMBLIES

CONTROL ROD SYSTEMS

POWER INSTRUMENTATION/GAS LINES

INSTRUMENT TREE/IVFH MACHINE

CLOSED LOOPS

REACTOR VESSEL, GUARD VESSEL

CORE SUPPORT STRUCTURE, RESTRAINT SYSTEM

REACTOR HEAD

BAFFLE PLATE

PRIMARY AND SECONDARY PUMPS

PRIMARY AND SECONDARY PIPING

PRIM. AND SEC. SODIUM PURIFICATION

DUMP Hx, IHx

STEAM GENERATORS

INERT GAS SYSTEMS

NA AFFECTED CORR.-CONTAINMENT AREA

NA AFFECTED CORR.-OUTSIDE CONT.

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13.0 EXTERNAL CORROSION PROCESSES

13.1 INTRODUCTION

13.1.1 Scope of Chapter

The external corrosion review will be limited to corrosion and general degradation agencies which are of potential importance to the LMFBF system affected by sodium excursions outside the primary and secondary system envelopes, i.e., spills, leaks, etc. A sodium-water interface will occur in the intermediate HX tubes for LMFBF plants using water/water steam generators and in the steam generator and superheater tubes for plants using the sodium/water steam generator concept (e.g., CRFBF). The special degradation problems associated with the sodium-water interface have been discussed in Chapter 12 in sufficient detail to introduce the general problem area and to serve as a basis for subsequent updating of this area. Such phenomenon as wastage will not, therefore, be within the scope of the external corrosion chapters.

Degradation processes within the scope of this chapter might be categorized as follows:

- a. Corrosion processes in which there is exchange of ambient species-- N_2 , O_2 , H_2O (vapor and liquid)--with the sodium.
- b. Corrosion processes in which there is limited exchange in the above respect because of thermal insulation and various protective envelopes.
- c. Corrosion and mass transfer effects associated with sodium events in which nitrogen is a principal ambient species

The unpredictable circumstances attending most of the above degradation categories precludes quantitative analysis and essentially limits any discussion to qualitative comments, qualified insofar as is possible, by service and laboratory experience. The major materials inventory of LMFBF systems may be separated into the broad categories

of austenitic and ferritic materials. The discussion of corrosion behavior under unstressed, and stressed, conditions, will attempt to identify common, and distinguishing, corrosion characteristics of these classes of materials.

Some of the chemistry and corrosion pertinent to this chapter overlap discussions given in Chapters 9 and 12. The present subject is complex enough to justify additional discussion of these common areas to the extent they relate to external corrosion.

13.1.2 Sodium Spill/Leak Potential

Published accounts do not support sodium spill/leak events attending the operation of LMFBR plants as a major problem area. For example, British experience with the Dounreay reactor over a 14 year span apparently involved only five small leaks with a NaK inventory of 100 tons.^(1,2) Up to December 1972, no major spills had been reported in U.S. systems.⁽³⁾ French experience with the Rapsodie and Phenix reactor plants, and the sodium leak detection and confinement techniques evolved therefrom, indicate some incidence of small sodium leaks of varying degrees of severity.⁽⁴⁾ The Germans experienced a loss of 500-1000 kg of sodium from a defective weld in a secondary storage system tank.⁽⁵⁾

An assessment of accident severity and probability given for the CRFBR is shown in Table 13.1.2-1 (Reference 6), and this reflects the encouraging spill/leak experience accumulated to-date. The universal recognition of the chemical reactivity of sodium has enforced close attention to the mechanical and metallurgical details of sodium plant systems which minimize manifestation of this reactivity. The tolerance for carelessness in design, maintenance, and surveillance is small, however, in connection with sodium. The practical significance of this fact can be demonstrated only by performance of the large scale commercial powerplant.

References for 13.1.2

1. J. Kirk, "UKEA Experience in the Detection of Liquid Metal Fires," Intl. Working Group on Fast Reactors-Specialist's Meeting on Sodium Combustion and Its Extinguishment-Techniques and Technology, Richland, WA, May 22-26, 1972.
2. R. R. Mathews, K. J. Henry, "Repair of DFR Leaks," Nucl. Eng., 10, October 1968, p. 840.
3. H. A. Morewitz, "Sodium Combustion and Its Extinguishment-Techniques and Technology," Part I, Intl. Working Group on Fast Reactors-Specialist's Meeting on Sodium Combustion and Its Extinguishment-Techniques and Technology, Richland, WA, May 22-26, 1972.
4. M. Sauvage, Y. Fruchard, "Sodium Combustion and Its Extinguishment-Techniques and Technology," ibid.

References for 13.1.2 (contd)

5. Element 5, Sodium Technology, WASH-1105, 2nd Ed., USAEC(ANL), December 1972.
6. J. Graham, L. E. Strawbridge, P. Bradbury, "Safety of the Clinch River Plant," Nucl Eng. Intl., October 1974, p. 854.

Table 13.1.2-1 (Ref. 6)

Classification of Accidents and Acceptance Criteria for CRFBR

Level	Event or accident class	Definition ● Examples only	Prob. (per reactor year)	Upper limit acceptance criteria*
1	Normal Operation	Events which will normally occur: ● Full power operation ● Startup & shutdown ● Random fuel pin failure	1	Accumulated cladding strain < 0.1%
2	Anticipated Transients	Events which, based on experience, are expected to occur at least once in the life of the plant: ● Loss of off-site power ● Loss of power to one pump ● Operator error ● Scrams	1—3·10 ⁻² (30 year plant life)	< 0.3%
	Unlikely Events	Events which are not expected to occur individually, but which might, based on the number of such possibilities, occur once during the life of the plant: ● Pump seizure ● Reactivity transient up to c/sec	3·10 ⁻² —10 ⁻⁴	< 0.7% Integrity limit (above this limit fuel cladding can fail)
3	Extremely Unlikely Events	Events never expected to occur: ● Maximum flood or earthquake or forest fire or tornado ● Large sodium fire ● Large sodium-water reaction ● Loss of off-site power and a diesel generator	~ 10 ⁻⁴ —~ 10 ⁻⁷	No loss of in-place coolable geometry Interpreted as: (1) No clad melting and relocation (2) No sodium boiling
	Hypothetical Events	Design margins to provide for unforeseen events		

* A fuel acceptance criterion is used here only as an example. Other criteria such as radioactivity release requirements also exist.

13.1.3 Possible Gas Atmospheres Ambient to Sodium Events

Sodium free surfaces in the reactor vessel and other primary circuit components will be protected by argon. Nitrogen is specified as the 'inert' gas cover for the reactor vessel, the space around the primary sodium circuit, and certain sodium sensitive work areas. Depending on the specific incident, sodium spills/leaks will be exposed to an ambient atmosphere ranging from nitrogen (plus deliberate, or inadvertent, impurities), to air with various water vapor contents. Liquid water, with various impurities, would be assigned an extreme position on the ambient environment spectrum with respect to harmful potential. The presence of liquid water in sodium sensitive zones would be classed as an accident, or improbable event.

Tentative specifications for the nitrogen gas for the FFTF⁽¹⁾ call for 1 +/- 0.2 vol% O₂. CO₂ is also being considered as an additive to nitrogen.⁽²⁾ Small amounts of oxidizing species are believed capable of reducing the potential corrosion effects of water vapor excursions into sodium sensitive areas. As will be discussed in Sections 13.2, 13.3 and 13.4, liquid water and water vapor, maximize the corrosion and damage consequences of a sodium spill/leak event. With respect to corrosion, the principal reaction product of sodium with H₂O, NaOH, has serious implications for both austenitic and ferritic materials, with emphasis on the ferritic materials.

The chemical reactivity of sodium will produce sodium compounds with many constituents of the ambient atmosphere. Sodium carbonate (Na₂CO₃), formed by the reaction of sodium with moist air⁽³⁾ is an expected reaction product with NaOH as an intermediate. Sodium carbonate appears, however, to be relatively innocuous with respect to corrosion and is possibly a desirable buffer between sodium and H₂O.⁽²⁾

References for 13.1.3

1. Fast Flux Test Facility Design Safety Assessment, HEDL-TME 72-92, July 1972.

References for 13.1.3 (contd)

2. Element 5, Sodium Technology; WASH-1105, 2nd Edition; USAEC(ANL), December 1972.
3. J. W. Mausteller, F. Tepper, S. J. Rodgers, Alkali Metal Handling and System Operating Techniques; Gordon and Breach Pub., NY, 1967.

13.1.4 Temperature Range Associated with Sodium Events

Figure 13.1.4-1 is a simplified schematic of various LMFBF plant systems. The sketches for the CRFBR and FFTF indicate temperatures associated with various circuit elements.^(1,2) Figure 13.1.4-2 is a more realistic schematic of major circuit components planned for the CRFBR system. Figure 13.1.4-3 is a schematic of a typical heat transfer loop for the FFTF, showing the disposition of guard vessels used to contain sodium spills/leaks. The CRFBR also uses guard vessels for the primary pumps, intermediate HX's, and the reactor vessel.

Temperatures attending sodium events in the external system may be expected to range from maximums indicated in the schematics (535-590°C) to near room temperature, depending on the event location and the temperature of the environment contiguous to the event. The exothermic nature of many sodium reactions presents some potential for excursions in excess of the temperature maximums indicated above. Temperature maximums would also depend on the thermal insulation, the rate of supply of reactants, and the heat dissipation agencies active in the event.

References for 13.1.4

1. W. M. Jacobi, "The Clinch River Breeder Reactor Project Nuclear Steam Supply System," Nucl. Eng. Intl, October 1974, p. 846.
2. Fast Flux Test Facility Design Safety Assessment, HEDL-TME 72-92 July 1972.
3. D. E. Simpson, "FFTF Design for Safety," Fast Reactor Safety Conf. Beverly Hills, CA, April 1974, CONF-740401, p. 1042.

Figure 13.1.4-1
Schematics of Various LMFBF Plant Systems

Figure 13.1.4-2 (Ref. 1)
Clinch River Schematic

Figure 13.1.4-3 (Ref. 3)
FFTF Heat Transfer System

13.1.5 Some General Maintenance and Surveillance Guide Lines

The proposition that the desirable physical properties of sodium outweigh its undesirable chemical reactivity will be tested in the FFTF (400 MWT) and CRFBR(970 MWT) systems. Demonstration of this proposition is underway, or imminent, at a number of foreign LMFBR plants exceeding the 500 MWT power category, namely: PFR(Dounreay, UK), BN-350(Shevchenko, USSR), Phenix(Marcoule, France), BN-600(Beloyarsk, USSR), SNR(Kalkar, W. Germany). To varying degrees, these plants will impose the operating and maintenance vagaries associated with large systems on the management of sodium. Obvious factors in the success of this management are: quality of design and construction, quality of the maintenance of the sodium associated systems. The latter factor is critically dependent on the surveillance given both the internal and external surfaces of the sodium containment systems. Internal surveillance and monitoring of sodium contaminants will give the first indication of the success of the system in accommodating to sodium. External monitoring is concerned with less subtle events, namely, sodium spills/leaks, which are final indicators of failure in sodium accommodation due to causes ranging from carelessness in some part of the fabrication-inspection-assembly sequence, to improper design, or operation beyond design limits.

The signals obtained from the internal monitoring will be used to corroborate design decisions, or to suggest improvements in design. The presence of sodium external to containment, signaled by the external monitors and visual inspection, allows relatively little time for correction. Sodium leaks and spills present: (1) a potential for strongly exothermic reactions with oxygen and water, plus generation of a powerful oxygen reducing agent, hydrogen; (2) a potential for forming a number of compounds, and ionic species, which can be inimical to the containment structure. While the austenitic materials are possibly less sensitive than the ferritic materials in this respect, caustic stress corrosion has affected virtually all materials pertinent to LMFBR systems.

Minimizing the consequences of probably inevitable leaks and spills will depend on the success in excluding reactive environmental constituents

from system zones with the greatest probability of high temperature sodium spills, on the speed with which an inert atmosphere can be applied to the trouble area, and on the quickness and thoroughness of cleanup action.

13.2 Na REACTIONS PERTINENT TO EXTERNAL CORROSION

13.2.1 Scope of Problem

The scope of chemical reactivity of sodium, within the reactant field presented by conceivable ambient conditions, is large and complex. Furthermore, it is difficult, a priori, to assign meaningful probabilities, to the various parts of this reactant field as a prelude to emphasizing particular reactions and reaction products. A suitably realistic approach to this problem appears to be a brief review of the principal Na reactions with the O_2 - H_2O , and air- H_2O systems and an identification of the reaction products which appear to have the greatest potential for corrosive effect on LMFBR structural materials. With respect to ultimate corrosive effect, H_2O is the most harmful reactant with sodium and this compound may be expected to obtain in vapor form over a wide range of concentrations, in the majority of sodium spill/leak events. Liquid water may also be involved as an immediate partner of sodium reaction through a somewhat improbable conjunction of accidents, or it may derive in various amounts from condensation of water vapor under chemical and/or physical encouragement.

The immediate reaction environment may favor heat dissipation and some dispersal of reactants and products. Or it may, as in the case of leaks behind thermal insulation, confine the reaction and permit local temperature escalation from the reaction heat input. In any event, the course of the sodium-ambient environment reaction will be dependent on the specific conditions attending the leak/spill event.

Table 13.2.1-1 from Reference 1 presents a summary of the principal reactions of sodium and sodium products with the O_2 - H_2O system. The intrusion of air to a sodium event will add the possibility of Na- N_2 and Na- CO_2 reactions to this list. These additional species will be discussed briefly later in this section. While some participation of both nitrogen and CO_2 are to be expected in the majority of sodium events, the reactions presented in Table 13.2.1-1 are considered to be the most important. Of

these reactions, several might be regarded as principal with respect to external sodium events and these will be discussed in the following parts of this section.

References for 13.2.1

1. O. J. Faust (Ed.), Sodium-NaK Engineering Handbook, VI, Gordon and Breach, N.Y. 1972.

Table 13.2.1-1 (Ref. 1)
Reactions of the Na-O-H System

<u>Equation</u>	<u>Equation Number</u>
$\text{Na} + \text{H}_2\text{O} = \text{NaOH} + 1/2\text{H}_2$	1
$2\text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{NaH}$	2
$\text{Na} + \text{NaOH} = \text{Na}_2\text{O} + 1/2\text{H}_2$	3
$2\text{Na} + \text{NaOH} = \text{Na}_2\text{O} + \text{NaH}$	4
$\text{NaH} = \text{Na} + 1/2\text{H}_2$	5
$\text{NaH} + \text{H}_2\text{O} = \text{NaOH} + \text{H}_2$	6
$2\text{Na} + 1/2\text{O}_2 = \text{Na}_2\text{O}$	7
$\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$	8
$2\text{Na} + \text{O}_2 = \text{Na}_2\text{O}_2$	9
$2\text{Na} + \text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{NaOH}$	10

13.2.2 Na + H₂O Reaction

The reactivity of sodium with water is indicated by the fact that solid sodium will react violently with ice at temperatures above about -98°C if the reactants are brought into hard contact.⁽¹⁾ Under small concentrations of water vapor [100-400 ppm (vol)] at temperatures ranging from 200-350°C sodium will react to form Na₂O, with hydrogen evolution. The Na₂O forms a layer on the surface of sodium which progressively lowers the reaction rate. The reaction rate appears to be roughly linear with H₂O concentration, and probably follows the reaction scheme,

At very low H₂O pressures, Reference 1 reported that no NaOH has been noted, possibly a result of the low hydrogen partial pressure favoring dissociation of NaOH. At H₂O pressures of about 15-65 mm, and temperatures greater than about 125°C, sodium and water react smoothly, forming an NaOH film over the sodium. The rate of NaOH formation is a function of the temperature and p_{H₂O}, and follows a rate law of the type,

$$p_{\text{H}_2\text{O}} = k t^n \quad (n \sim 1.2 \text{ at start and less than } 1/2 \text{ after a few seconds of reaction})$$

Above about 300°C, the Na-NaOH interaction becomes rate controlling (Equations 3 and 4 in Table 13.2.1-1). Below about 315°C, for any ratio of reactants and products, the consensus opinion⁽²⁾ appears to support the overall reaction,

Above about 315°C, this reaction also applies for an excess water condition. For the same temperature regime, an excess of sodium will lead to the overall reaction,

Generally, when oxygen is excluded from the Na-H₂O reaction, the reaction proceeds 'smoothly'. Violent effects are usually associated with the

O_2-H_2 secondary reaction under appropriate confinement conditions. Violence is, however, a relative term and the heat release potential of the $Na-H_2O$ reaction, plus the correlative hydrogen effects, must be regarded as prime degradation factors in systems with potential for sodium-water coupling. For temperatures above the MP of NaOH ($319^\circ C$) reactions 3 and 4 (see Table 13.2.1-1) are possible secondaries. The resulting NaH, NaOH and Na_2O reaction products, coupled with sodium, constitute a complex physical-chemical system which defeats simple reaction characterization. For example, NaH stability depends on the ambient hydrogen pressure at temperatures below about $385^\circ C$, according to the usual equilibrium predictions. Above this temperature, however, NaH dissociation appears to be controlled by the total ambient pressure.

References for 13.2.2

1. O. J. Faust (Ed.), Sodium-NaK Engineering Handbook, VI, Gordon and Breach, N.Y., 1972.
2. J. A. Ford, "Literature Review of the Sodium-Water Reactions" APDA-167, March 1967.

13.2.3 Na + O₂, H₂O and H₂ Effects

The principal Na-O₂ reaction product is Na₂O, given O₂ reaction 7 of Table 13.2.1-1 (Reference 1). At temperatures below about 48°C, dry oxygen reacts slowly with sodium and the rate law does not appear to fit conventional schemes.⁽¹⁾ For the T range 98-145°C, dry oxygen exhibits several reaction characteristics with sodium. Below about 110°C, the reaction follows the law,

$$x^n = kt \text{ (x is reaction parameter)}$$

This reaction may persist for several weeks exposure, with an n range of 1-3 which is constant for a given temperature and insensitive to oxygen pressure, while k is a function of both T and p_{O₂}. Above about 110°C, occasional spontaneous ignition will occur. After a time, the reaction appears to follow a law of the type,

$(x - x_0)^n = k(t - t_0)$, where x₀ and t₀ refer to the reaction coordinates at the time the above law is established.

Both H₂O and H₂ affect the Na-O₂ reactivity. A summary of the p_{H₂O} and p_{O₂} interaction with sodium is given in Table 13.2.3-1, from the work of Longton cited in Reference 2. The corresponding reaction modes and temperatures are given in the table. Similar effects of hydrogen on the Na-O₂ reaction are noted in Table 13.2.3-2.

References for 13.2.3

1. O. J. Faust (Ed.), Sodium-NaK Engineering Handbook, VI, Gordon and Breach, N.Y., 1972.
2. T. S. Krolikowski, "Violently Sprayed Sodium-Air Reactions in an Enclosed Volume;" ANL-7472, September 1968.

Table 13.2.3-1 (Ref. 2)

Interaction of H₂O (Vapor) and O₂ in Sodium ReactivityModes of Reactivity of Sodium at Various
Water Vapor-Oxygen Levels²¹

Partial Pressure of Water Vapor, mm Hg	Partial Pressure of Oxygen, mm Hg ^a									
	10	50	100	200	300	400	500	600	700	900
0.00002	N	N	N	N	N	N	N	N	N	N
0.0001	I	N	N	N	N	N	N	N	N	N
0.001	I	I	I	I	I	I	N	N	N	N
0.01	R	R	I	I	I	I	I	I	I	I
0.1	R	R	R	R	R	R	R	R	R	I
0.25	R	R	R	R	R	R	R	R	R	R

^aN: No detectable reaction at any temperature up to 550°C; reaction rate
<1 x 10⁻⁶ g Na/(cm²)(min).

I: No reaction until a certain temperature, the ignition temperature, is exceeded.

R: Immediate reaction, without ignition at 105°C.

Temperatures Corresponding to the
Sodium-reaction Modes²¹

Partial Pressure of Water Vapor, mm Hg	Partial Pressure of Oxygen, mm Hg									
	10	50	100	200	300	400	500	600	700	900
0.00002	550	550	550	550	550	550	550	550	550	550
0.00001	460	550	550	550	550	550	550	550	550	550
0.001	296	292	288	295	310	380	550	550	550	550
0.01	105	105	190	200	207	215	240	261	280	390
0.1	105	105	105	105	105	105	105	105	105	232
0.25	105	105	105	105	105	105	105	105	105	105

Table 13.2.3-2 (Ref. 2)
Effects of Water Vapor and Hydrogen on Na-O₂ Reactivity

P_{H_2O} , mm Hg	P_{O_2}/P_{H_2O}	Phenomenon	P_{H_2} , mm Hg	P_{O_2}/P_{H_2}	Phenomenon
0.00002	1×10^7	No detectable reaction at 550°C	nil	-	No detectable reaction at 550°C
0.0001	2×10^6	No detectable reaction at 550°C	0.00005	4×10^6	No detectable reaction at 550°C
0.001	2×10^5	Ignition at 295°C	0.0005	4×10^5	Ignition at 270°C
0.01	2×10^4	Ignition at 200°C	0.005	4×10^4	Ignition at 242°C
0.1	2×10^3	Immediate slow reaction at 105°C	0.05	4×10^3	Immediate slow reaction at 105°C

13.2.4 Na + CO₂, Na + N₂

Carbon dioxide will be present in the atmosphere ambient to sodium releases in concentration depending primarily on the amount of air incursion to the controlled atmosphere. As noted in Section 13.1.3, some consideration is being given to the use of small additions of CO₂ to the nitrogen 'inert' gas areas of sodium plants under the presumption that the principal oxidation product, Na₂CO₃, will tend to impede the Na-H₂O reaction.

Citing Japanese work, Mausteller⁽¹⁾ notes that sodium carbonate, Na₂CO₃, appears to be a principal reaction product between sodium and moist air. The carbonate is apparently formed directly from sodium, or through the reactions of Na₂O and NaOH with CO₂. Faust⁽²⁾ cites work showing that the reaction between Na and dry CO₂ is insignificant below about 200°C. Above about 300°C, various products are formed between Na and CO₂, namely, free carbon, NaCO, Na₂C₂, Na₂C₂O₄, NaHCO₂.⁽²⁾ The quantity and persistence of these products are dependent on the temperature of the reaction and the phases participating. Sodium carbonate, Na₂CO₃, is, however, the chief product in reaction between CO₂ and sodium in moist atmospheres. While data appear to be sparse, there is no evidence that Na₂CO₃ is a major factor in the corrosion of structural materials and it may, in fact, afford some protection against the Na-H₂O reaction via structural blocking of the H₂O.

Nitrogen will be a principal component of the atmosphere ambient to sodium releases within the containment areas protected by nitrogen and where air is present as a principal component, or as a contaminant. A number of sodium-nitrogen compounds are known, e.g., Na₃N, Na₃N₃, and Na(N₃)₂, the latter two compounds being the azide and diazide, respectively. The direct Na-N₂ reaction is, however, not expected to be a significant factor in external corrosion processes. Under conditions of an ambient nitrogen atmosphere and temperatures permitting sufficient mobility of nitrogen in sodium (via various carrier states), nitrogen may be of some importance in connection with the nitriding of certain structural materials. This phenomenon will be discussed in Section 13.5.

References for 13.2.4

1. J. W. Mausteller, F. Tepper, S. J. Rodgers, Alkali Metal Handling and System Operating Techniques; Gordon & Breach, N.Y., 1967.
2. O. J. Faust (Ed.), Sodium-NaK Engineering Handbook, VI, Gordon and Breach, N.Y., 1972.

13.2.5 Influence of Various Dissolved Species in Na Corrosion

Three 'interstitial' elements will be involved to some extent in reactions within the scope of this section, namely, carbon, oxygen and nitrogen.

Oxygen is believed to have a comprehensive influence in mass transport and corrosion processes involving the Na-O-H system. A solubility curve for oxygen in sodium is given in Figure 13.2.5-1.⁽¹⁾ The principal Na-O compound, as noted above, is believed to be Na₂O. The actual state of oxygen dissolved in liquid sodium is, however, not well established. In addition to the Na₂O compound, Nevzorov⁽²⁾ presents evidence to suggest that oxygen exists in the ionic form, O²⁻, within liquid sodium and that this species is active in both carbon transport and general corrosion effects involving oxygen in sodium.

Carbon solubility and state within liquid sodium are less well established. A carbon solubility summary given in Reference 1 indicates a carbon solubility ranging from about 50 ppm at the melting point of sodium (98.7°C), to about 200 ppm at 1100°C, although experimental confirmation of these carbon levels is apparently rather poor. CO is believed to be a principal compound between carbon and oxygen in sodium, and also the prime intermediate coupling in carbon transfer in sodium systems.⁽²⁾

Nitrogen solubility in sodium is low. Reference 1 cites a single value of about 4.4×10^{-10} moles N₂ per mole of Na at 500°C. The possibility of nitriding of structural materials by nitrogen-sodium cooperation at elevated temperatures will be discussed in Section 13.5.

References for 13.2.5

1. O. J. Faust (Ed.), Sodium-NaK Engineering Handbook, VI, Gordon, Breach, N.Y., 1972.
2. B. A. Nevzorov, Corrosion of Structural Materials in Sodium, IPST, Jerusalem, 1970.

Figure 13.2.5-1 (Ref. 1)
Oxygen Solubility in Sodium

13.2.6 Summary of Section 13.2

From the perspective of the external corrosion environment, the principal products of the Na-environment reaction appear to be NaOH, Na_2O , NaH and H_2 . These products will obtain, in various proportions, over a wide range of conceivable ambient atmosphere conditions. The structural effects of these products will depend on the temperature history of the sodium event, the residence time these species are allowed on structural materials, the local stress (strain) and metallurgical state of the material, the conditions which affect the mobility of the reaction products within, and from, the reaction environment, and on the presence of sodium independent ionic species and compounds which might sensitize (e.g., chloride ion) the material to sodium related corrosion processes.

Although Na_2O has been cited as a dangerous reaction product with respect to corrosion (cf Section 13.3), the quantitative data pertaining to this compound appear to be very sparse. Furthermore, Na_2O and NaOH can coexist under a wide range of reaction conditions and the presence and influence of NaOH should be suspect in some cases of reported Na_2O corrosion effects.

NaOH must be labeled the most generally significant reaction product of sodium with respect to corrosion potential for the principal structural materials of LMFBR systems. While, as noted in Section 13.2.2, NaOH is the main nongaseous reaction product of sodium with liquid H_2O , and a principal product of high water vapor atmospheres, the data pertaining to formation of NaOH at low $p_{\text{H}_2\text{O}}$ levels in inert gas, N_2 , or oxygen bearing atmospheres is very sparse. Over the temperature range 94-128°C, under static and flowing atmosphere conditions, Besson and Pelloux⁽¹⁾ observed NaOH and $\text{NaOH}\cdot\text{H}_2\text{O}$ as the sole reaction products down to $p_{\text{H}_2\text{O}}$ levels of 1 mm Hg. At a $p_{\text{H}_2\text{O}}$ of 10 mm Hg, Longton⁽²⁾ reported NaOH as the principal product for temperatures below about 300°C with Na_2O and NaH predominating at higher temperatures. Results of Addison and Manning cited by Henry⁽³⁾ indicate that NaOH is a sole, or principal

product, over the p_{H_2O} range 150-650 mm, and temperature range 125-175°C. In the latter work, NaH was observed as a co-product at the higher p_{H_2O} and temperature levels.

Longton⁽²⁾ has presented perhaps the most comprehensive summary of the reaction characteristics of the Na-H₂O-O₂ system. His work has illustrated many aspects of the interplay between O₂ and H₂O in sodium reaction. Inasmuch as oxygen will be a co-contaminant, or atmospheric constituent, attending virtually all sodium events in the external system, Na-H₂O reaction information, without some coupling with oxygen influence, would appear to be primarily of academic interest in the present context.

Figure 13.2.6-1 is an attempt at summarizing some of Longton's observations on the Na-O₂-H₂O system. Existence regions for NaOH, Na₂O and NaH, reported by the previously mentioned authors for the Na-H₂O reaction at moderate temperatures, are given along the ordinate (0% O₂). Water vapor pressures corresponding to 1% and 100% relative humidity are given for the temperature range 0-50°C (32-122°F). It is seen that both the 1% and 100% RH ranges are within the spontaneous reaction field established by Longton for temperatures not greater than 105°C. The temperatures determined by Longton for reaction within region 'I' are given in the figure at the limits of the 'I' field. It is to be noted that a temperature in excess of roughly 300°C will activate the Na-O₂-H₂O reaction over most conceivable values of p_{H_2O} and p_{O_2} obtainable in external system events.

The actual reaction products corresponding to various points of the p_{H_2O} - p_{O_2} grid is a complex function of temperature and specific reaction conditions. Newman and Smith,⁽⁴⁾ in analyzing the Na-H₂O reaction over a wide range of temperatures, state that below about 427°C NaOH, Na₂O and NaH will obtain in various proportions, whose sensitivity to specific reaction conditions discourages any generalization in this respect. Although their work did not include O₂ influence, this statement would not appear to be affected by O₂ presence.

The presence of NaOH as a significant, if not primary, reaction product attending most conceivable sodium events in the external system

Figure 13.2.6-1

Reaction Tendency and Products for Na-H₂O-O₂ System

appears to be well established. H_2O vapor may be expected as a reactant over a wide range of partial pressure. Liquid water is certainly not an improbable reactant, deriving either from 'accidents,' or from condensation. Condensation of water is encouraged by the presence of hygroscopic compounds on structural materials and by the capillary condensation phenomenon, whose power is suggested by the data of Table 13.2.6-1, where the ambient relative humidity at which condensation will begin is given as a function of the capillary radius. The corrosion significance of the presence of the OH^- ion will be discussed in Sections 13.3 and 13.4.

Table 13.2.6-1 (Ref. 5)
Capillary Condensation Data

Dependence of the Pressure P_1 of Saturated Water Vapor on the Radius of Curvature r of a Concave Meniscus

P_0 = Pressure of Water Vapor on a Flat Water Surface;
 q = Relative Humidity at Which Condensation Begins on a Concave Meniscus; Temperature 15° C

r , cm	P_1 , mm Hg	$\frac{P_1}{P_0}$	q , %
∞	12.7	1.000	100
69.4×10^{-7}	12.5	0.985	98
11.1×10^{-7}	11.5	0.906	91
2.1×10^{-7}	7.5	0.590	59
1.2×10^{-7}	5.0	0.390	39

References for 13.2.6

1. J. Besson, A. Pelloux, "La cinetique d'oxydation du sodium par la vapeur d'eau. Influence de la diffusion en phase gazeuse," Compts Rendu, Serie C, 262, 1966, p. 1579.
2. P. B. Longton, T. S. Krolikowski, data cited in: "Violently Sprayed Sodium-Air Reactions in an Enclosed Volume," ANL-7472, Sept. 1968.
3. J. L. Henry, "A Survey of the Sodium-Water Reaction and Reaction Products," USBM-RC-1469, 1970.
4. R. N. Newman, C. A. Smith, "Sodium/Water Combustion and the Chemistry of Wastage at Sodium/Water Leak Sites," J. Nucl. Matls, 52, 1974, p. 173.
5. N. D. Tomashov, Theory of Corrosion and Protection of Metals; The MacMillan Co., N.Y., 1966, p. 371.

13.3 UNSTRESSED CORROSION EFFECTS OF Na-H₂O-O₂ SYSTEM

13.3.1 Scope of Problem

The structural effects of a sodium spill/leak will depend on the subsequent temperature and chemical history of the sodium, including duration of contact, and particularly on the material in contact with the sodium. This discussion will be concerned principally with the corrosion behavior of austenitic and ferritic steels in contact with static liquid sodium and its principal reaction product with water and water vapor, namely, NaOH. Oxygen plays a pervasive role in sodium corrosion and some indication of its influence will also be given, although the mechanism of oxygen interaction in sodium and caustic (NaOH) degradation processes remains somewhat obscure. Nitrogen effects in the presence of sodium will be discussed in a separate Section (13.5).

The quantitative relation of a specific sodium spill/leak to structural degradation is virtually impossible, beyond indicating temperature and chemical conditions which can lead to significant corrosion with specific materials. There are sufficient data in this respect to indicate, however, that few materials are tolerant of sodium 'accidents,' with or without, conjoint stress action.

This section will review some information concerning both high and low temperature sodium effects on austenitic and ferritic alloys. The observations of sodium action will be followed by a discussion of caustic (NaOH) corrosion effects over a temperature range of significance to the LMFBR external system.

13.3.2 Austenitic Materials

13.3.2.1 Na Corrosion, Oxygen Influence

Up to temperatures of the order of 700°C, the austenitic stainless steels have exhibited relatively good stability to liquid sodium up to oxygen levels which are expected to obtain in practical working environments under reasonable contamination control. Table 13.3.2.1-1 is a summary of static corrosion data for a number of austenitic SS's in liquid sodium, at temperatures ranging from 274 to 1000°C. Data for flowing sodium systems are also included and it is seen that corrosion under flow conditions is generally more severe than under a static condition where adverse concentration (activity) gradients controlling the corrosion process might not be expected to persist for long periods.

The harmful effect of high oxygen levels in sodium are indicated in Table 13.3.2.1-2, for oxygen levels ranging from 50 to 5000 ppm. Oxygen is believed⁽²⁾ to function as an intermediary in the transport of carbon and alloying constituents from the alloy to the sodium. Electrochemical action in sodium systems is not well characterized at present. It is certainly not inconceivable that some of the potent oxygen influence may be ascribable to its ability to 'unblock' electrochemical corrosion processes even in systems with relatively low water contents. As will be noted in the following section, both the austenitic SS's and the low alloy chromium steels exhibit roughly similar corrosion behavior in liquid sodium and oxygen contaminated sodium up to the order of 100 ppm oxygen and temperatures of about 600°C. A consolidation of the effect of dissolved oxygen on sodium corrosion for these types of materials is given in Table 13.3.2.1-3, for oxygen levels ranging from 10-50 ppm.

References for 13.3.2.1

1. W. E. Berry, Corrosion in Nuclear Applications; John Wiley, NY 1971.
2. B. A. Nevzorov, Corrosion of Structural Materials in Sodium, IPST, Jerusalem, 1970.

Table 13.3.2.1-1 (Ref. 1)
Corrosion of Austenitic Alloys in Isothermal Sodium

Steel	Temperature, C	Flowing	Static	Exposure Time, hr	Weight Change Rate, mg/dm ² -month(b)
AISI Type 304	274		X	100	+77
	510	X		—	< .10
	566		X	1913	.3
	593	X		1000	+17
	593		X	1000	+15
	704		X	—	< .10
AISI Type 304 Welded and sensi- tized	593	X		500	+38
	593		X	500	+30
AISI Type 310	593	X		500	+75
	593		X	500	+27
	704		X	—	< .10
AISI Type 316	593	X		1000	+10
	593		X	1000	+13
AISI Type 316 Welded	593	X		1000	+11
	593		X	1000	+11
AISI Type 318	593	X		500	+86
	593		X	500	+27
AISI Type 347	510	X		—	< 10
	593	X		500	+146
	593		X	500	-22
	649	X		—	< 10
	704		X	—	< 10
18Cr-35Ni	704		X	—	< 10
AISI Type 304	1000		X	400	+2550
AISI Type 316	1000		X	400	+2960
AISI Type 310	1000		X	400	+2820
AISI Type 347	1000		X	400	+1420
Inconel 600	1000		X	400	+1870

(a) Containing a maximum of 100 ppm oxygen.

(b) Specimens not descaled.

Table 13.3.2.1-2 (Ref. 1)

Effect of Dissolved Oxygen in Sodium on Corrosion
of Ferritic and Austenitic Alloys

Steel	Oxygen in Sodium ppm	Temperature, C	Exposure Time, hr	Weight Change Rate, mg/dm ² -month ^(a)
Armco iron	50	538	163	-30
	100	538	163	-19
	250	538	71	-1500
	600	538	137	-4060
5Cr-1/2Mo	100	500	—	< -10
	1000	500	—	-180
	5000	500	—	-580
9Cr-1Mo	100	500	—	< -10
	1000	500	—	-200
	5000	500	—	-540
	100	704	—	-40
	5000	704	—	-3700
AISI Type 410	100	500	—	< -10
	1000	500	—	-70
	5000	500	—	-510
	100	704	—	-40
	5000	704	—	-2600
AISI Type 304	100	500	—	< -10
	5000	500	—	-20
AISI Type 347	100	500	—	< -10
	1000	500	—	-50
	5000	500	—	-50

(a) Specimens not descaled.

Table 13.3.2.1-3 (Ref. 1)

Consolidated Values for Effect of Dissolved Oxygen
on Corrosion of Ferritic and Austenitic Alloys
in Flowing Sodium

Specimen Temp. (hot leg), C	Oxygen Content of the Sodium			
	10-15 ppm		45-50 ppm	
	Average #	Maximum	Average	Maximum
538	0.05	0.25	0.25	1.25
593	0.15	0.75	0.75	3.75
649	0.39	1.95	1.9	9.5
704	0.95	4.95	4.7	23.5

Mils/yr

13.3.2.2 Mass Transfer Effects in Sodium

Liquid sodium may affect the metal structure by removing, or depositing, carbon and alloying constituents. These effects are sensitive to the temperature of the sodium/metal system, the ability of the system to establish, and maintain, adverse activity gradients for carbon and/or alloying constituents. Static sodium spills and the residuals from sodium leaks are not expected to be serious in this respect if reasonable attention is paid to cleanup. A large sodium accumulation, however, maintained at high temperature and providing a sodium bridge between alloys of markedly different carbon activity and alloy content might effect some significant carbon and alloy element exchange if allowed to persist beyond a few minutes, or hours. Mass transfer in sodium has been discussed in Chapter 9. A brief review of some carburization and leaching effects is pertinent here. An indication of the effect of carburization on the ductility of austenitic alloys is given in Table 13.3.2.2-1. The alloys were exposed at 1050°F to a sodium loop containing a plain C steel (carburized) carbon source for 700 hr. Figure 13.3.2.2-1 indicates the ability of sodium to 'leach' alloying constituents from an austenitic steel (316 SS) matrix. It is seen that both Cr and Ni have been removed down to a depth of about 8 μ after the indicated exposure. Removal of austenite formers, (e.g., Ni, C) from an austenitic matrix will produce ferrite. Ferrite and austenite differ in strength and thermal expansion coefficients, (6.5×10^{-6} in./in./°F for ferrite; 10.6×10^{-6} in./in./°F for austenite). This strength and expansion disparity could lead to local strain accumulation under stress and temperature cycling which could affect the corrosion response of the affected zone. They also differ in their susceptibility to embrittlement from hydrogen and other interstitials, (e.g., N), in their response to various other contaminants which might be present in the sodium, and in their electrochemical characteristics. Apart from adverse geometrical effects of leaching, (micro crack, or sensitizing to crack formation) it is seen that under sodium exposure conditions which allow both carbon and alloy element perturbation of the structure,

Table 13.3.2.2-1 (Ref. 1)

Fracture Strain after 300 hr Exposure to Sodium
with Carbon Source

Alloy	Strain	
	Pre-exposure, %	Post-exposure, %
Incoloy 800	17	14
Type 304	40	17
Type 316	38	19
Type 347	25	9

Figure 13.3.2.2-1 (Ref. 1)

Typical Compositional Changes Associated with Sodium Leaching (1200°F, 5704 hr, [O] 12 ppm, 316 SS)

considerable opportunity for corrosive action is created. Proper house-keeping should minimize these effects, which generally require a number of hours at high temperatures to be significant.

References for 13.3.2.2

1. F. A. Comprelli, F. J. Hetzler, T. A. Lauritzen, "Clad Compatibility with Mixed Oxide Fuel and Sodium," ANL-7120, p. 355.

13.3.2.3 Caustic (NaOH) and Na₂O Corrosion

With respect to the corrosion potential for structural materials, the principal reaction product between sodium and the external ambient atmosphere is NaOH. The austenitic SS's and high nickel-chromium alloys (INCO 800, 600 for example) are generally superior to ferritic materials in resistance to caustic attack over the range of temperatures pertinent to the external LMFBR system. This point is, in fact, a major distinguishing characteristic between these types of materials under both stressed and unstressed conditions.

Although caustic corrosion is given extensive publicity, good comparative data on caustic corrosion resistance are surprisingly scarce. Though the specific exposure conditions vary widely, compilations of industrial exposure to caustic solutions are valuable indices of general resistance to caustic solutions. Considering the broad range of metals which could be involved in LMFBR systems, and the potential importance of caustic corrosion to these metals, the inclusion in this review of a recent, comprehensive, caustic corrosion assessment for a number of metals is felt justified. Tables 13.3.2.3-1, -2, present the data obtained from four caustic soda producers (Reference 1). Table 13.3.2.3-3 gives the composition of the materials involved in this test. These data support the previous assertion that the austenitic stainless steels and high nickel-chromium alloys have generally good resistance to caustic solutions at temperatures of interest to this review. The attainment of concentrated NaOH solutions during the course of sodium spill/leak events is by no means improbable considering the concentrating possibilities of cracks and crevices, condensed water intervention, and a residence time of sodium on the structural material of more than a few minutes.

Garr⁽²⁾ studied the effect of 50% NaOH solutions on austenitic SS (304) at temperatures ranging from 150 to about 300°F. His criterion for corrosion effect was discoloration of the stainless steel. He tested both cold worked and annealed steels under both static and bubbled solutions, using air and argon for the latter tests. Figure 13.3.2.3-1 is a typical summary of his observations for the tests. Bubbling increased the corrosion

13.3.2.3-2
Table 13.3.2.3-1 (Ref. 1)

"Round Robin" Test Program by Four Caustic Soda Producers--Comparison of Corrosiveness of Diaphragm Cell Versus Mercury Cell Caustic--Conducted by NACE Committee T5A-3D

Material	Corrodent	Average Temperature				Corrosion Rate, mils per year			
		Company				Company			
		1	2	3	4	1	2	3	4
		C F	C F	C F	C F				
Nickel 200	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1	<0.1	<0.1	<0.1
Nickel 200	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
Nickel 200	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	1.0	<0.1
Nickel 200	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
Nickel 200	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
Nickel 200	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	<0.1		0.2	
Nickel 200	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	0.2			
Nickel 200	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.3			
INCONEL alloy 600	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1 (1)	<0.1	<0.1	<0.1
INCONEL alloy 600	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCONEL alloy 600	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	<0.1	<0.1
INCONEL alloy 600	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCONEL alloy 600	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCONEL alloy 600	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	<0.1		0.2	
INCONEL alloy 600	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	0.3			
INCONEL alloy 600	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.2			
MONEL alloy 400	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1	<0.1	<0.1	<0.1
MONEL alloy 400	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
MONEL alloy 400	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	0.1	0.2	<0.1
MONEL alloy 400	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
MONEL alloy 400	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
MONEL alloy 400	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	<0.1		0.8	
MONEL alloy 400	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	0.4			
MONEL alloy 400	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.5			
INCOLOY alloy 800	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1	<0.1	<0.1	<0.1
INCOLOY alloy 800	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCOLOY alloy 800	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	<0.1	<0.1
INCOLOY alloy 800	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCOLOY alloy 800	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
INCOLOY alloy 800	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	0.1		4.1 (2)	
INCOLOY alloy 800	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	0.5			
INCOLOY alloy 800	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.3 (1)			
CARPENTER alloy 20 Cb-3	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1	<0.1	<0.1	<0.1
CARPENTER alloy 20 Cb-3	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
CARPENTER alloy 20 Cb-3	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	<0.1	<0.1
CARPENTER alloy 20 Cb-3	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
CARPENTER alloy 20 Cb-3	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
CARPENTER alloy 20 Cb-3	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	0.4		1.5 (3)	
CARPENTER alloy 20 Cb-3	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	0.5			
CARPENTER alloy 20 Cb-3	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.4			
ACI CN-7M	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	<0.1	<0.1	<0.1	<0.1
ACI CN-7M	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	<0.1	<0.1	<0.1	<0.1
ACI CN-7M	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	<0.1	<0.1
ACI CN-7M	50% NaOH-Mercury Cell	37 98	45 113	— —	Ambient	<0.1	<0.1	<0.1	<0.1
ACI CN-7M	50% NaOH-Mercury Cell	— —	Ambient	— —	Ambient	<0.1	<0.1	<0.1	<0.1
ACI CN-7M	73% NaOH-Diaphragm Cell	119 246	— —	99 210	— —	0.1		9.3	
ACI CN-7M	73% NaOH-Diaphragm Cell	125 257	— —	— —	— —	1.2 (1)			
ACI CN-7M	73% NaOH-Mercury Cell	114 236	— —	— —	— —	0.4			
Ni-Resist Type 3	50% NaOH-Diaphragm Cell	35 95	29 85	88 190	54 130	0.2	<0.1	0.4 (4)	<0.1
Ni-Resist Type 3	50% NaOH-Diaphragm Cell	40 104	— —	— —	Ambient	0.6	<0.1	<0.1	0.2
Ni-Resist Type 3	50% NaOH-Mercury Cell	38 100	105 221	82 180	60 140	<0.1	<0.1	<0.1	<0.1

13.3.2.3-3

Table 13.3.2.3-2 (Ref. 1)

"Round Robin" Test Program by Four Caustic Soda Producers--Comparison of Corrosiveness of Diaphragm Cell Versus Mercury Cell Caustic--Conducted by NACE Committee T5A-3D

Material	Corrodent	Average Temperature								Corrosion Rate, mils per year			
		Company								Company			
		1		2		3		4		1		2	
		C	F	C	F	C	F	C	F	1	2	3	4
Ni-Resist Type 3	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient	Ambient	0.2	0.1		0.1
Ni-Resist Type 3	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient	<0.1	<0.1		0.2
Ni-Resist Type 3	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	0.3		8.4	
Ni-Resist Type 3	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	2.3			
Ni-Resist Type 3	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	1.2			
Type 316 Stainless Steel	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	3.3	<0.1
Type 316 Stainless Steel	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient	Ambient	0.2			<0.1
Type 316 Stainless Steel	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	0.2	<0.1
Type 316 Stainless Steel	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient	Ambient	<0.1	0.1		0.3
Type 316 Stainless Steel	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient	<0.1	<0.1		<0.1
Type 316 Stainless Steel	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	6 (4)		8.7	
Type 316 Stainless Steel	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	13.1 (5)			
Type 316 Stainless Steel	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	10 (4)			
Type 304 Stainless Steel	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	1.1	<0.1
Type 304 Stainless Steel	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient	Ambient	<0.1			<0.1
Type 304 Stainless Steel	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	0.1 (1, 6)	0.3	<0.1
Type 304 Stainless Steel	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient	<0.1	11.0		0.4
Type 304 Stainless Steel	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient	<0.1	<0.1		<0.1
Type 304 Stainless Steel	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	15 (4)		13 (7)	
Type 304 Stainless Steel	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	19.4 (5)			
Type 304 Stainless Steel	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	15 (4)			
Ductile Cast Iron	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	1.4	3.1	12	2.6
Ductile Cast Iron	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient	Ambient	1.5 (8)			5.2
Ductile Cast Iron	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	0.4	0.3	0.6	1.0
Ductile Cast Iron	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient	Ambient	1.8	2 (8)		6.2 (2)
Ductile Cast Iron	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient		3.7		2.6
Ductile Cast Iron	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	73		18	
Ductile Cast Iron	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	106			
Ductile Cast Iron	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	103			
Gray Cast Iron	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	2.1	1.9	13	2.9
Gray Cast Iron	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient	Ambient	1.9			7.9
Gray Cast Iron	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	0.4	2 (9)	2.6	1.7
Gray Cast Iron	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient	Ambient	2.1	3		5.7
Gray Cast Iron	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient		4.5		3.5
Gray Cast Iron	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	54		27	
Gray Cast Iron	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	44			
Gray Cast Iron	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	82			
Mild Steel	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	1.4 (5)	1.4 (10)	20	2.1
Mild Steel	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient	Ambient	1.5 (9)			3.2
Mild Steel	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	0.6 (8)	3 (6, 10)	1.8 (7)	1.2
Mild Steel	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient		21		
Mild Steel	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient	Ambient	1.4	2		2.9 (5)
Mild Steel	50% NaOH-Mercury Cell	—	—	Ambient	—	—	—	Ambient	Ambient		5.1		1.9
Mild Steel	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	59		5.7	
Mild Steel	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	dissolved			
Mild Steel	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	>38			
Mild Steel	73% NaOH-Mercury Cell	—	—	—	—	—	—	—	—	71			

(1) Pitted to a maximum depth of 1 mil.

(2) Pitted to a maximum depth of 4 mils.

(3) Pitted to a maximum depth of 5 mils.

(4) Stress-corrosion crack through one of the identifying punch marks.

(5) Pitted to a maximum depth of 3 mils.

(6) Mercury droplets in tank, 2 rates shown are for the duplicate specimens (not averaged); specimen with high rate showed stress-accelerated local attack.

(7) Pitted to a maximum depth of 8 mils.

(8) Pitted to a maximum depth of 2 mils.

(9) Pitted to a maximum depth of 12 mils.

(10) Pitted to a maximum depth of 11 mils.

3/31/75

13.3.2.3-4
Table 13.3.2.3-3 (Ref. 1)

Nominal Compositions of Nickel Alloys in Use or Corrosion
Tested in Caustic Solutions

Compositions, %									
Material	Ni	Fe	Cr	Mo	Cu	C	Si	Mn	Other
WROUGHT MATERIALS									
Nickel									
Nickel 200	99.5	0.15	—	—	0.05	0.06	0.05	0.25	—
Nickel 201	99.5	0.15	—	—	0.05	0.01	0.05	0.20	—
DURANICKEL* alloy 301	94.0	0.15	—	—	0.15	0.55	0.25	0.25	Al 4.5; Ti 0.5
Nickel-Chromium Alloys									
INCONEL* alloy 600	76.0	7.2	15.8	—	0.10	0.04	0.20	0.20	—
NIMONIC* alloy 75	77.4	0.5	20.5	—	—	0.10	—	—	Ti 0.35; Al 0.15
Nickel-Copper Alloys									
MONEL* alloy 400	66.0	1.35	—	—	31.5	0.12	0.15	0.90	—
MONEL* alloy K-500	65.0	1.0	—	—	29.5	0.15	0.15	0.60	Al 2.8; Ti 0.5
Copper-Nickel Alloys									
Copper-Nickel alloy CA 706	10.0	1.25	—	—	88.0	—	—	0.3	Pb 0.05 max; Zn 1.0 max
Copper-Nickel alloy CA 710	20.0	0.75	—	—	78.0	—	—	0.4	Pb 0.05 max; Zn 1.0 max
Copper-Nickel alloy CA 715	30.0	0.55	—	—	67.0	—	—	0.5	Pb 0.05 max; Zn 1.0 max
Iron-Nickel-Chromium Alloys									
INCOLOY* alloy 800	32.0	46.0	20.5	—	0.30	0.04	0.35	0.75	—
Stainless Steels									
AISI Type 202	5.0	67.0	18.0	—	—	0.15 max	1.0 max	8.7	N 0.25 max
AISI Type 302	9.0	70.5	18.0	—	—	0.15 max	0.5	1.5	—
AISI Type 304	9.5	70.0	18.0	—	—	0.08 max	0.5	1.5	—
AISI Type 304L	10.0	69.0	18.0	—	—	0.03 max	0.5	1.3	—
AISI Type 316	13.0	65.0	17.0	2.0 min	—	0.08 max	0.5	1.7	—
AISI Type 316L	13.0	65.0	17.0	2.0 min	—	0.03 max	0.5	1.8	—
AISI Type 309	13.5	60.5	23.0	—	—	0.20 max	1.0 max	2.0 max	—
AISI Type 310	20.0	52.0	25.0	—	—	0.25 max	1.0 max	2.0 max	—
AISI Type 330	35.0	47.0	15.0	—	—	0.25 max	1.0 max	2.0 max	—
AISI Type 347	11.0	68.0	18.0	—	—	0.08 max	1.0 max	2.0 max	Cb + Ta 10xC min
AISI Type 430	—	84.0	17.0	—	—	0.12 max	—	—	—
Iron Base Nickel-Chromium-Copper-Molybdenum Alloys									
CARPENTER* Stainless No. 20 (1)	29.0	43.0	20.0	2.0 min	3.0 min	0.07 max	1.0	0.8	—
CARPENTER* Stainless No. 20Cb-3	34.0	39.0	20.0	2.5	3.3	0.07 max	0.6	0.8	Cb + Ta 0.6
Nickel Base Iron-Chromium-Molybdenum Alloys									
INCOLOY* alloy 825	41.8	30.0	21.5	3.0	1.8	0.03	0.35	0.65	Al 0.15; Ti 0.9
HASTELLOY* alloy C	45.0	19.5	22.2	6.5	2.0	0.03	0.35	1.3	W 0.5; Cb + Ta 2.12
HASTELLOY* alloy C (2)	54.0	5.0	15.5	16.0	—	0.08 max	1.0 max	1.0 max	Co 2.5 max;
									W 4.0; V 0.4 max
HASTELLOY* alloy C-276	54.0	5.0	15.5	16.0	—	0.02 max	0.05 max	1.0 max	Co 2.5 max;
									W 4.0; V 0.4 max
INCONEL* alloy 625	60.0	5.0 max	21.5	9.0	—	0.10 max	0.5 max	0.5 max	Cb + Ta 3.65
Nickel Base Molybdenum Alloy									
HASTELLOY* alloy B	61.0	5.0	1.0 max	28.0	—	0.05 max	—	—	Co 2.5 max; V 0.2-0.4;
									P 0.025 max;
									S 0.030 max
CAST MATERIALS									
Nickel									
American Casting Institute									
ACI CZ-100	95.0 min	1.5 max	—	—	—	1.0 max	2.0	1.5 max	—
Nickel-Chromium-Iron Alloy									
ACI CY-40	70.0	9.5	15.5	—	—	0.3	3.0 max	1.5 max	—
Nickel-Copper Alloys									
Nickel-Copper alloy 505	64.0	2.0	—	—	29.0	0.08	4.0	0.80	—
ACI M-35	64.0	3.5 max	—	—	29.5	0.35 max	2.0 max	1.5 max	—
Stainless Steels									
ACI CF-8	19.5	66.0	9.5	—	—	0.08 max	2.0 max	1.5 max	—
ACI CF-8M	19.5	63.0	10.5	2.5	—	0.08 max	1.5 max	1.5 max	—
ACI CA-15	1.0 max	83.0	12.8	0.5 max	—	0.15 max	1.5 max	1.0 max	—
ACI HA	—	87.0	9.0	1.1	—	0.20 max	1.0 max	0.5	—
Iron Base Nickel-Chromium-Copper Alloys									
WORTHITE* Stainless	24.0	48.0	20.0	3.0	1.75	0.07 max	3.3	0.6	—
ACI CN-7M (3)	29.0	44.0	20.0	2.0 min	3.0 min	0.07 max	1.0	1.5 max	—
Nickel Base Iron-Chromium-Molybdenum Alloys									
CHLORIMET* 3	60.0	2.0	18.0	18.0	—	0.07 max	1.0	1.0	—
ILLIUM* alloy G	56.0	6.5	22.5	6.4	6.5	0.20	0.65	1.25	—
Nickel Base Molybdenum Alloy									
CHLORIMET* 2	63.0	3.0 max	—	32.0	—	0.15 max	1.0	1.0	—
Nickel Base Silicon Alloy									
HASTELLOY* alloy D	82.0	2.0 max	1.0 max	—	3.0	0.12 max	9.0	0.5-1.25	Co 1.5 max
Nickel Alloyed Cast Irons									
Ni-Resist Type 1	15.5	69.0	2.2	—	6.5	2.8	2.0	1.2	—
Ni-Resist Type 2	20.0	70.0	2.2	—	0.5 max	3.0 max	1.9	1.2	—
Ni-Resist Type 3	30.0	62.0	3.0	—	0.5 max	2.6 max	1.5	0.6	—
Ni-Resist Type 4	30.5	55.0	5.0	—	—	2.6 max	5.5	0.6	—
Ni-Resist Type D2	20.0	72.0	2.1	—	—	3.0 max	2.4	0.9	—
Ni-Resist Type D3	30.0	61.0	3.0	—	—	2.6 max	2.2	0.5 max	—

(1) An improved version of this alloy, CARPENTER* stainless No. 20Cb-3, has replaced CARPENTER* stainless No. 20.

(2) An improved version of this alloy, HASTELLOY* alloy C-276, has replaced HASTELLOY* alloy C.

(3) Cast Alloy 20 alloys such as DURIMET* alloy 20, ALOYCO* alloy 20, etc.

3/31/75

Figure 13.3.2.3-1 (Ref. 2)
Discoloration Threshold for Solution-Annealed
Type 304 Stainless Steel

effect (decreased time for discoloration), although he did not notice a substantial difference between argon and oxygen in this respect (oxygen appeared to be somewhat more aggressive). Data for static and bubbled solutions are summarized in Figure 13.3.2.3-2. In Figure 13.3.2.3-3, temperature-time characteristics are given for the annealed and cold worked materials, indicating that for a given temperature the annealed material exhibited somewhat less resistance to discoloration. In this figure a curve is also given for some HEDL results⁽³⁾ on the stress corrosion cracking of stressed bolts (304 SS) in concentrated caustic (NaOH). Although there is not much overlap in the temperature regimes of these data sets, it is indicated that, for example, a solution causing discoloration at about 300°F could lead to stress corrosion cracking after roughly 200 hr of exposure to the concentrated caustic under near yield stress conditions.

Comprelli, et al.,⁽⁴⁾ give some qualitative observations on sodium spills/leaks, indicating that where the ambient atmosphere permits formation of NaOH and Na₂O, intergranular penetration of austenitic SS's has been observed under deposits of these substances. On a micro scale, the work of Garr supports these observations and indicates that--particularly in conjunction with stress (or more generally, plastic strain caused by thermal or working stresses)--persistent caustic solutions can have a significant structural effect on austenitic materials at temperatures ranging from room temperature upwards. It would be difficult to separate the effects of NaOH and Na₂O under most working situations. Both of these compounds will be present to some extent under ambient atmospheres carrying both oxygen and water vapor.

The oxygen-water-sodium system, depending on the local conditions, can generate both chemical and electrochemical corrosion. This corrosion is aggravated by plastic straining of the metal and by physical and chemical heterogeneities on the metal surface which further activate electrochemical corrosion cells in the presence of any electrolyte formed by the Na-O₂-H₂O system.

Figure 13.3.2.3-2 (Ref. 2)

Log Time Versus $1/T$ for 304 SS Samples Exposed to 50 wt% NaOH,
With and Without Gas Being Bubbled Through Caustic Solution

Figure 13.3.2.3-3 (Ref. 2)

Comparison of Time to Discoloration and Time for Stress-Corrosion Cracking

References for 13.3.2.3

1. "Corrosion Resistance of Nickel and Nickel-Containing Alloys in Caustic Soda and Other Alkalies;" INCO Tech Bulletin C-EB-2, International Nickel Co. Inc.
2. K. R. Garr, "Corrosion of Type 304 Stainless Steel in NaOH," AI-AEC-13122, March 1974.
3. J. L. Ballif, et al., Sodium Removal and Requalification Handbook, St. No. 468, June 1973, p. 2.
4. F. A. Comprelli, F. J. Hetzler, T. A. Lauritzen, "Clad Compatibility with Mixed Oxide Fuel and Sodium," ANL-7120, p. 355.

13.3.3 Ferritic Materials

13.3.3.1 Na Corrosion, Oxygen Influence

Ferritic alloys, in particular the chromium-molybdenum alloys, exhibit good resistance to sodium over the range of temperature of present interest, namely, R T to about 500°C. Table 13.3.3.1-1 gives sodium corrosion data for various ferritic alloys over a temperature range of 274-593°C, for static and flowing sodium environments. As noted in Tables 13.3.2.1-2, -3, oxygen increases the corrosion of these materials in sodium. In general, however, the corrosion responses of the ferritic and austenitic alloys to sodium, and to oxygen contamination of sodium up to about 100 ppm, are roughly the same, as shown by Figure 13.3.3.1-1. At higher oxygen levels, the ferritic alloys appear to exhibit much greater sensitivity to oxygen, as shown by the high oxygen data of Table 13.3.2.1-2.

References for 13.3.3.1

1. W. E. Berry, Corrosion in Nuclear Applications; John Wiley, NY 1971.

Table 13.3.3.1-1 (Ref. 1)
Corrosion of Ferritic Alloys in Isothermal Sodium

Steel	Temperature, C	Flowing	Static	Exposure Time, hr	Weight Change Rate, mg/dm ² -month ^(b)
Iron	510	X		—	-20
Carbon Steel	500		X	—	-10
AISI 1010 Steel	593	X		1000	-49
	593		X	1000	-37
0.1C Steel	274		X	100	-63
0.5C Steel	274		X	100	0
1.0C Steel	274		X	130	+14
1/2Cr	593	X		1000	-69
	593		X	1000	-64
1-1/4Cr-1/2Mo	500		X	—	-10
	552	X		943	-26
	566		X	902	-25
	593	X		1000	-13
	593		X	1000	-11
2-1/4Cr-1Mo	510	X		—	<-10
	552	X		943	-12
	566		X	902	-12
	593	X		1000	-14
	593		X	1000	-9
5Cr-1/2Mo	510	X		—	<-10
	552	X		943	+22
	566		X	913	-6
	593	X		500	+23
	593		X	500	-8
7Cr-1/2Mo	500		X	—	<-10
	552	X		943	+22
	566		X	902	-70
	593	X		500	+42
	593		X	500	+7
9Cr-1Mo	510	X		—	<-10
	552	X		943	+35
	566		X	902	-5
	593	X		500	+70
	593		X	500	+29
AISI Type 410	250		X	1000	-7
	510	X		—	<-10
	593	X		1000	+38
	593		X	1000	+35
	704		X	—	-40
AISI Type 420	593	X		1000	+33
	593		X	1000	+31
AISI Type 440C	593	X		500	+68
	593		X	500	+28

a. Containing a maximum of 100 ppm oxygen.

b. Specimens not descaled.

Figure 13.3.3.1-1 (Ref. 1)

A Comparison of Sodium Corrosion Characteristics of Ferritic and Austenitic Alloys at Various Oxygen Levels in Flowing Sodium

13.3.3.2 Caustic (NaOH) Corrosion

A chief distinguishing characteristic between ferritic and austenitic materials is their corrosion response to caustic solutions, with NaOH solutions apparently having the greatest power to discriminate between the two materials.⁽¹⁾ In alkaline solutions, the principal corrosion product of ferritic materials is thought to be the ferroate ion, HFeO_2^- . Successive products of corrosion in caustic solutions are $\text{Fe}(\text{OH})_2$, Fe_3O_4 , gamma Fe_2O_3 and gamma FeOOH . This complex of reaction products of various structural characteristics leads to alternate periods of 'passivation' and corrosion in caustic solutions, as exemplified by Figure 13.3.3.2-1, depending on the physical and chemical conditions of the corrosion environment. Generally, the corrosion layer of ferritic alloys will be comprised of several layers of different structure and somewhat different chemical constitution. Figure 13.3.3.2-2 shows a typical layer development on mild steel under 13% NaOH at 340°C.

The corrosion response of ferritic alloys to caustic solutions is a function of the (OH), the associated cation (e.g., Na, K, Li), the temperature, the physical conditions which affect interchange of reactants and products with the metal surface, and species in the solution (e.g., O, Cl^- , Pb, Si, nitrate, chromate, etc.) which affect the protective character of corrosion product layers. The influence of caustic concentration, for relatively low caustic levels, is shown in Figure 13.3.3.2-3, for mild steel at 340°C. The influence of temperature, for a relatively weak solution (13%), is shown in Figure 13.3.3.2-4.

Rubright⁽²⁾ studied the corrosion behavior of the ferritic alloy, 21/4 Cr-1Mo, over a range of NaOH concentrations, and temperatures in aqueous solutions, and for various combinations of Na with NaOH. Table 13.3.3.2-1 gives his results for solutions ranging from sodium (plus 90 ppm oxygen) to sodium with NaOH loadings ranging from 0.18 to 10 wt%. One test with an overpressure of hydrogen (presumably adding NaH to the solution) is also given. His results for the 'pure' sodium plus oxygen tests are in fairly good agreement with data presented in Table 13.3.2.1-3. These data indicate the serious corrosion which can be effected by caustic in sodium at temperatures which certainly could obtain under conceivable spill/leak

Figure 13.3.3.2-1 (Ref. 1)

Corrosion Rate-Time Characteristic Showing Effect of Alternate Passive and Active Modes of Mild Steel in Caustic Solution

Figure 13.3.3.2-2 (Ref. 1)

Typical Layer Development on Mild Steel in NaOH

Figure 13.3.3.2-3 (Ref. 1)

Effect of Concentration of NaOH on Corrosion Rate

Figure 13.3.3.2-4 (Ref. 1)

Effect of Temperature on Mild Steel Corrosion in NaOH

Table 13.3.3.2-1 (Ref. 2)

Corrosion Rate of Croloy 2-1/4 Specimens in Sodium, in Sodium Hydroxide-Sodium Systems, and in a Sodium Hydroxide-Sodium Hydride-Sodium System at Various Temperatures

	<u>MEDIUM</u>	<u>TEMPERATURE</u>		<u>CORROSION RATE</u>
		(°F)	(C)	(Inches Per Year)
I	Sodium (=90 ppm Na ₂ O)	400	204	.0020
II	Sodium "	900	482	.0019
III	Sodium "	1250	677	.0023
IV	Sodium "	1400	760	.073
V	Sodium + 0.168 weight percent NaOH	900	482	.0020
VI	Sodium + 5 weight percent NaOH	900	482	.0072
VII	Sodium + 10 weight percent NaOH	900	482	.022
VIII	Sodium + 0.250 weight percent NaOH	1250	677	.036
IX	Sodium + 5 weight percent NaOH	1250	677	.105
X	Sodium + 5 weight percent NaOH	1375	746	.341
XI	Sodium + 5 weight percent NaOH + H ₂ over pressure (Na + NaOH + NaH)*	900	482	.0052

*Calculated equilibrium concentrations
at test conditions:

NaOH 0.2 weight percent
NaH 2.9 weight percent
Na₂O 7.3 weight percent

conditions of the external system. Rubright's data for aqueous NaOH solutions are, however, somewhat more spectacular in highlighting the potent influence of the OH⁻ ion on the corrosion of ferritic materials. Table 13.3.3.2-2 presents his results for aqueous solutions ranging in NaOH concentration from 24.2 to 98.6 wt%, at temperatures ranging from 60 to 482°C. It will be noted that he gives his corrosion effect in terms of in./year penetration and that, for example, an NaOH solution of 48.8 wt% gives a corrosion rate of about 1/2 in./year at a temperature of 141°C.

Table 13.3.3.2-2 (Ref. 2)

Summary of Corrosion Rates of Croloy 2-1/4 Steel
in Aqueous Sodium Hydroxide

<u>SOLUTION CONCENTRATION</u> (Weight Percent)	<u>PRESSURE</u>	<u>TEMPERATURE</u> (°F) (C)		<u>CORROSION RATE</u> (ipy)
24.2	Atmospheric	140	60	0.0001
24.2	Atmospheric	170	76	0.015
24.2	Atmospheric	200	93	0.032
24.2	Atmospheric	230	110	0.002
48.8	Atmospheric	200	93	0.035
48.8	Atmospheric	230	110	0.077
48.8	Atmospheric	260	127	0.141
48.8	Atmospheric	285	141	0.519
98.6	Atmospheric	700	371	1.00
98.6	40 psig	900	482	2.67

His results for the aqueous NaOH solutions are given in graphical form in Figure 13.3.3.2-5. Temperature-time characteristics for the three NaOH concentrations (24.2, 48.8 and 98.6 wt%) are given in Figures 13.3.3.2-6, -7, -8. Rubright observes that the corrosion in the aqueous NaOH solutions appeared to be simple solution attack (uniform penetration), with intergranular penetration, and oxide formation, observed only at the higher temperatures of his tests. For the Na-NaOH tests, he observed intergranular penetration, oxide formation, and whole grain removal, at the higher temperatures of this test series. Within the relatively short time span of his tests, he did not observe decarburization of the 2-1/4 Cr-1Mo steel for any of his test environments. An Arrhenius type plot for his aqueous NaOH test results is given in Figure 13.3.3.2-9, suggesting a substantial change in corrosion mechanism between the 48.8 and 98.8 wt% NaOH test solutions.

Even subject to the limits of interpretation imposed by one investigator and one experimental technique, Rubright's results give

Figure 13.3.3.2-5 (Ref. 2)
Corrosion of Croloy 2-1/4 in Aqueous NaOH

Figure 13.3.3.2-6 (Ref. 2)

Corrosion of Croloy 2-1/4 Steel Specimens (42.6 cm^2) in 24.2 Weight Percent Aqueous Sodium Hydroxide

Figure 13.3.3.2-7 (Ref. 2)

Corrosion of Croloy 2-1/4 Steel Specimens (42.6 cm^2) in 48.8 Weight Percent Aqueous Sodium Hydroxide

Figure 13.3.3.2-8 (Ref. 2)

Corrosion of Croloy 2-1/4 Steel Specimens (42.6 cm^2) in 98.6 Weight Percent Aqueous Sodium Hydroxide; Temperature--700°F

Figure 13.3.3.2-9 (Ref. 2)

Arrhenius Plot-Corrosion Loss Versus Temperature ($^\circ\text{K}$) for Aqueous Sodium Hydroxide Solutions

substantial illustration of a serious limitation of ferritic alloys, namely, susceptibility to corrosion in the presence of the OH^- ion, particularly under conditions permitting electrochemical action (aqueous electrolytes). As for the quantitative significance of his results, Subrahmanyam and Staehle⁽¹⁾ cite mild steel caustic corrosion data at corresponding temperatures and roughly equivalent caustic concentrations which agree, within a factor of two, or three, with Rubright's data, a discrepancy which could easily be accounted for by differences in alloy composition.

References for 13.3.3.2

1. D. V. Subrahmanyam and R. W. Staehle, "Stress Corrosion Cracking and General Corrosion of Iron, Nickel, Chromium, and Their Alloys in Caustic Solutions;" Ohio State Univ. Rept. No. C00-2018-4 (Q-1), 1969.
2. M. M. Rubright, "The Corrosion of Croloy 2-1/4 Steel in the Products of a Sodium-Water Reaction; Systems of Sodium Hydroxide in Water and in Molten Sodium;" BAW-1280-30, November 15, 1965.

13.3.4 Effects of Metal Cleaning Procedures

The cleaning of structural components which have been exposed to sodium, preparatory either to reuse, storage, or disposal, poses a number of problems due to the chemical reactivity of sodium and its propensity for permeating a metallic structure and subsequently 'bleeding' under appropriate environmental conditions. Apart from personal hazard potential, residual sodium--either surface or absorbed--may participate in the gamut of reactions discussed previously and generate corrosion products which are inimical to reuse of such components, and to those components which come within the radius of action of such products in the service, or storage, environments.

A number of schemes are under test for cleaning sodium affected materials and for tailoring cleaning procedures to specific components representing particular problems of sodium retention (e.g., steam generator). A recent review of current work by Atomics International on this aspect of sodium is given in Reference 1. Reference 2 discusses the general scope of sodium cleaning work within the purview of the ERDA and is an excellent concise review of sodium cleaning problems.

Cleaning agents may react chemically with sodium, or they may dissolve sodium. Examples of the former are water, alcohol, alkyl halides. Examples of the latter are mercury, molten lead, liquid ammonia. The current tendency is to emphasize the chemically reacting agents, such as water and alcohol. Water is usually applied as steam in the early stages with an inert diluent, usually nitrogen, for closer control of possible sodium and hydrogen reactions. Final cleanup usually involves liquid water for more complete removal of sodium and sodium products, and for ease in monitoring the cleanup efficacy. Of the alcohols, the low molecular weight varieties are more reactive with sodium. Tertiary butyl alcohol reacts slowly with sodium. It is, however, miscible with water. Various combinations of alcohol and water may be used depending on the severity, or stage, of the cleaning problem.

The final problem in cleaning is removal of the last cleaning agent(s) in the cleaning cycle. Following a final water treatment, a more volatile,

water miscible, solvent may be applied, which then might be removed by vacuum heating in the case of difficult components. Following cleaning, the metallic surface must be protected from adverse environmental effects if immediate, or eventual, reuse is planned. Large components present a substantial problem in this respect and optimum procedures for protection of a cleaned surface are under development.⁽²⁾

Sodium absorption by a metallic structure, with subsequent release of the sodium, poses a serious problem in cleaning. pH indicators, commonly used to monitor sodium removal, would not be sensitive to sodium within a structure which had not yet affected the wash solution. Nevzorov⁽³⁾ discusses the phenomenon of sodium penetration of a metal lattice, with subsequent 'bleeding' of this sodium for a period following exposure. His data pertain to high temperatures and do not indicate the temperature dependence of this action. Sodium apparently is not limited to grain boundaries in this penetration. A sodium advance more or less uniformly across a structure, has been noted for a number of different metals. Grain boundaries with strong composition perturbations from the basic structure, and gross structural defects, allow easy access to sodium, resulting in spike-like penetrations to considerable depth.

Smith, et al.,⁽⁴⁾ have noted sodium bleeding after exposure of austenitic SS to sodium. Figure 13.3.4-1 is a schematic of a test program used by these authors to study the effects of sodium exposure, subsequent cleaning, and atmospheric exposure, on the structural quality of austenitic SS. Following the various sodium and atmospheric exposures, the resistivity of the specimens was measured to indicate possible structural deterioration (Test A). The 'B' test consisted of exposing the specimen to the Strauss test (H_2SO_4 , $CuSO_4$ solution) and measuring the resistivity. In summary of this work, it was indicated that repeated sodium exposures adversely affected the metal structure (as indicated by the resistivity measurement following the Strauss test which is an indication of sensitization to stress corrosion cracking). Figure 13.3.4-2 shows the resistivity effects of the 3rd sodium exposure relative to those following the 2nd sodium exposure, plus a period of air storage. This figure, and other data from Reference 4, indicate that repeated sodium

Figure 13.3.4-1 (Ref. 4)

Test and Exposure Program

exposures progressively increase the response of the specimen to the Strauss reagent, and presumably the tendency of the material to develop cracks under stress and additional chemical encouragement, such as given by OH^- ions. Following a single sodium exposure, specimens were stored under water, dry air and normal air. Figure 13.3.4-3 shows the resistivity effect of water storage (180 days) and normal air storage (120 days) following a single sodium exposure. It is seen that the Strauss reagent indicates a pronounced sensitization to stress corrosion cracking following the water storage, with a relatively minor effect for the normal air storage. It was noted that dry air storage was more productive of resistivity change following the Strauss test than was normal air storage. This work indicated that a fairly aggressive cleaning procedure (moist air or nitrogen plus water rinsing of sodium contacted surfaces) may not be sufficient to remove residual sodium which, upon exposure to an oxygen-water vapor environment, participates in chemical and electrochemical corrosion action with the structural material. The corrosion effect appears to be aggravated by repeated sodium exposures and the pertinence of this observation to repeated sodium leaks/spills at a given site is obvious.

Figure 13.3.4-2 (Ref. 4)

Response to Strauss Reagent after 2nd and 3rd Na Exposures

References for 13.3.4

1. "Annual Technical Progress Report Sodium Technology and Cover Gas Seal Development Programs for FY 1974," AI-AEC-13132, August 1974.
2. "Element 5-Sodium Technology," WASH-1105, 2nd Ed. December 1972.
3. B. A. Nevzorov, Corrosion of Structural Materials in Sodium; IPST, Jerusalem, 1970.
4. F. A. Smith, E. L. Kimont, L. H. Bohne, "Water Cleaning and Air Storage Effects on Sodium Exposed Fuel Clad Alloys--304 and 304L Stainless Steel," ANL-7520, Pt. 1, p. 426.

Figure 13.3.4-3 (Ref. 4)

Comparison of Normal Air Storage and Water Storage
After Single Sodium Exposure

13.3.5 Summary of Section 13.3

Sodium spill/leak events in the external system present immediate problems of energy release from direct, or subsidiary reactions to the extent that air, or liquid water, or high water vapor concentrations, are contiguous to the event. The corrosion consequences of an event presents subtler problems of effects analysis. Sodium, per se, does not appear to present a serious problem in the latter respect unless the event escapes detection, or good housekeeping, for a considerable time period and the temperature history of the event allows sodium related mass transfer processes to work on adjoining structural materials.

Water vapor over a wide range of partial pressure will be an inevitable participant in sodium leak/spills. The available information appears to support the contention that NaOH will be a principal reaction product of sodium events under this circumstance. The caustic concentration which can be developed at an event site is impossible to predict, although a conservative viewpoint in this regard would allow a caustic presence ranging from virtually pure NaOH to very dilute aqueous or sodium base solutions of OH^- ions. It is submitted that caustic corrosion has not been given sufficient emphasis in materials considerations for LMFBFR plants and that the ferritic materials should be accorded special scrutiny in this respect prior to large scale commitments of ferritic materials to sodium sensitive zones in the external system.

Sodium is quite difficult to dissociate from its container material. The problem of cleaning, and qualifying for reuse, large complex components is a difficult one and many aspects of this problem will require the crucible of large scale experience before optimum procedures are developed.

13.4 STRESSED CORROSION EFFECTS OF THE Na-H₂O-O₂ SYSTEM

13.4.1 Scope of Problem

The influence of stress (strain) on corrosion is a complex subject which, in various respects, comprises a substantial part of the current corrosion literature under such headings as stress corrosion cracking, corrosion fatigue, thermal cycling effects, etc. A discussion of stress assisted corrosion will be confined to a brief review of stress corrosion information applicable to austenitic and ferritic alloys in caustic solutions. It is submitted that caustic (NaOH) involved corrosion is a prime potential degradation process in the sodium affected external surfaces of the LMFBR plants. It is unfortunate that caustic corrosion processes do not appear to enjoy the laboratory and engineering attention their damage potential appears to justify.

Generally, the warning signals for stress assisted corrosion in caustic media are similar to those for unstressed corrosion reviewed in the previous section. The austenitic stainless steels and high nickel alloys appear to exhibit substantially greater tolerance for the OH⁻ ion under stress than the ferritic alloys. Both types of material, however, will degrade seriously under appropriate conditions of stress, (OH⁻), temperature and time. The structural significance of this fact must be related to specific components, i.e., to the strength redundancy incorporated in the component and to the penalties for failure of various degrees of severity.

The stress corrosion characteristics of austenitic and ferritic alloys are perturbed by various contaminants of the basic corrosion environment. Certain species (e.g., Cl⁻, sulfides) can accelerate SCC damage, while other species (e.g., phosphates) have an inhibiting effect under certain conditions.

13.4.2 Austenitic Materials

13.4.2.1 Caustic (NaOH) Stress Corrosion Cracking

A comprehensive depiction of the factors affecting the stress corrosion cracking tendency would require an 'n dimensional plot involving parameters characterizing caustic concentration, the associated cation (i.e., Na^+ , Li^+ , K^+), the temperature history of the exposure, the stress field, the metallurgical and strain history of the affected site, the presence of aggressive, or inhibiting ions. A brief review of the effects of caustic concentration, stress and temperature will be given in this section for austenitic materials.

Figure 13.4.2.1-1 is an isocorrosion chart based on a number of laboratory and industrial observations. It will be noted that the stress corrosion cracking (SCC) phenomenon is sustained down to low caustic concentrations at sufficiently high temperatures. The inclusion of a stress dimension on such a chart would alter the details substantially. Specifically, it would be expected that stress conditions leading to considerable plastic strain would lower the tolerance of the austenitic materials for the OH^- ion with respect to both concentration and temperature. Additional indication of the effects of caustic concentration and temperature is given in Table 13.4.2.1-1, where the temperature levels are somewhat above those given in the figure. As indicated in this table, caustic effect does not necessarily increase with concentration. This effect is usually attributed to the ability of the material to passivate under the given exposure conditions. Figure 13.4.2.1-2 shows the dependence of the time for failure (θ_f) on the caustic concentration for a given stress and temperature. This figure also indicates the low level of caustic concentration which can be harmful under certain stress and temperature conditions. Presumably, an extension of the data of Figure 13.4.1-2 to high caustic concentrations would show some increase in θ_f , although this effect is sensitive to both stress and temperature and is complex enough to discourage predictions or extrapolations. Table 13.4.2.1-2 gives some SCC data for INCO 600 and 800 alloys, and 304 type SS. Although the 304 SS exhibits a greater tendency to SCC

Figure 13.4.2.1-1 (Ref. 1)

Isocorrosion Chart for Austenitic Chromium-Nickel
Stainless Steels in Sodium Hydroxide

Table 13.4.2.1-1 (Ref. 2)

Incidence of Cracking in Type 347 Stainless Steel
U-Bends Exposed to Sodium Hydroxide Solutions

Temp. °C	Mixture	Days	Cracking	
850°F	454	16% NaOH in Na	30	yes
	454	30% NaOH in Na	20	yes
	454	60% NaOH in Na	30	yes
	454	100% NaOH	14	yes
	454	96% NaOH in H ₂ O	30	no
750°F	399	100% NaOH	30	no
	399	95% NaOH in H ₂ O	30	no
684°F	362	100% NaOH	30	no
	362	80% NaOH in H ₂ O	1	yes

Figure 13.4.2.1-2 (Ref. 2)

Dependence of Time-to-Failure of Type 321 Stainless Steel on Concentration of NaOH Solution (Tests at 42,000 psi, 330°C)

Table 13.4.2.1-2 (Ref. 1)

Laboratory Tests--Results of U-Bend Specimens in 90% Caustic Soda at 300°C (572°F)

Material	Maximum Depth of Cracks, mils			
	Argon atm. 1 week	15 psig air 1 week	50 psig air 8 weeks	150 psig air 1 week
INCOLOY alloy 800	10	7	120 (a)	115 (b)
INCONEL alloy 600	0	0	75	115
Type 304 Stainless Steel	100	110	11	10

(a) Removed at four weeks.

(b) Two-week test.

Note: Testing performed in autoclaves under static conditions without replenishment of air or argon.

under the argon and low pressure air atmospheres, it is interesting that this work horse alloy generally compares very favorably with the high nickel inconels over the total range of corrosion environments.

Table 13.4.2.1-3 gives an indication of the stress, temperature and caustic concentration effects on the SCC tendency of an austenitic SS (18-9 Nb stabilized) for both KOH and NaOH solutions. The relatively greater effect of NaOH has been noted previously and is seen in these data.

Table 13.4.2.1-3 (Ref. 3)

Effects of Concentration, Stress and Temperature on SCC
in KOH and NaOH Solutions (18-9 Nb SS)

Effect of concentration at 300°C and 10 tons/in ²			Effect of stress at 300°C			Effect of temp. with 10 tons/in ² stress		
Wt.-%	Life with KOH, h	Life with NaOH, h	Applied stress, tons/in ²	Life with 80% KOH, h	Life with 80% NaOH, h	Temp., °C	Life with 80% KOH, h	Life with 80% NaOH, h
50	7-8	2-1	20	2-0	...	300	3-8, 19-8	1-1, 1-8
20	3-8, 19-8	1-1, 1-8	10	3-8, 19-8	1-1, 1-8	250	12-2, 55-7	3-6, 1-6
5	51-2, 17-6	6-4, 15-1	7-5	...	137	200	40-8, 82-8	177-8
1	17-9, 150 UB†		5	16-9, 30-3	112, 118	175	43-7, 195-8	
0-1	551 UB†		2	28-5, 88-5	400 UB†	150	500 UB†	

† UB = Unbroken

A stress corrosion cracking test of 304 SS in caustic saturated cleaning solutions (Dowanol-EB and ethanol) was reported in Reference (4). Specifically, bolt specimens were stressed to 100% yield and soaked in 20 wt% alcoholate solutions formed by dissolving sodium at 125°F under argon. No cracking was observed after an exposure time of 56 days to the 125°F solution.

Figure 13.3.2.3-3 indicated that apparently mild corrosion attack (discoloration) could eventually lead to SCC if the corrosion conditions were allowed to persist under appropriate levels of stress. The presence of a SCC sensitizing agent such as Cl⁻ might be expected to strongly affect the tolerance of austenitic components for sodium leaks/spills. There are indications, however, discussed in Reference (2), that the Cl⁻ ion may exert some inhibition on the SCC of austenitic materials in caustic solutions at certain Cl concentrations. This phenomenon will

doubtless receive greater attention considering the extensive application of austenitic materials to the sodium systems of LMFR's.

References for 13.4.2.1

1. Corrosion Resistance of Nickel and Nickel-Containing Alloys in Caustic Soda and Other Alkalies; INCO Tech. Bulletin CEB-2.
2. D. V. Subrahmanyam, R. W. Staehle; "Stress Corrosion Cracking and General Corrosion of Iron, Nickel, Chromium and Their Alloys in Caustic Solutions;" Ohio State Univ. Rept. No. COO-2018-4(Q-1).
3. P. P. Snowden, "Stress Corrosion of Austenitic Stainless Steel by High Temperature Solutions and Contaminated Steam;" J. Iron and Steel Inst., Feb. 1960, p. 181.
4. Annual Tech. Prog. Rept. Sodium Technology and Cover Gas Seal Development Programs Fiscal Year 1974; AI-AEC-13132. Aug. 1974.

13.4.3 Ferritic Materials

13.4.3.1 Some Qualifications and Potential Limitations

Ferritic alloys have virtually no competition in applications where high strength and resistance to deformation are required under conditions where a heavy section cannot be used to increase strength. In addition to their strength potential, certain alloying constituents can be incorporated in the ferritic matrix to achieve a substantial degree of 'tailoring' to specific corrosion environments. Generally, the economic advantage of ferritic alloys decreases rather rapidly when the composition is adjusted for maximum corrosion resistance within the ferritic framework. The 2 1/4 Cr-1Mo ferritic steel, now being considered for a number of applications within the LMFBR plant, appears to be an example of what is hoped to be a judicial balance between the economic factor and desirable general structural quality, including corrosion resistance. With respect to the important problem of decarburization within sodium circuits, and its mechanical property effects, this alloy is judged to be near its limit of utility at temperatures somewhat less than 500°C.⁽¹⁾ The ability of this alloy to resist the gamut of corrosion situations which may be presented by LMFBR service, including tubing for the sodium-water/steam heat exchangers and superheaters, is less well established and there appears to be need for conservatism in applications of this alloy. Some corrosion data supporting this attitude were presented in the previous section. Stress corrosion data for this alloy are evidently extremely scarce, particularly for caustic media which are of special importance for any material candidate which will be within the action scope of sodium. Accordingly, some stress corrosion cracking information generally pertinent to low alloy ferritic materials will be presented. Considering the susceptibility of the 2 1/4 Cr-1Mo alloy to caustic attack indicated in the previous section, these stress-involved data cannot be regarded as an overly conservative index of behavior for the low chromium-molybdenum alloys.

Reference for 13.4.3.1

1. H. Schnauder, R. A. Muller, "Modification of the Design of Intermediate Heat Exchangers for Sodium Cooled Reactors Using Ferritic Materials," EURFNR-924, 1971.

13.4.3.2 Caustic Stress Corrosion Cracking

The phenomenon of cracking of ferritic alloys in caustic environments has been a prime subject of corrosion literature for more than 50 years. Riveted boiler plates apparently provided favorable sites for caustic concentration which, under stress and appropriate temperature conditions, caused severe cracking problems. Considerable additional information on the behavior of ferritic alloys in caustic media has been provided by industrial manufacturers, and users, of caustic solutions. Berk and Waldeck⁽¹⁾ presented some definition of the 'danger zone' for caustic cracking based on U-bend tests with SAE 1020 steel. This is given in Figure 13.4.3.2-1, which suggests a maximum effect for solutions in the range of roughly 20-35% NaOH and a corresponding temperature limit for these concentrations of about 180°F. Schmidt et al.⁽²⁾ presented a somewhat more restrictive definition of the danger zone on the basis of an extensive NACE survey of caustic cracking. Their summary is presented in Figure 13.4.3.2-2, which gives a critical temperature-concentration characteristic somewhat more rigorous than Figure 13.4.3.2-1 with respect to temperature. Their data suggest a maximum effect at NaOH concentrations somewhat higher than the 20-35% range noted above and their 'critical' temperature comes close to 100°F. Table 13.4.3.2-1 gives some caustic cracking data with specimen specifics. The first entry in this table, namely, cracking at 35°C (95°F) for solutions in the range 4-60% would imply even more restrictive conditions than Figure 13.4.3.2-2. Electrochemical studies reported by Reinoehl and Berry⁽³⁾ indicate that, under conditions favoring electrochemical action, caustic solutions down to roughly 4% are aggressive to ferritic alloys at a temperature of 93°C (200°F), in agreement with the critical cracking characteristic established in Figure 13.4.3.2-2.

The effect of stress on caustic SCC is complex and depends on specific exposure conditions, time of exposure, and the chemical and metallurgical history of the metal. Figure 13.4.3.2-3 is a typical stress-failure time (θ_f) characteristic for a given temperature and caustic concentration. Plastic strain, rather than stress per se, is now considered

Figure 13.4.3.2-1 (Ref. 1)
Caustic SCC Danger Zone

Figure 13.4.3.2-2 (Ref. 2)
Relation of Temperature and Concentration
of NaOH to Cause Cracking

Table 13.4.3.2-1 (Ref. 3)

NaOH Concentrations at Which Caustic Cracking
Has Been Observed for Mild Steels

Caustic Cracking Concentration Range, % NaOH	Threshold Temperature,		Exposure Conditions	Reference
	F	C		
4-60	(95)	35	0.12% C-0.47% Mn steel (1/8" boiler plate)	10
5-73	130	(55)	NACE survey (service)	3
10-50	(160)	70	Boiler service	7
10-75	-	-	0.8% C steel, slow strain rate tensile tests	11
15-33	-	-	0.03, 0.09% C steels 3 mm thick U-bends	9
15-40	(175)	80	Various	8
18-40	180	(85)	1020 steel 1/4" thick U-bends	6
20-55	(180)	85	Bayer plants service	4
35-70	(160)	70	De-enamelling tanks • service	2

Points	C	N	Al	Si	Mn	P	S	Cu	O
○—○ B	0.04	0.014	0.001	< 0.001	< 0.001	0.003	0.002	--	0.002
△—△ C	0.02	0.006	< 0.003	0.003	0.018	0.011	0.009	< 0.003	--
●—● D	0.11	0.009	0.004	0.01	0.31	0.022	0.039	0.03	--

Figure 13.4.3.2-3 (Ref. 4)

Effect of Stress on Failure Times of Mild Steels in NaOH Solution
 (~250°C)

to be critical to SCC and the concept of a 'critical' stress appears to be of limited value. In other words, once sufficient plastic strain has developed as a result of various service conditions (temperature, stress cycling, steady stress, etc.), SCC will occur in the presence of caustic and sufficient stress to propagate the crack.

Relatively modest changes in temperature can drastically change the SCC tendency under given caustic and stress conditions. This is indicated by Figure 13.4.3.2-4 where the θ_f is given as a function of applied potential. It is seen that a temperature change of 50°C effects roughly an order of magnitude change in the failure time (θ_f). Strain rate is an important variable in SCC, with a slow strain rate generally being more harmful in the respect of SCC. This is indicated in Figure 13.4.3.2-5, where the cracking parameter (in this case reduction in area at fracture) is plotted against applied potential for various strain rates. Applied potentials which produce serious cracking at a strain rate of $1.6 \times 10^{-6} \text{ sec}^{-1}$, have no effect at the highest strain rate ($4.2 \times 10^{-5} \text{ sec}^{-1}$).

The ability of a metal to develop passive layers is crucial to its resistance to SCC. Figure 13.4.3.2-6 shows the effect of cold work on the ability to achieve passivation. Here the corrosion potential is plotted against time for mild steel in the 50%, 80% and zero cold worked conditions. The less negative potential is in the direction of passivity and it is seen that while the zero cold worked material exhibits a tendency to passivation after roughly 30 min, the cold worked materials persist in an active (corrosion mode) potential throughout the exposure to the caustic solution.

The damaging effect of caustic SCC is indicated by Figure 13.4.3.2-7 where maximum load sustained by the specimen, and the resulting reduction in area at fracture, are plotted against the applied potential for given caustic concentration, strain rate, and temperature conditions. While applied potential tests provide a possibly unnatural acceleration of the SCC process, the damage effects of these 'synthetic' tests is more than matched by observations of 'natural' SCC damage reported in surveys such as Reference (2). Summary remarks given by Schmidt et al. after their

Figure 13.4.3.2-4 (Ref. 4)

Effect of Temperature on the Failure Time of Mild Steel
in NaOH Solution

Figure 13.4.3.2-5 (Ref. 4)

Effect of Strain Rate on SCC

Figure 13.4.3.2-6 (Ref. 4)

Effect of Cold Deformation of Steels on Open Circuit Potential-Time Curves in NaOH Solution

Figure 13.4.3.2-7 (Ref. 4)

Embrittlement Effects of SCC at Various Applied Potentials

extensive survey of industrial participants are pertinent to this discussion. The following recommendations for minimizing caustic SCC were made:

- A. Decrease stress (residual and applied)
 - 1. Change design
 - 2. Stress relieve
- B. Decrease temperature
 - 1. Change design
 - 2. Change operating conditions
- C. Change material of construction
 - 1. Different metal
 - a. Nickel
 - b. Monel metal
 - c. Nickel clad steel
 - 2. Coatings
 - a. Spraying with nickel
 - b. Spraying with steel
 - c. Organic coatings (rubber has been used with considerable success in minimizing caustic attack)

The iron-chromium system has been the subject of considerable caustic corrosion research. Work cited in Reference (4) indicates that the 2 1/4 Cr-1Mo steel composition is far from optimum in this respect and that caustic resistance tends to increase with increasing chromium content. The compound $(\text{FeCr})_3\text{O}_4$ has been cited as responsible for passivity of iron-chromium alloys in caustic media, the influence of this compound apparently increasing with Cr content.

References for 13.4.3.2

1. A. A. Berk, W. F. Waldeck, "Caustic Danger Zone," Chem. Engr., June 1950, p. 235.
2. W. W. Schmidt, P. J. Gegner, G. Heinemann, C. F. Pogacar, E. H. Wyche, "Stress Corrosion Cracking in Alkaline Solutions," Corrosion, Sept. 1951, p. 295.
3. J. E. Reinoehl, W. E. Berry, "Natural Conditions for Caustic Cracking of a Mild Steel," Corrosion, 28, No. 4, April 1972, p. 151.
4. D. V. Subrahmanyam, R. W. Staehle, "Stress Corrosion Cracking and General Corrosion of Iron, Nickel, Chromium and Their Alloys in Caustic Solutions," Ohio State Univ. Report No. C00-2018-4(Q-1), 1969.

13.4.4 Summary of Section 13.4

The addition of stress (strain) to the corrosion conditions generally imposes more severe environmental limitations on structural materials. Specifically, temperatures and concentrations of corrosive species which might be tolerable under unstressed conditions may, under stress, be unacceptable for satisfactory performance. The interaction of plastic straining with the various sodium related corrosion processes which may be potentially important to external sodium events is not well understood. Much of the current information on sodium corrosion and mass transfer effects takes little, or no, cognizance of the straining variable and it is expected that much of this information must be qualified in this respect. Caustic stress corrosion cracking of austenitic and ferritic materials is probably better characterized than most stress assisted corrosion processes, although many important aspects of this problem remain unresolved to a satisfactory extent.

Components having surface stressed zones must be accorded special surveillance with respect to the corrosive action of sodium events, i.e., welded or flanged joints and connections, vibration prone locations, and all components where an appreciable stress field probably obtains at the surface. While it would be impractical to exclude thermal insulation from many such zones, provision must be made for detection of sodium events which could affect the zone, and the guideline of prompt attention to the event applies most particularly here. Stress generally lowers the tolerance of austenitic and ferritic materials for corrosion sensitizing agents, e.g., chlorides, fluorides, sulfides, etc., thereby invoking the demand for specially good housekeeping at stressed zones throughout the fabrication, installation and service phases.

13.5 NITROGEN REACTIVITY WITH STRUCTURAL MATERIALS

13.5.1 Scope of Problem

Nitrogen will be used as an 'inert' atmosphere for sodium sensitive zones within the containment envelope of LMFBR systems. In the absence of agencies, such as ionizing radiation, which can create a chemically active nitrogen species, nitrogen gas, per se, is not expected to pose any structural degradation problem at the temperatures which will obtain during normal operation for the external system. Data on pure nitrogen reactivity with various metals is surprisingly sparse, presumably because its principal areas of application, up to the present, have not involved temperatures where its reactivity with metals can be regarded as significant. Nitriding of the surface layer of various alloys has, of course, been a long used device to improve the wear and fatigue properties of metals with desirable general structural qualities. Nitriding may be applied in liquid or gaseous media. In liquid phase nitriding, nitrogen is introduced to the metal by nitrogenous compounds such as NaCN or KCN, with the assistance of cyanates such as NaCNO, or KCNO. Gas phase nitriding may employ an atmosphere of partly cracked ammonia, or a mixture of nitrogen and hydrogen may be used with the agency of glow discharge which chemically activates the nitrogen and prepares the metal surface for nitriding by removing oxide barriers. Thus, nitriding-the formation of nitrogenous compounds with alloy constituents plus a gradient of dissolved nitrogen in the base metal matrix-requires rather special chemical and physical conditions within the temperature regime of present interest (up to $\sim 500^{\circ}\text{C}$).

If a structural metal is exposed to liquid sodium under an ambient nitrogen atmosphere, some nitriding of the metal may occur at temperatures approaching the maximum which could exist under extreme external system conditions, i.e., a sodium spill/leak at a site permitting residence of the sodium for some time at a temperature of the order of 400°C or above under a nitrogen atmosphere. Sodium has a propensity for removing surface layers (oxides) which otherwise tend to discourage chemical reactivity of the metal. The actual state of nitrogen disposed in liquid

sodium is still uncertain. Evidently, the combination of sodium 'sensitizing' the metal surface plus some extra activity of nitrogen in sodium is sufficient to create a condition favorable for some nitriding at temperatures in excess of roughly 400°C. Some observations of this effect will be discussed for austenitic and ferritic metals.

13.5.2 Austenitic Materials

13.5.2.1 N₂-Na Effects

Table 13.5.2.1-1 lists some common nitrogen compounds with a number of elements found in austenitic and ferritic alloys. Aluminum, chromium, titanium, zirconium and vanadium are among the elements which have been used, to form nitride cases on iron base alloys. The nitride CrN has been identified in instances of the nitriding of austenitic alloys in sodium-nitrogen environments.⁽²⁾ Table 13.5.2.1-2 summarizes nitriding observations of Gill and Bokros⁽³⁾ with 304 SS. These specimens were positioned to allow both nitrogen and sodium exposure of the specimen and the table indicates the nitriding above (nitrogen side), below (sodium side) and at the sodium-nitrogen interface. The severest nitriding occurred close to the interface, with a gradual progression of nitriding effect in both directions from the interface with increasing exposure time. The long exposure times (660-1400 hr) for these tests at the relatively high temperature of 538°C (1000°F) for the external environment is to be emphasized. Figure 13.5.2.1-1 presents data of Wheeler⁽⁴⁾ cited in Reference 5, for 347 SS. There is surprisingly good agreement between these two data sets in the reported nitrided depths for 1000°F for comparable exposure times. Once again, the long exposure times and relatively high temperatures used to obtain the nitriding effects of Figure 13.5.2.1-1 are to be noted. Table 13.5.2.1-3 summarizes results of nitriding studies conducted at Knolls (cited in Reference 2), with a number of materials, including austenitic alloys and the ferritic alloy 2 1/4 Cr-1 Mo. The static capsule test at 900°F (482°C) comes closest to our present concern in that an apparently nitrided layer of 0.25 mil depth developed on 347 SS after 7 days exposure. The 1100°F (593°C) data, neglecting composition differences between 347 and 304 SS, are in good agreement with Figure 13.5.2.1-1.

As indicated by the data of Table 13.5.2.1-1, Ca and Mg exhibit strong nitriding tendencies. Reference 6 cites a recent patent granted for controlled additions of Cu or Mg to sodium to minimize nitriding of steels, especially the SS's. These elements presumably react with nitrogen carriers in the sodium placing the nitrogen in a less accessible form as a calcium, or magnesium, nitrogen complex.

Table 13.5.2.1-1 (Ref. 1)

Thermodynamic Data for Some Nitrides

nitride	ΔH^0 (Kcal/mole)	ΔG^0 (Kcal/mole)
AlN	-76.5	
BN	-60.7	
Ba ₃ N	-90	-73
Be ₃ N ₂	-135	
(CN) ₂	+74	+71
Ca ₃ N ₂	-105	-90
CrN	-29	
Fe ₄ N	-1.1	+2.4
Li ₃ N	-47	
Mg ₃ N ₂	-110	-96
Mn ₅ N ₂	-58	-47
Mo ₂ N	-17	-10
Si ₃ N ₄	-179	-155
TaN	-58	-52
Th ₃ N ₄	-310	-284
TiN	-80	-73
UN	-80	-78
VN	-41	-34.5
W ₂ N	-17	-11
ZrN	-87	

Table 13.5.2.1-2 (Ref. 3)

Nitride Case Thickness for Type 304 SS Exposures to 1000°F Sodium-Nitrogen System

Exposure Time (hr)	Specimen Position			
	Sodium Side Interface		Nitrogen Side Interface	
	Slightly Below (mil)	3 in. Below (mil)	Slightly Above (mil)	3 in. Above (mil)
660	0.9	0.1	None	None
1140	1.5	0.1	0.1	0.1
1400	2.0	0.3	-	0.4

Figure 13.5.2.1-1 (Ref. 4)

Nitriding of 347 SS in Static Sodium with Nitrogen
Cover Gas

Table 13.5.2.1-3 (Ref. 2)

Nitriding of Various Materials in Sodium Under a Nitrogen Cover Gas

Test	Material	Surface Area, dm ²	Weight Change, mg (Average, of 3 Specimens)	Thickness of Nitride Layer, mils	Knoop Hardness		X-Ray Diffraction Data
					Nitride Layer	Base Material	
Static Capsule Tests 900 F, 7 days O ₂ = 0.003 wt % Ca = 10 ppm	Be	0.072	+ 0.4(a)	None(b)	-	-	Film identified as Be ₃ N ₂
	347 SS	0.074	+ 1.0	0.25	285	178	None taken(c)
Static Container Tests 1100 F, 30 days O ₂ = 0.003 wt % Ca = 10 ppm	347 SS	0.196	+ 9.0	0.4	243	182	None taken(c)
	304 SS	0.163	+ 9.0	1.0	350	156	Layer identified as γCrN
	410 SS	0.163	+18.0	2.25	263	154	Layer identified as γCrN
	2.5Cr-1Mo	0.163	0.0	None	155(d)	131	-
	18-4-1 tool steel	0.102	+ 2.0	1.5	310	243	None taken(c)
	6-6-2 tool steel	0.163	+ 7.0	1.5	277	212	None taken(c)

(a) After descaling; film weight (per specimen) 1.6 mg.

(b) No visible nitride effect on descaled surface, except remaining nitride film caught in narrow irregularities owing to incomplete descaling.

(c) Structure similar between this film and X-ray identified films, plus the increase in hardness, are taken as evidence that this film carries a nitride.

(d) Too small an increase to be significant in the absence of a visible film.

References for 13.5.2.1

1. J. D. Fast, Interaction of Metals and Gases, Academic Press, N.Y., 1965.
2. J. H. Stang et al., "Compatibility of Liquid and Vapor Alkaline Metals with Construction Materials," DMIC Rpt-227, April 1966.
3. J. J. Gill, J. C. Bokros, "Nitriding of Type 304 Stainless Steel in a Sodium-Nitrogen System," NAA-SR-6162, May 1961.
4. G. C. Wheeler, "The Effect of Nitrogen Covered Sodium on S-20 Structural Materials," AECU-3656, 1957.
5. H. P. Maffei, "Cover Gas Impurities in Sodium Cooled Reactors: Literature Survey," BNWL-849, Aug. 1968.
6. Corrosion Abstracts, 13, No. 2, March 1974, Item 89-75.

13.5.2.2 The Influence of Oxidizing Gas Species on Na Effects

Without the conjoint action of sodium, nitrogen is not expected to pose any significant corrosion problem within the external environment. Figure 13.5.2.2-1 presents results of nitrogen-H₂O and nitrogen-O₂ corrosion studies conducted at Battelle Columbus⁽¹⁾ with a number of austenitic alloys. An oxidizing species, such as O₂ or H₂O, tends to counter any nitrogen reactivity with the metal by imposing an oxide layer. Figure 13.5.2.2-2 presents a graphical summary of the various nitrogen-O₂ tests at 1650°F (899°C). The 'attack' in this instance is oxidation. There was no identification of a nitrogen compound in these tests, although some nitrogen solution was apparently detected.

Reference for 13.5.2.2

1. D. L. Keller et al., "Corrosion of Stainless Alloys in High Temperature Nitrogenous Environments," BMI-1361, July 1959.

Figure 13.5.2.2-1 (Ref. 1)

Maximum Depth of Oxidation of Various Ferrous Alloys
Exposed for 100 hr in Nitrogen Containing Small
Amounts of Oxidizing Gases

Figure 13.5.2.2-2 (Ref. 1)

Effect of Oxygen in Nitrogen Atmospheres on the Oxidation of Type 318 SS at 1650°F

13.5.3 Ferritic Materials

13.5.3.1 Nitrogen Solubility and Equilibrium Thermodynamics Predictions of Nitrogen Reactivity

The formation of stable nitrides in a ferrous base depends on the presence of elements with a strong affinity for nitrogen. Pure iron possesses a relatively small solubility for nitrogen (see Table 13.5.3.1-1). Furthermore, its principal nitride, Fe_4N is relatively unstable as shown by the free energy-temperature diagram given in Figure 13.5.3.1-1. As an example of the use of this type of diagram, the reaction producing Fe_4N at 440°C requires an overpressure of nitrogen of about 4700 atmospheres to maintain the Fe_4N at equilibrium. The relative potency of $\text{NH}_3\text{-H}_2$ mixtures with respect to nitriding is also indicated by this diagram. Under the above conditions, NH_3+H_2 at 1 atmosphere pressure with a ratio $p(\text{NH}_3)^2/p(\text{H}_2)^3$ equal to about 0.26 will equilibrate with the Fe_4N . The N_2 overpressure for equilibrium is obtained by drawing a line between the 'D' point on the left hand scale and the intersection of the desired reaction line with the desired temperature and extending this line to the p_{N_2} scale on the right. The NH_3/H_2 ratio at 1 atm is determined by connecting the 'N' point on the left scale to the curve-temperature intersection and extending to the $(p_{\text{NH}_3})^2/(p_{\text{H}_2})^3$ scale on the right. This diagram also identifies the principal elements used for nitriding, namely, Al, Ti, Zr, etc., as noted in the previous section. The lower the reaction line on this diagram, the more stable the corresponding nitride according to the criterion of equilibrium thermodynamics.

References for 13.5.3.1

1. J. D. Fast, Interaction of Metals and Gases, Academic Press, N.Y., 1965.
2. J. Pearson, U.J.C. Ende, "The Thermodynamics of Metal Nitrides and of Nitrogen in Iron and Steel," J. Iron & Steel Inst., Sept. 1953, p. 52.

Table 13.5.3.1-1 (Ref. 1)Solubility of Nitrogen in Alpha Iron in Equilibrium with N₂ (1 atm)

T(C)	solubility(w/o)	(ppm)
20	4.1×10^{-7}	4.1×10^{-3}
100	5.9×10^{-6}	5.9×10^{-2}
200	4.6×10^{-5}	4.6×10^{-1}
300	1.7×10^{-4}	1.7
400	4.5×10^{-4}	4.5
500	9.0×10^{-4}	9.0
590	1.5×10^{-3}	15
700	2.4×10^{-3}	24
800	3.3×10^{-3}	33
880	4.2×10^{-3}	42

Standard Free-Energy/Temperature Diagram for the Formation of Metal Nitrides

13.5.3.2 Steel Compositions Favoring Nitriding and Na Influence on Nitrogen Effects

Table 13.5.3.2-1 lists the composition of some ferritic alloys tailored for nitriding, together with the composition of the 2 1/4 Cr-1Mo steel, of present interest to LMFBR systems. The latter alloy differs from the 'nitralloys' principally in C and Al content, with aluminum being the principal element distinguishing the nitriding characteristics of these alloys from the 2 1/4 Cr-1Mo alloy. In Table 13.5.2.1-3, it was noted that 2 1/4 Cr-1Mo did not nitride at 1100°F (593°C) under the sodium-nitrogen exposure conditions for up to 30 day's exposure. Other data on ferritic alloys with the sodium-nitrogen system have not been noticed. The 304 and 347 SS's differ from the 2 1/4 Cr-1Mo alloy in Cr content (2 1/4 compared to about 18%) and Ni content (0.09 compared to about 10), while the ferritic SS's (e.g., 410) differ in Cr content only to about the same extent. Nickel does not nitride appreciably, according to available data. Therefore, the chromium content must be assigned the responsibility for the relatively greater nitriding propensity compared to the low alloy ferritic materials such as 2 1/4 Cr-1Mo. CrN, as noted above, is the only nitride identified by the cited references in connection with nitriding of the 300 and 400 series SS's.

Nitrogen is one of the interstitials which can affect the stress corrosion cracking tendencies of a ferritic material. Dissolved nitrogen would be expected to be more important in this respect than nitride compounds. Nitrogen solution will occur in ferritic materials if exposed to nitrogen at temperatures near the maximums expected for LMFBR service. The presence of sodium might accelerate the nitrogen absorption at the somewhat lower temperatures which could obtain under sodium spill/leak conditions. The structural effects of this phenomenon are virtually unknown at this juncture and their elucidation will come principally from actual working experience with LMFBR systems.

Reference for 13.5.3.2

1. J. D. Fast, Interaction of Metals and Gases, Academic Press, N.Y., 1965.

Table 13.5.3.2-1 (Ref. 1)

Compositions of Some 'Nitralloys' Compared to 2 1/4 Cr-1Mo Steel

Identi- fication *	135	135 mod.	N	EZ	GR	2 1/4 Cr-1Mo
C	0.30-.40	0.38-.45	0.20-.27	0.3-.40	1.25-1.50	0.08
Mn	0.40-.70	0.40-.70	0.40-.70	0.50-1.10	0.4-0.6	0.6
Si	0.20-.40	0.20-0.4	0.20-.4	0.20-.40	1.25-1.5	0.30
Cr	0.90-1.4	1.4-1.8	1.00-1.5	1.00-1.5	0.20-.40	2.25
Al	0.85-1.20	0.85-1.2	0.85-1.20	0.85-1.20	1.00-1.5	0.009
Mo	0.15-0.25	0.30-.45	0.20-.30	0.15-.25	0.20-.30	0.87
Other			Ni(3.25)	Se(.15)		Ni(0.09)

* Identification according to Materials and Methods, March 1954.

13.5.4 Summary of Section 13.5

Although the nitriding 'problem' has received relatively little attention in connection with LMFBR systems, the available information indicates that, except under conditions permitting long residence of sodium on structural materials under nitrogen, at temperatures in excess of roughly 450°C, nitriding of the principal structural materials should present no significant problem. It is submitted that such conditions would very probably develop, or be indicative of, other problems somewhat more serious than nitrided spots on massive structural components. If the temperature factor is critical to this phenomenon, the time factor is not less so and prompt attention to sodium events should minimize nitrogen interaction with structural materials in the external environment.

13.6 REACTIVITY OF THE Na-H₂O-O₂ SYSTEM WITH THERMAL INSULATION MATERIALS

13.6.1 Scope of Problem

Thermal insulating material will be in close contact with the sodium circuits of the LMFBR, under various ambient atmosphere and temperature conditions. The annulus between the insulation and the sodium envelope may vary from less than an inch to several inches, depending on the requirements for instrumentation, heater circuits, etc. Insulation materials are invariably of complex chemical and physical structure. The spectrum of possible interactions between these materials and the Na-H₂O-O₂ system poses a problem in any quantitative predictions of structural effects resulting from sodium spills/leaks into an environment containing such materials, under atmospheric conditions which also can span a wide range of chemical activity.

This section will review some sodium-refractory interaction data. The data include some general chemical reactivity data for a number of compounds which may be incorporated either in insulation material or in oxide layers on the structural metal surface, and some recent engineering qualification tests with a number of commercial insulation materials which are candidates for LMFBR service.

13.6.2 Sodium Reactivity with Refractory Materials

Sodium reactivity with materials which could comprise thermal insulation materials is not well characterized because of the relatively complex chemistry involved, even with materials exceeding industrial standards of purity. Static sodium exposure tests over a range of temperature, including the possible extremes associated with the external system, will provide some discrimination among possible constituents of thermal insulation material. As noted in the previous sections, however, a properly comprehensive test program would involve all of the significant reaction products of the Na-H₂O-O₂ system. In this respect, present refractory and insulation data appear to be quite limited.

Table 13.6.2-1 gives the results of several studies of the reactivity of sodium with various refractory materials. The sodium data refer to static tests at 815°C, for 100 hr exposure. Of the oxides which could be incorporated in commercial insulation, Al₂O₃, MgO and BeO exhibit the best stability in this test, with ThO₂ and ZrO₂ progressively worse. Table 13.6.2-2 presents the results of another reactivity survey in sodium at temperatures of 932°F (499°C) and 1382°F (749°C). The effect of a temperature increase is somewhat surprising in several cases, although the mixed oxide systems used in some of these tests involve complex transitions, where reactivity effects would be difficult to predict. This is indicated by the results at 932°F for the BeO-ZrO₂ system, which, despite the presence of ZrO₂ (note Table 13.6.2-1 results for ZrO₂), performed better than the trio of better solo performers, namely, MgO-BeO-Al₂O₃. The other oxide complex incorporating ZrO₂ also gave the best stability at the higher test temperature.

Purity and physical state markedly influence the chemical response of a refractory and there are many opportunities for substantial variation in these factors between laboratory test specimens and commercial formulations sometimes using a number of refractory species in a given composite.

Table 13.6.2-1 (Refs. 1,2)
Corrosion Resistance of Ceramics to Sodium and NaK

Exposure to 815-C Static Sodium for 100 Hr	Exposure to NaK-50 for 168 Hours in Tilting- Furnace Equipment Where $T_{\text{High}} = 871\text{ C}$ and $T_{\text{Low}} = 650\text{ C}$
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Ceramics Showing No Observable Attack And Very Slight Weight Losses

Cr ₃ C (98.7)(a)	CbC (<1)(a)
TiC (97.4)	TiC (<1)
ZrC (100)	WC (<3)
Al ₂ O ₃ (single crystal) (100)	BeO (<1)
BeO (96)	
MgO (single crystal) (100)	
Mg ₂ AlO ₄ (single crystal) (100)	
Sm ₂ O ₃ (79)	
~49.5 Sm ₂ O ₃ -27 Gd ₂ O ₃ -balance:	
other rare-earth oxides (90)	
ZrB ₂	

Ceramics Showing Relatively Little Attack But Enough to Distinguish
Them From Materials in the Category Indicated Above

B ₄ C (80-90)	TiN (<3)
SiC	TiB ₂ (2)
ThO ₂ (75-80)	
Si ₃ N ₄ (67.7)	
MoSi ₂	

Ceramics Showing Significant Degrees of Attack

Zr-O ₂ (Ca-stabilized)	B ₄ C (0.5)
BN (60-98)	B ₄ C-20 wt percent ZrB ₂ (0.4)
	Mo ₂ C (8)
TiN	SiC-Si (0.3)
	ZrC (<1)
	Ta ₂ O ₅ (2)
	ThO ₂ (<2)
	UO ₂ (2)
	ZrB ₂ (0.7)
	CaF ₂ (1)
	MoSi ₂ (<1)
	MoS ₂ (19)
	CeS (19)

(a) In the left column the numbers in parenthesis refer to percent of theoretical density; in the right column, the corresponding numbers refer to apparent porosity in percent.

Table 13.6.2-2 (Refs. 1,3)

Resistance of Selected Ceramics and Cermets
to Attack by Aged and Filtered Sodium

Mole Compositions, Except as Indicated	Corrosion Rate, mg/(cm ²)(month)		Absorption, percent	Density, g/cc
	932 F	1382 F		
<u>Ceramics</u>				
Artificial periclase crystal (MgO)	-0.4	- 0.25		
BeO	0.14			
Stabilized ZrO	2.7			
1BeO : 1Al ₂ O ₃	0.0003		0.18	
1MgO : 4ZrO ₂	-0.091	-14.6	0.01	
1MgO : 8BeO : 1Al ₂ O ₃	-0.44	- 1.6	0.03	
76BeO : 4Al ₂ O ₃ : 20ZrO ₂ (+2 wt% CaO)	-0.64	0.54	0.01	
3MgO : 90BeO : 1ZrO ₂	-0.68	- 0.96	0.03	
Hot-pressed synthetic mica	Disintegrated			2.74
TiN	Spalled			2.39
CaZrO ₃	28.7			4.28
CdO	Missing			5.33
ZnO	Missing			2.33
Be ₂ C (swelled due to hydra- tion after test)	4.5			
MoSi ₂	Missing			6.10
<u>Cermets</u>				
K-138 (Co-bonded TiC)	-0.275			
K-138A (Co-bonded CbC)	-0.225			
K-L7 (Co-bonded WC)	-0.15	- 0.1		
K-152 (Ni-bonded TiC)	-0.15	- 1.77		
K-152B (Ni-bonded CbC)	-0.05	- 1.6		
100 percent TiC	-0.025	- 0.22		

References for 13.6.2

1. W. E. Berry, Corrosion in Nuclear Application, John Wiley, N.Y., 1971.
2. S. J. Basham, et al., "Corrosion Screening of Component Materials for NaK Heat Exchange Systems;" Chemical Engr. Prog. Symposium Series, 55(23), 1959, p. 53.
3. W. H. Cook, "Corrosion Resistance of Various Ceramics and Cermets in Liquid Metals;" ORNL-2391, June 1960.

13.6.3 General Chemical Reactivity of Various Oxides

The chemical reactivity of the various substances which could be incorporated in thermal insulation for sodium systems is a complex subject of vast scope. The previous section indicated some material guidelines with respect to sodium compatibility. Table 13.6.3-1 lists some additional reactivity information for some of these materials. While much of this information may not be immediately pertinent to the external system, general reactivity comments often furnish valuable clues to the analysis of specific corrosion situations, the effect of contaminant substances, etc. It is to be noted that, with the exception of MgO for which such information was not presented, all of the refractories listed in the table exhibit some reactivity with alkali metal and/or alkali metal reaction products at pertinent temperature levels. These oxides-- Al_2O_3 , ZrO_2 and BeO -- singly, and in combination, were rated with respect to sodium reactivity in Tables 13.6.2-1,-2. Caustic corrosion data, over a range of caustic (NaOH) concentration, would be of interest for these materials, although of less practical significance than similar data for commercial thermal insulation formulations.

Table 13.6.3-2 presents some general reactivity information for several oxides which are present to some extent on the protective oxide layers of austenitic and ferritic structural materials. Halogens (Cl, F, Br) are generally detrimental to oxidation products. Information on the effect of caustic solutions on these oxides is apparently very sparse. Sodium, above not well-defined temperatures, is aggressive towards the oxidation layers on ferritic and austenitic alloys. Nevzorov⁽²⁾ discusses a number of high-temperature ($\sim 800^\circ\text{C}$) tests with various sodium-oxide systems. The observations, however, are not particularly illuminating with respect to possible caustic interaction.

References for 13.6.2

1. G. V. Samsonov (Ed.), The Oxide Handbook; IFI/Plenum, N.Y. 1973.
2. B. A. Nevzorov, Corrosion of Structural Materials in Sodium; IPST, Jerusalem, 1970.

Table 13.6.3-1 (Ref. 1)
Misc. Reactivity of Refractory Oxides

Oxide	Reactant	T(C)	Comments	Oxide	Reactant	T(C)	Comments
Al ₂ O ₃	Nitrogen	1700	React in presence of carbon with formation of aluminum nitride	BeO	Beryllium, titanium	1400	No reaction in an inert medium
	Water	-	Insoluble		Water	-	Practically insoluble (0.002-0.008 mmole per liter H ₂ O)
	Hydrogen, carbon monoxide, hydrocarbons	Up to 1800	No reaction		Helium (liquid)	1000	No reaction
	Silicon	1800	React on heating in vacuum by the reaction $Al_2O_3 + 2Si = 2SiO + Al_2O$		Potassium bisulfate	-	React according to the equation $BeO + 2KHSO_4 = BeSO_4 + K_2SO_4 + H_2O$
Al ₂ O ₃ (cont.)	Sulfur, phosphorus, arsenic, and their compounds	1000	No reaction		Acids (solutions)	-	Dissolve BeO slightly
	Carbon	2000	React with formation of carbide Al ₄ C ₃		Hydrofluoric acid	-	React with the formation of the fluoride BeF ₂
	Potassium pyrosulfate	-	React on fusion		Carbon	1900	React on heating with the formation of the carbide Be ₂ C
	Acids and alkalis	-	Insoluble		Carbon tetrachloride	-	React with the formation of anhydrous chloride
	Alkalis (melts)	-	React with formation of aluminates		Alkalis (solutions)	-	Dissolve BeO slightly
					Alkalis (melts)	-	React with the formation of beryllates
MgO	Air	-	No reaction	ZrO ₂	Fluorine and fluorides	20	React
	Water	-	React with formation of hydroxide Mg(OH) ₂		Chlorine	800	React in the presence of carbon: $BeO + C + Cl_2 = BeCl_2 + CO$
	Acids	-	Dissolve		Ammonium acid fluoride	-	React with the formation of the fluoride: $ZrO_2 + 2NH_4HF_2 = ZrF_4 + 2NH_3 + 2H_2O$
	Magnesium chloride (30% solution)	-	React with formation of oxychloride Mg ₂ OCl ₂		Alkali metal carbonates and alkalis (melts)	-	React with the formation of zirconates: $ZrO_2 + 2NaOH = Na_2ZrO_3 + H_2O$; $ZrO_2 + 4NaOH = Na_4ZrO_4 + 2H_2O$
	Nitrogen + carbon disulfide vapor	800	React with formation of sulfide MgS		Nitric and hydrochloric acids	-	No reaction
	Carbon	-	React with formation of carbide MgC ₂		Sulfuric acid (concentrated)	Heating	Dissolves with formation of sulfate $Zr(SO_4)_2$
	Chlorine + carbon monoxide	750	React with formation of magnesium chloride $MgCl_2$: $MgO + Cl_2 + CO = MgCl_2 + CO_2$		Sulfuric acid (dilute)	-	No reaction
					Hydrofluoric acid	500	Dissolves by the reaction $ZrO_2 + 6HF = H_2[ZrF_6] + 2H_2O$
					Germanium, silicon, and titanium oxides	Fusion	React with the formation of silicates, titanates, and germanates
					Rare earth metal oxides	Fusion	React with the formation of zirconates of the type $Me_2Zr_2O_7$
					Alkaline earth metal oxides	-	React with the formation of zirconates $MeZrO_3$

Table 13.6.3-2 (Ref. 1)

Misc. Reactivity of Oxidation Products of Ferritic and Austenitic Structural Metals

Oxide	Reactant	T(C)	Comments	Oxide	Reactant	T(C)	Comments
Cr_2O_3	Hydrogen	1600	React with reduction to metallic chromium	FeO	Water	-	No reaction
	Potassium pyrosulfate (melt)	-	React with formation of the sulfate: $\text{Cr}_2\text{O}_3 + 3\text{K}_2\text{S}_2\text{O}_7 = \text{Cr}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4$		Hydrogen	-	React with reduction to metallic iron
	Lithium and sodium carbonates	Calcination	React with formation of the chromates LiCrO_2 and NaCrO_2	Fe_2O_3	Acids	-	React with formation of corresponding salts
	Sodium bromate	-	React by the equation $5\text{Cr}_2\text{O}_3 + 6\text{NaBrO}_3 + 2\text{H}_2\text{O} = 3\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{Cr}_2\text{O}_7 + 3\text{Br}_2$		Silicon oxide	Fusion	React with formation of silicates
	Sodium carbonate + nitrate (melt)	-	React by the equation $\text{Cr}_2\text{O}_3 + 3\text{NaNO}_3 + 2\text{Na}_2\text{CO}_3 = 2\text{Na}_2\text{CrO}_4 + 3\text{NaNO}_2 + 2\text{CO}_2$		Carbon, carbon monoxide	-	React with reduction to metallic iron
	Base metal oxides	-	React with formation of double compounds of the spinel type $\text{MeO} \cdot \text{Cr}_2\text{O}_3$		Water	-	No reaction
	Carbon	1200	React with formation of the carbides Cr_3C_2 and Cr_7C_3		Dry hydrogen	400	React with reduction to metallic iron
	Carbon tetrachloride	-	React with the formation of chromium chloride CrCl_3		Wet hydrogen	400	React with formation of Fe_3O_4
Cr_2O_3 (cont.)	Chlorine	800	React in the presence of carbon with the formation of chromium chloride CrCl_3		Wet hydrogen	800	React with formation of FeO
					Sulfuric acid (concentrated)	-	React with formation of the sulfate $\text{Fe}_2(\text{SO}_4)_3$
NiO	Acids	-	Dissolve slowly		Hydrochloric acid	-	React with formation of the chloride FeCl_3
	Barium oxide	-	React in oxygen atmosphere with formation of double salts $2\text{BaO}_2 \cdot \text{NiO}$		Chlorine	500	React with formation of the chloride FeCl_3
	Water	-	No reaction		Chlorine	400	React in the presence of carbon with formation of the chloride FeCl_3
	Hydrogen	-	React with reduction to metallic nickel				
NiO (cont.)	Sulfuric acid (dilute)	-	Dissolves with formation of the sulfate NiSO_4				
	Silicon oxide	-	React with formation of nickel orthosilicate $\text{Ni}_2(\text{SiO}_4)$				

13.6.4 LMFBR System Qualification Testing of Commercial Thermal Insulation Materials

13.6.4.1 Scope of Tests

While information on the pure constituents of thermal insulation material provides certain guidelines, the practical insulation materials are generally a complex of chemical species in various physical forms. Furthermore, commercial products will invariably have an impurity content which could markedly affect the desirability of the material under conceivable conditions of the external environment. Atomics International has performed an extensive program of qualification testing of a large number of thermal insulation candidates and their report, Reference 1, is the substance of this section. From the standpoint of corrosion effects compatibility, three types of tests were involved, namely, (a) sodium-air reaction tests within a cavity of the test material to see if the insulation aggravated the sodium-air reaction and the material exhibited satisfactory structural stability to local sodium-air reaction events; (b) chemical analysis of the materials to see if they satisfied certain standards for the chloride, sodium, and silicate content set forth in the RDT-M12-1 criteria for prevention of SCC of austenitic materials; (c) stress corrosion cracking tests with 304 SS in the neighborhood of 180-260°F, using U-bend specimens subject to chloride ions which might be leached from the insulation material by water.

References for 13.6.4.1

1. J. K. Balkwill, "Chemical and Physical Testing of Thermal Insulation Materials for Use at FFTF and SPTF," LMEC-74-6, April 1974.

13.6.4.2 Na-Air, Cl Contamination, Stress Corrosion Cracking Tests

Table 13.6.4.2-1 lists the commercial thermal insulation materials involved in the AI program. The (a) sodium-air tests were made by pouring liquid sodium (separately heated to 1050°F) into a cavity in a test block of the insulation material (initially at RT) under an ambient air atmosphere. The qualitative observations of the tests are given in Table 13.6.4.2-2. It was concluded that all of the candidate materials showed a 'satisfactory' compatibility with sodium under the test conditions, and did not aggravate the sodium-air reaction significantly. The volume of material affected by the sodium-air reaction depended on the porosity of the insulation--the reaction being confined essentially to the surface of the dense materials with some penetration of the more porous specimens. The materials containing calcium silicate exhibited the more vigorous reaction, presumably due to the involvement of water in the reaction. It was concluded that load-bearing candidates from their test selection would not suffer significant structural impairment from a sodium leak, under air, of considerably greater extent than represented by the test.

Figure 13.6.4.2-1 gives the chloride (Na + silicate) grid defining 'acceptable' chemistry for insulation materials, essentially based on the work of Karnes.⁽²⁾ The implication of this diagram is that chloride ions are not detrimental to the SCC tendency of austenitic alloys if balanced by a (Na + silicate) content of appropriate amount. Table 13.6.4.2-3 presents the results of the chemical analysis of the candidate materials and their rating based on the RDT-M12-1 criterion, summarized in Figure 13.6.4.2-1.

The insulation materials passing the chemical analysis test were used for the SCC test (c). This test consisted of placing U-bend specimens of sensitized 304 SS in contact with a heat source (steam or electrical heat). A block of the insulation under test was used as a wick to draw distilled water up to the surface of the 304 specimen, the placement of the test components being such as to insure that the tensile side of the specimen would be affected by any chloride ions leached from the

Table 13.6.4.2-1 (Ref. 1)

Thermal Insulation Materials for Sodium Compatibility Testing
(Sheet 1 of 2)

Trade Name	Manufacturer	Type and Form Tested	Density (lb/ft ³)	Contains Asbestos
Fiberfrax T-30R	Carborundum	Ceramic fiber paper, laminated into tubes	47	No
Glasrock Foam 50	Glasrock Products	Foamed, fused silica block	52	No
Kaylo-10	Owens Corning Fiberglas	Calcium silicate, pipe cover	11	Yes
Marimet-45	Johns-Manville	Calcium silicate, board	44	Yes
MMM-36, non-heat-treated	Johns-Manville	Calcium silicate, board	36	Yes
Min-K, standard	Johns-Manville	Refractory fiber, flexible blanket	16	Yes
Min-K, high-temp	Johns-Manville	Refractory fiber, flexible blanket	16	Yes
Super Caltemp	Fibreboard	Calcium silicate, pipe cover	12	No
Thermobestos	Johns-Manville	Calcium silicate, pipe cover	11	Yes
No. 10 Insulation	"48" Insulations	Refractory fiber, semi-rigid felt	10	Yes
Fiberfrax T-30LR	Carborundum	Ceramic fiber paper, laminated into blocks	47	No
Mono-Block	Keene	Mineral fiber block	15	No
MMM-36, heat-treated	Johns-Manville	Calcium silicate, board	37	Yes

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Table 13.6.4.2-1 (Ref. 1) (contd)

Thermal Insulation Materials for Sodium Compatibility Testing
(Sheet 2 of 2)

Trade Name	Manufacturer	Type and Form Tested	Density (lb/ft ³)	Contains Asbestos
PV Supertemp Block	Eagle-Picher	Mineral fiber, block	16	Yes
Superglas Moldable Felt	Eagle-Picher	Mineral fiber, felt	13	Yes
Cerafelt 600	Johns-Manville	Mineral fiber, blanket	6	No
Epitherm-1200	Eagle-Picher	Mineral fiber, molded pipe cover	10	No
Fiberfrax	Carborundum	Mineral fiber, blanket	6	No
Kaylo-10AF	Owens Corning Fiberglas	Calcium silicate, block	11	No
Min-K 1301	Johns-Manville	Mineral fiber, molded sheet	20	Yes
MF Pipe Insulation	"48" Insulations	Refractory fiber, pipe cover	9	No
Super "48" Cement	"48" Insulations	Refractory fiber, cement	25 (as-cast)	No
Super Caltemp	Fibreboard	Calcium silicate, block	12	No
Thermox-12	Johns-Manville	Calcium silicate, block	11	No
Wool	"48" Insulations	Refractory fiber, loose wool	8 (as-packed)	Yes

13.6.4.2-3

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Table 13.6.4.2-2 (Ref. 1)

Results of Sodium-Insulation Compatibility Testing

Trade Name	Duration of Sodium Burn (sec)	Maximum Flame Height (in.)	Sparks Ejected	Maximum Depth of Reaction
Stainless Steel Pan	90	1/4	No	DNA
Dense Materials				
Fiberfrax T-30R	45	4	Yes	1/4
Fiberfrax T-30LR	45	2	No	1/8
Glasrock Foam 50	65	1/2	No	None
Mono-Block	50	1	No	3/4
PV Supertemp Block	55	2	No	1
Super "48" Cement	60	4	No	3/4
Calcium Silicate Materials				
Kaylo-10	60	10	Yes	1/2
Kaylo-10AF	70	8	Yes	1/2
Super Caltemp	70	10	Yes	3/4
Super Caltemp	80	10	Yes	1
Thermobestos	45	10	Yes	1/2
Thermo-12	60	12	Yes	1/4
Dense Materials Containing Calcium Silicate				
Marimet-45	30	6	Yes	None
Molten Metal Marinite-36:				
Non-heat-treated	30	12	Yes	1/32
Heat-treated	35	4	Yes	3/8
Min-K 1301	70	12	Yes	1/4
Min-K, flexible, standard	25	8	Yes	1/2
Min-K, flexible, high-temp	25	8	Yes	1/4
Felted Materials				
Epitherm-1200	170	2	No	1
MF Pipe Insulation	145	4	No	1/2
Superglas Moldable Felt	130	2	No	1
No. 10 Insulation	120	2	No	1-1/4
Cerafelt 600	90	3	No	1
Fiberfrax	120	3	No	1/2
Wool	185	3	No	1

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Figure 13.6.4.2-1 (Ref. 1)

Acceptability of Insulation Material Based on Chemical Analysis

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13.6.4.2-5

Table 13.6.4.2-3 (Ref. 1)

Results of Chemical Analysis of Thermal Insulation Materials

Trade Name	Soluble Ion Concentration (ppm)				RDT M 12-1 Criteria
	Sodium	Silicate	Sodium & Silicate	Chloride	
Dense Materials					
Fiberfrax T-30R	1,300	6,050	7,350	1,040	Reject
Fiberfrax T-30LR	1,830	3,930	5,760	1,060	Reject
Recheck	-	-	-	956	Reject
Glasrock Foam 50	12	280	292	7	Accept
Mono-Block	1,680	945	2,625	260	Accept
PV Supertemp Block	214	292	506	36	Accept
Super "48" Cement	-	24,380	>24,380	1,200	Reject
Calcium Silicate Materials					
Kaylo-10AF	1,022	3,155	4,177	30	Accept
Super Caltemp	6,388	7,140	13,528	500	Accept
Recheck [†]	5,162	5,068	10,230	510	Accept
Thermo-12	550	4,690	5,240	180	Accept
Recheck [†]	446	4,450	4,896	198	Accept
Dense Materials Containing Calcium Silicate					
Marimet-45	35	2,885	2,920	12	Accept
MMM-36, non-heat-treated	540	7,105	7,645	138	Accept
MMM-36, heat-treated	420	1,860	2,280	47	Accept
Min-K 1301	3,112	3,135	6,247	40	Accept
Min-K 1301, asbestos-free	2,150	4,043	6,193	39	Accept
Min-K, flexible, standard	38	2,750	2,788	74	Accept
Min-K, high-temp	4	4,040	4,044	39	Accept
Felted Materials					
Epitherm-1200	-	367	>367	1,350	Reject
Recheck	350	654	1,004	46	Accept
Epitherm-1200 [†]	415	733	1,148	18	Accept
MF Pipe Insulation	279	798	1,077	91	Accept
Recheck [†]	169	634	803	24	Accept
Superglas Moldable Felt	92	326	418	254	Reject
No. 10 Insulation	338	362	700	351	Reject
Cerafelt 600	142	335	497	24	Accept
Fiberfrax	13	305	318	22	Accept
Recheck	6	340	346	25	Accept
Wool	98	868	966	96	Accept
Kaowool [§]	3	330	333	<25	Accept

[†]New sample used.[§]Kaowool: ceramic fiber blanket material, 8 lb/ft³, no asbestos, manufactured by Babcock & Wilcox.

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insulation. The summary of the SCC tests is given in Table 13.6.4.2-4. Failure was assigned to the material giving more than one cracked 304 specimen out of four specimens. Some of the 'failed' insulation materials were shown to have chloride contents which did not satisfy the criterion of Figure 13.6.4.2-1 (Fiberfrax T-30R and T-30LR). The 'failed' candidates included several which satisfied the chemical criteria, namely, Fiberfrax blanket, Min-K-1301, asbestos-free Min-K 1301 and Kaowool. Several materials were given an 'inconclusive' rating because the water leaching was not considered sufficient to reveal possible aggressive species. The summary of the materials passing the SCC tests is given in Table 13.6.4.2-5. Little information on the chemical constitution of these materials was given, presumably because of proprietary restrictions. "Calcium silicate types" were identified as: Kaylo-10AF, Super Caltemp, and Thermo-12. "Mineral fiber felted types" included: MF Pipe Insulation, Epitherm 1200, "48" Insulations Co. Wool, and Cerafelt 600. "Extreme-low-conductivity types" included: Min-K, flexible, both standard and high temperature versions.

References for 13.6.4.2

1. J. K. Balkwill, "Chemical and Physical Testing of Thermal Insulation Materials for Use at FFTF and SPTF;" LMEC-74-6, April 1974.
2. H. F. Karnes, "The Corrosion Potential of Wetted Thermal Insulation;" AICHE 57th Nat. Meeting, CONF-650905-2, September 1965.

Table 13.6.4.2-4 (Ref. 1)

Results of Stress Corrosion Cracking Tests
of Thermal Insulation Materials

Insulation Materials Tested	RDT M 12-1 Criteria	U-Bend Specimens Cracked/ Tested	Steam Heat (psig)	Electrical Heat (°F)	Water Evaporation Rate (ml/day)†
Min-K, flexible, high-temp	Pass	1/4	8.5 - 11.5	-	320
Min-K, flexible, standard	Pass	0/4	↓	-	341
Kaowool	Fail	4/4	↓	-	2700
Glasrock Foam 50	Pass	0/4	↓	-	368
Fiberfrax T-30R	Fail	4/4	8.7 - 11.8	-	602
Kaowool	Fail	2/4	↓	-	3510
Marimet-45	Pass	0/4	↓	-	234
MMM-36, non-heat-treated	Pass	0/4	↓	-	232
No.10 Insulation	I [§]	0/4	9.5 - 11.8	-	110
MMM-36, heat-treated	Pass	1/4	↓	-	275
Mono-Block	I [§]	0/4	↓	-	110
Fiberfrax T-30LR	Fail	3/4	↓	-	485
MF Pipe Insulation	Pass	0/4	-	199-239	365
Kaylo-10AF	Pass	0/4	-	203-240	225
Super Caltemp	Fail	2/4	-	203-229	330
Thermo-12	Fail	2/4	-	198-241	255
Epitherm-1200	Pass	0/4	-	181-230	435
Min-K 1301	Fail	3/4	-	211-240	160
Wool	Pass	0/4	-	195-229	465
Cerafelt 600	Pass	0/4	-	179-225	865
Min-K 1301, asbestos-free	Fail	4/4	-	208-260	265
Super Caltemp	Pass	1/4	-	211-238	605
Fiberfrax	Fail	2/4	-	225-230	880
Thermo-12	Pass	0/4	-	218-240	265

†Average over 28-day test.

§Inconclusive-wicking rate too low to meet RDT M 12-1 requirements.

Table 13.6.4.2-5 (Ref. 1)Thermal Insulation Materials Passing Chemical
and Stress Corrosion Tests

- 1) Min-K, flexible, standard temperature
- 2) Min-K, flexible, high temperature
- 3) Glasrock Foam 50
- 4) Marimet-45
- 5) Molten Metal Marinite-36, heat-treated
- 6) Molten Metal Marinite-36, non-heat-treated
- 7) MF Pipe Insulation
- 8) Kaylo-10AF
- 9) Super Caltemp
- 10) Thermo-12
- 11) Epitherm-1200
- 12) "48" Insulations Co. Wool
- 13) Cerafelt 600

13.6.5 Summary of Section 13.6

Thermal insulation will be used extensively in the sodium circuits of LMFBF plants. The interaction of these complex materials with sodium events of the external system cannot be described beyond the limits allowed by relatively simple laboratory tests and the information derived from working experience with plants of various size and complexity.

Apart from its obvious function, thermal insulation has a number of conceivable positive and negative attributes in the present context. On the positive side might be mentioned: insulation will serve as a partial barrier to the general atmosphere of a particular area and this may tend to limit the extent and the severity of a sodium event; the insulation provides some channeling for sodium reaction hydrogen which may assist in detecting sodium events. On the negative side: the insulation envelope screens the sodium circuit from visual inspection and places virtually total reliance on a detector array for early warning of sodium events. If a substantial exothermic sodium reaction does occur as a result of an adverse conjunction of factors, the thermal insulation can contribute to local temperature excursions, or to the maintenance of high average temperatures throughout the history of the event. This will tend to aggravate the attending corrosion processes and the consequent damage even if stripping the affected insulation from an event area is not a problem. Insulation will generally complicate the chemical and physical problems of cleanup and the partial containment quantities of the insulation could enlarge the structural area affected by the leak. The relative importance of these factors cannot be judged without substantial operating experience with large scale sodium systems.

The tests described in this section have provided considerable discrimination among commercial thermal insulation materials on the basis of chemical analysis and stress corrosion cracking tests oriented toward minimizing chloride cracking of austenitic SS's used with the insulation. A high temperature sodium event adjoining insulation will bring a complex chemistry into action, depending on the ambient environmental conditions.

It is probable that chloride ion leakage from the insulation will be a relatively minor factor in the totality of effects. The qualification provided by the AI program is, however, a valuable contribution to a very difficult problem of compatibility.

13.7 SUMMARY AND CONCLUSION

13.7.1 The Time Factor in Corrective Action

Most of the corrosion literature concerned with the LMFBR systems is dominated by sodium data. The external environment is concerned less with corrosion in pure sodium than with the corrosion effects of sodium reaction products with the ambient atmosphere. In this regard, it is submitted that NaOH, possibly also Na₂O, are paramount. Pertinent data for either austenitic or ferritic materials is limited and in the case of the ferritic materials the present indications of serious susceptibility to caustic concentrations, in either sodium or aqueous solutions, justify greater attention to this problem.

Although there is no chemical, or physical, justification for procrastination in correcting a sodium event, the austenitic materials appear to allow more time in dealing with sodium spills and leaks before significant structural damage can occur to massive components. This assertion rapidly loses validity, however, with increase in the prevailing temperature of the event and the involvement of water vapor or liquid water. The ferritic alloys appear to allow a very small tolerance for such incidents and the existing data support a philosophy of quickest attention to sodium excursions into the external environment which could affect ferritic alloy components. Steel cladding for floors and walls is certainly less critical in this respect than internally pressurized, or other highly stressed, zones where, beyond some penetration of the surface, the stress factor will start to augment chemical action.

13.7.2 Na Leak Monitoring Requirements

Except for virtually catastrophic incidents involving massive excursions of sodium into the external environment, the success in dealing with sodium events in the external system will depend on the quality of the monitoring system used to detect the presence of sodium, or sodium reaction products, outside the regular containment envelope. A number of physical, chemical and mechanical problems are involved in designing a comprehensive detector array for a large-scale system, and the design of detectors is under extensive research and development in most countries involved in the sodium reactor program. Detector types which are being used in various locations of the sodium system include the following: spark-plug, or electrical conductor, sensors; photoelectric smoke and flame detectors; flame photometers; pH meters; hydrogen detectors; radio-activity sensors. Comprehensive detection ability will depend on the use of a number of different types of monitors, located in positions which can take maximum advantage of the particular characteristics of the detector. Reference 1 is an excellent summary of current practice and testing in the monitoring of sodium events. French experience cited in this reference indicates that a satisfactory detector system must be designed as an integral part of the plant to insure that sodium events will come within the radius of effectiveness of the various monitors. Desensitization of detectors by dust, corrosion products, etc., is a prime problem and an aggressive maintenance policy for the detector system will always be a critically important aspect of monitoring capability.

References for 13.7.2

1. Element 5, Sodium Technology; WASH-1105, 2nd Ed. December 1972.

13.7.3 The Critical Corrosion Situations for Austenitic and Ferritic Materials

There are possibly two essential, qualitative guidelines for minimizing corrosion in the LMFBF external system, or any system, namely: minimize the opportunities for abnormal chemistry development; minimize the possibilities for stress-assisted corrosion.

Sites where abnormal chemical conditions can develop as a result of environment and/or system intervention include crevices and dead-end geometries. Crevices can be created by: overlays, or junctions of components, the edges of corrosion deposits, wires, marking devices, straps, insulation, etc. Dead-end geometries of small cross section and considerable depth can be created as an integral part of component design, or by the mating of components, various 'temporary' repair expediences, etc. Such zones are prime sites for water vapor condensation under appropriate conditions of temperature and relative humidity cycling. Condensation may occur by the chemical and/or physical water absorption of various chemical compounds, or by the capillary condensation phenomenon noted earlier in this chapter. The presence of condensed water, even down to layers of a few hundred angstroms thickness,⁽¹⁾ may trigger electrochemical corrosion action in the presence of electrically conducting species. The caustic stress corrosion cracking problem has been related in a number of instances to the concentration of the OH^- ion at such sites, particularly when the local heat input enables progressively higher boiling-point caustic solutions to develop.⁽²⁾ These sites tend to defeat normal, or sodium event, cleaning procedures and encourage the accumulation of chemical residues which can develop strong concentrations of chemical species inimical to the corrosion stability of the adjoining structural material. Furthermore, the progression of the chemistry in such zones is usually beyond the surveillance capability of the various monitoring systems.

The second guideline is to avoid near-surface stress concentrations, or conditions where plastic strain can accumulate as a result of combinations of thermal and applied stress cycling. Stress, or more generally,

conditions which can create plastic strain concentrations become increasingly significant as a damage agency with increasing temperature and time of exposure to the corroding media. As in the unstressed corrosion case, the austenitic stainless steels and high nickel alloys are substantially superior to the low alloy ferritic materials in their tolerance of these factors for caustic solutions. Inattention to sodium excursion events in the external system could, however, cause serious corrosion and stress corrosion effects on highly stressed austenitic materials. The ferritic materials, and in particular the 2-1/4 Cr - 1Mo steel, now being considered for wide application in the LMFBR plants, exhibit very little tolerance for caustic media throughout the temperature range of the external environment. Increases in stress, caustic concentration, and temperature, aggravate the caustic attack on ferritic materials. Tolerable exposure times to a dangerous combination of these factors would be expected to be very short. Any internally pressurized ferritic alloy component, irrespective of wall thickness, subject to a sodium spill/leak under conditions which could generate some caustic (and this would appear to apply to virtually all spills/leaks) should be given whatever in situ inspection is possible to determine the extent of structural damage.

Probable location and cause of sodium leaks and spills are not likely to be predictable until details of plant design and operation are known. The history of sodium facility operation shows that leaks have been discovered by operators inspecting the system visually rather than by the leak detection system.

At CRFBR operating temperatures and in areas covered by nitrogen plus 1% oxygen atmosphere sodium leaks may be expected to produce corrosion rates of tens to hundreds of mils/year. During shutdown, when the system is maintained at lower temperatures and where stresses equal or exceed yield stress for the material, failure through stress corrosion cracking can occur much more quickly.

Except under hopefully extreme and rare circumstances permitting prolonged contact of liquid sodium with structural material under a nitrogen atmosphere at temperatures in excess of roughly 450°C, nitriding is

not expected to be a significant problem in the LMFBR external environment. Within the scope of alloy compositions of present interest, high chromium contents appear to present the greatest potential for nitriding under the above circumstances.

References for 13.7.3

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2. H. A. Klein, "Corrosion of Fossil Fueled Steam Generators," Combustion, January 1973, p. 5.
3. Steels for High Temperature Service; U.S. Steel Publication.
4. R. N. Newman, C. A. Smith, "Sodium/Water Combustion and the Chemistry of Wastage at Sodium/Water Leak Sites," J. Nucl Matls, 52, 1974, p. 173.

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14.0 CORROSION/MASS TRANSFER AFFECTING MATERIALS
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	WELD ZONES OF ABOVE COMPONENTS

14.1 INTRODUCTION

The interface between the sodium cooling systems of the LMFBR and the water/steam system occurs at the steam generating components of the powerplant, specifically, at the evaporator and superheater components. Even without the material effects potential peculiar to liquid sodium, the steam generating components have accounted for the bulk of the inadvertent, costly, shutdowns of nuclear powerplants^(1,2). There are a number of reasons for this circumstance, among them:

- the steam generating components of nuclear powerplants represent a severe conjunction of mechanical, physical and chemical factors contributing to materials degradation; the ability of laboratory and prototypical equipment testing to analyze the complex synergism among these working factors remains quite limited, particularly where extrapolation to long service times is involved;
- the quality control procedures that have evolved for the construction and operation of the nuclear reactor and its primary cooling system have generally not been extended to the water/steam circuit of the associated electric power generation complex; the penalty for this relative inattention has been an unexpectedly high incidence of steam generation equipment failures.
- welding is used extensively in steam generation system components; the difficulties involved in standardizing the welding process and, accordingly, in characterizing the effect of welding on the structural performance of the involved materials, has been a prime factor in steam generation equipment failures;
- design inattention to some qualitative basics of corrosion knowledge; e.g., where there is potential for deposition from the working fluid, minimize the corrosion implications of deposit buildup by design strategy and/or by providing cleaning facility for the equipment; minimize mechanical crevices in zones of minimal corrosion tolerance; there have been numerous instances of neglect of these principles, particularly in the lower tube-sheet region of vertical evaporators for LWR powerplants.

Carbon and low alloy ferritic steels have been used extensively in the water/steam piping networks of fossil fueled powerplants and for various piping applications in the petrochemical industry. In this country, there is interest in the use of the 2 1/4Cr-1Mo steel as the tubing, tube-sheet and shell material for the evaporators and superheaters of LMFBR powerplants. This steel, in the Nb stabilized grade, has some application in foreign LMFBR powerplants.

It is the purpose of the ferritic steel section of this chapter to briefly review the water/steam-side and the sodium-side corrosion and mass transfer factors that may affect the performance of the 2 1/4Cr-1Mo steel, and to attempt some identification of problem areas related to the corrosion characteristics of this steel.

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14.2 SOME GENERAL FACTORS AFFECTING WATER/STEAM CORROSION

Reactor heat is transferred via the primary-secondary sodium coupling to the electric power generating system at the evaporator and superheater components. The sodium/water/steam interface at the evaporator and superheater represents only a very small segment of the total flow path for the water/steam circuit, which comprises the turbine, condenser, demineralizer, feedwater heaters and pumps, and miscellaneous components appropriate to a modern, high pressure steam electric power generating system. Considering all components in contact with the water/steam circuit, a variety of metallic and nonmetallic structural materials is involved, each distinguished to some extent in its interaction with the water/steam working fluid and the deliberate and adventitious constituents of this fluid.

Using the results of a comprehensive ASME review of steam powerplant problems, Klein⁽¹⁾ lists the following causes of working fluid contamination:

- condenser in-leakage
- evaporator carryover
- chemical discharge from demineralizer
- contamination following chemical cleaning

Condenser in-leakage is regarded as the principal contamination source, the potential corrosion significance of such leakage being determined by the chemical constitution of the condenser cooling water. The total burden of deliberate and adventitious chemical species and forms present in the water/steam working fluid is derived from: water treatment chemicals, impurities from various sources, corrosion products, erosion products and products from reactions among the foregoing. Jonas⁽²⁾ has listed some of the array of compounds that can deposit at various sites in the power generating circuit. Some appreciation for the complexity of typical boiler water and condensate chemistry may be had from Table 14.2-1, taken from Jonas' paper. An indication of the concentration of various gases that can occur in fossil and nuclear powerplant working fluid is given at the bottom of this table. Some of the sources/sinks and factors affecting the transfer of various chemical species within the water/steam circuit are listed in Table 14.2-2.

TABLE 14.2-1. Typical Boiler Water and Condensate Chemistry for High Pressure Steam/Electric Powerplants(2)

	Salt Water Cooling Avg (std)	Fresh Water Cooling Avg (std)	Drum Type Boiler Avg (std)	Super Critical Boiler Avg (std)	Pressurized Water Reactor Avg (std)
<u>Boiler</u>					
pH	9.7(.6)	9.5(.6)	9.7(.6)	9.4(.16)	9.4(.4)
Conductivity (Micro- MHOS)	118 (280)	80.8 (157)	110 (176)	6.7 (1.9)	66.6 (41.0)
Dissolved Oxygen (ppb)	2.7 (3.3)	15.5 47.6	1.9 (3.4)	4.7 (4.4)	3.3 (2.4)
Sodium (ppm)	7.7 (10.8)	6.7 (10.6)	5.6 (7.7)	.003 (.003)	16.8 (15.1)
Silica (ppm)	.17 (.12)	2.0 (5.4)	2.0 (5.6)	.012 (.007)	1.4 (1.7)
Copper (ppb)	-	6.1 (5.3)	6.2 (9.2)	2.6 (1.5)	14.0 (15.1)
Phosphates (ppm)	17.2 (31.1)	11.2 (13.0)	8.7 (8.5)	-	53.4 (87.2)
Sulfates (ppm)	10.0 (14.1)	48.8 (124)	50.5 (124)	0.007 (0.12)	1.5 (2.1)
Chlorides (ppm)	63.1 (177)	1.7 (4.4)	1.8 (4.7)	<.025 (.05)	.66 (.57)
Free NaOH (ppm)	-	30.3 (98.5)	11.1 (29.0)	-	-
Ammonia (ppm)	-	1.05 (.70)	.17 (.04)	1.21 (.50)	-
Hydrazine (ppb)	-	13.0 (9.9)	6.6 (4.15)	19.4 (11.7)	-
Maximum Allowable Chlorides in Boiler (ppm)	2.2 (3.0)	33.4 (77.5)	28.5 (96.6)	.003 (.008)	67.6 (23.4)
<u>Condenser Hot Well</u>					
pH	9.0(.7)	9.0(.4)	3.8(.3)	9.3(.3)	9.0(.04)
Conductivity (Micro- MHOS)	4.7(2.9)	4.4(11.7)	4.9(13.4)	6.2(2.2)	3.2(1.9)
Dissolved Oxygen (ppb)	7.8(9.1)	12.(16.2)	3.3(7.1)	10.8(8.2)	37.(54.9)
Sodium (ppm)	-	.93(2.6)	.20(.63)	.003(.003)	.07(1.2)
Silica (ppm)	.015(.01)	1.3(3.5)	.62(2.7)	.011(.006)	1.7(2.9)
Iron (ppm)	.01(.01)	.28(1.5)	.01(.02)	.077(.003)	.51(1.1)
Copper (ppb)	4.3(4.4)	2.7(4.3)	3.3(5.1)	3.0(1.9)	1.5(1.7)
Chlorides (ppm)	.01(.01)	.11(.27)	-	.03(.04)	.08(.03)

CONCENTRATION OF GASES IN PWP AND FOSSIL STEAM

	Concentration (ppm)	
	Mean	STD Dev.
H ₂	1.13	1.80
N ₂	1.69	2.12
O ₂	.011	.017
CO ₂	1.34	1.76
Hydrocarbons	.060	.066

TABLE 14.2-2. Sources/Factors Participating in Transfer of Chemicals Within Water/Steam System⁽²⁾

Sources/Sinks

Condenser leakage
Demineralization and sodium throw
Primary to secondary leakage in nuclear SGS
Oxygen in leakage
Corrosion of condenser, FWH and boiler tubes
Hideout of chemicals in boiler or SG sludge
Steam separation (mechanical carry-over)
Separation of chemicals (vaporous carry-over)
Steam washing
Dry-out, hideout and leaching in superheater and/or reheater
Deposition of dried particles and oxides in HP turbine
Precipitation of salts from steam and deposition
Interaction of the precipitates with H₂O
Evaporation and dry-out of wet steam in a turbine
Chemical interactions throughout the system

Physico-Chemical Factors

Solubility in water
Solubility in steam
Separation from water to steam
Chemical reactions in water
Chemical reactions in steam
Chemical reactions in oxides
Adsorption and absorption by oxides and other surfaces
Capillary condensation in oxides
Condensation of steam with impurities
Demineralization
Drying and washing

Typical operating parameters for the steam generation system of an LMFB powerplant are indicated by the specifications for the CRBRP (Clinch River). The evaporator and superheater components (two evaporators and one superheater for each of three separate loops) will transfer 975 MWt to the steam electric system. The steam cycle is a nonreheat cycle with 900°F superheated steam supplied to the turbine at 1450 psig. Figure 14.2-1 illustrates some specifics of the operating conditions for the steam generation system of the CRBRP. Figure 14.2-2 is a schematic of the sodium and water/steam flow distribution among the components of a single loop. The evaporator and superheater components for the CRBRP are identical. A schematic of the design for these components is given in Figure 14.2-3. The 2 1/4 Cr-1Mo steel has been selected for the tubing and shells of both components as well as for the sodium piping connecting the evaporator outlet to the inlets of the two evaporators for each of three loops.

The details of the maintenance of acceptable quality for the water/steam circuit of modern steam-electric powerplants still provide considerable opportunity for debate. Some of the chemical additions which have been used for water quality control are given in Table 14.2-3. Additives such as morpholine and hydrazine (so-called zero-solids treatment) are used for control of oxygen concentration and pH. Sodium phosphates have been the principal additives for control of corrosion troublesome impurities such as the chloride ion and for some degree of pH control. Numerous incidents of localized corrosion attack attributable to sodium phosphate, and its derivatives (e.g., NaOH), have tended to discourage regular phosphate treatment in favor of spot treatment upon signal of contaminant intrusion, followed by blowdown to eliminate phosphate precipitates and reduce the residual phosphate of the system. Full condensate polishing (demineralization) is another recourse being used, or proposed, toward improvement of water quality for modern, high-pressure, powerplants. As noted in Table 14.2-2, slippage of aggressive ions through demineralizers is, however, a significant problem, particularly under conditions that encourage concentration of the ions (e.g., heavy deposit buildup in high heat flux zones).

Figure 14.2-4 illustrates the principal justification for maintaining the pH of the water/steam circuit near neutral, or slightly alkaline, conditions. Ferritic steels comprise the bulk of the materials of the water/steam circuit. The normal oxidation product(s) of ferritic steels are unstable

Figure 14.2-1. Water/Steam System Parameters for the CRBRP Powerplant (3)

Figure 14.2-3. Reference CRBRP Superheater/Evaporator Component (4)

TABLE 14.2-3. Chemicals Used To Adjust Boiler Water Chemistry⁽⁵⁾

Chemical	Purpose	Comment
Sodium hydroxide NaOH (caustic soda)	Increase alkalinity, raise pH, precipitate magnesium	Contains no carbonate, precluding formation of CO ₂ in steam: pH control improves form of calcium precipitate (see sodium phosphates)
Sodium carbonate Na ₂ CO ₃ (soda ash)	Increase alkalinity and pH, precipitate calcium in the form of carbonate	Lower cost, more easily handled than caustic, but some carbonate breaks down to release CO ₂ with steam
Sodium phosphates NaH ₂ PO ₄ , Na ₂ HPO ₄ , Na ₃ PO ₄ , NaPO ₃	Precipitate calcium as hydroxyapatite, Ca ₁₀ (OH) ₂ (PO ₄) ₆	Alkalinity and resulting pH must be kept high enough for this reaction
Sodium aluminate NaAl ₂ O ₄	Precipitate calcium, magnesium	Forms a flocculant sludge
Chelants EDTA, NTA	Control scaling by forming heat-stable soluble complexes with calcium and magnesium	Prevents precipitation of scale-forming compounds onto metal surfaces. May dissociate at high pressures. Use oxygen-free water
Polymers Polyacrylates, etc.	Disperse sludge and distort crystal structure of calcium deposits, prevent fouling due to corrosion products	Distortion of crystal structure of precipitate prevents its adherence to metal surface. May be used in conjunction with phosphate, carbonate or chelate program
Tannins, starches, glucose and lignin derivatives	Prevent feedline deposits, coat scale crystals to produce sludge that does not adhere as readily to boiler heating surfaces	Organic dispersants (often called protective colloids) used with soda ash, phosphate. Also distort scale growth, inhibit caustic embrittlement
Seaweed derivatives Sodium alginate, sodium mannuronate	Provide a more fluid sludge and minimize carryover to turbine	Organics (often classed as reactive colloid) react with calcium and magnesium, absorb scale crystals
Sodium sulfite Na ₂ SO ₃	Prevent oxygen corrosion	Neutralizes residual oxygen by forming sodium sulfate. May decompose at high temperatures and pressures to form H ₂ S in steam. Available in catalyzed form for faster action
Hydrazine N ₂ H ₄ (normally supplied as solution)	Prevent oxygen corrosion	Removes residual oxygen to form nitrogen and water--one part oxygen to one part hydrazine is N ₂ H ₄ . Also available as catalyzed hydrazine
Filming amines Octadecylamine, etc.	Control return-line corrosion by forming protective film on metal surfaces	Protects against oxygen and carbon-dioxide attack. Small amounts of continuous feed maintains film.
Neutralizing amines Morpholine, cyclohexylamine, etc.	Control return-line corrosion by adjusting condensate pH	Protection through neutralization of carbonic acid formed from carbon dioxide
Sodium nitrate NaNO ₃	Inhibit caustic embrittlement	Used where water may have embrittling characteristics
Antifoams Polyglycols, silicones, polyamides	Reduce foaming tendency of highly concentrated boiler water	Usually added with other chemicals for scale control and sludge dispersion

(soluble, nonadherent) under extremes of either acid, or basic, conditions. This leads to either gross corrosion loss, or localized corrosion phenomena, such as caustic, or acid associated (e.g., chloride) cracking. As noted above, the type and schedule of chemical additions to provide acceptable buffering against contaminants that can warp the local pH towards either acid, or basic, conditions remains unresolved to a considerable extent.

The dissolved oxygen concentration of the water/steam circuit can affect the ability of ferritic, and particularly austenitic, steels to develop and maintain the oxide films crucial to passivity. Dissolved oxygen is also a cathodic depolarizer and, in this role, can tend to accelerate electrochemical corrosion processes. These characteristics of oxygen are in opposition with respect to the corrosion resistance. Presently, the general practice is to maintain the dissolved oxygen level at low-as-possible levels (see Table 14.2-1). There has been consideration of periodic oxygen 'conditioning' of circuit materials through additions of oxygen, or H_2O_2 . Indeed, the practice of minimizing the bulk oxygen concentration in the water/steam circuit is currently under some challenge.⁽⁷⁾ Current specifications for the feedwater and recirculating water quality for the Clinch River powerplant are given in Table 14.2-4.

As noted by Wranglen,⁽⁸⁾ the ability of anions to adsorb and perturb the structure of colloids also provides some indication of their general tendency toward aggressive corrosion behavior. Figure 14.2-5 is a summary Wranglen has made of a number of physico-chemical properties of anions that are commonly encountered in industrial processes. The corrosivity would tend to increase toward the right end of the 'scale'. Obviously, the participation of a given ion is strongly dependent on the specific corrosion situation. The hydroxide (OH^-) and chloride (Cl^-) ions have generally received most of the publicity in water/steam circuit corrosion processes. Corrosion significant concentrations of OH^- ion have arisen due to use of caustic (NaOH) for pH tailoring, and sodium phosphate additions for impurity control. Chloride ions have entered largely through in-leakage of chloride bearing cooling water at condensers.⁽¹⁾ There is obviously opportunity for the intervention of many other chemical species in the corrosion processes of the water/steam circuit. The corrosion credentials of a given material

Figure 14.2-4. Correlation Between Corrosion and Magnetite Solubility (6)

Table 14.2-4. CRBRP Feedwater Quality Specifications (4)

Total Solids	50 ppb (MAX)
Dissolved Oxygen	7 ppb (MAX)
Silica	20 ppb (MAX)
Iron	10 ppb (MAX)
Copper	2 ppb (MAX)
pH at 25°C	8.7 to 9.1
Hydrazine (Residual)	5 ppb (MAX)
Conductivity (Cation) at 25°C	0.3 micro-mho/cm
Sodium	1 ppb (MAX)

**CRBRP RECIRCULATING WATER
QUALITY SPECIFICATIONS**

Total Dissolved Solids	300 ppb (MAX)
Sodium	6 ppb (MAX)
pH at 25°C	8.5 to 9.0
Conductivity (Cation) at 25°C	2 micro-mho/cm

Steady-State Conditions
Full-Flow Demineralization
10% Drain

F^- , ClO_4^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , CrO_4^{2-} , OH^-	Cl^- , NO_3^- , Br^- , HS^- , I^- , SCN^- , S^{2-}
Low molar polarization	High molar polarization
Low adsorbability	High adsorbability
High overpotential	Low overpotential
Smooth, fine-grained electrodeposits	Treeing, coarse-crystalline electrodeposits
Low corrosivity	High corrosivity
Weakly peptizing	Strongly peptizing
Passivating	Activating
Weak electrocapillarity effect	Strong electrocapillarity effect
Weak hydrogen embrittlement	Strong hydrogen embrittlement

Figure 14.2-5. Physico-chemical Characteristics of Various Anions Important to Corrosion Processes (8)

Figure 14.2-6. Illustration of Concentrating Mechanism (3)

for service in this circuit are, however, generally judged on the basis of its resistance to stressed and unstressed corrosion attack by caustic and chloride solutions.

The development of an aggressive corrosion situation generally depends on the following conditions:

- some content of a potentially aggressive species in the bulk stream
- local conditions conducive to concentration of the species:
 - heat transfer providing a temperature gradient to support progressively higher boiling point solutions (see Figure 14.2-6) ;
 - conditions, such a crevice, or a porous oxide layer, or imperfections in an oxide layer, that enable transport of aggressive ions into the concentrating zone, yet shield the concentrated solution from dilution by the natural, or forced convection of the bulk solution ;
- local conditions conducive to the participation of electro-chemical processes in the corrosion action:
 - development of relatively large cathodic areas electrically accessible to small anodic (metal dissolution) areas on a continuous, or periodic, basis ;
 - stress/temperature conditions developing plastic deformation that tends to decrease passivation ability, and increase the possibilities for intrusion of the metal structure by corrosion hydrogen and/or other potentially damaging species ;
 - solution conditions (pH, chemical composition) that tend to encourage the formation of nonprotective oxidation products .

The oxidation behavior inherent to a given material at a given circuit site can account for a significant oxide buildup and metal attrition when several decades of service time are involved. Another important source

of deposit on heat exchanger surfaces is the corrosion/erosion products carried by the bulk stream. The deposition of this material in a boiling zone is apparently a function of heat flux to a power index that may range from 2 to 5.⁽⁹⁾ Thus, heat flux aggravates both the local corrosion response and the deposition of circuit impurities. In addition to degrading the heat transfer qualities of the heat exchanger and increasing the flow resistance (pressure drop), these phenomena contribute to the buildup of an aggregate of corrosion/impurity/additive products whose structure provides the conditions favorable to concentration of aggressive ions. Buildup on various circuit surfaces is controlled to some extent by periodic chemical cleaning. Klein⁽¹⁾ states that a cleaning frequency of once per three years is normally recommended for modern high pressure steam plants.

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14.3.1 Water/Steam Corrosion

The oxidation characteristics of a material in the water/steam environment of the evaporator and superheater, without significant intervention by contaminants, is the obvious base for consideration of the corrosion qualifications for such service. For temperatures of interest to powerplant service, the low alloy ferritic steels exhibit a water/steam corrosion response (e.g., depth of penetration of metal by oxidation front) an order of magnitude, or more, greater than that of the austenitic stainless steels, or Inconels. This is illustrated in Figure 14.3.1-1, where data bands are given for the low Cr ferritic steel family and the austenitic steels for a pure water/steam environment. Under sensibly isothermal conditions, the ferritic steels generally display a gradual improvement in oxidation resistance with increase in Cr content. While the effect of Cr is sensitive to some extent on the total alloy composition, an indication of improvement in oxidation resistance with increase in Cr content is shown in Figure 14.3.1-2.

The reaction,

is generally used to represent the water steam oxidation of ferritic steels under T/P conditions relevant to modern high pressure powerplants. The actual complexity of iron oxidation products under various temperature and oxidizing conditions is indicated by Table 14.3.1-1. Various products given in this table could be generated under conceivable ranges of temperature and ambient atmospheric conditions encountered by steam generation equipment over the installation-operation-maintenance-rehabilitation history of the equipment. A duplex structure is usually assigned to the Fe_3O_4 (magnetite) layer, consisting of an inner layer of fine crystallites and an outer layer of coarser crystals. The inner layer generally has an alloy element composition about the same as the parent metal, while the outer layer is virtually pure Fe_3O_4 .⁽¹⁾ Actually, micro inspection of typical oxide layers reveals a far more complex banding, with changes in both structure and composition across the thickness of the oxide layer. Under near neutral conditions (pH) magnetite is insoluble (see Figure 14.2-4) and unless the structure is perturbed by aggressive ion action, or mechanical/hydrodynamic action, it is the basis for the passive state of ferritic steels in water/steam environments.

Figure 14.3.1-1. Oxidation of Steels in Pure Water/Steam⁽¹⁾

Figure 14.3.1-2. Effect of Increasing Chromium Content of Ferritic Steels on Maximum Service Temperature Based on Scaling Resistance⁽²⁾

TABLE 14.3.1-1. Various Corrosion Products of Iron⁽³⁾

Composition (Mineral Name)	Color	Structural Type 8	Magnetic Character	Electrical Resistivity	Density	Thermal Behavior
$\text{Fe}(\text{OH})_2$	White	$\text{Mg}(\text{OH})_2$ (Brucite)	Paramagnetic	Insulator ⁽¹⁾	3.40	Decomposes at about 100°C to Fe_3O_4 and H_2 ⁽²⁾
$\text{Fe}_{.95}\text{O}$ to $\text{Fe}_{.83}\text{O}$ (Wustite)	Black	NaCl	Paramagnetic	Semiconductor	5.4-5.73	Melts at 1371-1424°C. Below 570°C decomposes to Fe and Fe_3O_4
Fe_3O_4 (Magnetite)	Black	Spinel	Ferromagnetic	Electronic Conductor 8	5.20 (4)	Melts at 1597°C
$\alpha\text{-FeOOH}$ (Goethite)	Yellow	$\alpha\text{-FeOOH}$ (Goethite)	Paramagnetic	Insulator ⁽¹⁾	4.20	Dehydrates ⁽³⁾ to $\alpha\text{-Fe}_2\text{O}_3$ at about 200°C
$\beta\text{-FeOOH}$	Light Brown	Not completely determined	--	--	--	Dehydrates ⁽³⁾ to $\alpha\text{-Fe}_2\text{O}_3$ at about 230°C
$\gamma\text{-FeOOH}$	Orange	$\gamma\text{-FeOOH}$ (Lepidocrocite)	Paramagnetic	Insulator ⁽¹⁾	3.97	Dehydrates ⁽³⁾ to $\gamma\text{-Fe}_2\text{O}_3$ at about 200°C
$\gamma\text{-Fe}_2\text{O}_3$ (Maghemite)	Brown	Spinel (with vacancies)	Ferromagnetic	Semiconductor to insulator	4.88	Transforms ⁽³⁾ to $\alpha\text{-Fe}_2\text{O}_3$ above 250°C
$\alpha\text{-Fe}_2\text{O}_3$ (Hematite)	Brick Red to Black	Al_2O_3 (Corundum)	Paramagnetic	Insulator	5.25	Decomposes to magnetite at 1457°C and 1 atm.

⁽¹⁾ Color indicates that these are insulators.

⁽²⁾ In contact with traces of oxygen, $\text{Fe}(\text{OH})_2$ is unstable at room temperature and transforms to $\gamma\text{-FeOOH}$, $\alpha\text{-FeOOH}$, or Fe_3O_4 depending on the conditions of the system (15).

⁽³⁾ Presence of water causes conversion to $\alpha\text{-Fe}_2\text{O}_3$ at lower temperature.

Water/steam oxidation data for the 2 1/4 Cr-1Mo steel are apparently very sparse within the temperature range 260-538°C (500-1000°F). Figure 14.3.1-3 displays some recent data obtained under isothermal and heat flux conditions. These data illustrate the important fact that isothermal data do not provide a satisfactory indication of the corrosion response under steady state, or transient heat flux conditions that will obtain in the heat exchanger assignments for this material. As indicated by this figure, the corrosion effect is aggravated by steady state heat flux. Some intensification of this effect might be expected under variable heat flux and mean temperature conditions, inasmuch as thermal stress is believed to be involved to some extent in this phenomenon.⁽¹⁾ Tomlinson, et al.,⁽⁵⁾ report somewhat erratic heat flux effects for a Nb stabilized 2 1/4 Cr-1Mo steel, at a mean temperature level of roughly 350°C, and a heat flux ranging up to 660 kW/m². Oxidation layer thickness increases with heat flux ranged from virtually nil to about 70% after 2000 hour exposure under 660 kW/m² heat flux. As noted in Figure 14.3.1-3, the steady-state oxidation under a steady heat flux displays a linear characteristic. The divergence between the heat flux and the isothermal data (which, according to Figure 14.3.1-3, tends more to a parabolic behavior) is increasing with exposure time. Assessment of heat flux effect based on the relatively short exposure of 2000 hours would, according to these data, be virtually meaningless. The present understanding of heat flux/temperature transient effects on the long-term oxidation characteristics of 2 1/4 Cr-1Mo steel is not satisfactory for confident specification of limiting mean temperature and heat flux conditions for this steel. According to a recent British assessment of the steam generator problems for LMFBR powerplants, this situation is generally applicable to all the ferritic steel candidates for structural service in steam generators.⁽⁶⁾ Present water-side corrosion allowances for the 2 1/4 Cr-1Mo steel are largely based on isothermal oxidation data.⁽⁷⁾

Figure 14.3.1-3. Oxidation of 2 1/4Cr-1Mo Steel Under Isothermal and Heat Flux Conditions in Superheated Steam (4)

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14.3.2 Chloride Affected Water/Steam Corrosion

Under a reasonable evolution of water quality control practice for steam-electric powerplants, the intrusion of potentially aggressive species must be recognized as a fact of the working environment of steam generating system materials for some time. Of these species, the chloride ion (Cl^-) is probably of greatest importance because of its prevalence, over a wide range of concentration, in the heat sink reservoirs available to commercial powerplants. Chloride corrosion action can be manifested in pitting and in stress corrosion cracking. Either phenomenon has more than adequate potential to disable various components of the water/steam circuit, ranging from the heat exchangers to the turbine. Both austenitic and ferritic steels are subject to chloride action. A strong susceptibility to stress corrosion cracking in chloride solutions is a well advertised weakness of certain austenitic steels (e.g., 300 series stainless steels). The vulnerability of ferritic steels to serious pitting in chloride environments has been known for many years. Although there has been frequent attribution to low alloy ferritic steels of 'invulnerability' to chloride stress corrosion cracking, there are laboratory and service data that can support a considerable challenge to this assessment.

In comprehensive reviews of chloride ion corrosion activity, Foley⁽¹⁾, Kolotyrkin⁽²⁾ and Hoar⁽³⁾ have noted the following possible action of the chloride ion:

- structural perturbation of normally passivating, or stabilizing, layers, leading to the creation of low resistance paths for physico-chemical interaction between the ambient solution and the metal;
- adsorption on metallic surface preferentially to normally passivating species under appropriate surface potential and physico-chemical conditions;
- creation of a field effect by adsorbed chloride ions that encourages metal ionization (dissolution);
- the formation of surface and solution complexes with metallic ions that are inimical to establishing passivity of the metal;

- encouragement of hydrolysis reactions, involving metal ions, that release protons (H^+) to the solution; this local acidic excursion can reduce passivation ability of the metal and stimulate local electrochemical action leading to pitting, or cracking under appropriate stress, metallurgical, and chemical stimuli.

With respect to resistance to chloride related pitting/cracking, it is difficult to assess the significance of the composition represented by the 2 1/4 Cr-1Mo steel relative to that of the low carbon steel family. On the basis of Cr content alone, the relative advantage of the 2 1/4 Cr-1Mo steel would appear to be of marginal practical significance. This is indicated by numerous laboratory studies of Fe-Cr alloys that generally support a gradual improvement in various chloride related corrosion criteria as the Cr level is raised over a Cr range of roughly 0-10%. A brief discussion of some of this work is appropriate in view of the sparcity of data on 2 1/4 Cr-1Mo steel, or closely related steels, in chloride environments.

Mann and Teare⁽⁴⁾ exposed a series of Fe-Cr alloys to a nickel chloride solution at 300°C. Stating the corrosion effect as follows: $w = kt^n$, where w is the metal loss in time t , the various alloys gave the following values of n :

<u>Material</u>	<u>n</u>	
pure Fe	0.80	(showing a gradual decrease in corrosion rate, $dw/dt = nk/t^{1-n}$ with increase in Cr content)
Fe-1Cr	0.81	
Fe-2Cr	0.64	
Fe-4Cr	0.38	
Fe-8Cr	0.31	

Verink and Pourbaix⁽⁵⁾ using a potentiokinetic electrochemical hysteresis technique, delineated zones of general corrosion, pitting susceptibility and passivity for a series of Fe-Cr alloys in solutions of various pH and chloride concentration (as NaCl) values. Figure 14.3.2-1 shows the contraction of the general corrosion field and the expansion in the passivity field as the Cr content is raised.

Stolica,^(6,7) using the potentiostatic technique at 25°C, passivated various Fe-Cr alloys in a H_2SO_4 solution and then observed the corrosion response to the addition of chloride solution (1N HCl + 2N NaCl solution was added in various amounts to the passivating solution). For his specific test conditions, Stolica reported the following chloride concentrations needed to initiate chloride attack, based on observation of pitting:

<u>Alloy</u>	<u>Cl^- (N)_{minimum}</u>	
pure Fe	0.0003	
Fe-5.6 Cr	0.017	
Fe-11.6 Cr	0.069	(showing increase in Cl^- conc. needed
Fe-20 Cr	0.10	to initiate attack as Cr content is raised)
Fe-24.5 Cr	~1.0	
Fe-29.4 Cr	~1.0	

Figure 14.3.2-2 illustrates the induction period phenomenon reported in numerous studies of chloride action. Figure 14.3.2-3 shows the relationship between the reciprocal of the induction time and the chloride concentration for the Fe-5.6 Cr alloy observed by Stolica.⁽⁶⁾ Similar plots were made for the other alloys noted above. The minimum Cl^- concentration was determined by extrapolating the plot to the zero of the reciprocal induction time (infinite time for attack). As a comment on the close similarity between the chloride corrosion response of a low Cr alloy and pure Fe, Stolica noted that the post-induction corrosion current increase characteristics for both materials were virtually identical.

Harrison, et al.,⁽⁸⁾ used the hydrogen effusion technique to monitor the corrosion progress of pure Fe and several low Cr alloys in a 0.1M $NiCl_2$ solution at temperatures of 250, 300, and 350°C. Over a 100-hour observation period, these authors described the corrosion effect by the relation: $dm/dt = k_1 e^{-k_2 t} + k_3$, which denotes an initial, exponentially decaying period (k_1, k_2), followed by a steady state, linear period (k_3). These studies showed a complex dependence of the various parameters (k values) on temperature and Cr content. The k_1 and k_2 values tended to exhibit a maximum near 300°C, while the k_3 value was greatest for the lowest temperature of the

Figure 14.3.2-1. Schematic Potential-pH Diagrams Showing Influence of Cr on Corrosion Behavior of Fe-Cr Alloys (5)

Figure 14.3.2-2. Potential-Time Characteristic for Fe-Cr Alloy (5.6%Cr) in 1N H_2SO_4 + 0.07N Cl^- (7)

tests, 250°C. The k_1 value decreased as the Cr content was raised, while the k_2 and k_3 values showed less correlation with Cr. K_3 , in fact, exhibited some increase with Cr increase, i.e., the long term (100 hours in this case) corrosion effect appeared to be greater for the higher Cr alloys. Southwell⁽⁹⁾ reported on long-term exposures of various Fe-Cr alloys to sea water. He observed that, while the Cr alloys (3 and 5% Cr) were superior to the carbon steel for up to about 4 years, for longer times the carbon steel stabilized at a lower corrosion rate resulting in a lower overall corrosion effect for the carbon steel. These latter references are cited to illustrate the point that where low alloy additions are involved, it is very difficult to support generalizations of alloy element influence on long-term corrosion behavior. Further, the intuition that increasing temperature will increase the corrosion effect is not necessarily true, depending on the change with temperature of all the kinetic factors that affect corrosion (e.g., corrosion product stability and permeability, electrochemical process parameters, such as solubility of depolarizing and passivating species in the solution, etc.).

The difficulty of relating the corrosion characteristics of relatively pure laboratory study alloys to those of commercial alloys of the same primary alloy content (e.g., Cr) is illustrated by Figure 14.3.2-4, where the corrosion behavior of high purity Fe-Cr binary alloys and a high purity Fe is compared to that of a single heat of a commercial alloy of 1% Cr. Mann and Teare⁽⁴⁾ attribute the superiority of the commercial alloy relative to its high purity counterpart to the silicon content of the commercial alloy. Data permitting a more comprehensive appraisal of the chloride corrosion behavior of low Cr alloys of present interest, containing the nominal background composition of commercial alloys, appear to be very sparse. The contribution of Mo, at the 1% level, to the corrosion characteristics of these low Cr alloys would not be expected to be large, considering the substantial alloy additions that are made to the ferritic matrix to achieve alloys of good corrosion properties under severe chloride exposure conditions (e.g., the Fe-28Cr-4Mo alloy discussed by Streicher).⁽¹⁰⁾

Figure 14.3.2-3. Reciprocal Induction Time vs. $[Cl^-]$ for 5.6%Cr-Fe Alloy in $1NH_2SO_4$ Solution (6)

Figure 14.3.2-4. Corrosion of Iron and Iron-Chromium Alloys in $0.1M NiCl_2$ at $300^\circ C$ (4)

Strauss and Bloom⁽¹¹⁾ conducted an interesting series of tests with low carbon steel under chloride bearing solutions and stressed conditions. Closed (welded) capsules, filled with various test solutions, were heated to 316°C (resulting pressure about 1,550 psi; burst pressure about 4,000 psi). Some of the observations of these authors are noted in Table 14.3.2-1. Figure 14.3.2-5 shows typical cracks observed in these tests. The observations on the high purity water test (see table), under similar capsule conditions, confirm a Cl^- influence. Furthermore, the observation that loose (unstressed) specimens inside the capsule exhibited no cracking under conditions that cracked the capsule, tend to confirm a stress influence on the observed cracking. These tests, representing an interesting conjunction of conditions that could obtain under service conditions (stress, temperature, weld zone, Cl^- presence) appear to offer some challenge to complacency regarding the 'invulnerability' of low alloy ferritic steels to chloride stress corrosion cracking. There is, as noted above, little evidence to support the contention that the 2 1/4 Cr-1Mo steel composition represents a significantly superior bulwark against chloride corrosion effects relative to low carbon steel. Some confirmation of this opinion, based on tests with 2 1/4 Cr-1Mo steel, is discussed below.

Howells, et al.,⁽¹²⁾ conducted model boiler tests with a variety of materials candidates for steam generator tubing/tubesheet applications. Generally, the tubing and tubesheet for a given test were made from the same material. Primary water was on the inside of the tubing. Specifications for the primary and secondary water used in these tests are given in Table 14.3.2-2, together with a schedule of test conditions designed to simulate various phases of the operating life. The observations of the corrosion response of the test materials are summarized in Table 14.3.2-3. These authors gave the following rating of the test materials in order of decreasing merit: Monel, Inconel, nickel, Croloy 16-1, Croloy 2 1/4 (2 1/4 Cr-1Mo steel). It was the author's opinion that the 2 1/4 Cr-1Mo steel exhibited too much tendency to serious pitting to be considered for steam generation system service.

14.3.2-8

TABLE 14.3.2-1. Capsule Tests of Mild Steel with Various Solutions Containing Cl^- and/or Fe(III) at 316°C (11)

Capsule Contents	Result of Treatment
(1) 0.001 M. FeCl_3	Capsules cracked and leaked within 6 to 15 hours.
(2) 0.0001 M. FeCl_3	Very shallow cracks were produced within one week.
(3) 0.0005 M. $\text{Fe}_2(\text{SO}_4)_3$	No cracking observed with one week.
(4) 0.001 M. $\text{Fe}(\text{NO}_3)_3$	No cracking observed within one week.
(5) 0.003 M. NaCl	No cracking observed within one week.
(6) 0.01 M. NaCl	No cracking observed within one week.
(7) 0.1 M. NaCl	Slight attack at weld junction during one week.
(8) 1 M. NaCl	Localized corrosion in martensite penetrated welds within 20 hours.
(9) Aqueous slurry of $\gamma\text{-FeOOH}$ containing 0.6% Cl^-	Capsules cracked and leaked within 6 hours.
(10) Aqueous slurry of $\gamma\text{-FeOOH}$ generated by corrosion in H_2O_2 containing 0.0005% Cl^-	Capsules cracked and leaked within 12 hours.
(11) Aqueous slurry of $\gamma\text{-FeOOH}$ generated by corrosion in high purity water	No cracking observed within one week.
(12) Slurry of $\gamma\text{-FeOOH}$ in line 11 and 0.0001 M. FeCl_3	Capsules cracked and leaked within 16 to 18 hours.
(13) Aqueous slurry of $\alpha\text{-FeOOH}$ containing* 0.01% Cl^-	Shallow cracks were produced within one week.
(14) Supernatant liquid $\gamma\text{-FeOOH}$ slurry in line 9	No cracking observed within one week.
(15) Slurry of $\gamma\text{-FeOOH}$ in line 13 and liquid in line 14	Capsules cracked and leaked within 3 to 4 hours.
(16) Slurry of $\alpha\text{-FeOOH}$ containing 0.01% Cl^- and 0.003 M. NaCl	Moderately deep cracks were produced within one week.
(17) Slurry of $\gamma\text{-Fe}_2\text{O}_3$ containing 0.01% Cl^- and 0.003 M. NaCl	Moderately deep cracks were produced within one week.
(18) Slurry of $\alpha\text{-Fe}_2\text{O}_3$ containing 0.02% Cl^- and 0.003 M. NaCl	Very deep cracks were produced within one week. One capsule cracked and leaked within 4 days.
(19) Slurry of Fe_3O_4 containing <0.01% Cl^- and 0.003 M. NaCl	No cracking observed within one week.

*At least 3 and usually more capsules were given each treatment.

mild steel specimens (0.09C, 0.017P, 0.032S, 0.007N, 0.57Mn, 0.075Si, 0.10Cr, 0.07Ni)
 H annealed before fabrication; after fab., 875C vacuum anneal; no weld stress relief
 20 mil thick tubing used for capsules

- high purity water test solution showed no significant penetration after 4 weeks' exposure; after 4 years, maximum penetration was 2 mils
- loose (unstressed) specimens inside capsule showed no cracking under solution that cracked capsule

(80X)

Figure 14.3.2-5. Typical Cracks Observed in Mild Steel Under Capsule Tests with Chloride Solutions(11)

Table 14.3.2-2. Test Conditions for Ref. 12 Tests

Water Conditions :

primary: deionized and deaerated
2,000 psi, 600F

secondary: pH: 10.9 +/- 3 (adjusted with NaOH)

Cl⁻: 500 +/- 50ppm(synthetic sea water)

PO₄⁻: 250 +/- 50ppm(Na₂HPO₄)

O₂ : 0.2-0.5 ppm(by aeration)

T : 480-490F

P : 600 psig

Test Conditions :

- . heat flux(based on tube ID) 40-60,000 Btuhr⁻¹ft⁻²;
- . heat exchanger laid-up dry after 48, 192, 336 hrs for period of 8 hrs; the secondary system was purged with air saturated water during layup;
- . after 96, 240 and 424 hrs operation, 60-90% of the heat exchanger area was exposed to vapor phase for 1 hr;
- . after 144, 288 and 472 hrs operation, the heat exchanger was laid-up wet for 8 hrs with treated, aerated boiler water on the secondary side;
- . 500 hr total test period
- . [O] control: 85% of time, [O] was between undetectable to 0.5ppm; remainder of time [O] was between 0.5-2.0 ppm.

Table 14.3.2-3. Test Results of Ref. 12

Croloy 21/4(21/4Cr-1Mo steel):

all surfaces on secondary side were affected by general roughening and severe pitting up to 15 mils deep; pitting was randomly distributed over the secondary surface, but of greater density in crevice areas; all corrosion advanced in 'gross manner' without regard to microstructure;

Croloy 16-1:

general pitting and corrosion similar to Croloy 21/4, but less severe;

Nickel:

all open secondary surfaces in excellent condition, only very slight dulling; pits up to 6 mils deep were noticed under support plates in crevice regions;

Inconel:

open surfaces in excellent condition; some incipient pitting/roughening under support plates; crevice region showed mild general attack and scattered small pits up to 3 mils deep;

Monel:

no significant corrosion on any surfaces; no evidence of preferential attack at crevice zones;

347SS:

small SCC in crevice regions, predominantly transgranular, up to 6 mils deep; negligible general corrosion on open surfaces or crevice surfaces.

White and Johnson⁽¹³⁾ used a tilting autoclave (Monel) to simulate the alternate wet/dry conditions obtaining in the upper stages of the evaporator component. Over a 24-hour period, the test specimens experienced 144 wet/dry cycles. Test temperature was 500°F (260°C). The test solution was as follows: PO_4 (250-350 ppm as Na_2HPO_4); Cl^- (500-550 ppm as synthetic sea water); pH (10.6-11.2, with NaOH); O_2 (7-9 ppm (air saturated at RT)). U-bend specimens made from annealed sheet stock were used for these tests. While the significance of the short (24-hr) test period is questionable, the observations of these authors are interesting.

<u>Material</u>	<u>Observation</u>
347 SS	transgranular cracking in all specimens
Inconel	no SCC
nickel	no SCC
Monel	no SCC
Croloy 16-1-----	heavy oxidation, localized attack (pitting, blunt cracks) favoring martensitic structure; heavy oxide layer on tensile side of bend
Croloy-2 1/4-----	heavy oxidation; general attack was more severe than that noted for Croloy 16-1

Although chloride apparently was not involved, an incident of severe pitting and general corrosion for 2 1/4 Cr-1Mo steel reported by Ruther and Hart⁽¹⁴⁾ is pertinent to this discussion. These authors were studying the effect of dissolved oxygen level on the aqueous corrosion of iron and low alloy steels. Tests were run with unstressed specimens in a refreshed autoclave at 260°C, at oxygen levels of 50 ppm and less than 100 ppb. The corrosion response of as-received commercial 2 1/4 Cr-1Mo steel was substantially less in the high oxygen solution (50 ppm). After 25 days' exposure, they reported 1 mg/cm² metal loss for the 50 ppm solution and 6 mg/cm² for the low (100 ppb) oxygen solution. Linear oxidation characteristics were observed for 2 1/4 Cr-1Mo steel in both solutions. The severe pitting incident occurred under the following conditions:

- after 24 days' exposure under high O conditions, the tests were interrupted to remove equipment; samples were placed in a dessicator;
- upon restarting the test, the specimen developed deep pits and the general corrosion was sufficient to discolor the effluent water;
- test analysis revealed that the rate of temperature increase for the restart test was lower than usual;
- subsequent testing revealed that the 2 1/4 Cr-1Mo specimens consistently pitted under a slow heat up, as opposed to forming temper colors when the specimen and autoclave were preheated before the test solution was introduced.

Considering the possible range of ambient environmental conditions steam generation equipment may experience throughout its history, these observations on 2 1/4 Cr-1Mo behavior, even without the apparent intervention of aggressive ions, are a somewhat disquieting addendum to the recorded credentials of this material.

Hammond, et al.,⁽¹⁵⁾ and Griess, et al.,⁽¹⁶⁾ report on more recent chloride related test work with 2 1/4 Cr-1Mo steel. These tests were designed to simulate the wet/dry cyclic conditions in the upper stages of an evaporator, and, possibly, the lower stages of a superheater. The test conditions for the chloride solution studies are summarized in Table 14.3.2-4. Unfortunately, neither report gives specifics on the general corrosion response of the 2 1/4 Cr-1Mo steel under these test conditions, other than the observation that this steel exhibited 'heavy scaling' under the conditions reported by Griess, et al.⁽¹⁶⁾ The only additional qualification given to this steel on the basis of these tests is that it is 'immune' to chloride stress corrosion cracking.

Griess, et al.,⁽¹⁷⁾ discuss test work with 2 1/4 Cr-1Mo steel in a recirculating boiler system. Test specimens made from tubular stock were segmented and sprung onto a 2 1/4 Cr-1Mo sheathed heater element. This method of mounting imposed a maximum tensile-side stress probably exceeding

Table 14.3.2-4. Test Conditions for Work of Refs.15 & 16

The loop operating conditions for Ref.15 work were as follows:

<u>test cycles</u>	three per week between superheated and saturated conditions
<u>saturation periods</u>	24hr each, followed by 24hrs at superheat (except 48hrs on weekends)
<u>superheat T</u>	800 or 700F(427 or 371C)
<u>saturation T</u>	540F(282C)
<u>pressure</u>	900psi(6.2 MPa)
<u>oxygen injected</u>	20 ppm max(based on total mass)
<u>chloride injected</u>	10 max ppm(based on total mass)

Test Conditions for Ref.16 work were as follows:

T cycled on 48hr period between 385 and 318C(725 and 605F); during superheat part of cycle the $[Cl^-]$ as NaCl was held at 4.2ppm for the first 3146 hrs of test and 2.7ppm(as $CaCl_2$) for the rest of the test (2960hr); during saturated phase of cyclic test, the $[Cl^-]$ was increased to 10ppm;

pressure was held at 1625 psi

$[O]$ was held at about 9 ppm

the yield stress. Both unwelded specimens and specimens incorporating a weld seam were used. Based on the heated area of the steel sheath, a heat flux of about $48,000 \text{ Btu-hr}^{-1} \text{ ft}^{-2}$ was used for all tests. The specifics of these tests are given in Table 14.3.2-5, together with observations reported on the overall corrosion response of the 2 1/4 Cr-1Mo steel specimens and heater sheathing. The test conditions allowed exposure to sub-cooled water at the lower portion of test section, and to a nucleate boiling regime on the heated section proper. The specimen-sheathing coupling provided opportunities for crevice conditions over this range of water/steam states.

The corrosion response of the 2 1/4 Cr-1Mo steel observed in this study may be summarized as follows from the authors' comments:

- under Cl^- contamination (either dilute NaCl solution, or cooling tower water containing Cl^-) random pitting was observed throughout the heated section; severe crevice corrosion was noted on the upper part of the heated section; there was evidence of SCC on the tensile side of specimens located on the upper heated section;
- with the dilute NaOH solutions, there was severe corrosion on the heated sections with some SCC evidence; pitting was observed on the unheated section.

An example of massive pitting and an example of stress corrosion cracking evidence observed during this program are shown in Figure 14.3.2-6.

The steam generating system components, particularly the evaporator component with its complex multi-phase conditions on the water side, pose an environmental simulation problem of unique difficulty. As noted by Klein⁽¹⁸⁾ and many others, there is a strong correlation between debilitating corrosion and massive deposit buildup on the heat exchanging surfaces. Contributions to this buildup come from the local corrosion response to the working fluid as well as from the other sources discussed in Section 14.2. The stimulative influence of deposit buildup on corrosion processes is extremely difficult to model. Nevertheless, corrosion assessments made

Table 14.3.2-5. Test Conditions and Test Observations for Ref.17 Work

1st test:

- . pH 11.3-11.4 at start
- . 100 ppm NaOH(contained some dissolved O, unspecified amount)
- . saturation T of 532, 607, 662F, with time at T of 1692, 898 and 1072hr, respectively

Observations :

- . pitting observed near center of heated section; welded specimens exhibited no particular difference in corrosion response

2nd test:

- . typical water from cooling tower of following composition:

calcium	183ppm	27ppm after one week of testing
magnesium	48	7.7 "
chromium(VI)	7.1	0.05 "
chloride	27	6.0 "
sulfate	370	220 "
- . pH 6.8 at start; 7.2 after one week
- . T was 605F(1600 psi)
- . test time was 1481 hr

Observations:

- . many shallow pits on lower end of heater rod
- . heavy attack on all heated areas of specimens and sleeve; complete penetration of sleeve(30 mils)at top of heated section
- . all specimens had deep pits under heavy oxidation layer
- . cracks were filled with oxidation product on both welded and unwelded specimens
- . above observations apply to both open zones and crevice regions

3rd test:

- . 10 ppm Cl⁻(no attempt at deoxygenation)
- . 650F(1600 psi)
- . test time 2065 hr

Observations:

- . numerous shallow pits on unheated part of assembly
- . specimens on lower end of heated section exhibited occasional mounds of oxide, overlying large pits
- . near top of heated section, very heavy crevice attack on both sleeve and specimens, in some cases penetrating the 30 mil sheathing; severe corrosion appeared confined to crevice zones, in contrast to 'catastrophic' general corrosion noted in test 2
- . intergranular crack 15 mils deep was noted on unwelded specimen

4th test:

- . specimens exposed to high purity boiling water at 604F for 2 weeks to develop oxide; hot well of circuit had air exposure
- . above specimens then exposed to 100 ppm NaOH and hot well was blanketed with N₂ to reduce [O] and neutralization of caustic by CO₂
- . test time 618 hr

Observations:

- . pitting similiar to that observed on test 1 on heated section
- . crevice corrosion observed near middle of heated section; severe attack on sleeve and specimens leading to near penetration(30 mils) of sleeve
- . number of shallow(5 mil) cracks observed under oxide on tensile side of specimen where there was heavy oxidation

pitting (140X)
2nd test

cracking (140X)
3rd test

Figure 14.3.2-6. Corrosion Observations with 2 1/4Cr-1Mo Steel
From Ref. 17 Work(see Table 14.3.2-5)

without cognizance of this factor are of very doubtful practical significance for a material, such as 2 1/4 Cr-1Mo steel, that is demonstrably prone to deposit buildup from both of the sources noted above. In a recent review of nuclear reactor steam generation equipment problems, Bolt and Garnsey⁽¹⁹⁾ question the extent to which the test work to date on prominent materials candidates for such service provides an adequate basis for large-scale commitment of the materials.

Chloride ion intrusion, over a fairly wide range of bulk solution concentration, may be anticipated for commercial powerplants over the foreseeable future. There is ample support for the belief that the chloride ion is the corrosion agent of greatest damage potential for the general steam power complex. The 2 1/4 Cr-1Mo steel is presently a prime candidate for the crucial tubing, tubesheet and shells of the evaporator and superheater components of the U.S. LMFBR powerplants. The extant evidence on the performance of this particular steel in chloride affected environments does not appear to give acceptable support for these assignments on the following bases:

- a propensity for severe pitting corrosion under crevice and heavy deposit conditions that is a more than adequate incentive for caution in critical applications of this steel, irrespective of stress corrosion cracking tendencies;
- a propensity for development of nonprotective oxidation products under a chloride environment, leading to heavy deposit buildup and a severe metal attrition rate;
- the scope of validity of the well advertised 'invulnerability' of the 2 1/4 Cr-1Mo steel to chloride related stress corrosion cracking could support much closer scrutiny; cracking has been observed for this steel, and low carbon steels of roughly similar corrosion properties, under conditions that are not unrealistic with respect to LMFBR steam generator conditions; the effect of various stress states, fatigue in particular, on chloride SCC tendency has been barely explored for the 2 1/4 Cr-1Mo steel; although electrochemical processes affecting the chloride SCC

phenomenon would be expected to be far more active in the liquid stages of the evaporator, there has been relatively little test emphasis on this component.

- under local acidification conditions characteristic of chloride affected corrosion, low alloy ferritic steels have exhibited embrittlement possibly related to abnormal hydrogen intrusion of the metal^(e.g., 18,20,21); the relationship of this embrittlement to gross alloy composition, and metallurgical structure is not well known; the general similarity of the corrosion characteristics and mechanical properties of the 2 1/4 Cr-1Mo steel to those of the family of steels that is the basis for these embrittlement observations does not imply any degree of immunity of 2 1/4 Cr-1Mo steel from this embrittlement.

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14.3.3 Caustic Affected Water/Steam Corrosion

Caustic (NaOH) can intrude the working life of an LMFBR steam generating system material from several sources:

- use of NaOH to tailor the pH of the water circuit;
- use of sodium phosphate additions to control impurities; subsequent hydrolysis of impurity-phosphate reaction products to produce NaOH as a product;
- breach of the Na/H₂O containment (tubing) in the evaporator or superheater components, resulting in NaOH and H₂ as the primary reaction products;
- carryover of NaOH generated by maintenance/cleaning operations on sodium exposed equipment; deionizer slippage/breakthrough

The concentration agencies discussed under the chloride section of this chapter apply to NaOH as well. NaCl liquid solubility imposes a limit on the concentration potential at a given pressure. The concentration of NaOH is not solubility limited, the concentration being a function of the temperature gradient accessible to the bulk solution, and the shielding afforded the concentrated solution from the dilution action of the bulk stream. These points are illustrated in Figure 14.3.3-1, where the boiling point elevation for NaOH and NaCl solutions are given for a wide range of pressure and solute concentration. Figure 14.3.3-2, on a different scale, indicates the NaOH concentration that can arise from small temperature differentials across a deposit, or crevice. This curve is fairly insensitive to pressure level. In the case of NaOH, it is evident that given some small content of NaOH in the bulk solution, plus a powerful concentration agency (thick porous deposit or deep crevice in a zone of large heat flux) the bulk water NaOH analysis is a virtually worthless guide to the possibility of serious local caustic attack.

The bulk of NaOH related study with LMFBR materials candidates has been concentrated on the so-called wastage phenomenon. This term is applied to the complex of action attending the rupture of a water/steam tube in the presence of liquid sodium at high temperature, the resulting sodium-water/steam reaction, and the damage to the parent tube and that of the adjacent

Figure 14.3.3-1. Boiling Point Elevation and Solubility of NaCl and NaOH as a Function of T and P (1)

Figure 14.3.3-2. Boiling Point Elevation vs. $[\text{NaOH}]^{(2)}$

tubes in the array. Wastage is a safety concern of the first magnitude for an LMFBR powerplant. Study of this complex phenomenon has, however, yielded no more than rough qualitative indications of the resistance of various materials to caustic related corrosion action. Wastage is discussed in Chapters 12 and 13 of this report. A recent summary of comparative wastage data obtained by GEAP is given in Table 14.3.3-1. These data affirm trends established in earlier work, namely: substantial inferiority of 2 1/4 Cr-1Mo steel to Inconel 800 on the basis of wastage damage criteria; the differential between these materials increases at the lower test temperatures of significance to the evaporator component.

As noted in Chapter 13, wastage is essentially a post facto corrosion phenomenon and is the immediate consequence of a chain of events culminating in through-wall pitting, cracking, thinning. Detection of such events will hopefully be early enough to preclude multiple tube failure, with its operational and energy release implications. At the least, however, detection of a tube failure will force shutdown and plugging of the affected tube, an operation capable of imposing very substantial cost and manpower penalties on a nuclear powerplant.⁽⁴⁾

Inasmuch as caustic can participate in the pre-tube rupture corrosion action for a variety of reasons, it is unfortunate that, up to the present, caustic related corrosion work with 2 1/4 Cr-1Mo steel has apparently been extremely limited in this country and abroad.

The susceptibility of carbon and low alloy ferritic steel to stressed and unstressed corrosion action by caustic solutions is discussed in Chapter 13 of this report (Sections 13.3.3.2 and 13.4.3.2). Figure 14.3.3-3 is reproduced from this prior discussion. This figure is a necessarily qualitative summary of caustic cracking experience obtained from many years of commercial use of carbon and low alloy steels in a wide variety of caustic affected working environments. This figure also represents a broad spectrum of compositions within the carbon and low alloy steel families as well as heat treatment and mechanical working histories. In Chapter 13 of this report, the opinion was submitted that the 2 1/4 Cr-1Mo steel composition does not represent any practically significant protection advantage

Table 14.3.3-1. Comparative Wastage Resistance⁽³⁾

Material	High Temperature 860F(460C)	Low Temperature 650F(343C)
21/4Cr-1Mo	1	2 1/2
304 Stainless Steel	4	30
Incoloy 800	6	100

(based on damage criteria discussed in Reference 3)

Figure 14.3.3-3. Caustic SCC Field Established by Industrial and Laboratory Experience for Carbon and Low Alloy Ferritic Steels

against caustic related corrosion action relative to the background material of Figure 14.3.3-3. Figure 14.3.3-4 displays the suspect caustic SCC field on the T- [NaOH] grid. Superimposed on this field are some of the caustic related SCC incidents reported for 2 1/4 Cr-1Mo steel, or closely related steels. Some details of the incidents spotted on Figure 14.3.3-4 are given in Table 14.3.3-2. This experience suggests that, under appropriate stress and physico-chemical stimuli, the 2 1/4 Cr-1Mo steel is vulnerable to caustic SCC throughout this field, and possibly somewhat beyond the lower temperature boundary of the indicated field inasmuch as this zone is relatively unexplored because of limited practical interest.

Propensity to deep pitting and/or cracking in caustic affected media is a prime consideration for LMFBR steam generation system materials. There are two other aspects of caustic action that could affect material suitability, namely: encouragement of rapid water/steam corrosion by small caustic concentrations in the working fluid; catastrophic general corrosion in a steam/water environment caused by concentrated caustic solutions. Apart from the general attrition of the metal associated with such oxidation, the voluminous corrosion products generally increase problems arising from bulk stream product deposition and contaminant concentration. Some review of general caustic corrosion, over a wide range of temperature and caustic concentration, is given in Chapter 13 of this report (Section 13.3.3.2). Figure 14.3.3-6 shows some of the sparse general caustic corrosion data for 2 1/4 Cr-1Mo steel reported in Chapter 13. Recently reported incidents of the general corrosion of 2 1/4 Cr-1Mo steel in caustic affected media are given in Table 14.3.3-4. The only quantitative measure of corrosion response given in these observations is obtained from Indig's report.⁽⁸⁾ These points (about 1 in./yr at 482°C under 5-10 ppm NaOH for tubular specimen; 0.35-1.4 in./yr under 316°C and 10% NaOH, estimated from dimensional changes of welded tensile specimens) are plotted on Figure 14.3.3-6. Both of these points fall close to data obtained by Rubright⁽¹⁰⁾ for 99% NaOH. This is not necessarily illogical agreement, considering the reported wide variability in caustic attack with concentration (see Figure 13.3.3.2-8 of Chapter 13).

Figure 14.3.3-4. Corrosion Parameters for Caustic SCC Incidents Reported for 2 1/4Cr-1Mo or Closely Related Steels

Table 14.3.3-2. Some Observations of Pitting/Cracking Behavior of 2 1/4Cr-1Mo, or Closely Related Steels in Caustic (NaOH) Media

Ref. 9

conditions: 1st test(see table 14.3.2-5); 100 ppm NaOH; 532, 607, 662F;900-1700 hr

observations: pitting near center of heated section; both welded and unwelded specimens showed similiar response

conditions: 4th test(see Table 14.3.2-5); 100 ppm NaOH; 604F; 2 weeks

observations: pitting similiar to that observed in 1st test(above); severe crevice corrosion on specimens and sleeve(30 mil penetration); shallow (5 mil) cracks observed on tensile side of specimen under heavy oxidation

Ref. 8

conditions: 5 and 10% NaOH; 316C; constant strain rate test; static autoclave technique

observations: specimen strained to failure in 5% NaOH showed numerous shall surface cracks; in 10% NaOH 'marginal' case of SCC observed

conditions: 5 and 15% NaOH; 232C(450F); constant strain rate test; static autoclave technique

observations: both transgranular and intergranular SCC for both annealed and welded specimens(see Figure 14.3.3-5)

conditions: 5 and 15% NaOH; 316C; straining electrode test technique

observations: under anodic polarization, shallow surface cracking observed; cracking more severe under 10% NaOH medium; under cathodic polarization, shallow cracking occurred

Ref. 5

conditions: 3Cr-1/2Mo steel; 28% NaOH; 110C; constant strain rate test under polarization control

observations: SCC occurred over potential range -700 to -900 mv(Reference Hg/HgO electrode); hydrogen embrittlement(cracking) was observed for potentials more negative than about - 950mv; thorough deoxygenation increased both the SCC and hydrogen embrittlement

Ref. 6

conditions: 50% NaOH; 316C(deaerated); U-bend specimens

observations: thru specimen(120 mils) SCC observed for coldrolled/annealed specimen within 1 week

Ref. 7

conditions: 3Cr-1/2Mo steel; potentiostatic test technique; 33% NaOH; 100C; specimen stressed to YS

observations: SCC observed within two potential regions: -290^{to}-640mv and -740 to -940mv(hydrogen electrode reference)

Table 14.3.3-2 (concluded)

Ref. 8 (work by H. S. Isaacs (ORNL) cited by Indig⁽⁸⁾)

conditions: 33% NaOH; potentiostatic control under constant strain rate

observations: all specimens susceptible to SCC, but degree of severity depended on: metallurgical condition; oxidizing potential; carbon content
cold worked state had highest SCC resistance, with quenched/tempered and annealed material next in order
over carbon range of 0.08-0.135, the higher carbon material was more resistant to SCC for a given heat treatment

conditions: 33% NaOH; 118C; constant load technique

observations: for each increase of 10ksi in stress, the cracking time decreased by a factor of five

Ref. 8 (work by Dahl et al, referenced by Indig⁽⁸⁾)

conditions: 3Cr-1.2Mo steel; 20% NaOH; 226C(437F); potentiostatic control; specimens stressed to YS

observations: SCC observed over a range of potential (anodic to cathodic polarization w.r.t. to rest potential); anodic polarization of 300 mv, or more, from rest potential resulted in high rates of general corrosion rather than SCC

(see Table 14.3.3-3 for specimen heat treatment, where reported)

Table 14.3.3-3. Reported Heat Treatment for 2 1/4Cr-1Mo or Other Steel For References Cited in Tables 14.3.3-2 and -4.

<u>Reference</u>	<u>Reported Heat Treatment of 2 1/4Cr-1Mo (or other) steel</u>
<u>9</u> (2 1/4Cr-1Mo)	no details; presumably annealed tubing used
<u>8</u> "	<u>annealed:</u> 1695F/20min; furnace cool to 1350F; hold 45 min., air cool <u>normalized/tempered:</u> 1695F/30min.; air cool; temper at 1250F/1 hr; air cool <u>cold worked:</u> annealed; cold rolled 25% <u>cold worked:</u> normalized/tempered; cold worked 25% <u>welded tensile samples and tube samples:</u> after welding, given post-weld heat treatment of 1350F/1 hr
<u>5</u> (3Cr-1/2Mo)	austenitized at 920C/4hr; tempered at 630C/slow furnace cool
<u>6</u> (2 1/4Cr-1Mo)	<u>Ac treatment:</u> cold rolled 40%; 106601122C/1hr; water Q <u>Ac + L treatment:</u> above plus: 649-677C/1 hr; air cooled
<u>7</u> (3Cr-1/2Mo)	no details
<u>8</u> (2 1/4Cr-1Mo)	H.S. Isaacs work reported by Indig ⁽⁸⁾ ; no details given; see Table 14.3.3-2 for general comments on types of material tested by Isaacs
<u>10</u> (2 1/4Cr-1Mo)	no details, presumably annealed tubing

a

b

Figure 14.3.3-5. SCC Observed in 2 1/4Cr-1Mo Steel
10% NaOH, 232C(450F)(see Table 14.3.3-2) (8)

Figure 14.3.3-6. Unstressed Caustic Corrosion Data for
Mild Steel, 2 1/4Cr-1Mo Steel and Ni/Inconel

Table 14.3.3-4. Observations of General Corrosion Behavior of 2 1/4Cr-1Mo Steel in Caustic(NaOH) Media

Ref. 9

conditions: 100 ppm NaOH; 600F; model boiler loop; specimens mounted on electrically heated section

observations: severe general corrosion on heated section

conditions: 100 ppm NaOH; model boiler loop with specimens mounted on electrical heater; saturation steam conditions, with T varying over range 280-350C(530-660F); test times ranged from 900-1700 hr; no attempt at deaeration

observations: heavy loose scale observed for specimens at low temperature end of heated section(~100C)

conditions: 100 ppm NaOH; model boiler loop same as above; specimens exposed for 2 weeks to pure boiling water to develop oxide; 100 ppm NaOH solution then introduced and attempt made to exclude oxygen by nitrogen blanketing; test time 618hr determined by failure of heater section by corrosion

observations: moderate corrosion of specimens on unheated section(~100C); severe general attack on heated specimens over T range 280-350C

Ref. 6

conditions: 50% NaOH(deaerated); 316C; static autoclave technique; U-bend specimens

observations: very severe general corrosion after 2 weeks for specimens given 871C/air cool plus 649C/2hr heat treatment(see Table 14.3.3-3)

Ref. 8

conditions: 10% NaOH; 316C; constant load test; static autoclave technique

observations: simulated tube/tubesheet weld specimens showed catastrophic general corrosion(see Figure 14.3.3-7) in range of 0.4 to 1.4 inches per yr(estimated from dimensional changes reported by by Indig); electroslog remelted unwelded specimens showed good corrosion behavior; of the air melted material; the normalized and tempered material showed somewhat better corrosion behavior than annealed material

conditions: 5 and 10% NaOH; 316C; constant strain rate test

observations: cold worked specimens(20%) showed severe general corrosion; welded and stress relieved specimens showed severe general corrosion; no oxidation details given for annealed and normalized/tempered specimens under 5 and 10% NaOH; annealed specimens exhibited about 50% less reduction in area(relative to pure water tests) in both 5 and 10% NaOH; normalized/tempered material showed about 50% less reduction in area under 10% NaOH

conditions: 5 and 10% NaOH; 316C; straining electrode technique

observations: under anodic polarization, severe general attack noted in 10% NaOH

conditions: 5-10ppm NaOH; 482C(900F); 1750psi; pressurized tubing, superheater simulation tests

observations: test time was limited by rapid failure of tubing by general oxidation; maximum test time was 144 hr; both annealed and normalized/tempered material exhibited a catastrophic corrosion rate of the order of 1 inch/yr

Ref. 10

conditions: unstressed corrosion tests in NaOH solutions ranging from 24 to 99% NaOH; test temperature range was 140-700F at atmospheric pressure; 900F was used for 99% NaOH, under 40 psig of water vapor

observations: corrosion rate is a function of temperature and [NaOH], with temperature having the greatest effect; corrosion was linear with time, with no induction period observed; corrosion rate was very high at temperatures above about 200F, reaching a maximum of the order of 2.7 in/yr at 900F

(see Table 14.3.3-3 for heat treatment details, where given)

Figure 14.3.3-7. Weld Sample Before and After Exposure to 10% NaOH, 316C(600F); see Table 14.3.3-4

The current caustic related corrosion information for the 2 1/4Cr-1Mo steel represents only a very limited exploration of the effects of alloy preparation technique, impurity background, self-self and dissimilar welds, heat/mechanical treatments, on the caustic corrosion characteristics of this steel. From the local caustic corrosion perspective (pitting and cracking propensity over a wide range of the T-[NaOH] field) the extant caustic corrosion information is not supportive of working assignments where some caustic presence at various stages of the working life is a virtual certainty. Also, there appears to have been a preoccupation with the caustic cracking of this steel that has tended to obscure the equally important general caustic corrosion behavior. In view of numerous demonstrations of catastrophic general corrosion of this steel, over a wide range of the T-[NaOH] field, it is difficult to understand the relative importance of the caustic cracking phenomenon in much of the current literature on this steel (e.g.8). Unwelded specimens are the basis for this unsatisfactory general caustic corrosion picture for 2 1/4Cr-1Mo steel. The few recent observations on welded specimens⁽⁸⁾, presumably representing some measure of the current state-of-the-art, are particularly disturbing, considering the prominence of the welded structure in proposed applications of this steel to evaporator and superheater components.

It is impossible to forecast the extent to which free caustic (NaOH) will intrude the working life of LMFBR steam generation system materials. Unless pH and impurity control techniques can evolve to the point of eliminating even sporadic nonvolatile chemical additions with caustic generating potential, then resistance to the full gamut of caustic corrosion action will continue to be an important prerequisite for steam generation system materials. Under this criterion, on the basis of existing evidence, it is submitted that the support for the 2 1/4Cr-1Mo steel is not adequate.

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14.3.4 Sodium-Side Corrosion/Mass Transfer

The intermediate heat transfer system (IHTS) which includes the superheater and evaporator, contains the lowest temperatures of the sodium system in an LMFBF powerplant. Figure 14.3.4-1 shows the temperature distribution of the sodium streams affecting the IHTS for the Clinch River reactor. The secondary sodium flows inside the tubing of the intermediate heat exchanger (IHx) and outside the tubing of the superheater and evaporator components. Although low relative to that of the primary sodium circuit that traverses the reactor core, the sodium temperature profile indicated in Figure 14.3.4-1 includes a temperature range where very substantial mass transfer (dissolution-transport-deposition) can occur over an operating lifetime of 20 to 30 years. All basic substitutional (e.g., Cr, Ni, Mo, Mn) and interstitial (e.g., C, O, N, B) elements of the structural materials comprised by the IHTS are affected to some extent by this mass transfer action of sodium. Some of the complex of factors affecting this phenomenon are noted below:

- oxygen, possibly nitrogen, concentration and disposition in sodium
- local hydrodynamics
- metallurgical condition (i.e., heat treatment/mechanical working history of metal(s))
- physico-chemical nature of prior surface deposits
- temperature profile of the total circuit, including average and transient values
- chemical and physico-chemical properties of the complex sodium contaminants that determine the propensity to mass transport, the form of the transported material, its deposited form and structure, and the long term stability of the components of the deposit with respect to both the ambient sodium and the underlying metal

General corrosion of ferritic steels in sodium is discussed in Chapters 9 and 13 of this report. On the basis of the simple metal loss criterion, existing data indicate that, under nominally expected control of sodium impurities (oxygen is of principle concern), there should be no serious design limitation attributable to this factor.

Figure 14.3.4-1. Fullpower Secondary Sodium Circuit Temperature Profile for CRBRP(1 & 2)

Figure 14.3.4-2. Carbon Concentration-Distance Profiles; 2 1/4Cr-1Mo Steel, Normalized; After Exposure to Flowing Na at 480C (3)

The mass transfer and redistribution of interstitial elements is, however, a factor of some concern for both the austenitic and ferritic materials of the IHTS. Carbon has received the bulk of this attention because of its power, in various forms, to affect the mechanical properties of ferritic and austenitic steels. Also, carbon is prominent because the proposed IHTS materials mix provides a massive carburizing source (ferritic steel) in the superheater and evaporator components and a massive decarburizing sink in the austenitic steels of the IHX and the secondary sodium piping network. The decarburizing/carburizing process is affected by many of the factors noted above. Figure 14.3.4-2 displays a typical carbon profile obtained for normalized 2 1/4 Cr-1Mo steel at 480°C. If carbon loss is interpreted as a parabolic corrosion process, carbon loss may be expressed as: $W = Kt^{0.5}$, where W is the integrated carbon loss per unit area (g/cm^2), t is the exposure time and K is the rate constant. Figure 14.3.4-3 displays carbon loss rate constant data as a function of temperature for 2 1/4 Cr-1Mo steel with various heat treatments (annealed, normalized, normalized and tempered). The data of Matsumoto, et al.,⁽⁴⁾ for the annealed material exhibits somewhat higher loss rates than the normalized and normalized plus tempered material of Natesan, et al.⁽³⁾ Figure 14.3.4-4 illustrates some predictions of changes in carbon profile over long periods of sodium exposure. Figure 14.3.4-5 illustrates the reduction in carbon loss that can be effected by the presence of a carbide stabilizing element (Nb in this case). The effect of stress state/history on carbon loss appears to have received little attention. Figure 14.3.4-6 presents some Russian data reported by Fidler and Collins,⁽⁵⁾ showing a progressive lowering of the carbon profile of 2 1/4 Cr-1Mo steel with increase in stress (state unspecified), after 500 hours' exposure to sodium at 550°C.

In addition to carbon effects on the source and receptor metals, redistribution of various elements of the IHTS structural materials can lead to the creation of surface zones that bear very little similarity to the parent metal in either mechanical or corrosion properties. Under appropriate progressive attrition by the total service environment, such a 'surface' layer may very well determine the service life of the parent metal. The weld zones of the IHTS must be accorded particular attention, especially

Figure 14.3.4-3. Temperature Dependence of Rate Constants for Decarburization of 2 1/4Cr-1Mo Steel in Sodium (3)

Figure 14.3.4-4. Expected Long Term Decarburization Profiles of 2 1/4Cr-1Mo Steel (5)

Figure 14.3.4-5. Decarburization of Stabilized and Unstabilized 2 1/4Cr-1Mo Steel (5)

Figure 14.3.4-6. Observed Decarburization Profiles of 2 1/4Cr-1Mo Steel Under Various Stress Conditions (5)

those between the ferritic and austenitic components. Some of the difficulty in standardizing such a weld, and characterizing it for the working environment, is indicated by a typical weld proposal for this joint, namely: 2 1/4 Cr-1Mo/I-82/I-800/unknown filler/316SS.⁽⁶⁾

The corrosion/mass transfer phenomena noted above are internal to the IHTS and can operate without malfunction of any IHTS component. A major potential source for external contamination of the IHTS sodium is the water-side of the steam generation components. Apart from the products of Na-H₂O reaction (NaOH and H₂), leaks in the superheater and evaporator components can introduce various contaminants peculiar to the water system at the time of the leak, namely: corrosion products derived from the entire water/steam circuit, contaminants from condenser in-leakage, water treatment chemicals, gas from in-leakage at various points of the steam system. These contaminants may be in elemental form, or in ionic form in a host of chemical compounds of widely varying reactivity with sodium. These substances have some potential for perturbing the 'normal' corrosion/mass transfer processes of the IHTS.

At present, the knowledge of corrosion/mass transfer action in sodium environments is of very limited utility in assessing the long-term in-service performance of structural materials. For example, the test foil procedure for characterizing the carburizing/decarburizing potential of sodium⁽⁷⁾ and the interpretation of carbon loss in terms of simple, uniform, rates,⁽³⁾ are only preliminary design/analysis expedients. Practical design significance for such information can be achieved only by a comprehensive mechanical property correlation under a reasonable simulation of the working environmental factors. Specifically, there is now very little knowledge of the effect of fatigue, excited by a combination of mechanical and thermal agencies, on the long-term structural significance of interstitial transfer within the sodium circuit. Modeling of fatigue action, under even partial simulation of the complex of factors operative in a working IHTS, is a formidable experimental challenge. Attempts at correlation of mechanical properties with corrosion/mass transfer action are planned.⁽⁶⁾ It is reasonable to expect, however, that prediction of long-term behavior in IHTS systems will remain, to a large extent, beyond the capacity of laboratory, or prototypical engineering testing.

A number of factors will be influential in the sodium-side performance of 2 1/4 Cr-1Mo steel in proposed steam generating system applications:

- chance conjunctions of abnormal metal structure/composition factors (e.g., sulfide, phosphide inclusions, martensitic islands) with conditions conducive to structural degradation (e.g., fatigue, corrosion/erosion); the practical significance of this factor will depend on the general metallurgical quality of the as-installed tubing and, in particular, the quality of weld zones;
- the long-term effect of interstitial element loss/redistribution on the creep and fatigue properties of the total metal cross-section; carbon is of principal concern;
- the ability of selected fabrication techniques and pre-service heat/mechanical working treatments to achieve metallurgical states for the installed metal that do not present opportunities for selective (e.g., grain boundary) attack by the ambient sodium environment;
- the degree of control exercised on the dissolved and particulate species accessible to the secondary sodium circuit that can perturb the general, and local, corrosion/mass transfer response of the 2 1/4 Cr-1Mo steel.

A proper appraisal of most of the above factors will require the materials commitment and operational vagaries peculiar to a large-scale LMFBR powerplant. There is, as noted above, a substantial area of uncertainty with respect to the sodium-side performance of 2 1/4 Cr-1Mo steel, centered on the ability of sodium to alter the content and disposition of the carbon in this steel.

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14.3.5 Miscellaneous Corrosion Related Processes

The steam generation system of an LMFBR powerplant represents a virtually unique conjunction of mechanical, chemical, and thermal factors that can affect the performance of structural materials. Some of these factors, imposed by the functional requirements of the steam generation equipment, are as follows:

- a secondary sodium/water-steam interface in both the evaporator and superheater components, thereby subjecting heat exchanger tubing simultaneously to the gamut of corrosion/mass transfer agencies peculiar to both the sodium and the water circuits;
- tube vibration potential of the secondary sodium stream and the multiphase regimes of the water-steam stream;
- metal-metal contact situations at tube shrouds, support plates, anti-vibration devices;
- a multiplicity of welded connections
- tubing temperature transients imposed by bulk temperature changes in the sodium and/or water streams and by shifts in the heat transfer burden among tubes of the array due to variability of deposit buildup within the array;
- complex stress transients imposed on tubing by pressure, temperature and flow variations in the sodium and/or water streams.

Some review of miscellaneous corrosion related processes, somewhat beyond the scope of the conventional water-side and sodium-side discussions given previously in this chapter is appropriate.

The generic term, fretting, involves some factors not discussed previously in this report. There have been a number of incidents where fretting has been suspected as a participant in steam generator tubing damage.⁽¹⁾ The potential importance of fretting to LMFBR steam generation system equipment justifies some review of the fretting process. Because of the

sparsity of fretting information for virtually all materials, and the 2 1/4 Cr-1Mo steel in particular, the comments will necessarily be fairly general.

Both fretting corrosion and erosion involve contact-surface forces imposed by environmental partners of the metal. These may be solids (e.g., as in metal-metal, metal/oxide-metal/oxide contact situations), liquids, or gases. Generally, metal attrition from liquid, or gas, contact is labeled erosion. All of these media can impose both shear and impact type forces on a metal surface and some similarity of effects is to be expected. Both fretting and erosion processes can involve chemical and electrochemical action to various extents, depending on the specific environmental conditions and the properties of the participants. Where there is vibration leading to relative motion between contiguous metal surfaces, high liquid or gas velocities in linear or turbulent modes, two-phase flow regimes having high throughput rates, then both fretting and erosion may become active after some time of exposure to these conditions. With greater appreciation of the number of factors which can influence these processes, arbitrary phenomenological boundaries tend to recede in importance. The factor common to both fretting and erosion is surface forces, whose orientation-intensity-time characteristic is usually an unplanned aspect of the service environment. Metal loss will occur when the integrated effect of these forces, and the service stresses, exceeds the structural binding strength for various zones, whose size will depend on the extent of the surface stress field, and structural strength details within this field. The latter aspect is sensitive to chemical and electrochemical activity which occurs during the time of the applied forces and to the metallurgical history of the metal.

Generally, an oxide layer of various thickness intervenes between the metal and the fretting, or eroding, agency. Partial, or full, destruction of the oxide will usually precede metal damage in the absence of prior metal defects. The fretting and erosion resistance of many metals is attributable to the structural stability of their oxide(s). This may result from a combination of intrinsic structural quality of the oxide layer and the ability of the metal to regenerate the oxide under the fretting or erosion conditions. The sodium-side of the heat exchanger

tubing will tolerate virtually no oxide. Apart from deposits of miscellaneous corrosion/mass transfer products, the metal surfaces involved in sodium-side fretting will be unprotected.

Even excluding chemical action, there are many variables involved in the fretting process, for example: vibration mode(s) and frequencies, clearance, contact pressure, shearing stresses, relative slip and motion between fretting partners, time, and metallurgical state of partners. In addition, such properties as melting point, hardness and fatigue strength of the participating metals and compounds have been used to correlate and explain fretting data.

When fretting occurs under a corrosive environment, virtually the whole spectrum of chemical and electrochemical factors can come into play, compounding the prediction problem considerably beyond current theoretical capacity. Most fretting correlations, involving some of the above factors, are only of very limited use. At this time, there is almost total reliance on experimental analysis of suspect fretting situations. As in the case with stress corrosion cracking, long exposure time may be needed to develop fretting damage. Attempts to drastically condense the time frame of the phenomenon may, as is also the case with SCC, seriously affect the conception of, and the accommodation to, the process.

Fretting data pertinent to the steam generation system applications of the low alloy ferritic steels are very sparse. This fact is emphasized by a fretting study program at the Chalk River Laboratory oriented toward steam generator tubing.⁽²⁾ It is the objective of this program to relate vibration characteristics of the working environment to long-term fretting damage, with the consequent objective of identifying acceptable vibration and contact situations. The present Canadian philosophy is that the vibration characteristics of the steam generator components should be known before installation. Design limits taking cognizance of such analysis will, at the least, tend to improve the working environment of the tubing. They will also tend to clarify the actual working situation, presumably a prerequisite for deliberate improvement of tube working life. The Canadian approach is strongly supported by Nelms and Segaser⁽³⁾ in their study of vibration related problems in nuclear powerplant systems. The principal

conclusion of the latter work is that much current design practice does not reflect sufficient concern for vibration effects in critical components. The report of Irvine, et al.,⁽⁴⁾ discusses another aspect, namely, plastic strain accumulation as a result of operational conditions. Plastic strain is now held to be a prerequisite for crack propagation. It is not difficult to associate this factor with a lowering of the resistance to fretting and erosion.

Electrochemical techniques are being used increasingly in the analysis of fretting corrosion. Their ability to quantify corrosion processes associated with the fretting process is a powerful aid in relating general corrosion characteristics to fretting susceptibility in a given service environment. Recently, Taylor and Waterhouse⁽⁵⁾ reported on an electrochemical study of the fretting behavior of a number of metals of varying electrochemical activity and oxidation characteristics, namely, Ta, Zn, Al, Ag, Cu, Cr, and Ni. They used an electrolyte of 0.5M NaCl. Hemispheres of 6.3 mm radius, loaded to 300 gm, were vibrated against flat plate specimens of the same material using a vibration generator. Amplitude and frequency were 50 microns and 120 Hz, respectively. Prior to testing, the specimens were mechanically polished to a 1 micron finish. Tests were run with both air and nitrogen saturated solutions and corresponding ambient atmospheres. Two types of electrochemical tests were conducted: (a) the corrosion potential of the fretting couple was measured before, during, and after fretting; (b) galvanostatic (constant imposed current) tests were run in both air and nitrogen, with, and without, fretting. Table 14.3.5-1 shows the effect of fretting action on the corrosion potential. It is seen that, with the exception of Ag and Cu, all metals showed a more reactive (negative) corrosion potential under fretting, with Cr and Al giving the largest effect. The authors attribute the increased anodic activity to breakdown of the oxide layer, with specific voltage effects being determined by the electrochemical activity and the kinetics of regenerating an oxide under the contact conditions. Figure 14.3.5-1 shows the effect of fretting on the potential of Cr and Al. Upon cessation of fretting, the potential generally climbed to the initial value, although more time was needed to reestablish this value. Similar effects were noted for both air and nitrogen

Table 14.3.5-1. The Mean Free Potential Fall on Fretting in 0.5M NaCl ⁽⁵⁾

<u>Material</u>	<u>Fall in ϕ on Fretting(mv)</u>
Ag/Ag ⁺	0
Cu/Cu ²⁺	0
Ni/Ni ²⁺	35
Ta/Ta ⁵⁺	130
Cr/Cr ³⁺	310
Zn/Zn ²⁺	10
Al/Al ³⁺	450

Figure 14.3.5-1. Potential-Time Characteristics During Fretting Under Air-Saturated 0.5M NaCl ⁽⁵⁾

saturated solutions. The galvanostatic data showed increased anodic activity for Cr, Al and Ta under fretting, with very little change for Ag, Cu, or Ni.

Recent French work cited in Corrosion Abstracts⁽⁶⁾ also demonstrated that austenitic and martensitic stainless steels exhibit sharp increases in electrochemical activity (depassivation) when self-fretted under neutral NaCl solutions (30g/liter). Stress-wise, these laboratory studies may not be overly conservative with respect to service conditions. Chemically, the laboratory work may represent some departure from reality. The abnormal chemistry potential of crevices and thick deposits has, however, been emphasized in this chapter. A fretting situation will create 'dynamic' crevices of various geometries. Opportunity for chemical exchange with the ambient stream will be determined by the specific contact situation. Severe stress corrosion cracking of many structural alloys has been observed under static crevice conditions. The imposition of periodic surface stresses on this corrosion arena certainly does not tend to bias the metal toward greater stability. Quite the contrary, as shown by the above work.

Hutchings and Sanderson⁽⁷⁾ measured the effect of fatigue cycling (slow cycle, reverse bend; stress amplitude $\pm 112 \times 10^3$ psi, frequency 0.08Hz) on the corrosion current developed by an 18% manganizing steel. The metal was fatigued under cathodic polarization in an aerated neutral 3% NaCl solution. Following a number of fatigue cycles, current measurement was made in the same solution without simultaneous fatigue. The results followed the relationship,

$$\log (\text{current parameter}) = K(N/N_f)^3$$

where K was between 1 and 2, N is the number of fatigue cycles, and N_f is the fatigue limit for the given stress situation. Figure 14.3.5-2 displays the observed relationship between the current parameter and the N/N_f ratio, showing the rapid increase in corrosion current as the fatigue limit is approached. These results may have more implication for corrosion fatigue than for fretting. Some association of these results with fretting appears plausible, however, considering that a fretting situation can impose a fatigue type stress through impact and sliding modes. The long 'induction'

Figure 14.3.5-2. Effect of Fatigue Cycling in Air on Corrosion Current Density (7)

time observed for some fretting action suggests some correspondence with a fatigue, or endurance, type situation. The above authors suggest that accumulated fatigue damage may result in an increase in electrochemically active atoms and/or a decrease in the activation energy for anodic and/or cathodic processes, effects that could accelerate the deterioration of the metal structure.

Fretting corrosion has received relatively little research attention. The complexity and potential importance of this problem will probably require tests of partial segments of full-scale components. Some work of this nature is planned, or underway, in connection with steam generator components for the CRBRP.⁽⁸⁾ In-service vibration monitors, positioned at points identified as sensitive by prior vibration analysis, would be of great value in correlating any observed damage with the operating history. Electrochemical studies, with realistic electrolytes, can provide a sensitive monitoring of structural decay, as well as of the conjoint action among mechanical, metallurgical and corrosion factors whose effects envelope determine fretting damage.

With sodium exterior to the heat exchanger tubing, the sodium side will bear the full brunt of metal-metal contact situations. Most wear/self welding studies in sodium have been in connection with materials suitable for bearing surfaces and wear pads. These materials bear very little structural relation to 2 1/4 Cr-1Mo steel. As noted above, sodium is intolerant of the nonmetallic layers usually associated with protection against fretting damage. The fretting characteristics of this steel under sodium, within the range of metallurgical and chemical conditions possible for commercial material, appear to be largely unknown. Furthermore, a severe sodium-side fretting situation could transmit some influence (vibration, stress pulse) to the water-side of the tubing. This could result in some perturbation of the water-side corrosion response of the 2 1/4 Cr-1Mo steel. If a voluminous, porous, oxide developed at the affected site, this secondary fretting effect could lead to serious local attack in the presence of aggressive ions such as OH^- , or Cl^- .

There is now more general recognition of the importance of vibration analysis to the design of heat exchanger equipment. While minimization of corrosion fatigue is a primary objective, experience has shown that fretting situations are also to be avoided. In LMFBF steam generation equipment, the sodium-side will be the principal arena for direct fretting action. Under sodium exposure, the conception of fretting influence must also include some potential for enlarging the zone of material affected by sodium leaching of interstitial and substitutional elements important to long-range structural stability. The sensitivity of 2 1/4 Cr-1Mo steel to this sodium-side action, as well as to water-side influence of this action, needs substantial clarification before large-scale commitment of this steel to LMFBF steam generation components.

References for 14.3.5

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14.5 SUMMARY AND CONCLUSIONS

14.5.1 Ferritic Materials

The possibility of crucial assignments for the 2 1/4 Cr-1Mo steel within LMFBR steam generation systems has been anticipated for over a decade. Despite this knowledge, from the perspective of general corrosion credentials pertinent to this service, it is submitted that the evidence in support of this steel remains inadequate in several important respects.

- The water/steam behavior of a tubing material for evaporator and superheater service is a fundamental qualification;. Even without the intervention of aggressive ions (e.g., OH^- , Cl^-), the long-term oxidation behavior of 2 1/4 Cr-1Mo steel in high heat flux zones appears to afford very marginal support for this steel. The effect of periodic chemical cleaning on the overall water/steam oxidation behavior of this steel is unknown.
- Laboratory experience with aggressive ion presence during water/steam oxidation of this steel are sparse, particularly under the various cyclic temperature and fatigue/steady stress modes operative in the steam generation equipment. Recent data for both Cl^- and OH^- affected environments indicate that very severe perturbation of the water/steam corrosion response can be effected for this steel by low concentrations of either of these ions in the bulk stream. Irrespective of local attack (pitting, cracking), the general metal attrition from such action could impose impractical design penalties on this steel when service times in excess of 20 years are involved.
- Well publicized claims to the contrary, the 2 1/4 Cr-1Mo steel has exhibited both severe pitting and cracking under chloride and caustic environments not unrealistic with respect to potential steam generation system conditions.
- Embrittlement, probably related to some direct, or indirect, form of corrosion induced hydrogen action, has been observed

during water/steam exposure of carbon and low alloy ferritic steels. There has been some correlation of this effect with local conditions leading to acidification under electrochemical action, the chloride ion being the chief suspect as an intermediary in this phenomenon. The demonstrable sensitivity of 2 1/4 Cr-1Mo steel to chloride presence, as well as the qualitative similarity in general corrosion behavior among steels of the low alloy ferritic family, does not imply any degree of immunity of 2 1/4 Cr-1Mo steel from this embrittlement. Relatively hard structural inhomogeneities resulting from fabrication (e.g., welding) may be particularly susceptible to this embrittlement.

Figure 14.5.1-1 gives sodium and water/steam temperature ranges (full power to refueling mode for sodium; full power to room temperature maintenance modes for water/steam) for the steam generation system of the Clinch River plant. On the basis of the corrosion review of 2 1/4 Cr-1Mo steel given in this report, temperature ranges over which various corrosion processes have a significant potential of occurring are indicated on this figure. In view of various concentration agencies discussed earlier in this chapter, and the indefiniteness of what might be termed a 'critical' aggressive ion concentration under complex working conditions, specification of mean bulk concentrations of caustic, or chloride ion, pertaining to these ranges of corrosion activity would be virtually meaningless. Dissolved oxygen, as noted previously in this chapter, has a broad scope of action in the corrosion processes noted in Figure 14.5.1-1. It is submitted that the negative, and positive, influences of dissolved oxygen are not known to an extent that justifies any quantitative relation of [O] to these corrosion processes.

The caustic SCC regime is extended to the maximum sodium temperature level because penetration of a superheater tube near the upper stage could conceivably bring caustic processes into play at close to the maximum sodium temperature in the superheater. Caustic pitting is regarded as essentially a water-side process. This process, and the other clearly water-side

Figure 14.5.1-1. An Assessment of Potential Corrosion Trouble Areas for the 2 1/4Cr-1Mo Steel in LMFBR Steam Generation System Service

processes, are terminated at the maximum steam temperature level. Room temperature was selected as the lower temperature for all the water-side processes, including caustic pitting. The cross hatched zone is an indication of the temperature regime where maximum corrosion activity might be expected, by virtue of temperature and/or opportunities for electrochemical participation in the corrosion activity. The double arrow denotes a regime (A) where no strong temperature bias is expected; the single arrow a regime (B) where an increase in corrosion activity with temperature would be expected. Some factors that might be expected to aggravate the propensity of 2 1/4 Cr-1Mo steel to the corrosion action displayed in Figure 14.5.1-1 are as follows:

- fatigue, over a wide range of temperature and stress parameters, with tensile superposition;
- high heat flux in conjunction with deposit buildup/crevices
- fretting on sodium-side; possible water-side influence
- metal inclusions (sulfides and phosphides emphasis)
- rapid water-side temperature transients
- metal structural inhomogeneities (e.g., martensitic islands), with weld zones of particular concern
- crud buildup on water-side surfaces
- structural defects introduced during fabrication/testing/maintenance/rehabilitation phases due to mechanical and/or chemical action.
- poor management of the particulate and dissolved species, on both the water and sodium sides, with potential for adversely affecting corrosion response; Cl^- and OH^- excursions are to be avoided; [O] tolerance range is poorly identified at present and many particulars of chemistry management of sodium and water sides will be resolved only by operational experience.

As noted previously in this chapter, there is a considerable area of uncertainty in the sodium-side response of 2 1/4 Cr-1Mo steel, centered principally in the loss and redistribution of carbon over long-term exposure to sodium of various impurity backgrounds. The corrosion implications of this carbon effect are not known to any extent. The immediate concern of this effect is for mechanical properties, and it is reasonable to expect that satisfactory resolution of this mass transfer problem will require substantial in-service experience under the full scope of working factors and the vagaries peculiar to commercial powerplant operation. Stabilizing elements (e.g., Nb, Ti) can retard carbon loss. The general property effects of such stabilizers are not, however, well enough known to justify their introduction on the basis of only carbon stabilization.

It is submitted that the potential general water-side behavior of 2 1/4 Cr-1Mo steel provides an immediate and severe criticism of this steel for the proposed LMFBR steam generation system applications. Some improvement in water-side corrosion characteristics may be effected for the nominal 2 1/4 Cr-1Mo composition by careful impurity control during melting and primary fabrication. The effects of metallurgical structure, and structural inhomogeneity, on the water-side corrosion behavior of 2 1/4 Cr-1Mo steel are not well established. The prominence of welding in the fabrication of steam generation equipment, and the difficulties in standardizing the welding operation, suggest, however, that the broadest possible structural and impurity tolerances are desirable for a tubing material.

Prior to large-scale commitment of the 2 1/4 Cr-1Mo steel to a U.S. LMFBR powerplant with prime demonstration responsibility, further broad scoped study of the production, fabricability, and mechanical and corrosion property spectrum, of this material is certainly in order. On the basis of the published information accessible to this review of the corrosion characteristics of the 2 1/4 Cr-1Mo steel, it is submitted that there is a considerable basis to question the adequacy of the incentive for a continuation of this work with this particular material.