**SUMMARY REPORT
SODIUM MASS
TRANSFER PROGRAM
EFFECTS OF SODIUM EXPOSURE
ON THE CORROSION AND
STRENGTH OF STAINLESS STEELS**

U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT(04-3)-189 PROJECT AGREEMENT 15

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SUMMARY REPORT
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AND STRENGTH OF STAINLESS STEELS

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Project Agreement 15

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HIGHLIGHTS OF PROGRAM ACCOMPLISHMENTS

GENERAL PROGRAM HIGHLIGHTS

All program objectives have been accomplished, involving a total of 135,000 hours of operation of seven loops and twelve test rigs during a period of 34 months with well controlled analytical surveillance to reproduce as closely as possible typical LMFBR coolant conditions.

Five candidate alloys were investigated in this program to establish corrosion and stress-to-rupture properties in flowing sodium environment typical of LMFBR systems. The alloys were Types-316 and -304 stainless, which were investigated in depth, as well as Types 347, 321 and Incoloy-800 which were examined in less detail.

This report covers the period October 1, 1968 to August 31, 1971, during which time over 5000 corrosion/deposition samples were exposed from 2000 to 16,000 hours, at 800 to 1300°F. In addition, 176 samples of cladding were tested under biaxial stress in flowing sodium at 1300 and 1150°F. Control tests were carried out on samples in argon atmosphere at the same temperatures for comparison with results obtained in sodium.

Corrosion data were reproducible within 10% from one loop run to another and compared well with published data in the literature. Relative corrosion rates were established for the austenitic alloys tested with Incoloy-800 found to corrode at twice the rate of Type-316 stainless steel.

Deposition of particulates was discovered, measured and characterized in this program. These particulates are composites of elements removed from the hot leg of sodium circuit and were found mainly in cooler parts of the loops. Deposits must be considered in the design of power plant components in terms of hydraulics, heat transfer effects and radioactivity deposition.

Stress-to-rupture properties of unstabilized steels (304, 316) were found to diminish because sodium removed carbon, nitrogen, and boron and accelerated the formation of sigma phase in the stainless specimens exposed in the hot leg at 1300°F. This observation dictates major design considerations for LMFBR cores, and provides the basis for considering stabilized steels for fuel cladding applications.

One experimental run was performed to study radioactive specie (Cobalt-60) movement in flowing sodium. The results obtained indicated that contact maintenance of reactor components such as the Intermediate Heat Exchanger is not feasible at the present state of technology.

Electrochemical oxygen cells with air reference electrodes showed some promise, but considerable development of ceramics for the electrolyte is needed before they can be used as reliable on-line meters.

The impurities in the sodium were maintained within typical LMFBR limits according to the guidelines of report ANL ST/5. Measurement by vanadium wire technique (ANL ST/6) showed 0.96 ± 0.1 ppm oxygen. Surveillance and monitoring were accomplished by both on-line techniques and periodic sampling. A stirred cold trap was developed which demonstrated 100% efficiency for removal of hydrogen and oxygen from sodium by enabling cold zone turbulence to be increased independent of residence time without increasing cold trap size. Thus it is a potential solution for economic cold trap design for power plant systems.

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ABSTRACT

This document includes results of investigations on the effects of high temperature (to 1300°F) flowing sodium on five stainless steel alloys which are candidates for use as structural materials of LMFBR primary coolant systems. Precision of control and measurement of parameters such as oxygen concentration and temperature were substantially improved relative to prior work. Corrosion rate for Type-316 stainless steel at 1300°F is 0.84 ± 0.3 mil/year (3 ± 2 ppm oxygen, > 20 ft/sec, and essentially zero downstream).

Mechanical properties important to cladding design were significantly degraded by exposure to typical central core sodium conditions. The degradation was found to be caused by both changes in chemical composition and mass transfer.

On long exposure, several effects of sodium were found, including removal of minor elements such as carbon, nitrogen, and boron; formation of sigma phase; and formation of subsurface voids. These effects combine to produce time- and temperature-dependent limits on the retention of any given level of design properties. Typical times for significant reduction in useful properties range from about 3,000 hours at 1300°F to more than 10,000 hours at 1200°F.

Another significant byproduct of the mass transfer process is the transport of radioactivity within the primary system. The desirability of providing the capability for remote handling and maintenance of LMFBR primary system components was indicated in a test which measured cobalt-60 transfer, quantitatively, from the high temperature zone (1300°F) of a test loop to zones corresponding to IHX, pump, and piping regions.

In another series of tests, particulate materials were observed, both as surface deposits (by scanning electron microscope) and as particles filtered from sodium streams. The limited data to date indicate that particle deposition may be significant to system design and operation under extreme conditions through fouling of IHX surfaces, potential blockage of small diameter flow passages, as well as its contribution to radioactivity buildup in components.

The question of use of small-loop data for large subsystems was approached by calculation of effective boundary layer thicknesses as a function of duct size and flow velocity. To the limited extent of this work, it appears feasible to duplicate the full range of the hydrodynamic conditions important to mass transfer in large system designs using only small test loops.

During this phase of the program, typical oxygen levels in sodium were maintained at about 3 ppm (extreme range 1 to 4 ppm). Cold traps were controlled to $\pm 2^\circ\text{F}$. The efficiency of standard cold traps was improved from 50% to 99% by increasing crystallizer turbulence without increasing net mass flow. This improvement will allow reductions of size and cost of cold traps for large LMFBR systems. Impurities in sodium were monitored by a combination of on-line distillation, oxygen meters, plugging meters, and chemical analysis of samples. Amalgamation analysis was made more specific for sodium oxide by an improved method which corrected for hydride and carbonate. Precision of analysis was enhanced by improving the procedure and reproducibility of the blank correction. (A proposed revised standard has been prepared and circulated.)

Application to Design

Data were obtained from tests in seven dynamic recirculating loops, with heat transfer (ΔT to 500°F) simulating thermal, hydraulic, and chemical conditions of reactor cooling systems.

The results provide a basis for development of LMFBR design criteria in areas concerning compatibility of sodium with stainless steel. Results show that design corrosion allowances should be of the order of 1 mil per year at 1300°F where oxygen concentration is less than 5 ppm. Fuel cladding design should allow for reductions in stress-to-rupture life of up to 50% at 1300°F during the life of an LMFBR core, with the loss of strength due to loss of interstitial and minor alloying elements such as carbon, nitrogen, and boron.

Handling and maintenance procedures for the intermediate heat exchanger, pumps, and piping of a primary reactor cooling system must be based on radiation levels up to 50 to 70 R/h or more, due to corrosion and transport of cobalt-60. Other long-lived isotopes (Mn-54, Co-58, Cr-51), as well as fission products transported from the core, will add to radiation levels over the life of an LMFBR.

Sodium purification and monitoring procedures and equipment developed in the program show promise for application to LMFBR coolant systems.

Data obtained in this program are applicable for use in design, but additional work in certain areas, such as mechanical properties and radioactivity buildup in primary systems, and steam generator and heat exchanger materials corrosion, and mechanical properties, could potentially lead to reductions in design uncertainties and consequently reduce LMFBR plant costs.

SECTION I

INTRODUCTION

1. INTRODUCTION

This phase of the Sodium Mass Transfer Program summarized here was operated for the Atomic Energy Commission by General Electric to obtain improved design data for materials used in sodium systems. In addition, data were obtained on a variety of phenomena which can affect the successful long-term operation of sodium systems.

The earlier phase of the program consisted of systematic tests to obtain statistical correlations of parameters that control corrosion rate for austenitic (mainly Type 316) and ferritic (mainly 2-1/4 Cr-1 Mo and 5 Cr-Ti) steels in flowing sodium. The summary of Phase I results^{2,2*} indicated the trends in corrosion rates with temperature, oxygen concentration, velocity, and downstream position. These results were incomplete for design purposes, especially at higher temperatures. Also, the data had large scatter due to relatively crude techniques of oxygen control and determination.

In Phase II, a primary objective was to reduce the relatively large uncertainty limits of corrosion rate data and extend them to cover LMFBR design conditions. In addition, studies were initiated on the nature and extent of changes in properties and composition of fuel cladding due to high temperature flowing sodium.

The Phase II Program established substantially more precise and reliable corrosion data, suitable for design use, by improved techniques of control and measurement of operating variables, especially oxygen. Routine control of total oxygen to less than 5 ppm was maintained, and levels of 2 to 3 ppm have been common. The improved precision and control have also permitted reliable discrimination of the relative corrosion rates of various types of stainless steel.

Perhaps even more important than the improvement in reliability of corrosion data has been the recognition that many design applications of materials in sodium at higher temperatures are more severely limited by changes in mechanical properties than by corrosion itself. Carbon transfer was observed in Phase I in ferritic and austenitic steels. In Phase II, such effects in austenitic steels were more quantitatively determined, and a few rates of changes were measured for design-limiting conditions. In addition, it was discovered that large changes in composition of many of the minor elements—including nitrogen, silicon, boron, as well as carbon—commonly occurred in stainless steel at rates increasing with temperature and becoming significant to design above 1150 to 1200°F.

Most of the properties and behavior of stainless steels in design applications are strongly influenced by the amount and distribution of such minor alloying elements; for example all of the following properties:

- Ultimate strength
- Ductility
- Creep strength
- Response to fast-neutron irradiation
 - Swelling rate
 - Strength and ductility changes
- Response to chemical attack
 - Stress induced attack (caustic or chloride)
 - Intergranular attack

The foregoing circumstances require that materials property data intended for design application in sodium above 1200°F must take account of both composition changes and consequent structure changes. For example most measurements of radiation-induced swelling to date have been made on samples at or near the as-received composition. In actual core design and analysis, account must be taken of the change in concentration (by factors of two to five) of minor elements such as carbon, nitrogen, and boron, which are known to affect swelling rate and ductility after irradiation.

While experiments with full temperature and sodium exposure have been started in EBR-II, these will take some time before systematic data coverage can be attained. Meanwhile, the irradiation of specimens previously exposed to sodium (in P.A. 15 loops) can provide some initial data on the swelling and ductility behavior of such modified alloys under neutron irradiation.

*See References for Section 3.

SECTION 2

IMPURITY MONITORING AND CONTROL

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2. IMPURITY MONITORING AND CONTROL

To reduce and assess the errors associated with the study of mass transfer phenomena, precise control and measurement of impurities, particularly oxygen, are required. Described in this section are improvements in purification procedures evolved during the course of the program, and the methods used and data obtained in monitoring impurity species, both in the laboratory and in-line, are summarized.

2.1 LOOP PURITY CONTROL

Full time operation of the cold traps on all loops was implemented to ensure constant impurity concentrations and minimize recovery time after maintenance operations or in case of inadvertent introduction of contaminants. Two other improvements were effected in the mode of cold trap operation: precise temperature control which was used routinely, and the introduction of turbulence (stirring) was investigated, tested, and used occasionally to raise the efficiency of the cold trap.

2.1.1 Precise Control of Cold-Trap Temperature

Initially, loop cold traps were regulated with semiautomatic temperature control equipment. This equipment was an improvement over the prior methods of cold-trap control since it enabled full-time operation within narrower limits than was formerly possible by manual adjustments. Nevertheless, the equipment lacked features necessary for precise control of loop purity (i.e., closer than $\pm 5^\circ\text{F}$). Hence, a new, improved, solid-state device for cold-trap temperature control was designed, constructed, and placed in operation on loops during 1970. The new system overcomes the disadvantages of the previous equipment and has features which increase its flexibility while providing control within $\pm 2^\circ\text{F}$.

2.1.2 An Improved Cold Trap for Sodium Systems

A twofold increase in cold-trap effectiveness for impurity removal was achieved by producing high turbulence in the crystallizer of a standard cold trap. Conventional cold traps have relatively low cleanup efficiencies, thus limiting their potential capability for rapid system purity recovery following an excursion.

It has been observed^{1,2} in flowing sodium systems that an increase of fluid turbulence greatly enhances the precipitation of materials at supersaturated concentrations in sodium. The reason for this can be seen in the following equation, where the impurity precipitation rate can be expressed as:

$$\frac{dm}{dt} = K A (C - C_s), \quad (1)$$

where

$\frac{dm}{dt}$ = precipitation rate (gm/sec),

A = deposition surface area (cm^2),

C = concentration of supersaturated impurities,

C_s = saturation solubility of impurities at the precipitation temperature, and

K = mass transfer coefficient ($\text{gm}/\text{cm}^2\text{-sec}$).

K has been observed to increase linearly with increasing sodium turbulence (i.e., increasing Reynolds number $[N_R]$). This equation shows that by increasing K, the precipitation rate will be increased, provided other terms in the equation are kept constant.

Based on this observation, a new cold trap was designed (see Figure 2-0) utilizing an electromagnetic stirring device. Tests were conducted in loop 9 to measure the oxygen and hydrogen cleanup rates under laminar (unstirred) and turbulent (stirred) modes of cold trap operation. The initial impurity concentration and the cold-trapping temperature were kept the same during both modes of operation in order to determine the effect of varying K alone. The decrease of oxygen with time was measured with an air-reference electrochemical cell, while hydrogen was monitored by a diffusion membrane connected to a sputter ion pump on the vacuum side.

Figure 2-0. Stirred Cold Trap

Figures 2-1 and 2-2 show the results of this test for hydrogen and oxygen removal, respectively. Increasing the turbulence (stirred mode) doubled the rate of hydrogen removal (Figure 2-1). A similar effect is shown for oxygen removal in Figure 2-2, where increased oxygen cell voltage represents decreased oxygen activity in sodium.

The calculated cold trap efficiency, using the mass balance equation and assuming ideal mixing, can be expressed as

$$\ln_e \frac{C - C_e}{C_0 - C_e} = -\epsilon\lambda, \quad (2)$$

where

- C = instantaneous concentration of hydrogen in sodium,
- C_e = minimum or equilibrium concentration of hydrogen at particular cold trap temperature,
- C₀ = initial concentration of the hydrogen in sodium prior to cold trap operation,
- ε = cold trap efficiency, and
- λ = number of system turnovers through the cold trap.

Figure 2-1. Hydrogen Removal for Two Modes of Cold Trap Operation

Figure 2-2. Rate of Oxygen Removal by Cold Trap

A diffusion type hydrogen meter with ion current readout, developed in this program, was calibrated and applied as an on-line hydrogen monitor. Hydrogen removal (Figure 2-1) was monitored continuously by the meter. Since the flux of hydrogen diffusing through the membrane is proportional to the concentration of hydrogen in sodium, and since the current generated by the sputter ion pump is directly proportional to the hydrogen flux, the ion current is a direct measure of the hydrogen concentration in sodium. Hence, Equation (2) can be expressed as

$$\ln_e \frac{I - I_e}{I_0 - I_e} = -\epsilon\lambda, \quad (3)$$

where the subscripts on the ion current "I" have the same meaning as in Equation (2). The calculation of efficiencies from the plot of

$$\ln_e \frac{I - I_e}{I_0 - I_e}$$

versus system turnover (Figure 2-3) showed that creating a hydraulic turbulence in a conventional cold trap increased its efficiency for removal of hydrogen to ~99%, from ~51% for removal of the same species in the same cold trap.

2.2 ON-LINE MONITORING

2.2.1 Plugging Indicator

For routine continuous monitoring of impurities in sodium, the plugging indicator probably is the best measuring tool available at present.

The plugging indicators used for P.A. 15 sodium systems are all of the thermally regenerative design, as shown in Figure 2-4. Of the two orifice plate designs, B was used originally; however, due to excessive pressure drop and difficulty in unplugging, the design was changed to A. Although no difference in plugging temperature was observed, the A design has successfully eliminated the problems associated with B.

The standard plugging run has advanced to an automatically controlled combination of the bare orifice and oscillating runs.^{2,5} It begins with a steady sodium flow rate at >800°F and proceeds with a temperature ramp of -10°F/min. When a temperature ~50 degrees greater than the expected plugging temperature is reached, the ramp is slowed to -1.5°F/min and continues to a minimum temperature of ~220°F. If no plug forms after 2 hours at 220°F, the results are reported as "no break". If a plug does form, the cooling is switched off when the flow reaches ~50% of its initial value, which initiates the oscillating portion of the run. The theory of oscillating runs has been discussed in detail elsewhere.^{1,2} An average of ten oscillations is reported as the oscillating plugging temperature and has proved to be more reproducible than the bare orifice break. By starting with the bare orifice run, all plugging temperatures present are identified.

The useful range of the plugging indicator extends from very high saturation temperatures (>450°F) down to 250 to 300°F. At the lower saturation temperatures, the ability to identify the correct plugging temperature depends significantly on the design and operating techniques used. At higher impurity levels, these factors are less important.

a. Plugging Temperature Correspondence with Cold Trap Temperature

Much of the experience in plugging indicator operation was obtained at two cold trap temperatures: 432°F (high oxygen), and 270°F (low oxygen). Results of over 100 runs are shown in Figures 2-5 and 2-6.

Results obtained in P.A. 15 work show the useful range of plugging indicator data. The high-oxygen run 8-6, for example, shows good reproducibility for both bare orifice and oscillating runs at 432°F cold-trap temperature. Some short-term work at 335°F cold-trap showed good oscillating run values, but the bare orifice results were ~50 degrees lower than expected. At low-oxygen conditions (250 to 270°F cold-trap), plugging indicator results are normally obtainable for only a few days after initiating loop flow. An oscillating run can often be extended for several days or more at these conditions; however, after approximately 1 week at 270°F cold-trap, a plug can usually no longer be formed on a clean orifice. This—a "no break" result—indicates a saturation temperature below ~300°F for a bare orifice run and below ~270°F for an oscillating run. Both cases are well below 5ppm oxygen.

Figure 2-3. Cold Trap Efficiency for Two Modes of Operation

Figure 2-4. Plugging Indicator Design

Figure 2-5. Plugging Indicator Data From Run 8-6 (All Runs, Normal and Off-normal)

Figure 2-6. Plugging Indicator Data From Run 9-3 (All Runs, Normal and Off-normal)

b. Plugging at Temperatures Above that of Cold Trap

The greatest difficulty in interpreting plugging indicator data is in the upper break, or multiple impurity, system. This condition is characterized by two or more plugging breaks in a single run (bare orifice or oscillating). Typically, one of the breaks is at a considerably higher temperature than the cold-trap temperature. Frequently, the lower break, corresponding to the cold trap temperature, is not obtained at all. Multiple breaks often occur in systems that either have inadequate cold trapping or have been exposed to atmospheric contamination shortly before the plugging run.

An investigation was carried out during the program to identify the species causing these high-temperature flow stoppages. A special device (plugging compound collector) was designed to operate as a plugging indicator, but with the capability of collecting amounts of these precipitants large enough to be identified. The details of this work have been published.⁵ It was found that sodium-hydrogen compounds were the materials causing premature stoppage. It was also found that even when only a single break was present, corresponding to the cold-trap temperature 300°F or less, the predominant species was sodium hydride, although sodium oxide was also detected. The persistence of hydrogen compounds in loop sodium at temperatures greater than that of the cold trap is an indication that the conventional trap, without stirring (forced internal turbulence) has low efficiency with respect to hydrogen removal.

2.2.2 On-Line Vacuum Distillation of Oxygen

One of the sodium mass transfer loops (loop 8) is equipped with a vacuum distillation system which has been described elsewhere in detail.⁶ The amount of oxygen found at any given cold-trap temperature was reproducible. Furthermore, the oxygen measured was proportional to the concentration expected on the basis of solubility data⁷, albeit somewhat higher.

Three temperatures of major interest, where a significant amount of data was available, are listed with their values in Table 2-1.

TABLE 2-1
ANALYSIS OF OXYGEN BY ON-LINE VACUUM DISTILLATION

Cold Trap Temperature (°F)	Oxygen Concentration (ppm)
270	2.7±1.8
300	3.5±1.2
432	15±3.2

2.2.3 Electrochemical Oxygen Meter

Some experience was gained with the use of electrochemical cells for the measurement of oxygen in sodium during the test program. Two cells were operated successfully out of approximately 15 attempts. One of the successes was an early UNC Cu/Cu₂O reference electrode, which logged 7500 hours at a controlled temperature of 600°F. During its long time in project loop 8, its operation was characterized by good stability, but with a slight calibration shift during loop shutdown between runs. The initial calibration run (against the cold trap) is shown in Figure 2-7, and indicates a slope close to that of theoretical but the absolute values were somewhat lower than theoretical. The cell broke on restart of the system; i.e., warmup from frozen state.

The second successful cell used a ceramic tube of Zircoa's slip cast variety, which was hydrogen fired; reference electrode was air. The cell was calibrated by oxygen gas addition to sodium. The cell operated for about 4800 hours at 800°F, 700 hours at 1000°F, and 150 hours at 1300°F. It too cracked on startup from sodium in the solid state. The remaining cells either did not function properly to begin with, or cracked after short periods in service, with evidence of sodium attack on the ceramic. The problem of sodium attack on the ThO₂/Y₂O₃ ceramic electrolyte must be solved before this device can be reliably applied in nuclear power plants.

Figure 2-7. Oxygen Meter Calibration Curve

2.2.4 On-Line Hydrogen Monitoring

a. Diffusion Tube Type H₂ Detector

Because of the need for continuous monitoring of hydrogen as an indicator of water or steam leaks in LMFBR secondary systems, and because the presence of hydrogen in sodium causes problems in interpretation of plugging indicator traces, strong incentive exists for developing an on-line hydrogen meter. Diffusion type hydrogen monitoring devices have shown considerable promise for measuring the partial pressures of hydrogen in liquid sodium systems.^{8,9,10} These devices employ a thin diffusion membrane (nickel or stainless steel tube) which is submerged in liquid sodium. A high vacuum is maintained on the inside of the membrane, which allows the hydrogen to diffuse from the sodium into the vacuum. Earlier, it was shown that the current of the sputter ion pump used to maintain the high vacuum is proportional to the hydrogen content of the sodium.¹⁰

A study was undertaken to develop the hydrogen detector as a standard process instrument for sodium-cooled fast breeder reactor systems.

A Type-304 stainless steel diffusion tube (see Figure 2-8) was selected because of its resistance to attack by sodium and for its high permeability to hydrogen diffusion. Although nickel is sometimes used as the diffusion tube material, it is subject to a higher corrosion rate than stainless steel, and to deposition of iron and chromium on the membrane which may change its diffusion characteristics.

The effect of sensor temperature on the behavior of the H₂ detector was studied at various concentrations of hydrogen in sodium, controlled by adjusting the cold trap temperature. The ion current generated by a sputter ion pump in the vacuum side of the diffusion tube was used to monitor the flux of hydrogen diffusing through the membrane.

Because the limiting step for diffusion of hydrogen is the diffusion through the stainless steel wall, the hydrogen flux is exponentially dependent on the diffusion-tube temperature:

$$\text{ion current} \propto \text{H}_2 \text{ flux} \propto \exp(-Q_D/RT), \quad (4)$$

where

Q_D = activation energy of the diffusion process,

R = gas law constant,

T = absolute temperature.

An experiment was conducted to calibrate a hydrogen meter, consisting of a Type-304 stainless steel membrane and a sputter ion pump readout. Before the start of the experiment to calibrate the hydrogen meter, the stirred cold trap was heated in order to remove impurity deposits. Then the conventional cold trap was operated at 250°F for several days to clean up the loop sodium. After the cleanup, the conventional trap was valved out of the system and hydrogen was added to the loop by bubbling a mixture of hydrogen and argon under the sodium surface in the cold zone surge tank. The hydrogen was then collected in the stirred cold trap, and the trap temperature was used to control the hydrogen concentration in the loop sodium.

A matrix of points was determined by measuring the sputter ion pump current versus the sensor temperature at four cold-trap temperatures. The results are shown in Figure 2-9. The data were fitted to the equation:

$$\text{Log } P_{\text{H}_2} = \text{Constant} - Q_D/RT, \quad (5)$$

where

P_{H_2} = pressure inside the diffusion tube,

T = absolute sensor temperature,

Q_D = activation energy of the diffusion process, and

R = gas law constant,

by the method of least squares. The values for Q_D were computed to 95% confidence limits and are shown in Figure 2-9.

Figure 2-8. Hydrogen Diffusion Meter with Ion Current Readout

Figure 2-9. Temperature Dependence of Hydrogen Meter (Type-304 Stainless Steel Membrane)

The temperature dependence of the flux of hydrogen "J" permeating through the diffusion barrier can be expressed as:

$$J \propto (p_1^{1/2} - p_2^{1/2}) \exp\left(-\frac{Q_D}{RT}\right) \quad (6)$$

where

- p_1 = partial pressure or activity of hydrogen in sodium,
- p_2 = apparent partial pressure of hydrogen in the vacuum side,
- Q_D = activation energy of diffusion of hydrogen through the membrane, and
- T = temperature of the sodium at the sensor.

Since the partial pressure of hydrogen on the vacuum side is considerably lower than the partial pressure or activity of hydrogen in sodium (p_1), Equation (6) becomes

$$J \propto p_1^{1/2} \exp\left(-\frac{Q_D}{RT}\right). \quad (7)$$

Using the Clausius-Clapeyron approximation, the temperature dependence of the partial pressure or activity of hydrogen, p_1 , in sodium at constant concentration of hydrogen, can be expressed as

$$p_1 \propto \exp\left(\frac{-\Delta\bar{H}}{RT}\right), \quad (8)$$

where $\Delta\bar{H}$ is the partial molar heat of solution of hydrogen in liquid sodium below saturation. Hence, Equation (7) becomes

$$J \propto \exp\left(-\left(\frac{\frac{\Delta\bar{H}}{2} + Q_D}{RT}\right)\right). \quad (9)$$

As can be seen from Figure 2-9, at higher concentrations of hydrogen (>2 ppm, 240°C cold trap temperature^{1,2}), the Q_D obtained in this experiment is found to be 15.7 kcal, which is in good agreement with gaseous diffusion data.¹¹ This result indicates that at higher concentrations of hydrogen, the diffusion of hydrogen through the membrane is the rate controlling step and that the activity of hydrogen in sodium is independent of temperature, which is also in agreement with the literature.¹² However, at lower hydrogen concentrations (<2 ppm), the Q_D value obtained in this experiment is 13.5 kcal, indicating that the hydrogen activity below the saturation concentration of hydrogen decreases with sodium temperature, and contradicting other observations.^{12,13,14}

Calibration of specific hydrogen meters will depend on design and application factors such as temperature, effective membrane area, and membrane composition. It should be noted that changes in the composition of the membrane due to mass transfer effects, corrosion, and deposition in sodium can be expected to affect long-term stability of hydrogen meter calibrations.

In summary, the conclusions of the study are:

- The activity of hydrogen in the cover gas and the sodium of an LMFBF coolant system is controlled by cold trap temperature.
- At lower concentrations of hydrogen (<2 ppm), the hydrogen activity decreases with increasing sodium temperature. This is believed to be due to the interaction of oxygen with hydrogen as the molar ratio of hydrogen and oxygen approaches unity.
- At higher concentrations of hydrogen (>2 ppm), the hydrogen activity in liquid sodium is independent of temperature. This implies that the heat of solution of hydrogen in sodium is zero.
- In a cold-trapped dynamic sodium system, permeation of dissolved hydrogen through a stainless steel membrane is a diffusion-controlled process.

- The chemical potential of hydrogen and the membrane temperature and composition uniquely determine the hydrogen permeation rate into a vacuum.
- The thermodynamic behavior of hydrogen in a flowing liquid sodium system under a temperature gradient can be determined by studying the rate of permeation of hydrogen from sodium through a membrane.

b. Cover Gas Chromatography

To check the assumption that the hydrogen concentration in the sodium was controlled by the cold trap, the partial pressure of hydrogen in the cold-zone surge tank was measured by gas chromatography. The results of these measurements, which are plotted in Figure 2-10, indicate that the partial pressure of hydrogen in the cover gas is in good agreement with the dissociation pressure of sodium hydride in equilibrium with liquid sodium. This agreement implies that the hydrogen concentration in the sodium and the cover gas of a dynamic sodium system is controlled by the cold-trap temperature.

The line in Figure 2-10 is the result of correlating the present partial measurements with the sodium hydride dissociation pressure measurements of a number of other investigators.¹⁵⁻²² The measurements, which span a range of nearly nine orders of magnitude, were fitted to Equation (10) by the method of least squares:

$$\log_{10} p_{H_2} = 11.6 \pm 0.2 - \frac{6100 \pm 100}{T} \quad (10)$$

where

- p_{H_2} = partial pressure of hydrogen, torr,
 T = hydrogen saturation temperature, °K, and
 $\pm$ = indicates 95% confidence limits.

Figure 2-10. Dissociation Pressure of NaH in Equilibrium with Na(l) Versus Temperature

2.3 ANALYTICAL CHEMISTRY

2.3.1 Oxygen by Amalgamation

A flow-through pipe sampler^{2,3} (see Figure 2-11) was developed and used for sodium sampling on all loops. The flow-through, or on-line, sampler is a length of 1/2-inch-diameter stainless steel tubing used to sample loop sodium at specified operating conditions. These conditions have ranged from approximately 500 to 1300°F in the project loops. After the fabricated sampler is cleaned with reagent grade acetone, it is connected into the loop sampling manifold with threaded connections, and the sampler is preheated and evacuated to <10 microns before initiating sodium flow.

Sodium is pumped through the tube to remove surface contamination as well as to ensure that a representative sample of the loop sodium is obtained. A flow-through period of 4 hours minimum has been employed for sampling sodium at temperatures 600°F or higher. For lower temperatures, the flow-through period is increased to at least 8 hours. The tube is then valved off, quickly cooled to freeze the sodium, removed from the loop, and sealed.

The standard procedure used for the amalgamation analysis was initially tested in the ASTM round robin,^{1,2} and subsequently proposed as a standard by the National Analytical Standards Working Group.^{2,2} Toward the final days of the project, a high blank, uncorrected for in the procedure, was discovered. This had led to data which were biased high. The blank was due to contamination on the outer walls of the sampling tubes, probably moisture, which was not removed by either evacuation or equilibration in the dry box atmosphere. The blank was reduced from the 20 to 30 µg range to 6 µg by changing the mode of surface cleaning from grit blasting to wire brushing. In addition, a revision was made in the procedure to include the tubing blank as well as the usual operational blank.

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Figure 2-11. Flow-through Sampler

The standard amalgamation procedure assumes the separated impurity consists only of sodium oxide while it is known that other alkaline species; e.g., sodium hydride, sodium carbonate, and sodium hydroxide may be present and may lead to erroneous results. To obtain more specific data for oxygen, a new procedure was developed to correct for the presence of residual sodium hydride and sodium carbonate. The procedure also permits analysis for hydride hydrogen and for carbonate on a single sample. The method involves (a) in-box amalgamation under vacuum, (b) removal of the vessel to a vacuum system after amalgamation is complete for determination of hydrogen, (c) addition of water followed by determination of hydrogen (i.e., that evolved from undecomposed hydride), (d) addition of dilute acid followed by analysis of gases released (i.e., those resulting from decomposition of carbonate), and (e) analysis of the acidified sample for total sodium. The data from steps (b) and (c) give the amount of total hydride. The data from step (d) give the carbonate present. The data from steps (c) and (d) permit correction of the total alkalinity value (data from step (e) for undecomposed hydride and carbonate). The corrected value reflects only Na_2O and NaOH in the samples.

Termination of the P.A. 15 program limited the number of analyses performed by this technique, and it was applied only before the blank procedure was changed as described above. The results of analyses performed were reported in Reference 23. Further development and application of this technique will be conducted in future work.

The data obtained by the standard method with the improved blank correction are listed against cold trap temperature for a number of loop samples in Table 2-2.

Table 2-2
SUMMARY OF TOTAL ALKALINITY DATA
FLOW-THROUGH SAMPLES – AMALGAMATION DETERMINATION

Sample Designation	Total Alkalinity (ppm)	Cold Trap Temperature (°F)
a. Data obtained at cold trap temperatures around 300°F		
1R-1-7A	9.5	290
4R-2-9	3.8	294
4R-2-12A	2.9	290
5-5-5	7.0	300
6-2-1	7.6	290
6-4-2	3.9	300
8-5-2A	5.0	310
8-5-4A	7.5	295
9-2-16	5.5	292
9-2-18	6.4	292

Mean = 5.7 ± 2.0 ppm

b. Data obtained at 270°F cold trap temperature

4R-2-14	5.4
4R-2-21	6.0
4R-2-26	5.9
4R-2-27	6.1
5-5-22	4.6
6-4-13	4.1
6-4-16	4.8
6-4-21	4.0
8-6-34	5.1
9-3-19	3.5
9-3-20	3.4

Mean = 4.8 ± 1.1 ppm

Table 2-2 (Continued)

Sample Designation	Total Alkalinity (ppm)	Cold Trap Temperature (°F)
--------------------	------------------------	----------------------------

c. Cold trap at 250°F and stirred

9-3-21	3.3
9-3-24	3.2
9-3-25	2.5
9-3-26	2.0
9-3-27	4.9
9-3-28	5.1

Mean = 3.5 ± 1.2 ppm

d. Cold trap temperature 432°F

1R-3-1A	48
1R-3-2A	17
1R-3-3A	37
1R-3-5A	14
1R-3-6A	22
1R-3-8A	19
8-6-16A	47
8-6-17A	27
8-6-18A	35
8-6-19A	36
8-6-20A	33
8-6-22A	24

Mean = 30 ± 11 ppm ($\pm 1\sigma$)

e. Cold trap temperature below 250°F.

5R-5A-2A	2.8	250
5R-5A-3A	1.7	240
5R-5A-4A	2.8	230
5R-5A-5A	1.4	220
5R-5A-6A	2.8, 2.5	215

- The data in Section a. of Table 2-2 reflect operation of a number of systems where the cold-trap temperature was maintained at about 300°F, when the precise temperature control of the cold trap and full-time operation of the trap, discussed earlier, were not in effect. The mean total alkalinity was 5.7 ± 2.0 ppm.
- The data in Section b. were for samples taken with higher precision temperature control at 270°F and full-time operation of the cold trap. The results, 4.8 ± 1.1 ppm total alkalinity, show a lower impurity level and less scatter. The modified method was also used for the analysis of several of these samples. A result of 2.0 ± 2.0 ppm oxygen was obtained, which reflects the correction for the presence of the non-oxide impurities.
- A brief period of operation at 250°F in which the crystallizer zone of the cold trap was stirred in the manner discussed previously led to still lower data, 3.5 ± 1.2 ppm (Section c., Table 2-2).
- Section d. shows data obtained when two systems were deliberately run at high oxygen levels, i.e., at a cold trap temperature of 432°F. The mean value obtained was 30 ± 11 ppm total alkalinity. The more specific technique gave a value of 13 ± 2 ppm oxygen, showing that at higher cold-trap temperatures the amounts of non-oxide impurities are large.
- Section e. shows results of analyses from loop 5R when the cold-trap temperature was lowered in steps to 215°F.

It should be noted that precision of the analyses is probably better than that shown since the data also include the errors associated with sampling and with loop control over an extended period.

It is clear that all the methods are in reasonable agreement and all are capable of reaching the specification limits for oxygen in sodium less than 5 ppm. The results are also in fair agreement with the saturation solubility value at 270°F, 1.6 ppm. Thus, these methods are all acceptable tools for the routine surveillance of oxygen in sodium.

Of these techniques, the plugging indicator is the most satisfactory tool for this purpose since it can be run continuously on-line. Distillation, although it is capable of greater reproducibility and is more specific, is essentially an in-line grab method and has the further disadvantage of requiring sophisticated equipment and operation. The standard amalgamation technique, like any laboratory method, has the disadvantage of potential sampling errors and does not provide continuous data. However, it is a good backup to the plugging indicator, can be run rapidly with good precision, and has the advantage of the longest history of application and the most extensive testing and standardization of any of the methods. The improved amalgamation technique requires more complicated equipment and operation but does have the advantage of being more specific and in addition, yields information on hydride and carbonate content.

However, since distillation, amalgamation, and plugging measurements are not specific for oxygen, they tend to be biased high and do not provide a true value, particularly as the oxygen concentration decreases to low levels; e.g., less than 2 ppm. Thus, these tools are not adequate when exact oxygen concentrations are needed.

Both the electrochemical cell technique and the vanadium wire method give promise of surmounting the specificity problem; i.e., they respond only to oxygen. A properly operating cell is the ideal tool since it gives continuously valid estimates for the oxygen activity. The difficulties in obtaining such a cell have been discussed.

The vanadium wire technique should also measure the oxygen activity although it depends on an experimentally determined distribution coefficient. Experience with its use is meager and the effect of possible interferences is under study. It is essentially an instantaneous method rather than a continuous one. Thus, when proven, it will substitute for amalgamation as a backup to on-line methods.

2.3.2 Refractory Metal Wire Equilibration

Vanadium wires were exposed to loop sodium in run 5R-5A, at a cold-trap temperature of 250°F, the analysis showed 0.96 ± 0.1 ppm. Vanadium wire exposure was in accordance with Standard Procedure No. 7, ANL/ST-6, January 1971.

A summary of the oxygen determinations at 270°F cold trap temperature by various methods is shown in Table 2-3.

Table 2-3
MEASUREMENT OF OXYGEN AT 270°F COLD TRAP TEMPERATURES

Method of Measurement	Oxygen ppm
On-Line Distillation	2.7 ± 1.8
Plugging Indicator	< 2.7 (a)
Standard Amalgamation (Total Alkalinity)	4.8 ± 1.1
Specific Amalgamation (Oxygen)	2.0 (b)
Vanadium Wire	0.96 ± 0.1 (250°F Cold Trap)

(a) The less-than value is used since the majority of actual data points showed "no break".

(b) Precision has not been established but at these low concentrations it is estimated to be within 50%.

2.3.3 Analysis of Carbon and Metals

a. Carbon Analyses

The monitoring of these species was less frequent because no direct relationship was apparent between the data obtained and the phenomena under study in the loops.

Typical data for the analysis of carbon in loop sodium range from 15 to 65 ppm. The procedure used is the "wet combustion" technique, published as a project topical report.²⁴

A typical sample of loop sodium was analyzed by this technique at G.E.-VNC, and at two other laboratories by high temperature combustion techniques. The data were as follows:

Laboratory	Carbon (ppm)
WADCO	1.7
EBR-II	0.5 ± 0.1
G.E.-VNC	15.0 ± 5.0

The large discrepancy in the results remains unexplained. No source of contamination has been found to cause the high G.E. results, and there are no apparent losses in the procedures followed by the other laboratories to account for the lower results. This observation should be investigated. However, more important is the fact that no laboratory technique has yet successfully indicated a carbon potential in a flowing system. Thus, emphasis should be placed on the development of an electrochemical, or on wire or tab techniques for the determination of carbon activities.

In addition, some interesting observations relative to carbonate were made during the course of the studies. Carbonate is apparently present in all loop samples in the range of 1 to 5 ppm expressed as carbon. This was observed during the standard carbon analysis, and confirmed by distillation and amalgamation data.

b. Analysis for Metals

Analyses for metallic impurities were performed by conventional emission spectrographic or spectrophotometric techniques. Typical results appear in the following table:

Metal Impurity	Concentration (ppm)
Fe	2 to 10
Cr	1 to 7
Ni	0.5 to 2
Ca	1 to 5

Difficulties were encountered with obtaining uncontaminated representative sub-samples from flow-through sampler tubes. The combination of over-flow cup sampling followed by distillation is a better approach. It was noted that particulates may be present, and mild dissolution techniques are insufficient to put the metals quantitatively in solution. This is probably also true for the overflow cup samples and, thus, a vigorous dissolution technique should be applied to all residues in which metallic species are sought.

c. Miscellaneous Analyses

Several other species have been analyzed for special purposes during the course of the program and are shown in Table 2-4.

Table 2-4
ANALYSIS OF THE NON-METALS IN SODIUM

Species	Concentration (ppm)
Chloride	0.4 to 1.0
Silicon	<0.5
Cyanide	0.05 to 0.6

2.4 HYDROGEN-OXYGEN INTERACTION

Since hydrogen has been a persistent impurity in the mass transfer systems, the potential for interaction with oxygen required assessment, particularly insofar as the effects on monitoring devices were concerned. Specifically, the effect of hydrogen on the electrochemical oxygen meter, and oxygen on diffusion measurements of hydrogen, required evaluation.

A test apparatus was constructed (see Figure 2-12) consisting of a stainless steel pot with a stirrer, provided with means for gaseous additions of hydrogen and oxygen. A uranium foil was used to reduce the oxygen level, and a diffusion tube to reduce the hydrogen content. Oxygen was monitored with an electrochemical cell, and hydrogen both by chromatography in the cover-gas phase and by the diffusion tube meter with ion current readout.

Two types of experiments were run. In the first experiment, oxygen was gettered by uranium foil to a low value, 0.7 ppm. Known increments of hydrogen were added. The EMF of the oxygen cell was monitored, and the change in ion current noted after each addition. The data (Table 2-5) show that oxygen activity did not change within the measurement error (± 0.005 mV or ± 0.1 ppm). The range of hydrogen present in the pot during the test was from 0.1 to 5 ppm.

Table 2-5
OXYGEN-HYDROGEN INTERACTION DATA

	ΔH , in Sodium (ppm)	EMF of Oxygen Meter (Volts)	Oxygen (ppm)	Δ Ion Current (Hydrogen) (Microamperes)
Section A	0.19	1.820	0.7	18
	0.19	1.822		19
	0.70	1.817		44
	1.06	1.820		63
	1.09	1.815		60
	2.20	1.820		109
	2.16	1.824		110
	2.20	1.823		110
Section B	0.74	1.680	90	46
	1.09	1.702	50	62
	1.09	1.700		60
	1.28	1.720		70
	1.09	1.720	25	60
Section C	1.09	1.800	2	01
	1.09	1.773		59
	1.09	1.756		60
	1.09	1.732	16	59

Figure 2-12. Hydrogen-Oxygen Interaction Apparatus

In the second experiment, a large amount of oxygen, 90 ppm, was added. A known increment of hydrogen was added, and the change in ion current noted. The oxygen was gettered to a lower oxygen level in stages, and the addition of hydrogen was repeated. These data are shown in Section B of Table 2-5. The same experiment was carried out in reverse; i.e., hydrogen was added to the system gettered to 2 ppm oxygen, and then oxygen was added in stages up to 16 ppm while the response of ion current was recorded for hydrogen addition at each stage. Section C of Table 2-5 provides the data.

An examination of Table 2-5 shows that the response of the ion current, which is proportional to the hydrogen content of the sodium is the same for a given increment of hydrogen regardless of the oxygen in the system. For example, for an addition equivalent to 1.09 ppm hydrogen at 0.7 ppm oxygen, the ion current change is 60 μ A; at 25 ppm oxygen, it was also 60 μ A; and at 16 ppm oxygen, it was 59 μ A.

In summary, the data indicate that over the concentration ranges of normal interest—hydrogen 0.1 to 5.0 ppm, oxygen 0.7 to 90 ppm—there is no apparent interaction between the species, and no effect of one species on the monitoring of the other. The data here were predominantly taken at 800°F; a limited amount obtained at 1000°F also showed no interaction. Data obtained by experimenters at Brookhaven National Laboratory which were taken in a flowing system, disagree with these findings. The cause for disagreement has not been found.

2.5 LIST OF ACCOMPLISHMENTS

- The efficiency for hydrogen removal by cold trapping, was nearly doubled, from ~51% for a conventional laminar operation to ~99% for turbulent operation. The effectiveness of a cold trap for oxygen removal showed a similar benefit. This is believed to be due to the increase in the mass transfer coefficient of deposition of the impurities, due to internal stirring.
- Localized high turbulence in the zone of precipitation in a cold trap increase the impurity removal efficiency by a factor of two without increasing the throughput, and should be incorporated in future cold-trap designs.
- Lower impurity levels can be achieved in much shorter time by creating local high turbulence in a cold trap. Use of this concept in reactor systems will permit faster recovery from fault conditions than is possible with a conventional cold trap. Increasing the cold-trap efficiency will enable a plant operator to cope with unpredictable inputs of impurities into the system for a longer time, and reduce the size (cost) of an LMFBR cold trap.
- Analysis of plugging runs indicates that, for loops operating at 270°F, the impurity saturation temperature is less than 300°F. Improvements in PI design and operating procedure have resulted in increased accuracy for PI run results.
- A plugging compound collector has permitted the identification of plug-forming materials from single- and multiple-impurity systems. X-ray diffraction and chemical analysis show the materials to be primarily Na-H and Na-O-H compounds.
- The plugging indicator is the most satisfactory device for continuous purity monitoring in sodium systems. Although a plugging indicator is not a specific instrument, its response to overall impurity changes are reproducible, and provides reliable on-line surveillance.
- On-line distillation yields reproducible values for the oxygen content of a system. However, manipulations are presently complex and limit its usefulness as a routine monitoring device. At levels below 2 ppm, its specificity for oxygen needs further investigation because of potential interferences from other low-level, sodium-containing impurities.
- Although two units operated for over 7000 hours, performance of electrochemical oxygen cells during this program was unsatisfactory. Considerable development of ceramics for the electrolyte is needed before they can be used as reliable instruments.
- The hydrogen concentration in cover gas over sodium is controlled by the temperature of the sodium cold trap.
- At lower concentrations of hydrogen (~ < 2 ppm in sodium), the hydrogen activity decreases with increasing sodium temperature. At higher concentrations of hydrogen (> 2 ppm in sodium), the hydrogen activity in liquid sodium is independent of temperature, which is consistent with data available in the literature.
- In a cold-trapped dynamic sodium system, the permeation of dissolved hydrogen through a stainless steel membrane is a diffusion-controlled process.
- The amalgamation procedure for the laboratory determination of oxygen in sodium has been perfected as a useful backup to the plugging meter. An understanding and correction of the blank problem has extended the useful range of the technique to meet the demands of specifications for this species, <5 ppm.
- A more sophisticated version of the amalgamation has been developed which yields specific data for oxygen and also permits estimation of the hydrogen and carbonate levels in the sodium.

- The laboratory method for hydrogen is of barely adequate sensitivity for loop monitoring. The analysis for this species can be best accomplished on-line with diffusion tube, sputter ion gage techniques, and by gas chromatography.
- The laboratory method for carbon analysis is of value to indicate gross contamination, but is useless in identifying carburization potential. Development of a continuous-reading, on-line carbon activity device is an essential long-term goal; development of a wire or tab technique is needed for the short term.
- The monitoring of other species in loop sodium has surveillance value only to guard against unlikely introduction of contaminants, and should be performed only rarely.
- Over the concentration ranges of normal interest—hydrogen <5.0 ppm, oxygen 0.7 to 90 ppm—there is no apparent interaction between the species and no effect of one species on the monitoring of the other. The temperature range studied was 800°F to 1000°F.

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SECTION 3

CORROSION AND MASS TRANSFER

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3. CORROSION AND MASS TRANSFER

The Corrosion/Deposition studies in the P.A. 15 program were aimed at producing data suitable for use in LMFBR coolant system designs. Tests were conducted to measure accurately the average corrosion rates of selected stainless steels as well as the effects of individual parameters. Seven test loops were operated—both corrosion mock-ups of LMFBR systems and loops designed for studies of specific parameters and effects. All tests were in recirculating, nonisothermal, sodium loops. Test conditions included the following ranges:

Sodium Temperature
 Hot leg — 1300°F
 Cold leg — 800–900°F
 Velocity — up to 28 ft/sec
 On-line cold trap temperature — 210–432°F controlled to $\pm 2^\circ\text{F}$

The precision achieved permitted measurement of the relative corrosion rates of Types 316, 304, 321, and Incoloy-800. Average corrosion rates were determined by weight changes of hollow cylindrical specimens. On-line monitoring of a test of corrosion and deposition of cobalt-60 produced time-dependent data on deposition (radioactivity buildup). A mass balance for cobalt-60 was accomplished from post-test analyses. Also, the first systematic measurements of dimensional changes due to sodium corrosion were made.

The interdependence of velocity, oxygen, and loop position (downstream) was identified in individual parameter tests.

Both the cobalt-60 test and the observation of deposition of chromium and nickel on pure ion samples in a corroding zone (where adjacent stainless steel was losing chromium and nickel) led to the hypothesis that the Mass Transfer process is a form of atomic exchange with a driving force related to solution and activity gradients between the alloy metals and sodium.

3.1 CORROSION

Types-304 and -316 stainless steel have been selected as structural materials for fuel cladding, control rod cladding, core components, and the primary-secondary piping systems of the sodium-cooled FFTF reactor.¹

To explore the limits of performance of stainless steels at potential hot-spot conditions, extended corrosion studies have been conducted at 1300°F. More detailed evaluations of the effects of velocity, downstream and oxygen were also made.

One of the LMFBR Mockup Loops used to study corrosion and mass transfer in an all austenitic stainless steel system is shown in Figure 3-1. Detailed descriptions of the loop and sample configurations were reported in 1967.² The nominal range of operating conditions is shown in Table 3-1.

Table 3-1
 NOMINAL OPERATING CONDITIONS

Hot-leg material	316 SS
Cold-leg material	316 SS and 304 SS
Hot-leg temperature	1300°F
$\Delta T^\circ\text{F}$	400 to 500°F
Hot-leg velocity	3 to 28 ft/sec
Cold-leg velocity	3 to 15 ft/sec
Cold trap temperature	270°F and 432°F
Oxygen concentration by chemical analyses	<5 ppm and 15 ppm
Exposure time	to 3500 hours

Figure 3-1. LMFBR Corrosion Mock-up Loop 8

3.1.1 Effect of Velocity on Corrosion Rate

The corrosion rate of Type-316 stainless steel at 1300°F is shown in Figure 3-2 as a function of velocity at several downstream[†] conditions. In the velocity range up to about 20 ft/sec, the dependence of corrosion rate on velocity is approximately linear in accordance with previous results. With increasing velocity, the dependence becomes much less. For comparative purposes, available United Kingdom (U.K.) data at 1200°F³ are included in Figure 3-2; they show similar trends of alloy corrosion with increasing velocity.

The effect of sodium velocity on corrosion rate suggests that the rate-determining step in the corrosion process is velocity-dependent in the low-velocity range. This hypothesis is valid in the temperature range 1200 to 1300°F. At lower temperatures the diffusivity of the solute atoms through the laminar boundary layer will be slower. Consequently, one may expect that at lower temperatures the effect of velocity on corrosion will be somewhat different. These data support the hypothesis⁴ that up to approximately 12 to 20 ft/sec, the diffusion of solutes and/or corrosion products across the liquid boundary layer is rate-determining. At higher velocities, the laminar boundary layer of the liquid diminishes sufficiently so that a surface reaction rate becomes the rate-controlling step and is independent of velocity. The thickness of the laminar boundary layer depends both on the fluid velocity and pipe dimension. Hence, if the present hypothesis is correct, the critical velocity at which corrosion becomes independent of velocity will depend on the flow change geometry. Consequently, the critical parameter to describe corrosion is the thickness of the laminar boundary layer rather than the sodium velocity. An attempt was made to correlate the limited corrosion data in the literature (where the geometry and sodium flow are known). The thickness of the laminar boundary layer, at various conditions, was calculated using the following equation from Schlichting.

The laminar boundary layer thickness in a pipe:

$$\delta = 5 \times \frac{\nu}{V_*}$$

$$V_* = \sqrt{\tau_0/\rho}$$

$$\tau_0 = 0.04 \times \rho \times V_{AV}^{7/4} \times \gamma^{1/4} \times d^{-1/4}$$

where

- ρ = sodium density,
- V_{AV} = average velocity,
- ν = kinematic viscosity = μ/ρ ,
- d = diameter, and
- μ = absolute viscosity.

A plot of corrosion rate versus boundary layer thickness is shown in Figure 3-3. The data from G.E., Westinghouse, and the U.K. seem to indicate that the corrosion rate of steels becomes independent of fluid turbulence below a boundary layer thickness of 0.0002 inch. Figure 3-4 shows a plot of boundary layer thickness as a function of velocity at several pipe diameters. The theoretical explanation for the convergence of two curves is that as the boundary laminar layer thickness increases, corrosion rate decreases, until the boundary layer thickness becomes so thick (e.g., static sodium) that corrosion rate approaches zero. Consequently, both curves converge toward zero corrosion rate.

The oxygen level of loop 3R was below 5 ppm, based on cold trap temperature, but no flow-through samples were taken for chemical analysis during the run. The effects of oxygen level on corrosion rate were therefore not evaluated. Also, since the limited data indicate a very low corrosion rate, the data must be considered somewhat uncertain. Further study at various oxygen levels and higher corrosion rates will be necessary to further determine the nature and relationships of the variables.

[†]The term "downstream" is used to signify that the quantity of corrosion product in the sodium changes an incremental amount, over a finite distance along the loop, as it seeks equilibrium saturation at a rate corresponding to the driving force for corrosion or deposition at the point.

Figure 3-2. Corrosion Rate at 1300°F As a Function of Sodium Velocity at an Oxygen Level of Less than 10 ppm

Figure 3-3. Influence of Laminar Boundary Layer Thickness on the Corrosion of Stainless Steels

Figure 3-4. Boundary Layer Thickness in Pipes
Sodium at 1300°F

To verify the hypothesis and to determine the critical parameter, tests were planned in loop 3R (described corrosion specimens. Limited data from loop 3R obtained in the thicker boundary layer (low corrosion) range, as shown in Figure 3-3, are in agreement with existing data. It is believed that comparison of corrosion data from various investigators in various loops should be made on the basis of thickness of the laminar boundary layer and not the sodium velocity per se. Finally, it is recommended that the extrapolation of the corrosion data from small loops to large systems should be made on the same basis.

3.1.2 Effect of Downstream (L/D) on Corrosion

The corresponding effect of downstream on corrosion rate at 1300°F is shown in Figure 3-5 at several velocity levels. The reduction in corrosion rate with increasing downstream can be attributed to the increase in the chemical activities of solute (corrosion products) elements in sodium as they are removed from the alloy steel.

It is interesting to note that the effect of downstream (L/D) on corrosion depends on the sodium velocity (boundary layer). At higher velocity (higher corrosion), the corrosion of steels predictably decreases more sharply with downstream (L/D) than at lower velocity (lower corrosion). Hence, the present data indicate that effect of velocity (boundary layer thinning) and downstream (L/D) on corrosion are dependent on each other.

3.1.3 Effect of Oxygen on Corrosion

A high-oxygen (432°F CT temperature) corrosion test was completed during this period. The cold trap in loop 8 was stacked with Na₂O in order to maintain a high oxygen level. The resulting corrosion rates of Type-316 stainless steel are shown in Figure 3-6, along with low-oxygen (270°F CT temperature) corrosion data which were obtained at the same velocity and temperature conditions.

As can be seen in Figure 3-6, there is a considerable increase in the corrosion rate due to the increase in oxygen concentration. The most interesting feature of the results is that downstream (L/D) has a much stronger effect on corrosion rates at higher oxygen levels. This is caused by the higher corrosion rates at upstream positions, and more rapid saturation of the sodium with corrosion products, which decreases the chemical driving force for corrosion at downstream positions. This observation also emphasizes the point that effects of oxygen concentration on corrosion rates of stainless steels are dependent on the downstream position of the sample. For example, at zero downstream (extrapolated value), the corrosion rate of stainless steel is 0.5 to 2.75 mils/year (~5 times) for cold-trap temperatures of 270 to 432°F, respectively. However, at a downstream position of ~540, the corrosion rate is greater by only a factor of 2 (from 0.25 to 0.5 mil/year. It is generally agreed that the oxygen dependence for corrosion of stainless steels (presumably at zero downstream position) is about 1.0 to 1.2 to the power of oxygen [$O_x^{1.0-1.2}$]. The oxygen dependency of corrosion at zero downstream position, based on on-line vacuum distillation analyses for oxygen, was found to be [$O_x^{1.0-1.2}$]. However, if Eichelberger's recommended oxygen solubility expression⁷ is used to calculate the oxygen coefficient, then the oxygen dependence of corrosion becomes [$O_x^{0.63}$].

Assuming that the oxygen dependence of corrosion to be [$O^{1.0-1.2}$], the present data indicate that the temperature dependence of Eichelberger's⁷ recommended oxygen solubility expression is not correct.

3.1.4 Effect of Temperature on Corrosion

Phase I of P.A. 15 produced statistical corrosion rate data for a matrix of variables. Primary variables were maximum loop temperature, oxygen (cold trap temperature), materials (Type-316 stainless steel, 2-1/4 Cr-1 Mo, 5 Cr-1/2 Mo-Ti), and Loop ΔT. Secondary variables were velocity, temperature, and time. Downstream distance was recognized as a variable from measured weight change results. The data had a large variance factor: 95% of the test sample corrosion rates within a factor of 5 compared with the average.

In Phase II, initial objectives were to decrease the uncertainty factor, and it was reduced to a factor of about 1.4. Upper limits were used in estimating corrosion rates. The data are listed in Table 3-1A.

The average corrosion rate from Phase II for 1300°F, 22 ft/sec, cold trap temperature 270°F, is 0.84 ± 0.3 mil per year (extrapolated linearly to zero downstream).

In the high oxygen run (15 to 20 ppm) (Run 8-6, Phase II), the effects of downstream and velocity were found to depend on each other. As can be seen in Figure 3-6, downstream has a much stronger effect at higher oxygen concentrations. The increased corrosion rate causes more rapid saturation of sodium by corrosion products, thereby decreasing the solution potential at downstream positions (other factors constant). Therefore, it is concluded that a general corrosion equation with single variation terms (such as generated in Phase I) is inaccurate to the extent that cross-product terms (two or more variables per term) are required to correlate test results.

Figure 3-5. 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

Figure 3-6. Comparison of Corrosion Rates of Type-316 Stainless Steels in High-Oxygen and Low-Oxygen Sodium

Table 3-1A
EFFECT OF TEMPERATURE ON CORROSION

Temperature (°F)	Corrosion Rates (mils/yr)	
	Phase I (a) Average	Phase II (b) Upper Limits 95% Confidence Range
1300	0.95	1.15
1200	0.39	0.65
1100	0.15	0.33
1000	0.05	0.17

(a) GEAP-4831

- Cold trap temperature 305°F. Velocity and downstream not separated.
- Velocity 20 ft/sec
- $\frac{\text{Maximum Corrosion Rate}}{\text{Average Corrosion Rate}} \approx 5.3$

(b) GEAP-13671

- Cold trap temperature 270°F
- Velocity >22 ft/sec (velocity-independent range)
- $\frac{\text{Maximum Corrosion Rate}}{\text{Average Corrosion Rate}} \approx 1.4$
- All data extrapolated linearly

For design purposes, corrosion rates as recommended in GEAP-13761, GEAP-13544, and this report should be used. For other conditions outside the test range, the current state-of-the-art forces the designer to ratio the rates, using data in Table 3-1A. At conditions near 1300°F at >22 ft/sec, with oxygen controlled by on-line cold traps at 270°F or below, the error involved in using the assumption will be acceptably small. These conditions were chosen as typical of LMFBR core hot-spot (maximum corrosion rate). Conditions which vary widely from these will be at lower temperatures or lower velocities, and consequently lower corrosion rates. Intermediate heat exchangers and steam generators are not expected to corrode. Carbon movement is discussed in Section 4. Carburization and decarburization rates at lower temperatures will be studied in follow-on work.

3.1.5 Corrosion Data Correlation

A general observation that may be implied by the foregoing results is that a change in any parameter which affects corrosion rates will change the downstream effect when impurities are not at saturation solution concentration. The data from this program show that effects of oxygen, velocity, and downstream are interdependent. However, the effects of temperature on the oxygen, downstream, and velocity were not studied, nor was the effect of oxygen concentration on velocity. The data in Figures 3-5 and 3-6 show that oxygen and downstream are interdependent variables.

The equation that correlates these data is:

$$\text{C.R.} = -0.33 - 0.119(X_O) + 1.7 \times 10^{-4} (L/D) + 1.98 \times 10^{-4} (X_O) (L/D)$$

where:

C.R. is corrosion rate, mils per year,

X_O is oxygen concentration in ppm (unsaturated).

Further test data are needed to generate a more general analytical expression for corrosion as a function of velocity, downstream, oxygen, and temperature.

3.1.6 Mass Transfer of Major Alloy Constituents

The movement of various alloying elements around the experimental loop was monitored by x-ray fluorescence analysis of surface compositions of the hot- and cold-leg samples from all experiments. Representative results are shown in Figures 3-7 and 3-8. The data show the change of the elemental compositions at the surface after exposure at various positions and temperature distributions in the loop. For comparative purposes, the total weight change is also shown.

In all experiments, selective leaching of chromium, nickel, and manganese was observed; this increased with the increase in total corrosion. Results show that the nature of the relative movements of alloy constituents in stainless steel will be sensitive to sodium velocity, oxygen level, and temperature. In Figures 3-7 and 3-8, the corrosion and deposition of various elements' patterns for the two separate experiments are shown. Although the relative change in composition of chromium and nickel at the surface was radically different, the selective leaching of manganese, within experimental error, was not affected. An increase in corrosion, shown in Figure 3-8, was due to higher velocity for that experiment. The increase in total corrosion for the high-velocity run resulted in an increase in nickel and chromium movement, but the increase of nickel movement was greater than that of chromium. Therefore, nickel loss due to corrosion is much more sensitive to velocity than chromium loss at equal oxygen concentration.

Based on the stability of double oxide of sodium and chromium, it was postulated that the removal of chromium from stainless steels involves reaction with oxygen at the surface.⁹ If this model is correct, then one should expect the selective leaching of chromium to be affected by oxygen concentration in sodium. Figure 3-8 shows that an increase in oxygen concentration (432°F CT temperature) radically increased the chromium depletion, which indicates that chromium movement does involve reaction with oxygen. The movement of nickel, however, was not changed by increase in oxygen concentration. The corrosion of nickel base alloys was found to be independent of oxygen concentration.³ The present data are consistent with that observation.

A few pure iron samples were inserted in a loop in order to determine the effect of substrate composition on mass transfer; the results are shown in Figure 3-10. The iron samples in the hot leg picked up a considerable amount of nickel and chromium, whereas the adjacent stainless steel specimens lost both metals.

This observation implies that concentrations of nickel and chromium in sodium in the hot leg were below saturation. Consequently, the deposition mechanism of these metals on the iron samples was by an atomic exchange due to activity gradient of the solutes between the iron and sodium. The movement of interstitials, minor elements, and microstructural changes are discussed in detail in Section 4.

3.2 DEPOSITION

The deposition of corrosion products in sodium systems is likely to influence hydraulic and heat transfer characteristics, and control the rate and locations of radioactivity buildup. Consequently, it is important to study the nature, degree, and rate of deposition in sodium systems.

3.2.1 Effect of Velocity and Downstream on Deposition Rate

In an isothermal region, the flowing sodium tends to saturate with respect to solute elements (corrosion products). As the sodium enters the first cooler (Zone J in Figure 3-1), the sodium temperature decreases, and the sodium becomes slightly supersaturated with respect to dissolved elements. The degree of supersaturation depends on the temperature coefficients of the solubility of various elements and on the amount of solutes present.

The effect of sodium velocity on the rate of deposition in an isothermal region is shown in Figure 3-10. The rate of deposition, like the rate of corrosion, increases with the increase of sodium velocity. As the velocity is increased, the degree of turbulence increases, and the thickness of the liquid boundary layer decreases. It is believed that turbulence enhances (1) the nucleation of particulate in the bulk stream, (2) the frequency with which these particulates can move through the liquid boundary layer and impinge on the substrate, and (3) the nucleation of particulate on the substrate itself. As the sodium becomes depleted of solute elements with increasing downstream, the rate of deposition is decreased.

3.2.2 Particulates

The study of the deposition process, through identification of the species (composition and structure) deposited in a flowing nonisothermal system, should provide technical insight into the influence of temperature, temperature gradient, impurity level, and flow characteristics of the sodium upon:

- The mechanisms of the corrosion and deposition processes,
- The predominant species involved in the mass transfer process,
- The morphology of the particulate and the nature of the bond to the substrate (and, by inference, the long-term effect upon heat transfer characteristics of the component),
- The probable distribution of radioactive corrosion products throughout the primary system of the reactor, and
- Potential procedures to control the rate, amount, and location of deposition.

Figure 3-7. Weight Change and X-ray Fluorescence Data from Exposed Surface as a Function of Position after 3000 Hours Exposure to Sodium with Less Than 5 ppm Oxygen (Run 8-1)

Figure 3-8. Weight Change and X-ray Fluorescence Data from Exposed Surfaces as a Function of Loop Position after 3000 Hours Exposure in Sodium

Figure 3-9. X-ray Fluorescence Analysis of Sample Surfaces

Figure 3-10. Rate of Deposition as a Function of Velocity and Downstream Position at 800°F

Large amounts of particulates were collected from the mass transfer loops by using 2- to 5-micron-pore-size micrometallic filters, and placing specimens in the loop to create a local turbulence at the points of interest. The temperatures and locations at which the particulates were collected are shown in Table 3-2.

Table 3-2
REGIONS OF PARTICULATE COLLECTION

Sample Source	Temperature and Cumulative Hours	Location of Deposit
Impingement samples	~1070°F ~3000 hours	~24 ft downstream from the main heater
Economizer	~300-700°F ~15,400 hours	~35 ft downstream from the main heater
Ni Filter	600°F ~700 hours	~25 ft downstream from the main heater

3.2.2.1 Nominal Operating Conditions

All of the mass transfer experiments were carried out at a maximum loop temperature of 1300°F and a cold zone temperature of 800 to 900°F, except in the case of the particulate collection loop (loop 1R) where the minimum temperature was 600°F. The sodium velocity was varied from 2 to 25 ft/sec in the hot leg and from 2 to 15 ft/sec in the cold leg, depending on the particular test conditions. For comparative purposes, particulates were collected at 3 to 4 ppm oxygen (270°F CT temperature) and 15 ppm oxygen (432°F CT temperature).

3.2.2.2 Chemical Analysis

The compositions of the deposits removed from the various loop positions are listed in Table 3-3. These values are accurate to within $\pm 5\%$ of the value stated. In addition to the elements shown in Table 3-3, fractional percentage concentrations of cobalt, molybdenum, magnesium, silicon, and tin were observed in the spectrographic analyses.

The most distinctive change in the elemental compositions of the filter residue is the increase in the silicon component. This observation indicates that the loss of silicon from stainless steel involves reaction with oxygen. The silicon leaching out of steels reacts with oxygen and sodium, and deposits as amorphous silicate. The available thermodynamic data for Gibb's energy of formation of Na_2SiO_2 indicates that the compound can exist in sodium with less than 0.1 ppm oxygen.¹⁰ All the silicon present in the filter residue was found to be water soluble. This is a strong indication that water-soluble Na_2SiO_2 was present in the filter residue.

Table 3-3
AVERAGE ELEMENTAL COMPOSITION OF VARIOUS DEPOSITS

Source of Deposit (and Temperature)	(Element (%))							
	Fe	Cr	Ni	Na	Mn	Si	Ca	C
Impingement Cartridge (1070°F) (Low O ₂)	6	35	25	10	7	—	—	~3
Economizer (300-700°F) (Low O ₂)	21	13	10	14	—	6	—	—
Ni Filter (600°F) (Low O ₂)	5	4	2	40	6.0	6	1.1	~2
Ni Filter (600°F) (High O ₂)	2	5	1.6	40	1	17	—	—
— Analysis not performed								

3.2.2.3 Structural Analysis

A description of the structural analysis is given elsewhere in detail.¹¹ The major differences in the nature of particulates as determined by XRD analysis in high- and low-oxygen sodium are shown in Table 3-4.

Table 3-4
MAJOR DIFFERENCES IN PARTICULATES AS DETERMINED BY XRD ANALYSIS

<u>Location</u>	<u>Constituents</u>	<u>Low Oxygen (1-3 ppm)</u>	<u>High Oxygen (15-20 ppm)</u>
Hot Leg (1290°F)	NaCrO ₂	None	Major
Cooler Impingement Samples (1100-1000°F)	Austenitic Phase	Major	Major
	NaCrO ₂	Minor	Major
	α Fe	Trace	Minor
	M ₂₃ C ₆	Strong Minor	Trace
Filter Residue (600°F)	NaCrO ₂	Major	Major
	α Fe	None	None
	M ₂₃ C ₆	Minor	Trace

Existence of NaCrO₂ in the deposits from higher-temperature regions is consistent with available thermodynamic data.¹² However, in low-oxygen runs (1 to 3 ppm), the considerable amount of chromium is present as chromium carbide, whereas at higher-oxygen levels, chromium exists primarily as NaCrO₂. It is most likely that at higher-oxygen levels, carbides become unstable with respect to NaCrO₂ according to the following reaction:

The movement of nickel and its presence in the particulate essentially remained unchanged with the increase of oxygen. This confirms the assumption that transfer of nickel in the stainless steel system does not involve reaction with oxygen, and double oxide of Na and Ni is not stable in liquid sodium.¹³

It has been proposed^{3,6} that corrosion and deposition of iron in liquid sodium is influenced by oxygen concentration. Analysis of the deposits from colder regions of the U.K. sodium mass transfer loops showed presence of sodium ferrate $[\text{FeO}(\text{Na}_2\text{O})_2]$.¹⁴ Recent thermodynamic measurements of double oxides of iron and sodium reveal that $\text{FeO}(\text{Na}_2\text{O})_2$ is not stable in liquid sodium containing normal oxygen concentrations.¹⁴ For example, at 1150°F , about 1000 ppm of oxygen are needed for the formation of $\text{FeO}(\text{Na}_2\text{O})_2$ as a separate phase. Analyses from both high- and low-oxygen runs showed that iron is primarily present in metallic form as alpha iron. There was no evidence of formation of double oxides of iron and sodium up to 15 ppm oxygen in sodium. Hence, from the present data it is difficult to confirm the hypothesis that corrosion of pure iron in liquid sodium depends on oxygen concentration. Absence of manganese in the filter residue of the high-oxygen run indicated that all of the manganese was precipitated in upstream higher temperature regions. This could be due to formation and deposition of a double oxide of manganese and sodium in high-temperature regions.

3.2.2.4 Morphology of the Particulates

To determine the physical characteristics of surfaces after corrosion and the particulates after deposition, samples from various regions of the heated and cooled sections of the loops were examined by scanning electron microscopy. The morphology of the particulates that deposit in a typical cooler region (1200 to 1100°F) of a sodium system is shown in Figures 3-11 and 3-12. As can be seen the particulates have a distinct crystalline structure which is consistent with the XRD analysis of particulates from a similar temperature region (impingement cartridges at 1070°F). These particulates were identified as an austenitic phase, carbides, and NaMO_2 .

However, as the sodium is cooled to lower temperatures, ($\sim 800^\circ\text{F}$), the crystalline appearance of the particulates disappears (Figure 3-12), which is consistent with the emergence of alpha iron as the major constituent of the particulate in this temperature region. These observations indicate that the composition and structure of the particulate, and perhaps the mechanism of deposition, are a function of the temperature of the region in which the deposition is occurring. It has been shown previously⁹ that the velocity profile can also affect deposition, but the influence of velocity appears to be limited to the rate of deposition and not the chemical nature of the deposits. It is believed that the chemical nature of the deposits at a constant oxygen concentration depends on the temperature at which the deposition takes place.

3.3 COBALT-60 TRANSFER (SCOPING TEST)

To date, a number of analytical studies^{15,16,17} have been made to estimate the magnitude of radioactive materials transport in a large system. These analytical studies, however, have been based on very limited experimental information.^{18,19} Some of the major uncertainties in these studies have been the locations and rates of deposition of cobalt-60 in flowing, nonisothermal sodium systems. In one study the assumption has been made that the corrosion and deposition behavior of cobalt is identical to that of nickel. In other studies, it has been assumed that cobalt and nickel do not behave similarly and that the bulk of the radioactive cobalt is retained in the core and plenum region of the reactor. The latter approach has been based on experimental evidence of such an effect.^{18,19}

The long-term objectives of these tests were to provide more experimental data on the release and deposition of radioactive corrosion products (cobalt-60, manganese-54) in flowing sodium systems. Because of redirection of the program, the present studies were limited to a single scoping run. The objective of this scoping test was to establish the sensitivity and operability of radioisotope techniques for measuring the corrosion and deposition rates of cobalt-60.

3.3.1 Sample Preparation

Radioactive samples consisted of Type-316 stainless steel rings (1.0 inch long $\times$ 0.441 inch o.d. $\times$ 0.020 inch wall). The samples were electroplated with cobalt-60 (on the outer surface only) and heat-treated in vacuum at 1000°C for 3 hours. The diffusion cycle was determined from a solution of Fick's Second Law for diffusion into a semi-infinite solid from a nonreplenished source of negligible thickness. Values of the diffusion coefficient of cobalt in stainless steels were not available; consequently, diffusion coefficients for nickel in stainless steel were used in these calculations.²⁰ The penetration profile for cobalt-60 into the samples (calculated on the basis of $D_{\text{Co}} = D_{\text{Ni}}$) is shown in Figure 3-13.

As shown in Figure 3-13, approximately 40% of the cobalt-60 remains within 0.0001 inch of the metal surface when the sample is diffused for 3 hours. Even higher surface activities can be attained by shorter exposures. However, it was observed that smearable contamination was undesirably high for diffusion anneals of 1-hour duration. The obvious advantage of this type of specimen is that it combines a high specific surface activity with a low total activity. In addition, there is a negligible increase in the total cobalt concentration of the steel because only very small amounts (in the order of 10^{-6} gm cobalt-60) are diffused into each sample. Weights and activities of the samples tested in Run 9-3 are shown in Table 3-5.

Figure 3-11. Deposit on Surface of Type-316 Stainless Steel after 3356 hours at $\sim 1200^{\circ}\text{F}$ in Flowing Sodium (3000X)

Figure 3-12. Deposit on Surface of Type-316 Stainless Steel after 3356 hours at $\sim 800^{\circ}\text{F}$ in Flowing Sodium (3000X)

Figure 3-13. Calculated Concentration Profile for Cobalt-60 Diffusion into Stainless Steel at 1000°C

Table 3-5
WEIGHTS AND ACTIVITY OF PLATED RING SAMPLES

Sample Number	Sample Weights (grams)	Activity Cobalt-60 (1-19-71) (millicuries)
R3(571-9-E)	3.2409	0.71
R5(571-9-D)	3.3193	0.48
R4(571-9-C)	3.1538	0.35
R1(571-9-B)	3.3607	0.78
R7(571-9-A)	3.2345	0.68
		Total 3.00

3.3.2 Experimental

The forced convection sodium mass transfer loop used to study the mass transport of cobalt-60 is shown in Figure 3-15. The nominal run conditions are as follows:

Hot-leg temperature—1200°F

Cold-leg temperature—850°F

Sodium velocity in hot-leg test section—~10 ft/sec

Cold-trap temperature—250°F

Oxygen (chemical analysis)—<5 ppm

Total run time—2100 hours

Five tubular samples with a total activity of 3 mCi were placed on a mandrel in the hot leg (Figure 3-14). On-line counting during the course of the run was carried out with a NaI detector and single-channel analyzer. The counting stations were selected primarily on the basis of accessibility of the detector and shieldings near the pipe walls of the loop. After the insertion of the radioactive samples in the hot leg, background counts at each monitoring station were established. The disintegration counts taken during the run were corrected for background activity with the established background counts.

A series of removable tubular sample cartridges were placed in the loop. After the conclusion of the run, the sample cartridges were removed in an argon atmosphere, and were individually counted to determine the activity buildup. One cartridge was leached in acid to remove 99% of its activity, and the leached solution was counted for absolute activity, which was subsequently used to convert the disintegration counts from all the cartridges into absolute microcuries.

3.3.3 Discussion

On-line counting: The buildup of cobalt-60 activity during the course of the run is shown in Figure 3-15. During the first 500 to 600 hours, the cobalt-60 activity on the loop rose sharply with time, after which the rate of buildup attained a steady state. The initial rate of activity buildup was found to be proportional to the square root of time ($t^{1/2}$). This indicates that the initial rate of buildup was being controlled by a diffusion process.

Activity released: Total amounts of cobalt-60 activity released from the source are shown in Table 3-6.

Table 3-6
TOTAL AMOUNTS OF COBALT-60 ACTIVITY

Sample	Cobalt-60 Prior to test in mCi	Cobalt-60 After Test in mCi	Change in Cobalt-60 in mCi
1	0.708	0.686	-0.022
2	0.476	0.466	-0.010
3	0.350	0.262	-0.088
4	0.785	0.742	-0.043
5	0.682	0.688	+0.006

Net loss = -0.157 mCi

The corrosion rate of Type-316 stainless steel at 1200°F, <5 ppm oxygen at 15 ft/sec sodium velocity, is 0.2 mil/year³. Hence, for 2100 hours of exposure, the calculated total corrosion in the hot leg in this experiment was about 0.05 mil. The calculated penetration profile shows that about 20% of the cobalt-60 would remain within 0.05 mil of the metal surface. Based on 0.05-mil corrosion, the total cobalt-60 lost from the source should have been ~600 μ Ci (3000 $\times$ 0.2). This is four times higher than the amount of cobalt-60 released in this experiment. This discrepancy can probably be accounted for by the cumulative uncertainties in the assumed value of the diffusion coefficient and the corrosion rates.

3.3.4 Deposition Pattern of the Cobalt-60

3.3.4.1 Isothermal Section and Coolers

The deposition pattern of cobalt-60 in the isothermal section (Zone P), located at immediate downstream position of the sample holder, is shown in Table 3-7. As can be seen from Table 3-7, most of the cobalt-60 released from the source was deposited in the hot-leg isothermal region. This observation is in general agreement with the radioactive materials transport study at BNWL.¹⁸ The driving potential for deposition cobalt-60 in the isothermal section is most likely due to the activity gradient of cobalt-60 between stainless steel and liquid sodium. This hypothesis is based on previous study¹¹ which showed that pure iron and nickel samples placed in the hot leg of an all-stainless-steel system pick up a considerable amount of chromium, which is also believed to be due to the chromium activity gradient between the liquid sodium and the substrate. It is believed that as the concentration of cobalt-60 in the stainless steels in the hot leg increases, the cobalt-60 will eventually migrate toward the downstream position.

Previous studies²¹ on transport of radioactive corrosion products for longer periods (up to 6000 hours) showed that a considerable amount of cobalt-60 migrates to the cold leg of the loop. Hence, the present data, as well as the results from BNWL experiments, may be misleading due to the shorter durations of both tests.

* - ON-LINE COUNTING STATIONS

Figure 3-14. Radioactive Cobalt-60 Transport Test (Loop 9)

Figure 3-15. On-Line Cobalt-60 Transport Data

Table 3-7
MASS BALANCE FOR COBALT-60, CORROSION/DEPOSITION

Cobalt Deposited on Samples

Location ^(a) (Zone)	Na Velocity (~fps)	Temperature (°F)	Activity (Microcuries)
Source ^(b)	10	1200	33.1
P	10	1200	37.0
Cooler I	4	1190 to 1135	9.5
G & H	4	1135	4.0
Cooler II	9	1135 to 1060	7.5
Cooler III		1060 to 990	1.1
Cooler V		910 to 860	<u>4.3</u>
Subtotal, Samples			96.6

Cobalt-60 Deposited on Pipe Walls

Source	19.7	
P	20.3	
F	5.6	
J	<u>5.4</u>	
	Subtotal, Pipes	<u>51.1</u>
	Total Deposits	147.7
	Total Released from Source	157.0

(a) Figure 3-15

(b) Deposits in source zone, other than source samples

3.3.4.2 Mass Balance

A mass balance between corrosion (release from source specimens) and deposition was attempted for cobalt-60. The results, shown in Table 3-7, indicate that 148 of the total 157 microcuries (or 94% of the activity) have been accounted for in the mass balance.

The activity from piping walls was measured in the following manner. All loop zones, including the source zone, were counted "on line" at a number of positions. One section (P) was run cut away, and the cobalt-60 was removed by acid etching. The relative counts of other loop sections were converted to absolute counts by comparison with the counts obtained from section P.

3.4 CONCLUSIONS**3.4.1 Corrosion**

- The P.A. 15 Phase II corrosion data show that the effect of downstream (L/D) on corrosion depends on the velocity of liquid sodium.
- It has been observed that corrosion of steels becomes independent of sodium velocity as velocity increases. In the velocity-dependent range, the diffusion of solutes across the laminar boundary layer is believed to be the rate determining step. Hence, the critical parameter to describe corrosion is the thickness of the laminar boundary layer rather than the sodium velocity. It is well known that the boundary layer thickness depends both on the fluid velocity and the pipe dimensions. Hence, it is recommended that the comparison and large system extrapolation of the corrosion data from various investigators should be made on the basis of the boundary layer thickness.
- High (432°F CT temperature) and low (270°F CT temperature) oxygen corrosion studies showed that the effect of oxygen in sodium on the corrosion of stainless steels is dependent on downstream (L/D) position. For example, at zero downstream, the corrosion rate is dependent on $[O_x^{1.0-1.2}]$, whereas at "L/D" of 540, it is only $[O_x^{0.49}]$.

- At zero downstream, the calculated oxygen dependency of corrosion based on chemical analysis (vacuum distillation) of oxygen is $[O_x^{1.0-1.2}]$. The calculation based on Eichelberger's recommended expression for oxygen solubility in sodium shows the oxygen dependency to be $[O_x^{0.63}]$.
- Assuming the oxygen dependency of corrosion of $[O_x^{1.0-1.2}]$ to be correct, it is believed that the temperature dependency of the Eichelberger recommended oxygen solubility expression is erroneous.
- Earlier mass transfer studies²² of General Electric Company produced data for a semi-empirical corrosion correlation. The effects of oxygen, velocity and downstream (L/D) on corrosion of steels were treated as independent parameters. The present mass transfer results show that the effects of oxygen, velocity, and downstream on corrosion are all interdependent. The assumption of independent, separable variables for correlation is thus untenable and cross-product terms are required.

3.4.2 Mass Transfer and Deposition

- Selective leaching of chromium is enhanced by high oxygen concentrations in the sodium, while the movement of nickel is not affected. This observation implies that mass transport of chromium involves reaction with oxygen in sodium, and nickel movement does not. Selective leaching of silicon is increased with increase in oxygen, indicating transfer of silicon also involves reaction with oxygen.
- Increasing fluid turbulence enhances the rate of deposition. The mechanism of deposition probably involves the diffusion of solute atoms, and the particulates nucleated in stream across the liquid boundary layer on to the substrate.
- Fluid turbulence at the deposition site controls the magnitude of the deposit; however, the temperature at the deposition zone governs the chemical nature of the particulate.
- Deposition of corrosion products in the hot leg depends on alloy composition of the substrate. For example, pure iron samples placed in the hot leg picked up considerable amounts of chromium and nickel, whereas the adjacent stainless steel samples lost both of these elements. These results indicate that the liquid sodium in the hot leg is not saturated with respect to chromium and nickel. The predominant mechanism of deposition of elements is believed to be atomic exchange. The driving potential for the exchange process is the activity gradient of the solutes between liquid sodium and the substrate.
- The alloy composition of the substrate has little or no effect on the deposition of materials in colder regions. Supersaturation of the solutes in sodium on cooling is the driving force for deposition in the cold leg.

3.4.3 Particulates

- In the present program, large amounts of particulates were collected from flowing-sodium systems and characterized.
- In sodium containing 15 ppm oxygen, chromium is primarily present as $NaCrO_2$ in the deposited residue. In low-oxygen sodium (3 to 4 ppm), only part of the chromium combines with sodium and oxygen; the remainder forms carbides.
- Up to 15 ppm oxygen, double oxides of nickel, or iron and sodium, were not detected in the deposited particulates. Absence of nickel in oxide form is consistent with the corrosion of nickel-base alloys, which is found to be independent of oxygen concentration. It is generally believed that mass transfer of iron involves reaction with the oxygen in sodium. The absence of double oxides of iron and sodium in the particulates contradicts the foregoing hypothesis.
- Presence of $M_{23}C_6$, $NaCrO_2$, and Na_2SiO_2 in sodium containing 3 and 15 ppm oxygen is consistent with available thermodynamic data. Absence of double oxides of iron or nickel and sodium in this range of oxygen concentrations is also in agreement with thermodynamic data in the literature.

3.4.4 Cobalt-60 Transfer (Scoping Test)

- Diffusion of small quantities of activated corrosion products (e.g., cobalt-60 or manganese-54) into the surface of stainless steel specimens provides good sensitivity and low total activity for studying transport of radioactive corrosion products in flowing sodium.
- Use of this type of sample eliminates interference from background radiation and minimizes safety problems associated with specimens irradiated in the reactor.
- On-line counting methods are capable of resolving activity changes in the order of 10 μCi in a low-activity test loop.

- The present ~2100-hour test shows that 70% of cobalt-60 released from the source remains in the hot-leg isothermal section.
- It is believed the cobalt-60 will migrate downstream to colder regions as soon as the cobalt-60 reaches a critical concentration in the hot-leg specimens; consequently, long-term tests are required.

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SECTION 4

**INFLUENCE OF HIGH TEMPERATURE EXPOSURE IN FLOWING SODIUM
ON THE COMPOSITION, MICROSTRUCTURE, AND MECHANICAL
PROPERTIES OF STAINLESS STEELS**

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4. INFLUENCE OF HIGH TEMPERATURE EXPOSURE IN FLOWING SODIUM ON THE COMPOSITION, MICROSTRUCTURE, AND MECHANICAL PROPERTIES OF STAINLESS STEELS

4.1 OBJECTIVES

The objective of this task was to determine the effects of mass transfer on the long-term structural properties of the LMFBR cladding materials. More specifically, the objectives were to measure the stress-rupture properties of cladding during exposure to typical primary-sodium conditions. This included tests in sodium and control tests in argon at the same temperature, as well as the measurements of changes in microstructure and measurements of changes in the content of major and minor elements. Relative corrosion rates of the selected cladding materials were also measured concurrently with the exposure of the stressed specimens.

The following materials were tested in the solution annealed and in the carbide agglomerated conditions: Types-304, -316, -321 and -347 stainless steel, and Incoloy-800. This section summarizes the major findings which are discussed in detail in a topical report.¹

4.2 TEST METHODS

The corrosion and mechanical property testing was performed in three identical test facilities (Figure 4-1), designated loops 4R, 5R, and 6R. The loops are constructed of Type-304 stainless steel, except for the heat transfer surfaces which are of Type-316 stainless steel. Eleven loop runs were completed: two in loop 4R, five in loop 5R, and four in loop 6R.

The nominal operating conditions for 10 of the 11 runs were: 1300°F (T_{max}), $\Delta T = 500^\circ\text{F}$, a flow of 10 gpm (1.25 gpm/channel in Zone F, eight channels), and an oxygen content 2.5 ± 1.5 ppm based on a cold trap temperature (T_s) of $270 \pm 2^\circ\text{F}$. The other run was at 1150°F (T_{max}) and a $\Delta T = 445^\circ\text{F}$. The sodium velocity was 17 ft/sec in each channel of Zone F, and 10 ft/sec in Zones E, G, and J.

Two types of specimens used in these tests have been reported previously.³ Briefly, these included ring specimens (0.5 inch o.d. x 0.035 inch wall), tube specimens (0.875 inch o.d. x 0.035 inch wall), and cladding specimens (0.250 inch o.d. x 0.015 inch wall). Tube and ring specimens were exposed in Zones E, G, and J (Figure 4-1) while pressurized and nonpressurized cladding specimens were tested in Zone F.

The chemical compositions of the materials used in these tests are shown in Table 4-1.

4.3 RESULTS AND DISCUSSION

4.3.1 Comparative Corrosion

Because of the downstream position of the sample sections in loops 4R, 5R, and 6R, it is not possible to produce maximum corrosion rates (or, for that matter, maximum rates of decarburization, major element losses, degradation of mechanical properties, etc.). However, it has been possible to measure the comparative corrosion behavior of various steels. A compilation of corrosion data from runs 4R-1, 4R-2, 5R-1, 5R-2, 5R-3, 5R-4, 5R-5, 6R-1, 6R-2, and 6R-4 is shown in Figure 4-2.

In addition, the equations describing the best fits through the data and the 95% confidence limits for the parameters are given in Table 4-2. As shown in Figure 4-2, the corrosion data from nine different test runs at 1300°F and three separate loops exhibit good self-consistency. The most corrosion-resistant material at 1150 and 1300°F is Type-316 stainless steel. Progressively higher corrosion rates are observed at both temperatures for Types-304 and -347 stainless steels and Incoloy-800. In an earlier report,² corrosion rates were given in the form of linear equations.

Further analysis of the data indicates that linear corrosion rates are the exception, not the rule. Statistical analysis showed that the index of determination for an exponential function was always greater than the index for a linear function. The closer the value of this index is to unity, the better the analytical expression fits the data. A comparison of the indices of determination for linear and exponential fits to the corrosion data for the steels exposed in these tests is given in Table 4-2.

4.3.2 Compositional Changes

Analysis of corrosion samples revealed that weight changes were accompanied by selective removal of alloying elements from the steels. These compositional changes (which are responsible for the microstructural and mechanical property changes of the steels) are presented in this section for major and minor elements. Major elements are defined by initial concentrations greater than 1%, whereas minor elements are defined by initial concentrations of $<0.1\%$.

Table 4-1
CHEMICAL COMPOSITIONS OF THE TEST MATERIALS
As Certified by Vendor

	Material	Heat Number	C	Mn	Si	Ni	Cr	Co	Mo	Cb&Ta	Al	Ti	S	P	Cu
Seamless Tubing (Stress Rupture)	Incoloy-800 (a)	HH2051A	0.08	0.88	0.35	31.09	20.30	—	—	—	0.30	0.44	0.007	—	0.41
	304H SS (a)	20184	0.05	1.59	0.47	9.15	18.85	—	—	—	—	—	0.011	0.017	—
	316H SS (a)	20303	0.06	1.48	0.57	13.23	17.95	—	2.26	—	—	—	0.012	0.018	—
	321H SS (a)	28967	0.06	1.79	0.52	11.23	17.45	—	—	—	—	0.44	0.014	0.017	—
	347H SS (a)	24772X	0.06	1.77	0.54	11.65	18.29	—	—	0.75	—	—	0.006	0.013	—
Weld Drawn Tubing (Corrosion)	Incoloy-800 (b)	HH2930-A	0.09	0.90	0.50	31.43	21.04	—	—	0.11	0.44	0.51	0.007	—	0.48
	Incoloy-800 (c)	HH2930-A	0.09	0.90	0.50	31.43	21.04	—	—	0.11	0.44	0.51	0.007	—	0.48
	304 SS (b)	860289	0.05	1.39	0.65	9.45	18.52	0.09	0.20	—	—	—	0.004	0.015	0.14
	304 SS (c)	860578	0.07	1.38	0.62	9.66	18.47	0.15	0.30	—	—	—	0.009	0.012	0.13
	316 SS (b)	156146	0.05	1.76	0.52	13.44	16.72	—	2.09	—	—	—	0.017	0.029	—
	316 SS (c)	7X3463	0.08	1.64	0.40	13.10	17.28	—	2.60	—	—	—	0.006	0.021	—
	321 SS (b)	137365	0.05	1.58	0.58	9.82	17.37	—	0.21	—	—	0.50	0.012	0.031	0.27
	321 SS (c)	M1837	0.05	1.82	0.64	11.22	17.58	—	0.23	—	—	0.43	0.010	0.010	0.15
	347 SS (b)	860682	0.06	1.44	0.56	10.00	18.61	0.13	0.30	0.75	—	—	0.012	0.011	0.21
	347 SS (c)	830617	0.05	1.44	0.65	11.14	17.31	0.15	0.30	0.79	—	0.02	0.011	0.016	0.18

- (a) Stress-Rupture Samples 0.250-in. o.d. x 0.015-in. wall - zone F. Ordered to ASTM 213-65 (300 series) and ASTM B-163-66 (Incoloy-800).
- (b) In-Pipe Corrosion Samples 0.500-in. o.d. x 0.035-in. wall - zones E, G, and J. Ordered to ASTM A269 (300 series) and ASTM B163 (Incoloy-800).
- (c) In-Pipe Corrosion Samples 0.875-in. o.d. x 0.035-in. wall - zones E, G, and J. Ordered to ASTM A269 (300 series) and ASTM B163 (Incoloy-800).

Table 4-2
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 $4.96 \times 10^{-4} \frac{\text{mils}}{\text{mg/dm}^2}$

4.3.2.1 Major Elements

X-ray fluorescence analyses were performed on the surfaces of specimens that were exposed, at 1150 and 1300°F, to flowing sodium for times ranging from 538 to 15,726 hours. The fluorescence analysis represents the composition of a surface layer <0.1 mil thick.

The results of these analyses are shown in Figure 4-3. All the alloys exhibited progressive losses of chromium, nickel, and manganese with increasing exposure time. The alloys lost approximately 65 to 80% of their manganese, 50 to 65% of their chromium, and 55 to 90% of their nickel content during these exposures. This selective depletion of alloying elements leaves an iron-rich surface that can transform to the commonly observed ferritic layer. The molybdenum concentration in the alloys appears to be stable, since no significant changes in composition were measured. It is evident from Figure 4-3 that the surface compositions after 15,726 hours of exposure are comparable with those after approximately 10,000 hours exposure. This indicates that steady-state mass transfer conditions at the surface are attained only after 10,000 hours at 1300°F. Fluorescence data from specimens exposed at 1150°F showed that losses in major elements occurred at the lower temperature, but at a slower rate.

To establish the nature of the compositional disturbances in the bulk of the steel, electron microprobe analyses were performed on Types-304, -316, and -347 stainless steels, and on Incoloy-800 corrosion samples. The samples were taken from the maximum upstream position (Zone E) of the loop after a 15,726-hour exposure. Results of similar examinations after a 2,083-hour exposure have been reported previously³ and are in general agreement. Typical results of the microprobe studies are shown in Figures 4-4, 4-5, and 4-5A for Types-316 and -347 stainless steels and Incoloy-800, respectively.

All the alloys exhibited the same general trends; i.e., depletion of chromium, nickel, manganese, and silicon within a surface layer up to 5.0 mils thick. The maximum compositional changes were observed in the Types-304 and -347 stainless steels where chromium, nickel, manganese, and silicon losses were detectable to depths of 2.0 to 5 mils. The minimum changes were observed in Type-316 stainless steel and Incoloy-800 where the compositional changes were detected to depths of 0.5 to 0.75 mil.

Metallographic examination of the specimens (see following subsections) was used to identify the microstructure of the alloys as a function of distance from the surface. The microstructures and composition profiles were consistent. The ferritic surface layers of Types-304, -316, and -347 steels contain 5 to 7% chromium, 1 to 2% nickel, <0.5% silicon, <0.5% manganese, and a balance of approximately 90% iron. The ternary phase diagram (iron, chromium, nickel) shows that this composition should produce a ferrite layer, while the surface composition, (9% chromium—16% nickel) of the Incoloy-800 should remain austenitic, as was observed.

Figure 4-1. LMFBF Cladding Test and Screening Loops, 4R, 5R, and 6R

Figure 4-2. Corrosion of Stainless Steels in Flowing Sodium at 1150°F and 1300°F

In comparing Figure 4-2 with Figures 4-4 and 4-5, it could be concluded that there is a correlation between the depth of chromium and nickel depletion and the differences in general corrosion observed between Types 316 and 347 stainless steel. However, the volume of intergranular cavities present in Type 347 (see Subsection 4.3.3) accounts for most, if not all, of the observed difference in weight loss between Types 316 and 347. The depth of depletion of substitutional alloying elements in Type 347 corresponds roughly to the depth of penetration of the intergranular cavities. It is possible that the cavities provide diffusion paths for chromium, nickel, etc., which are not present in Type 316. This concept is confused somewhat by the concentration profiles for Incoloy-800 for which the depth of substitutional element loss is similar to Type 316 even though Incoloy-800 had more pronounced intergranular cavities than Type 347. Because of the considerable difference in initial alloy content between Incoloy-800 and the stainless steels, it is not possible to make direct comparisons or draw definite conclusions with the present data.

Figure 4-3. Surface Concentration of Alloying Element as a Function of Exposure Time in 1300°F and 1150°F Flowing Sodium

Figure 4-4. Composition Profile of Solution-Annealed Type-316 Stainless Steel After 15,726 hours Exposure to 1300°F Flowing Sodium

Figure 4-5. Composition Profile of Solution-Annealed Type-347 Stainless Steel After 15,726 hours Exposure to 1300°F Flowing Sodium

Figure 4-5A. Composition Profile of Solution-Annealed Incoloy-800 after 15,726 Hours Exposure to 1300°F Flowing Sodium

4.3.2.2 Minor Elements

The analytical methods used to determine the quantity of interstitial or minor alloying elements are given in Table 4-3. Bulk analyses were performed on 1-gram quantities of the specimens, with an equal amount of material for the standard condition.

Table 4-3
ANALYTICAL METHODS FOR THE DETERMINATION OF MINOR ELEMENTS

Element	Method of Analysis	Accuracy (ppm)
C	Leco Combustion Conductometric	±10
N	Kjeldahl or Vacuum Fusion	±10
S	Combustion-Titration	±10
P	Modified Heteropoly Blue Method	±10
Si	Perchlorate Acid Dehydration	±200
B	Spark Source Mass Spectrometry	±0.04

Changes in carbon content were observed in Zones E, F, and G of the test loops. Types-304 and -316 tube specimens and cladding specimens decarburized in most (but not all) of the runs at 1300°F, while Types-321, -347, and Incoloy-800 carburized. Summaries of the data for various tests are given in Tables 4-5 and 4-6. Examination of these data showed that the carbon transfer results from the various test runs were not entirely consistent. Decarburization at 1300°F was observed in all but two (6R-1 and 5R-2) of the test runs; however, the magnitude of decarburization varied substantially. The reasons for this scatter have not yet been determined, and will require further analysis of the data. However, certain consistent relations can be made between the decarburization data and the stress-rupture properties of the steels. It has been observed that the maximum degradation in stress-rupture properties during sodium exposure at 1300°F was observed in tests 4R-2 and 5R-4, while substantially smaller effects were observed in test 5R-5. Examination of Tables 4-4 and 4-5 shows that the former runs exhibited rapid decarburization, while the latter decarburized slowly.

Also shown in Tables 4-4 and 4-5 are the results of exposures at 1150°F (run 6R-4). As shown in the tables, real, but negligible, decreases in carbon content were observed in specimens of Types-304 and -316 stainless steel. These small changes were consistent with the 1150°F stress-rupture data.

Changes in nitrogen content of the steels were also observed in these tests. As shown in Figure 4-6 and Table 4-6, losses in nitrogen were observed in all Zone E specimens during these tests. Losses in nitrogen were observed for both stabilized and nonstabilized steels, with the major changes occurring in Types-304 and -316. In addition, significant nitrogen loss from Type 316 occurred during the 1150°F test.

Results obtained at lower downstream positions (Zone F) were not as consistent. In these tests, the stabilized steels were nitrided, whereas the nonstabilized steels gained or lost nitrogen, depending on the test run. One of the major observations of these analyses is the very rapid nitrogen gain for all the steels at 1150°F. As shown in Table 4-6, at 1150°F the rate of nitrogen pickup was as fast or faster than at 1300°F. This effect could be related to the higher solubility of nitrogen⁴ at 1150°F than at 1300°F.

Results of analyses for boron, sulfur, and phosphorus are shown in Table 4-7. As shown, sodium exposure did not affect the sulfur and phosphorus contents of stabilized or nonstabilized steels at 1150 and 1300°F. Examination of the phosphorus data shown in the table were unusually high (ASTM maximum is 0.040%). Comparison of these values with original records for these cladding specimens reveals that the original analyses were substantially lower. Therefore, it is probable that the absolute values of the phosphorus concentrations are not correct. The relative amounts before and after sodium exposure, however, are significant, and it is concluded that no phosphorus changes occurred. Sulfur analyses listed here agreed well with prior vendor and check analysis.

As shown in Table 4-7, both the stabilized and nonstabilized steels lost substantial quantities of boron during exposures at 1150 and 1300°F. These results are significant because boron has major effects on the high-temperature creep and stress-rupture properties of austenitic alloys.⁵

Table 4-4
CARBON ANALYSES OF CLADDING SPECIMENS
From Zone F (0.015 x 0.250 o.d.)

Run Number	Temperature (° F)	Time (hours)	Weight Percent Carbon				
			304	316	347	I-800	321
	Standards		0.056, 0.055, 0.053 0.054, 0.051, 0.055	0.068, 0.060, 0.061 0.053, 0.061, 0.060	0.068, 0.084, 0.076	0.075, 0.069, 0.078	0.079, 0.070, 0.073
6R-2	1300	538	0.042, 0.051	0.055, 0.057, 0.051	0.083	0.105	—
6R-1	1300	1,008	—	0.070, 0.071, 0.068, 0.069	—	—	—
6R-3	1300	1,768	0.037, 0.054	0.064, 0.052, 0.058	0.096	0.087	0.087
5R-4	1300	4,838	0.012, 0.015	0.037, 0.048, 0.032	—	—	—
5R-5	1300	10,352	0.031	0.036	0.075	0.110	0.210
4R-2	1300	15,726	0.003	0.013	—	0.190	0.160
6R-4	1150	11,379	0.050	0.057	0.085	0.070	0.079

Table 4-5
CARBON ANALYSES OF TUBE SPECIMENS
FROM ZONE E (0.035 x 0.875 o. d.)

Run Number	Temperature (°F)	Time (hours)	Weight Percent Carbon			
			304	316	347	I-800
	Standards		0.075,0.075,0.062	0.074,0.073,0.076	0.055,0.051,0.052	0.088,0.095
6R-2	1300	538	0.052	0.056	0.049	0.096
4R-1	1300	743	0.055	0.062	0.057	0.097
6R-1	1300	1,008	—	0.075	—	—
5R-2	1300	1,745	—	0.074	—	—
5R-1	1300	2,083	—	0.042	—	—
5R-3	1300	3,044	—	0.051	—	—
5R-4	1300	4,838	0.027,0.017	0.038,0.036	0.052,0.053	0.098
5R-5	1300	10,352	—	0.051	—	—
4R-2	1300	15,726	0.005,0.005	0.025,0.005	0.046,0.046	0.116
6R-4	1150	11,379	—	0.070	—	—

4.3.2.3 Decarburization Kinetics

Analysis of the decarburization data for Types-304 and -316 stainless steel cladding specimens was done to develop an equation that would describe the rate at which carbon was lost. Preliminary evaluation of available data (Table 4-5) revealed that decarburization was substantially faster in test runs 6R-2, 6R-3, 5R-4, and 4R-2 than in test runs 6R-1 and 5R-5. Data were therefore selected for analysis on a conservative basis; i.e., emphasis was placed on the data that exhibited the fastest decarburization. It will be shown later that this approach was not conservative, and that the decarburization rate of stainless steels in the hot leg of a flowing sodium system can be faster than the rates measured in these tests.

The average carbon concentration ($\bar{C}$) in a cladding specimen of thickness (h) can be described as a function of $\frac{D_t}{h^2}$. A tabular compilation of the relation of $\bar{C}$ to $\frac{D_{ct}}{h^2}$ may be found in Darken and Gurry.⁶

$$\bar{C} = C_i + (C_s - C_i) f\left(\frac{D_{ct}}{h^2}\right), \quad (4-1)$$

where:

- C_i = Initial carbon concentration,
- C_s = carbon concentration at the specimen surface,
- t = exposure time (sec), and
- D_c = diffusion coefficient of carbon in the steel (cm^2/sec).

Initial calculations for cladding specimens were made, using the diffusivity data of Argawala, et al.⁷ The value of $C_s = 0.003$ wt % was chosen on the basis that this was the minimum carbon content measured in any specimen during these tests. Initial calculations based on these values revealed that the calculated decarburization rates were much faster than the measured rates. For this reason, Equation (4-1) was modified by multiplying the diffusion coefficients by an empirical coefficient (k). This coefficient is a measure of the efficiency of the decarburization process; i.e., if $k = 1$, the system is capable of decarburizing the steel at the maximum theoretical rate. K was determined by fitting Equation (4-1) to one data point for each steel. The modified equation was then used to calculate the decarburization behavior of both steels at 1150 and 1300°F (k for Type-304 stainless steel = 0.0425; k for Type-316 stainless steel = 0.0166).

The results of this calculation are shown in Figure 4-7, along with the experimental data. As shown, there is good agreement between the semi-empirical equation and the measured data at 1300°F. The empirical equation, however, does not agree with the 1150°F data. Therefore, this analysis shows only that an empirical equation based on a conventional diffusion equation can describe the time dependence of decarburization of some (but not all) of the test runs. Also shown in Figure 4-7 are the data from similar tests at A.I.⁸ These data were obtained at 1200°F on Type-316

Table 4-6
NITROGEN ANALYSES OF CLADDING SPECIMENS
From Zone F (0.015 x 0.250 o.d.)

Run Number	Temperature (°F)	Time (hours)	Weight Percent Nitrogen				
			304	316	347	I-800	321
	Standards		0.066, 0.069, 0.056	0.063, 0.060	0.051, 0.052	0.023, 0.030, 0.022	0.024, 0.038, 0.023
5R-5	1300	10,539	0.045	0.055	0.078	0.063	0.046
4R-2	1300	15,726	0.082	0.064	0.083	0.076	0.070
6R-4	1150	11,379	0.091	0.086	0.086	0.054	0.060

NITROGEN ANALYSES OF TUBE SPECIMENS
From Zone E (0.035 x 0.875 o.d.)

Run Number	Temperature (°F)	Time (hours)	Weight Percent Nitrogen			
			304	316	347	I-800
	Standards		0.056, 0.052	0.058, 0.053, 0.055, 0.054	0.064, 0.063	0.058
5R-5	1300	10,539	—	0.012	—	—
4R-2	1300	15,726	0.013	0.011	0.059	0.042
6R-4	1150	11,379	—	0.041	—	—

Table 4-7
MINOR ELEMENT ANALYSES OF SPECIMENS
From Zone F (0.015 x 0.250 o.d.)

Run Number	Temperature (°F)	Time (hours)	Boron (ppm)	Sulfur (wt %)	Phosphorous (wt %)
	Standard (316)		2.2, 2.5	0.022, 0.015	0.035, 0.038
5R-5	1300	10,352	0.6	0.017	0.036
6R-4	1150	11,379	0.4	0.020	0.040
	Standard (321)		1.1, 1.1	0.017, 0.014	0.046, 0.038
5R-5	1300	10,352	0.9	0.011	0.030
6R-4	1150	11,379	0.2	0.014	0.039

From Zone G (0.035 x 0.875 o.d.)

	Standard (316)		1.7	—	—
4R-2	1300	15,726	0.07	—	—
	Standard (321)		5.0	—	—
4R-2	1300	15,726	0.08	—	—

stainless steel cladding 0.010 inch in thickness. The data were corrected for difference in thickness (by multiplying the exposure time by the ratio of the squares of the wall thicknesses $\frac{0.015^2}{0.010^2}$ of the respective claddings). Even with this correction, it is evident that the decarburization rate obtained by A.I. at 1200°F was much faster than the decarburization rate obtained in this study at 1300°F. This comparison shows that more efficient decarburizing conditions were established in the A.I. tests than in the present study. This, in turn, suggests that even more efficient conditions could be established in the core (zero downstream) position of a reactor. Consequently, the decarburization rates and effects on mechanical properties measured in the present studies are not conservative. Data required for conservative design must be obtained in experimental test loops where the specimens are in a zero downstream position of the hot leg.

Part of the carbon loss is accounted for by deposition in the heat exchanger. The results of an examination of the economizer tubing from Loop 4R is given in Appendix A.

4.3.3 Microstructural Changes

Metallographic examination of the corrosion samples from Zones E, F, and G revealed structural changes in all the steels tested. Figure 4-8 shows the effect of 1300°F flowing sodium on the microstructure of the corrosion samples for various exposure times. The most outstanding change at the short-time exposure of 538 hours is the existence of the sigma phase near the surface of Type-316 stainless steel. This precipitation along the denuded grain boundaries is a direct consequence of compositional changes; that is, the loss of carbon along the grain boundaries causes the $M_{23}C_6$ carbides to become unstable and consequently to dissolve, thus nucleating a grain boundary network of sigma phase. At longer exposures, where there are substantial losses of carbon, the grain boundaries throughout the structure contain large sigma particles. The x-ray fluorescence and the electron microprobe data agree with the metallographic observations on Type-316 stainless steel concerning the initiation and growth of the ferritic layer. This layer is visible after ~2000 hours exposure, and reaches a maximum thickness (0.6 to 0.7 mil) between 10,352 and 15,726 hours (Figure 4-8A).

Figure 4-6. Effects of Exposure in Flowing Sodium on the Nitrogen Contents of Stainless Steels

Figure 4-7. Time and Temperature Dependence of Decarburization of Stainless Steels in Flowing Sodium

A major microstructural change in Type-304 stainless steel is the formation of martensite. The concurrent losses of nickel, chromium, manganese, and carbon are sufficient to allow the austenite to transform to martensite on cooling. After 10,352 to 15,726 hours exposure, the microstructure of Type-347 stainless steel consists predominantly of grain boundary sigma particles (grain boundary delineation is lost), a (0.70 mil) ferritic surface phase, and void formation 4 to 5 mils below the ferritic surface phase.

Subsurface void formation is also present in the Type-321 stainless steel corrosion samples in Zone G (Figure 4-9A). Microprobe traces of Types-321 and -347 stainless steel show major depletions of chromium, nickel, and manganese from the subsurface regions of these steels. It was first thought that the cavities might have been the result of losses of major alloy elements. If this depletion was not compensated by densification of the remaining material, Kirkendahl porosity could form by precipitation of vacancies. However, when the materials were examined by thin-foil transmission electron microscopy, no minor voids could be found, so a different reason for the cavities was sought. Figure 4-9B shows the Type-316 stainless steel at a depth of 0.9 mil below the outside surface. The main features are large sigma phase particles and dislocations. In Figure 4-9C, it can be seen that in the Type 321 there was an absence of sigma phase. The main features in the structure are dislocations, stacking faults, and what appears to be small precipitates. Also visible in Figure 4-9C is a polygonal network of light areas on the micrograph which is an etching characteristic. This regular array of light spots was also observed in another sodium-exposed Type-316 specimen which was thinned to a different depth.

In a further attempt to find microporosity in the Type-321 stainless steel, a metallographic specimen was reground and polished for examination by a scanning electron microscope (SEM). A Type-316 sample was included for comparison. Figure 4-9D shows the Type-316 sample which had been lightly etched with glyceregia. There are extensive amounts of sigma phase visible in the micrograph and a few pits, possibly caused by the brittle sigma phase falling out during specimen preparation, if not similar to the pits in Type 321 stainless steel. Figure 4-9E shows the Type-321 stainless steel at the same magnification and distance from the outside surface as Figure 4-9D. The large cavity is typical of the many to be found in this sample. No microporosity was found; precipitates were not evident.

The SEM was then used to examine the surface of the Type-321 tubing (Figure 4-9F shows one of the surface pits). These pits are apparently connected to the subsurface cavities along grain boundaries. While these limited observations do not permit firm generalized conclusions, they do show new information on the effects of cladding alloys due to exposure in nonisothermal flowing sodium.

Figure 4-8. Effects of Sodium Exposure on the Microstructure of Solution-Annealed Stainless Steels.

Figure 4-8. Specimens Exposed in Zone E to 1300°F Flowing Sodium. All photos 500X, Etchant Glyceregia.

Figure 4-8A. Rate of Ferrite Layer Formation in Type-316 Stainless Steel Exposed to Flowing Sodium at 1300°F

Figure 4-9A. Subsurface Void Formation in Solution-Annealed Type-321 Stainless Steel Exposed in Zone G to 1300°F Flowing Sodium for 15,700 Hours

Figure 4-9B. Transmission Electron Microscopy, Type 316 Stainless Steel Exposed to Flowing Sodium 15,726 Hours at 1300°F, 0.9 mil Below Outer Surface

Figure 4-9C. Transmission Electron Microscopy, Type-321 Stainless Steel Exposed to Flowing Sodium 15,726 Hours at 1300°F, 1 mil Below Outer Surface

Figure 4-9D. Scanning Electron Microscopy, Type-316 Stainless Steel Exposed to Flowing Sodium 15,726 Hours at 1300°F.

Figure 4-9E. Scanning Electron Microscopy, Type-321 Stainless Steel Exposed to Flowing Sodium 15,726 Hours at 1300°F. Cross Section of a Subsurface Cavity

Figure 4-9F. *Scanning Electron Microscopy, Outside Surface of Type-321 Stainless Steel Exposed to Flowing Sodium at 1300°F for 15,726 Hours*

A dramatic illustration of void formation is shown in Figure 4-8. Void formation in Incoloy-800 has progressed to the point where it is obviously intergranular and interconnected to the exposed surface. It is probable that the large percentages of chromium and nickel lost from Incoloy-800 along preferential diffusion paths (grain boundaries) are responsible for this apparent "intergranular attack." Initiation and growth of intergranular voids appear as early as 538 hours, and they do not reach a limiting thickness (as do the surface phases of Types-304 and -316 stainless steel) but progress with time (diffusion controlled).

The presence of these intergranular cavities has not previously been noted in any great quantity. This is because the cavities are only observed to form in stabilized stainless alloys and only become evident after exposure to high temperature (1300°F) flowing sodium for long times (>5000 hours). It is now recognized that these cavities were also present in specimens exposed for shorter times, but the size and distribution of the cavities were such that their presence was not detected. The formation of these cavities may also be associated with impurity concentrations in the alloys and so may vary with the melting process or heat treatment. Therefore, the cavity formation observed in air-melted stabilized alloys may not necessarily be representative of other melting practices; e.g. vacuum melting.

The effect of stress on the formation of sigma in solution-annealed Type 316 stainless steel cladding is shown in Figure 4-10. Both steels were exposed to 1300°F flowing sodium for 15,726 hours in Zone F. It is evident that the stress (or more properly, strain) increases the rate of growth of the sigma phase. The unstressed steel contains large individual sigma particles in the grain boundaries and small acicular sigma particles within the grains. The stressed specimens contain larger inter- and intra-granular sigma particles and exhibit well-defined grain boundaries.

4.3.4 Stress Rupture Properties

Tests were performed at 1150 and 1300°F on both solution-annealed and carbide-agglomerated steels. Results of tests in sodium and control tests (in argon) are discussed in this subsection.

4.3.4.1 Type-304 Stainless Steel

Results of stress-rupture tests on Type-304 stainless steel are tabulated in Table 4-8, and shown graphically in Figure 4-11.

In Figure 4-11, no distinction is made between the stress-rupture properties of solution-annealed and carbide-agglomerated steels at 1300°F. A linear regression analysis of the data showed that the two heat treatments produce equivalent properties for both 1300°F sodium and argon tests. As shown in the figure, the 1300°F control data are in good agreement with literature data⁹ (uniaxial tests) for Type-304 stainless steel, and exhibit a narrow confidence band.

In contrast, the stress-rupture data from the 1300°F sodium tests exhibit considerably more scatter. This scatter is caused by run-to-run variations. The maximum reductions in stress-rupture properties were produced during runs 4R-2 and 5R-4. The minimum reduction was produced during run 5R-5. It is shown in the following subsection that similar run-to-run variations were observed in the Type-316 stainless steel data. It should be emphasized that all three test runs (4R-2, 5R-4, and 5R-5) were performed at the same nominal temperatures, flows, cold trap temperatures, etc. The only major variation in the 5R-5 test was the early replacement (after 2036 hours at 1300°F) of the main loop heater. This replacement introduced 5.5 square feet of new stainless steel surface area in the hot-leg region immediately upstream from the specimens. This replacement of 68% of the surface area in the heater section of the loop probably disturbed the steady-state conditions which had been developed in the loop in the previous run. Consequently, the replacement of the heaters had the effect of increasing the effective downstream position of the test specimens in run 5R-5, thus minimizing the degradation of mechanical properties.

This discussion should be taken into account in defining the "real" effect of sodium exposure on the design properties of cladding. The maximum degradation produced in these tests probably represents the minimum degradation that will be produced in the reactor core (for the same temperatures, flows, oxygen, etc.). Because of the high power density of the core, the peak temperature sections of the cladding will operate in essentially zero downstream conditions. Therefore, the maximum degradations reported here should be incorporated into the cladding design.

Measurements of rupture strain ($\Delta D/D$) were taken from stress-rupture specimens that had been tested in argon and in sodium. Although there was scatter in the data, both Types-304 and -316 stainless steel suffered losses in ductility as a result of sodium exposure. For example, in tests at 1300°F, lasting up to 6000 hours, the average value of $\Delta D/D$ for Type 304 was reduced from ~15% to ~7%. Similarly, in tests at 1300°F, lasting up to 12,000 hours, the average value of $\Delta D/D$ for Type 316 was reduced from ~10% to ~4%.

Table 4-8
 BIAxIAL STRESS-RUPTURE DATA FOR TYPE-304 STAINLESS STEEL

Sodium Tests — 1300°F

Rupture Time (hours)			
σ psi	SA	CA	Loop
5000	5187	4500	4R-2
	6547	6229	4R-2
5500	3939	9223	5R-5
	7806	—	5R-5
6000	6999	6709	5R-5
	8307	7678	5R-5
7000	2409	2409	5R-4
	2644	3342	5R-4
	2198	2188	4R-2
	2237	2263	4R-2
9000	1189	1184	5R-4
	1656	1487	5R-4

Control Tests — 1300°F

Rupture Time (hours)		
σ psi	SA	CA
5000	>16,000	>19,520
	—	>16,000
8000	3380	4165
	—	5965
9000	2511	2727
	3373	2895
	4374	3389
11,000	829	718
	901	—

Sodium Tests — 1150°F

Rupture Time (hours)			
σ psi	SA	CA	Loop
18,000	1710	5391	6R-4
	1947	6235	6R-4
20,000	514	1662	6R-4
	559	4006	6R-4

Control Tests — 1150°F

σ psi	SA	CA
19,000	2441	3012
	3640	3152
	3857

STRESSED, DURING EXPOSURE

UNSTRESSED, DURING EXPOSURE

GLYCEREGIA

1000X

Figure 4-10. Effect of Stress on Sigma Formation in Solution-Annealed Type-316 Stainless Steel Exposed to 1300°F Flowing Sodium for 15,700 hours

Figure 4-11. Stress-Rupture Properties of Type-304 Stainless Steel in Argon and Flowing Sodium

The test data at 1150°F show that carbide agglomeration produces a major improvement in the stress-rupture properties of Type-304 stainless steel in sodium. Comparison with ASTM data and five failures from the argon control tests indicates that the sodium data are within the scatter band for tests in inert environments. This conclusion is supported by the small changes in composition and microstructure produced at 1150°F.

4.3.4.2 Type-316 Stainless Steel

Results of stress-rupture tests on Type-316 stainless steel are given in Table 4-9 and Figure 4-12.

As shown, the data for carbide-agglomerated and solution-annealed steels are plotted separately. With the exception of the heat treatment effects, the results for Type-316 stainless steel at 1300°F are consistent with those of Type-304 stainless steel. Degradation of stress-rupture properties was observed for both solution-annealed and carbide-agglomerated steels, with the greatest changes occurring in the latter. In agreement with the data for Type-304 stainless steel, the decrease in the stress rupture strength produced during run 5R-5 was considerably less than in runs 4R-2 and 5R-4. Possible reasons for this effect are described in the previous subsection.

Only a limited number of tests in sodium at 1150°F were completed at the termination of these experiments. The data from these tests, although limited, do indicate that the stress-rupture properties of Type-316 stainless steel in sodium are consistent with the ASTM data for tests in inert environments.

4.3.4.3 Statistical Analysis of Stress-Rupture Data

Analytical expressions describing the experimental results for the various materials, heat treatments, and test environments at 1300°F are given in Table 4-10. These equations were obtained by conventional least-squares methods to determine the best fit through each set of data. In addition, calculations were made to determine the 95% confidence limits for the coefficients listed in Table 4-10.

Comparison of Table 4-10 with the experimental data supports the conclusion that the stress-rupture properties are substantially degraded by 1300°F sodium exposure. It should be pointed out that the confidence limits for the data from sodium tests would be improved substantially if the data from run 5R-5 were deleted. A conservative calculation for the expected degradation of cladding during reactor exposure should not include the data from run 5R-5.

4.3.4.4 Post-Exposure Stress-Rupture Tests

A limited number of specimens were also exposed to sodium at 1300°F in an unstressed condition for various exposure times. These specimens were subsequently stress-rupture tested in argon. A description and the results of these tests are given in Appendix B.

4.3.5 Confirmatory Results

Other investigators have confirmed the results presented here and in earlier reports^{10,11,12} Ragnall¹³ exposed thick-walled (>0.060 inch) Type-316 stainless steel to flowing (1 ft/sec), high-temperature (1275°F, ΔT 300°F) sodium for 3301 hours. The initial carbon concentration in the steel was not uniform. A concentration gradient ranging from 0.09 wt% carbon at the surface to 0.05 wt% carbon at a depth 25 mils below the surface was observed in the steel before testing. The average carbon content within a surface layer 15 mils thick (equivalent to cladding wall thickness) was about 0.07 wt%. After exposure, the carbon concentration gradient was reversed (less carbon at the surface than in the bulk), and the average carbon content in the 15-mil layer was reduced to about 0.035 wt%. Within one cladding thickness, this exposure reduced the average carbon content by 50%. No measurements were made in this study of the effects of the observed decarburization on the mechanical properties of the steel.

Similar results were observed by Shively.⁸ In these tests, samples of Type-316, 20% cold-worked stainless steel cladding with 10-mil wall thickness were exposed in flowing (6 ft/sec), high-temperature (1200°F ΔT 50°F) sodium for 2613 hours. Before exposure the bulk content in the steel was ~0.057 wt%. After exposure, the bulk carbon concentration was reduced to ~0.016 wt%—a reduction of more than 70%. In addition to the reduction in carbon content, degradation of stress-rupture properties were observed. In these relatively short-time tests, reductions of 25% in rupture strength and 50% in rupture strain were measured.

It should be emphasized that the compositional and mechanical property changes reported in these studies will not occur in static or flowing isothermal sodium. In tests at 1200 and 1400°F for 3000 and 1000 hours, respectively, Lee¹⁴ observed no significant degradation of mechanical properties of cold-worked Types-304 and -316 stainless steel during exposure to high-purity (~10 ppm oxygen) sodium.

However, Lee did observe major decarburization and degradation of mechanical properties when the same steels were tested in zirconium-gettered systems¹⁵. In these tests, specimens of cold-worked Type-304 and annealed Type-316 stainless steel were exposed at temperatures ranging from 1300 to 1400°F for times up to 1000 hours. In contrast to the tests without zirconium, the carbon contents of the steels were reduced by 30 to 50%, and the rupture strength of the Type-304 stainless steel was reduced by 25%.

Figure 4-12. Stress-Rupture Properties of Type-316 Stainless Steel in Argon and Flowing Sodium

Table 4-9
BIAXIAL STRESS-RUPTURE DATA FOR TYPE-316 STAINLESS STEEL

Sodium Tests — 1300°F

σ (psi)	Rupture Time (hours)		
	SA	CA	Loop
6000	10,883	10,852	4R-2
		14,239	4R-2
7000	7780	9543	5R-5
	9171	—	5R-5
8000	3822	5162	4R-2
	4415	5175	4R-2
9000	—	3526	5R-4
	4676	6124	5R-5
	6727	8426	5R-5
12,000	—	1497	5R-4
	—	1642	5R-4

Control Tests — 1300°F - Argon

σ (psi)	Rupture Time (hours)	
	SA	CA
7000	11,452	11,631
	11,618	>16,000
8000	11,760	15,960
9000	5460	>14,050
	5474	>11,000
11,000	3183	4874
	4551	9279
13,000	2415	1584
15,000	1374	925

Sodium Tests — 1150°F

σ (psi)	Rupture Time (hours)		
	SA	CA	Loop
22,000	10,788	7734	6R-4
	—	8570	6R-4

Table 4-10
ANALYTICAL EQUATIONS DESCRIBING THE
1300°F STRESS RUPTURE DATA

$$\ln tr = \ln a - B \ln \sigma$$

tr = rupture time (hours)
σ = initial biaxial hoop stress (psi)

Material and Heat Treatment	Test Environment	Equation and 95% Confidence Limits for A and B Parameters
304 SA	Argon	$\ln tr = 54.71 \pm (30.3) - 5.14 \pm (3.3) \ln \sigma$
304 SA	Sodium	$\ln tr = 33.23 \pm (10.3) - 2.85 \pm (1.1) \ln \sigma$
304 CA	Argon	$\ln tr = 62.77 \pm (19.0) - 6.02 \pm (2.1) \ln \sigma$
304 CA	Sodium	$\ln tr = 34.29 \pm (11.3) - 2.97 \pm (1.3) \ln \sigma$
316 SA	Argon	$\ln tr = 33.84 \pm (5.2) - 2.75 \pm (.58) \ln \sigma$
316 SA	Sodium	$\ln tr = 26.47 \pm (19.8) - 1.98 \pm (2.1) \ln \sigma$
316 CA	Argon	$\ln tr = 39.16 \pm (33.5) - 3.32 \pm (3.6) \ln \sigma$
316 CA	Sodium	$\ln tr = 34.55 \pm (9.0) - 2.87 \pm (1.0) \ln \sigma$

4.3.6 Post-Exposure Characterization

Cladding samples that were exposed to sodium for 10,350 hours and 15,760 hours at 1300°F, and 11,379 hours at 1150°F, were characterized for physical dimensions and defects. The results of these examinations are given in Appendix C.

4.4 CONCLUSIONS

Many observations have been made in this task, which are of major significance to designers of LMFBR core components. The results are of greatest significance for thin-walled components (such as cladding) which will be exposed at the highest temperatures in the reactor system.

In general, it can be concluded that the creep and stress rupture properties of the nonstabilized Types-304 and -316 stainless steel will be degraded during reactor service. This degradation will be proportional to the temperature and time of exposure. The contributors to this degradation are losses of minor elements from the bulk of the steel, precipitation of large quantities of sigma phase, losses of major elements from the surface layers of the steel, and corrosion. The major losses in strength, however, result from losses in high-temperature strengthening elements (C, B, N) and the precipitation of sigma phase.

Although stress-rupture tests were not performed on stabilized steels (321, 347) or Incoloy-800, it is probable that these materials will also suffer some degradation in properties during exposure. The basis for this conclusion is the evidence of intergranular cavity formation, the precipitation of sigma phase, and the decreases in both boron and nitrogen contents from these steels. With the exception of intergranular cavities, these effects are smaller in the stabilized steels than in the nonstabilized steels. Thus, it is probable that the stabilized steels will suffer less degradation in properties.

Specific conclusions derived from this work are:

- The stress-rupture properties of nonstabilized stainless steels are reduced during exposure in nonisothermal, flowing sodium systems. At 1300°F, the 10,000-hour rupture strengths of Types-304 and -316 stainless steels can be reduced by 30 to 40%. No changes in properties have been observed in 1150°F tests.
- These losses in strength are caused by major losses in carbon and boron contents of the steels, and concurrent sigma phase formation.

- In the upstream positions of the test loop, the nonstabilized steels can lose up to 95% of their bulk carbon content, 75% of their boron content, and 75% of their nitrogen content. Smaller losses of carbon and boron, and gains in nitrogen, are observed in downstream positions.
- Stabilized alloys (321, 347, I-800) do not lose carbon, but can lose boron and nitrogen in somewhat smaller quantities than the nonstabilized alloys.
- Sigma-phase formation is most prevalent in Type-316 stainless steel. Lower concentrations are observed in Types-304, -347, and 321 stainless steel and Incoloy-800.
- Intergranular cavity formation occurs in all stabilized steels exposed at 1300°F. Cavities have been found to depths of 4 to 5 mils from the surface of these steels. The effects of these cavities on the mechanical properties of the stabilized steels have not been measured.

4.5 REFERENCES FOR SECTION 4

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APPENDIX A

METALLURGICAL EXAMINATIONS, LOOP 4R

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APPENDIX A

METALLURGICAL EXAMINATIONS, LOOP 4R

An examination of the Type-316 stainless steel economizer tubing from loop 4R was conducted to measure the extent of carbon movement and intergranular attack in the tubing wall. In addition to the economizer tubing, the loop piping from the outlet of Zone G to the economizer was examined. The results of both examinations are presented here.

A.1 CLEANING AND REMOVAL OF COIL SPECIMENS

The coil consisted of two Type-316 stainless steel tubes (1 inch o.d. X 0.035 inch wall) that were coiled and "nested" together. One piece of tube was cut from each coil at five locations: the inlet, the outlet, and three equally spaced intermediate positions (see Figure A-1). The five sections removed from one coil were sealed off and stored in the dry box. The five sections from the other coil were washed with water. The remains of the coils were sealed and stored in Building D.

A.2 REMOVAL AND CLEANING OF LOOP PIPING SPECIMENS

All pieces of pipe cut from the loop had a sodium film which was washed with alcohol and water. Locations of the sections removed for examination are shown in Figure A-1.

A.3 RESULTS OF EXAMINATION

The microstructure of the inner and outer surfaces of the economizer tubing is shown in Figure A-2. The microstructure of the base metal is characteristic of the temperatures of exposure; i.e., very little precipitation at the outlet (800°F), whereas at the inlet there is correspondingly more carbide precipitation and sigma phase formation. At locations 15 and 21 (1/2 and 3/4 of the total distance through the economizer), gross carbide precipitation indicative of high carbon activity in sodium is beginning at the outer surface along slip lines. At location 6 (1/4 of total distance) and the inlet, there is a surface layer characteristic of sodium corrosion on both the inner and outer surfaces.

The carbon content of the economizer tube at the inlet, outlet, and three equally spaced locations on the coil are shown in Figure A-3. The bulk carbon content of the tube increases continuously from the inlet to the outlet of the coil. Since the carbon content of the as-received tube material is not known (the vendor's heat analysis of 0.06%C, was not considered adequate without a check analysis), it cannot be stated where the tube stopped decarburizing and began carburizing. The increase in carbon content from the elbow (1 inch o.d. X 0.062 inch wall thickness) at the inlet to the outlet, however, indicates that the carbon activity in both the heated and cooled sodium was definitely higher at the economizer outlet than at the inlet. The higher carbon content of the outer surface layer removed from the tubes at locations 15 and 21 confirms the observation of a carbide case on the outer surface of these tubes (see Figure A-2).

Analysis of a dark-gray metallic deposit found only on the inner surface of samples 6 and 15 is shown in Table A-1. The increase in carbon content of the deposit with downstream position indicates that the carbon activity was increasing as the sodium was cooled on the inner surface of the tube. The composition of the deposit indicates that it might be a mixture of carbides and a metal.

A-4 RESULTS: LOOP PIPING

Sections of the loop piping (Type-304 stainless steel) from the six locations shown in Figure A-1 were examined metallographically and visually. The most significant feature revealed in the examination was the presence of intergranular cracks 1 to 2 mils deep on the inner surface of the pipe section at the inlet to Zone H (Figure A-4). This attack was similar to that found on samples from the corresponding location (Zone H inlet) in loop 5R.* In the section examined from loop 4R, the intergranular attack occurred around half of the circumference of the pipe inner surface. In the same section, but at a different location on the circumference, a uniform attack (similar to oxidation) about 0.05-mil (or 1.2-micron) deep was observed. The uniform attack (0.05 mil) was also observed in the "mid-riser" section (Figure A-1) between the economizer and Zone J. "Grooves" on the inner surface in the axial direction were seen in every section. Examination of these grooves at high magnification with the scanning electron microscope (SEM) revealed corrosion but no cracks (Figure A-5). They were, therefore, probably present in the as-received piping.

One final observation worth noting was a group of unusual "growths" at the pipe tee at the outlet of Zone H (Figure A-6). These probably occurred during vacuum distillation. It was difficult to tell whether the filament type of growth originated from a deposit or from the pipe wall itself. The central portion of this growth was colored deep blue/purple. The other nodules were probably formed from unvaporized sodium.

* F. A. Comprelli, F. J. Hetzler, R. S. Young, "Observation Concerning Localized Corrosion in Piped Sodium Systems," Trans. ANS, Vol 8, No. 2, p. 411.

The observations are summarized as follows:

- a. Significant localized intergranular attack (1 to 2 mils) of Type-304 stainless steel was produced by sodium with low oxygen content (~ 2 ppm) in 17,628 hours. (This confirms similar observations made on material from loop 5R.)
- b. Type-316 stainless steel heat exchanger tubes were carburized (outer surface) by sodium that was being heated. The inner surface (decreasing temperature sodium) was found to be decarburizing at the entrance (higher temperature), and carburizing at lower temperatures downstream (assuming vendor analysis of as-received carbon content was correct). This effect should be further investigated for verification and to determine its significance to IHX operations.
- c. The carbon activity in loop 4R sodium was higher at low temperature than it was at high temperature--as expected.
- d. Relatively deep grooves (3 to 5 mils) originally present in the loop piping did not develop into cracks during 17,600 hours of exposure at 1300°F in flowing sodium.
- e. Deposits from sodium that was being cooled were probably a mixture of carbides and metal. They were easily removed by brushing or ultrasonic cleaning.

Table A-1
ANALYSIS OF DEPOSIT FROM TUBE INSIDE DIAMETER

Specimen number	4R-6	4R-15
Specimen location downstream from economizer inlet	1/4	1/2
Alloy content (%)		
Fe	17.8	15.8
Cr	60	38
Ni	18	43
Mn	2.1	2.6
Mo	1.1	0.8
Carbon	0.37/0.56	1.3/1.6

Figure A-1. Specimen Location and Identification Cut from Loop 4R Economizer and Piping

OUTER SURFACE

← HEATING SODIUM

(1160°F)*

(1040°F)

(925°F)

(800°F)

TEMPERATURE: 1275°F

1/4 (6)

1/2 (15)

3/4 (21)

→ COOLING SODIUM

INNER SURFACE
INLET

OUTLET

MAGNIFICATION: 400X
MATERIAL: TYPE-316
STAINLESS STEEL

*TEMPERATURES IN
PARENTHESES ARE
ESTIMATED (LINEAR
INTERPOLATION)

GEAP-10394

A-4

Figure A-2. Microstructure of Tube in Loop 4R Economizer

Figure A-3. Carbon Content of Tubes in Economizer (Loop 4R) (see Figure A-1)

500X
UNETCHED

1000X
UNETCHED

MATERIAL: TYPE-304 STAINLESS STEEL
LOCATION: ZONE H INLET (INNER SURFACE)
EXPOSURE: 17,628 hours AT 1300°F

Figure A-4. Intergranular Attack and Oxidation (Slight) at Same Location in Loop But at Different Location on Circumference.

500X
SCANNING ELECTRON
MICROSCOPY

MATERIAL: TYPE-304 STAINLESS STEEL
LOCATION: MID-RISER
EXPOSURE: 17,628 hours AT 1275°F

Figure A-5. Groove on Pipe Inner Surface

"A"

Figure A-6. Growth at Outlet of H Section (after Vacuum Distillation)

APPENDIX B

**POST-EXPOSURE STRESS-RUPTURE TESTS
OF STAINLESS STEEL**

APPENDIX B

POST-EXPOSURE STRESS-RUPTURE TESTS OF STAINLESS STEELS

A limited number of unstressed specimens of the steels described in this appendix were exposed in flowing sodium at 1300°F for times ranging from 538 to 15,726 hours, and at 1150°F for 11,379 hours. The specimens exposed at 1300°F for times up to 4,838 hours were cleaned, fabricated into stress-rupture specimens, and tested in argon at 1300°F. As stated in previous reports, these specimens exhibited major degradation in stress-rupture properties. For example, prior exposures of 4,838 hours in sodium reduced the stress-rupture life of Types-304 and -316 stainless steels by factors of ten. Smaller (but readily measurable) degradation was observed for the other sodium-exposed materials.

Although a "sodium effect" was demonstrated in these tests, metallographic examination showed that much of the damage was caused by accelerated oxidation of the sodium-exposed specimens due to residual impurities from the sodium exposure. An example of the accelerated oxidation of solution-annealed Type-316 stainless steel is shown in Figure B-1. The specimen was pre-tested in flowing sodium at 1300°F for 1768 hours and then tested in argon (at 1300°F and 13,000 psi) until failure (~960 hours). The unexposed specimen was tested in argon at the same temperature and pressure for ~2400 hours before failure. As shown in the figure, a thick oxide scale formed on the surface of the sodium-exposed specimen during the stress-rupture test. This oxide, which formed in a nominally-inert atmosphere, also penetrated the grain boundaries of the steel as fracture progressed. This accelerated oxidation cannot be explained on the basis of compositional changes in the steel, because the pre-exposure time was too short to produce a sufficient change in the alloy composition.

A plausible explanation for the accelerated oxidation exhibited by sodium-exposed steels is that residual impurities (Na_2O , NaOH) were retained on the surface. This conclusion is particularly disturbing because the effect was common to most of the sodium-exposed specimens despite prior cleaning in alcohol and water.

In summary, these tests have shown that: (a) residual impurities (in concentrations sufficient to produce major chemical attack) are not readily removed, by conventional cleaning, from sodium-exposed steels, and (b) high-temperature mechanical property tests of pre-exposed steels can reflect corrosive attack from residual impurities rather than inherent degradation of the materials.

Figure B-1. Microstructures of Type-316 Stainless Steels after Stress-Rupture Test in Argon at 1300°F

APPENDIX C
CLADDING CHARACTERIZATION

APPENDIX C

CLADDING CHARACTERIZATION

Cladding specimens exposed to flowing sodium were subjected to nondestructive examination to characterize the post-exposure condition of individual tubes. The examination included measurements of inside and outside diameter, plus wall thickness and ultrasonic determination of defects. This is believed to be the first systematic data on dimensional changes due to sodium corrosion.

The data generated from dimensional measurements are summarized in Table C-1. The diameter measurements are calibrated to a known standard and accurate to ± 0.0001 inch. One trend is immediately apparent in the data: the outside diameter of the tubes decreases with increasing exposure to sodium for all materials (see Table C-2). The diameters of Types-321 and -347 stainless steel cladding (~ 0.025 inch o.d.) were reduced by 0.6 and 0.9 mil, respectively after 10,000 hours in flowing sodium at 1300°F . In another test, the same materials, exposed to 1600 hours, showed the same reduction. Weight loss rate, however, continued constant. This observation may be related to the appearance of subsurface voids along grain boundaries, but studies to date have not been in enough depth to draw firm conclusions.

In a few instances there was also a decrease in inside diameter, as shown in Table C-3. This was most pronounced in the Type-304 stainless steel. Wall thickness measurements agreed quite well with the diameter measurements (Table C-4), with one notable exception. The absolute deviation of the difference between the outside diameter—inside diameter and measured wall thickness was ± 0.00011 inch. The exception was the as-received, cold-worked, Type-316 tubing for which the difference between the direct measurement and the value obtained by subtracting inside diameter from outside diameter was 0.00055 inch. Since the direct measurement of wall thickness involves an ultrasonic technique, it is possible that changes in the severely cold-worked structure interfered with the measurement.

The surface finish of the tubes was also made apparent by the diameter measurements since the diameter was traced as the tube rotated. In general, the surface appeared to be roughened after exposure to sodium at 1300°F , while there was little roughening at 1150°F . Of course, some of the observed roughness must be attributed to the longitudinal scratches introduced when the samples were removed from the sodium loop. However, excluding local variations in diameter, there appeared to be consistent trends in the diameter measurements over several inches of tubing. The unexposed tubing and the tubing exposed at 1150°F , on the other hand, usually varied less than ± 0.00005 inch from the mean.

It was found that a meaningful examination for defects by ultrasonic testing was impossible due to the aforementioned scratches on the specimen tubes. The equipment used did not distinguish between surface and subsurface defects. The system was calibrated to set off an alarm if a defect exceeded 10% of the tubing wall thickness based on a standard with an outside diameter and inside diameter notch. In some instances, the alarm was on constantly while the probe traversed the tube. Other tubes exhibited a constant noise level that was below the alarm threshold, but this did not appear to be related to microstructure or amount of sodium exposure. Some of the tubes (i.e., Types 321 and 347), which were exposed 15,726 hours at 1300°F and examined by microscopy, were known to have cavities under the outside diameter surface. However, ultrasonic testing indicated that the tubes were defect free, with no observable level of noise. All of the control samples were found to be free of defects.

Table C-1
SUMMARY OF CLADDING SPECIMEN DIMENSIONAL MEASUREMENTS

Sample	Material	Exposure		O.D.	I.D.	Wall Thickness	
		Time (hr)	Temperature (°F)			Average	Range
0011	304SA		Control	0.2496	0.2202	0.0146	0.0144 to 0.0149
0021	304CA		Control		No archive available		
0031	316SA		Control	0.2502	0.2197	0.0154	0.0149 to 0.0159
0041	316CA		Control		No archive available		
0051	347SA		Control	0.2501	0.2192	0.0156	0.0149 to 0.0161
0061	321SA		Control	0.2498	0.2202	0.0150	0.0147 to 0.0151
0071	I-800SA		Control	0.2499	0.2201	0.0152	0.0147 to 0.0156
0081	316CR		Control	0.2501	0.2206	0.0143	0.0141 to 0.0149
4211	304SA	15,726	1300	0.2482	0.2195	0.0142	0.0138 to 0.0147
4221	304CA	15,726	1300	0.2483	0.2195	0.0144	0.0140 to 0.0149
4231	316SA	15,726	1300	0.2495	0.2195	0.0150	0.0148 to 0.0153
4241	316CA	15,726	1300	0.2493	0.2194	0.0149	0.0146 to 0.0152
4251	347SA	15,726	1300	0.2492	0.2198	0.0147	0.0142 to 0.0153
4261	321SA	15,726	1300	0.2492	0.2200	0.0146	0.0141 to 0.0150
4271	I-800SA	15,726	1300	0.2491	0.2200	0.0147	0.0143 to 0.0149
4281	316CR	15,726	1300	0.2489	0.2198	0.0145	0.0143 to 0.0146
5511	304SA	10,352	1300	0.2486	0.2198	0.0142	0.0138 to 0.0145
5521	304CA	10,352	1300	0.2487	0.2198	0.0145	0.0141 to 0.0147
5531	316SA	10,352	1300	0.2496	0.2195	0.0151	0.0147 to 0.0153
5541	316CA	10,352	1300	0.2494	0.2195	0.0150	0.0147 to 0.0152
5551	347SA	10,352	1300	0.2492	0.2199	0.0147	0.0145 to 0.0148
5561	321SA	10,352	1300	0.2492	0.2200	0.0144	0.0139 to 0.0148
5571	I-800SA	10,352	1300	0.2493	0.2200	0.0146	0.0143 to 0.0149
5581	316CR	10,352	1300	0.2490	0.2200	0.0145	0.0143 to 0.0148
6411	304SA	11,379	1150	0.2494	0.2201	0.0146	0.0141 to 0.0151
6421	304CA	11,379	1150	0.2497	0.2202	0.0146	0.0141 to 0.0152
6431	347SA	11,379	1150	0.2500	0.2200	0.0149	0.0148 to 0.0151
6441	321SA	11,379	1150	0.2497	0.2203	0.0147	0.0143 to 0.0151
6451	316SA	11,379	1150	0.2500	0.2196	0.0152	0.0149 to 0.0154
6461	316CA	11,379	1150	0.2499	0.2198	0.0149	0.0147 to 0.0151
6471	I-800SA	11,379	1150	0.2496	0.2197	0.0149	0.0146 to 0.0152
6481	316CR	11,379	1150	0.2495	0.2208	0.0142	0.0138 to 0.0145

Table C-2
COMPARISON OF SPECIMEN O.D.'S AT VARIOUS LEVELS OF SODIUM EXPOSURE

Material	Control	Specimen Outside Diameters		
		1150°F 11,379 hours	1300°F 10,352 hours	1300°F 15,726 hours
304SA	0.2496	0.2494	0.2486	0.2482
304CA	NA ^(a)	0.2497	0.2487	0.2483
316SA	0.2502	0.2500	0.2496	0.2495
316CA	NA ^(a)	0.2499	0.2494	0.2493
316CR	0.2501	0.2495	0.2490	0.2489
312SA	0.2498	0.2497	0.2492	0.2492
347SA	0.2501	0.2500	0.2492	0.2492
I-800SA	0.2499	0.2496	0.2493	0.2491

(a) Not available

Table C-3
COMPARISON OF SPECIMEN I.D.'S AT VARIOUS LEVELS OF SODIUM EXPOSURE

Material	Control	1150°F 11,379 hours	1300°F 10,352 hours	1300°F 15,726 hours
304SA	0.2202	0.2201	0.2198	0.2195
304CA	NA ^(a)	0.2202	0.2198	0.2195
316SA	0.2197	0.2196	0.2195	0.2195
316CA	NA ^(a)	0.2198	0.2195	0.2194
316CR	0.2206	0.2208	0.2200	0.2198
321SA	0.2202	0.2203	0.2200	0.2200
347SA	0.2192 ^(b)	0.2200	0.2199	0.2198
I-800SA	0.2201	0.2197	0.2200	0.2200

(a) NA - Not available

(b) Very rough i.d. surface

Table C-4
COMPARISON OF WALL THICKNESS DETERMINED BY O.D. - I.D. AND DIRECT MEASUREMENT

o.d. - i.d. Exposure	Wall Specimen	Material	(inch)	(inch)	Difference (Wall - o.d./i.d.) (inch)
Controls	0011	304SA	0.0147	0.0146	-0.0001
	0021	304CA	NA(a)	NA(a)	NA(a)
	0031	316SA	0.0152	0.0154	0.0002
	0041	316CA	NA(a)	NA(a)	NA(a)
	0051	347SA	0.0154	0.0156	0.0002
	0061	321SA	0.0148	0.0150	0.0002
	0071	1-800SA	0.0149	0.0152	0.0003
	0081	316CR	0.01475	0.0142	-0.00055
1300° F 15726 hours	4211	304SA	0.0144	0.0142	-0.0002
	4221	304CA	0.0144	0.0144	0
	4231	316SA	0.0150	0.0150	0
	4241	316CA	0.01495	0.0149	-0.00005
	4251	347SA	0.0147	0.0147	0
	4261	321SA	0.0146	0.0146	0
	4271	1-800SA	0.01455	0.0147	0.00015
	4281	316CR	0.01455	0.0145	-0.00005
1300° F 10352 hours	5511	304SA	0.0144	0.0142	-0.0002
	5521	304CA	0.01445	0.0145	0.00005
	5531	316SA	0.01505	0.0151	0.00005
	5541	316CA	0.01495	0.0150	0.00005
	5551	347SA	0.01465	0.0147	0.00005
	5561	321SA	0.0146	0.0144	-0.0002
	5571	1-800SA	0.01465	0.0148	-0.00005
	5581	316CR	0.0145	0.0145	0
1150° F 11379 hours	6411	304SA	0.01465	0.0146	-0.00005
	6421	304CA	0.01475	0.0146	-0.00015
	6431	347SA	0.0150	0.0149	-0.0001
	6441	321CA	0.0147	0.0147	0
	6451	316SA	0.0152	0.0152	0
	6461	316CA	0.01505	0.0149	-0.00015
	6471	1-800SA	0.01495	0.0149	-0.00005
	6481	316CR	0.01435	0.0142	-0.00015

(a) NA - No archive available.

APPENDIX D

PUBLICATIONS ISSUED

APPENDIX D

PUBLICATIONS ISSUED

Topical Reports, October 1, 1968 through August 31, 1971

- GEAP-10048 Collins, G. D., *Plugging Indicator Operation*, September 1969. Task II, On-Line Monitors.
- GEAP-13545 Comprelli, F. S., and Krankota, J. L., *Interpretation of the ASME Code for Low-Alloy Steels in Bi-metallic Sodium Systems*, September 1969. Task III.
- GEAP-13544 Wozadlo, G. P., and Spalaris, C. N., *Corrosion of Stainless Steels and Deposition of Particulates in Flowing Sodium Systems*, September 1969. Task IV.
- GEAP-13559 Wozadlo, G. P., and Pohl, L. E., *Sodium Mass Transfer: Comparative Corrosion and Microstructural Effects for Austenitic Stainless Steels in Flowing Sodium*, October 1969. Task I.
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- GEAP-10008 Quarterly Report No. 8, December 1968–February 1969
- GEAP-10036 Quarterly Report No. 9, March–May 1969
- GEAP-13539 Quarterly Report No. 10, June–August 1969
- GEAP-13539-11 Quarterly Report No. 11, September–November 1969
- GEAP-13539-12 Quarterly Report No. 12, December 1969–February 1970
- GEAP-13539-13 Quarterly Report No. 13, March–May 1970
- GEAP-13539-14 Quarterly Report No. 14, June–August 1970
- GEAP-13539-15 Quarterly Report No. 15, September–November 1970
- GEAP-13539-16 Quarterly Report No. 16, December 1970–February 1971

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