MASTER

SODIUM TECHNOLOGY PROGRAM
PROGRESS REPORT
FOR THE PERIOD ENDING AUGUST 31, 1971

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SECTION 1 INTRODUCTION

1.0 GENERAL

This progress report on the Sodium Technology Program covers the work performed during the period from June 1, 1971 to August 31, 1971. The program is divided into the following subtasks:

Sodium Wear Test Program (see Section 2)

Wear, Bearing Tests

Self Welding Evaluation in Sodium

Component Materials Compatibility (see Section 3)

On-Line Meter Characterization (see Section 4)

The Component Materials Compatibility subtask is a continuation of work reported as CEL continuation in WARD-4210T1-1, a progress report for the period ending November 30, 1970. The Sodium Wear Test Program and the On-Line Meter Characterization subtask were initiated during the third quarter of FY-1971.

2.0 SUMMARY OF OBJECTIVES

The primary objectives of each of the subtasks of this program are given below:

2.1 Sodium Wear Test Program

The objectives are to experimentally measure the wear rates and friction coefficients of several material combinations in interface configurations simulating FFTF core components under prototypic operating conditions; also to provide reactor designers with the quantitative data and experience factors necessary to successfully design components or component interfaces which will experience sliding or rubbing contact while immersed in high-temperature sodium.

The objective of the second part of this program is to determine self-welding potential between various material couples that are typical of FFTF loadings and configurations.

2.2 Component Materials Compatibility

The objectives are to provide experimental information and analytical relationships for design data so that the rate and direction of carbon and nitrogen transfer and associated mechanical property changes of structural materials within liquid metal systems, representative of primary and secondary circuits of an LMFBFR, may be predicted.

2.3 On-Line Meter Characterization

The objectives are to characterize fully the state-of-the-art liquid metal oxygen meters and provide the needed information on the performance characteristics of a standard electrochemical oxygen meter for FFTF and subsequent LMFBFR applications.

3.0 SUMMARY OF PRIOR WORK

All work related to the present investigations and performed prior to the present period has been fully documented in:

AEC Contract AT(30-1)-4173

WARD-4173-1, "Sodium Technology Program Quarterly Progress Report for the Period Ending March 31, 1970."

WARD-4173-2, "Sodium Technology Program Quarterly Progress Report for the Period Ending June 30, 1970."

AEC Contract AT(30-1)4210, Task 1

WARD-4210T1-1, "Sodium Technology Program Progress Report for the Period Ending November 30, 1970."

WARD-4210T1-2, "Sodium Technology Program Progress Report for the Period Ending May 31, 1971."

4.0 SUMMARY OF CURRENT PROGRESS

4.1 Sodium Wear Test Program

Construction of the first Sodium Wear Test Rig (SWEATER 1) is approximately 75 percent complete. Loop components are installed, and installation of interconnecting piping is in progress. The test chambers have been welded and stress relieved, and final machining is in progress. However, schedule slippage occurred as a result of delays in delivery of components for the test chambers. Machining of components for the drive system is essentially complete.

All design drawings for the sodium loop and test chambers have been completed, approved and issued. Components for the sodium loop have been fabricated and assembly is 90% complete; the twelve test chamber components have been machined and the assembly is in progress. Installation of the electrical and electronic system is 90% complete.

A System-Design-Description Report has been issued.

4.2 Component Materials Compatibility

The conceptual design for the Interstitial Transfer Facility (ITF) was completed during this reporting period. ITF experimentation will yield data on carbon and nitrogen transfer 'rates' whereas the current CEL work serves to establish 'equilibrium levels' of carbon and nitrogen in sodium system component materials.

Use of carbon meters in this phase of the work would greatly reduce costs and improve schedules. To date, the diffusion-type meter experience has been marred by the high background carbon levels remaining from its earlier use (by MSAR) at extremely high carbon activities. Replacement of the contaminated meter components is about 90% complete. The electrolytic carbon meter has been strongly affected by hydrogen introduced into the CEL-1 system by the diffusion type meter. This is being corrected by locating diffusion type meters on CEL-1 and electrolytic-type meters on CEL-2. The problem of limited electrode life in the latter type of meter (previously reported by BNL, ANL, and ARD) remains to be resolved.

Experience with the electrolytic oxygen meter on CEL-1 has been generally successful, though improvements in the thermal shock resistance of the electrolyte are needed. A new platinizing process by WRL shows promise in this connection.

Using CEL-1, five additional runs were made to provide needed data on Type 304 stainless steel in the low (<80 ppm) and middle (200-700 ppm) ranges. The requisite values were obtained, and a number of interesting comparisons with the behaviors of ARMCO iron, 2.25 Cr-1Mo ferritic steel, Types 316 and 321 stainless steels, and Incoloy 800 were achieved. In particular, a tendency for Type 321 stainless steel and Incoloy 800 to not decarburize below a minimum level was noted. The ferritic materials continued to exhibit decarburization at all carbon activity levels.

4.3 On-Line Meter Characterization

Drafting of the meter loop for FPL-2 has been completed. Materials purchases are 90% completed, and fabrication of the system is in progress with a scheduled start of shakedown operations in mid-September, about three weeks behind the original schedule. Agreement was reached with ANL on the details of operations during the meter test.

Characterization of the WADCO and ZIRCOA manufactured ceramic electrolyte tubes

has shown that the impurity level at the inside diameter is significantly higher than at the outer diameter with the impurities concentrating at grain boundaries. Fractographic analysis of tube failures has shown that the fractures are transgranular from the OD through about 80% of the thickness with the last 20% of the fracture being intergranular. It is inferred that the grain boundaries in the latter region have been weakened by reaction of the impurities during the platinizing process (reference electrode formation). A modified platinizing process has been adopted which decreases the affected intergranular region by about 90%.

Initial tests of meters using ZIRCOA electrolyte tubes are in progress in CEL's while awaiting completion of FPL-2. The oxygen sensitivity of these meters is the same as that of the WADCO meters with a somewhat lower absolute EMF output.

SECTION 2

SODIUM WEAR TEST PROGRAM

1.0 WEAR, BEARING TESTS

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1.1 Objectives

The objectives of the wear test program are:

1. To experimentally measure the friction coefficients and wear rates for several material combinations in interface configurations simulating FFTF core components under prototypic operating conditions.
2. To provide reactor designers with the quantitative data and experience factors necessary to successfully design components or component interfaces which will experience sliding or static contact under load while immersed in high-temperature sodium.

1.2 Background

The success of many design features and mechanisms for FFTF and LMFBR cores is dependent upon the ability of metallic surfaces, which are in contact under sodium, to slide over one another. The motion originates during operation of various mechanical components such as the core restraint device, control rod drives, and refueling machines; or as the result of differential thermal expansion and/or flow or mechanically induced vibrations.

Design of these components and structures must include allowances for frictional loads and wear phenomena in sodium; these allowances must be based on data obtained in tests which accurately simulate the surface contact and sodium conditions anticipated in the reactor system.

During the last half of CY-1970, an extensive review of FFTF core, control rod drive mechanism, and in-vessel fuel handling machine designs was performed (AEC Contract AT(45-1)-2171) to identify components and interfaces that will be subject to frictional loads and wear while immersed in sodium. The need for data on friction coefficients and wear rates was established, and a Westinghouse Development Test Requirement Specification (WDTRS 1.27) [1]

[1] WDTRS 1.27, "Wear Testing - FFTF Components (Revision 2 with Addendum)," Tables I and II and Tables 1 and 2 of Addendum, February 17, 1971, Contract AT(45-1)-2171 Task 1, Westinghouse Advanced Reactors Division, Madison, Pennsylvania.

was prepared that defined the important components and interfaces, their operating conditions, and the test plan needed to obtain the friction and wear data. WDTRS 2.43^[2] and WDTRS 2.46^[3] were also established.

1.3 Prior Work

The basic experimental approach selected in the ARD program is to press two diametrically opposed horizontal pin specimens against plate specimens mounted on a vertically reciprocating rod immersed in flowing, well-characterized sodium. The contact bearing load (normal static load), the force necessary to move the plate (frictional load), and the displacement are continuously measured. Friction coefficients are calculated as the ratio of the frictional and the measured normal static loads on the pin-plate specimen.

Wear data will be obtained from measured length and width changes of the pin and from quantitative analysis of wear scars on the plate specimens using a surface profiling instrument.

Additional information will be obtained on surface morphology, chemical composition, and metallurgical changes. Current plans include the testing of specimen surfaces in the "as-received" condition and after pre-exposure to sodium under conditions selected to produce the same surface composition and metallurgical conditions as anticipated for the actual FFTF component.

Design of the friction and wear test machines and sodium supply loop was completed, and construction of two facilities was started. Each facility will consist of two wear test machines and a sodium supply loop. The equipment was described in detail in the previous quarterly.^[4] Figures 2-1, 2-2, and 2-3 show the wear test machine, reciprocating drive system, and the sodium supply loop, respectively. Operating and test parameters for the facility are summarized in Table 2-1.

1.4 Current Progress

Construction of the first Sodium Wear Test Rig (SWEATER #1) is nearing completion. All loop components have been fabricated (or received) and installed in the enclosure. Approximately 75 percent of the interconnecting piping has been completed. The remainder of the piping has been fabricated, and field installation and welding is in progress. A photograph of the loop during construction is shown in Figure 2-4. The control consoles, shown in Figure 2-5, have been assembled and interpanel and service wiring completed.

[2] WDTRS 2.43, "Fuel Cladding Corrosion Wastage Allowances Tests," May 1971, Westinghouse Advanced Reactors Division, Madison, Pennsylvania.

[3] WDTRS 2.46, "FTR Duct Load Pad Materials Evaluation," July 1971, Westinghouse Advanced Reactors Division, Madison, Pennsylvania.

[4] WARD-4210T1-2, "Sodium Technology Program Progress Report for the Period Ending May 31, 1971," August 1971.

Figure 2-2. SWEATER Drive Mechanism

4340-4

Figure 2-3. Loop Assembly Isometric

Fabrication of the test chambers was delayed due to delays in delivery of the six-inch Conoseal flanges. At present, test chamber (TS-1 and TS-2) welds have been completed and stress relieved in an inert atmosphere furnace at 1550 to 1650°F. Final machining of the flange cover plates is in progress. A photograph of the test chambers after welding and stress relief is shown in Figure 2-6.

Table 2-1. Test Parameters for SWEATER

Wear Test Machine	
Operating Temperature	400 to 1350°F
Specimen Configuration	a. Flat-on-flat b. Cylinder on-flat
Contact Pressure	200 to 10,000 psi
Motion	a. Reciprocating, 0.02 to 3-inch displacement b. Rotational $\sim \pm 7-1/2^\circ$ c. Reciprocating plus rotation d. a or b or c plus vibration
Total Travel	Up to 10,000 inches
Velocity	1 to 37.5 ipm
Dwell Time	0 to ~ 6 month
Specimen Surface Condition	a. As-fabricated and installed b. Pre-exposed to reproduce expected surface compositional changes
Sodium Supply Loop	
Purity	<5 ppm oxygen, <2 ppm hydrogen, maintained by cold trap, 25 micron particulate filter
Flow	0.1 to 2 feet per second past wear surfaces
Characterization	On-line oxygen meters. Bypass sampling for metals, O, H, N, C, and particulates as required.

Figure 2-4. SWEATER - Sodium Supply Loop During Construction
4500-29

Figure 2-5. SWEATER - Control Console

Figure 2-6. SWEATER - Test Chamber

Machining of drive system components is more than 80 percent complete and assembly of the drives for TS1 and TS-2 was started. Figure 2-7 shows the various drive system components prior to assembly.

Purchase orders have been placed for solution annealed Type 316 and 304 stainless steel specimen material. Some difficulties have been encountered in locating a vendor for small quantities of 20% cold worked Type 316 stainless steel and Inconel 718 strip. Since no quotes were received for material to RDT specifications, all material is being ordered to conventional ASTM specifications and will be upgraded at ARD.

2.0 SELF-WELDING EVALUATION IN SODIUM

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2.1 Objectives

The objectives of these tests are to provide information on self-welding characteristics for FFTF reactor materials with relevance to the component configurations anticipated in the reactor and reactor system.

2.2 Prior Work

2.2.1 Preparatory Work

The basic need and specifications for this program were identified in a Westinghouse Development Test Requirements Specification.^[1] Prior work^[5] outside of Westinghouse has provided preliminary information on suitable material combinations for use in high temperature sodium, however, the data were obtained under conditions not prototypic of those anticipated for the many components of the FFTF.

2.2.2 Facilities

In order to perform the self-welding tests identified in Reference 1, design efforts were initiated at Westinghouse on modifications to an existing sodium facility. The prior work at Westinghouse can be summarized as follows:

1. Operational parameters of the sodium loop were finalized.
2. All loop components and auxiliary systems were designed.
3. Details of sample geometry and test procedures were finalized.
4. Materials required to construct the necessary loop components were identified and placed on order.

[5] K. Bendorf, "Experimental Investigations of Self-Welding of Structural Materials Under Sodium," Nucl. Eng. Des. 14, pp. 83-98 (1970).

Figure 2-7. SWEATER - Drive System Components
4500-30

2.3 Current Progress

2.3.1 Sodium Loop

Design modifications on the Thermal Fluids Loop have been completed. The resulting system is called the Self-Welding System (SWS). The surge tanks have been redesigned to adequately control the sodium levels in the system, particularly under emergency dump conditions. The cold traps have been designed to give a residence time >5 minutes at a flow rate of 0.2 gpm. Non-isothermal conditions are achieved in the system by a 10 kw "clam-shell" heater assembly, economizer, and sodium to air heat exchanger. An isometric of the resulting system is shown in Figure 2-8. Sampling and Westinghouse oxygen meter sections have been added to the system to give the necessary purity monitoring capabilities. All drafting effort on the SWS has been completed. Modifications to the existing framework have been completed. All components for the system have been fabricated, and the system has been assembled (Fig. 2-9) with the exception of the heaters and insulation.

An analysis has been performed on the test chamber force rod to predict the rod temperature profile. The analysis satisfied the 400°F maximum seal temperature for the maximum temperature case. From this analysis it has been determined that no heating of the vapor cooling column will be necessary.

2.3.2 Test Chambers

The drawings for the test chambers have been revised, based on fabrication related problems. All components, with the exception of the test samples, have been machined for 12 test chambers. One set of the chamber components and assembly are shown in Figure 2-10 and 2-11, respectively. Most components are made of Types 304 or 316 stainless steel with the exception of the seal head which is carbon steel. This component does not come in contact with liquid sodium.

To study the wiping conditions between two sample surfaces, an assembled test chamber with dummy specimens was tested under a compressive stress of 1467 psi at room temperature. A torque of 34 foot-lbs was required to perform the necessary wiping action. After the test, the mating surfaces indicated some degree of scratch marks as a result of the wiping action.

The partially assembled control panel is shown in Figure 2-12. The control panel contains all necessary instrumentation for the monitoring and control of temperatures, sodium flow rates, and hydraulic pressures.

The System-Design-Description report has been completed, and the Westinghouse required Stored Energy Committee Safety Report is being prepared.

Figure 2-8. Self-Welding System Isometric

Figure 2-9. Rear View of Self-Welding Loop Partially Constructed
4500-7

Figure 2-10. Self-Welding Test Chamber Components

4500-6

Figure 2-11. Completely Assembled Self-Welding Test Chamber
4500-5

Figure 2-12. Self-Welding Control Panel Partially Constructed
4500-4

SECTION 3

COMPONENT MATERIALS COMPATIBILITY

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1.0 OBJECTIVES

The objectives of this program are to provide experimental information and analytical relationships for FFTF and LMFBR design uses, so that the rate and direction of carbon and nitrogen transfer and the associated mechanical property changes of structural materials within liquid metal circuits representative of primary and secondary reactor plant systems may be predicted.

2.0 PRIOR WORK

2.1 Related Work Outside Westinghouse

The current AEC sponsored interstitial transfer program is part of an overall national program on sodium technology. The work at Westinghouse interfaces with, and in some areas complements, work being performed at ANL. Programs at AI, BNL, GE, MSAR, and UNC, which have now been terminated, are also relevant to the Westinghouse effort.

In the area of carbon meter calibration and operation, the Westinghouse program will benefit from past work at UNC and BNL where the meters were developed and at MSAR where the UNC meter was used successfully in high-carbon environments. The ANL program is perhaps the most extensive one outside Westinghouse. ANL personnel are concentrating primarily on relating carbon transport to chemical species fundamental studies of interstitial activities in structural materials and on adapting experimental meters for on-line use in EBR-II. The meter program is of particular interest to Westinghouse.

AI's program (now terminated) interfaced in the area of material properties. They were to investigate the effect of carbon and nitrogen content of stainless steel on mechanical properties.

2.2 Facilities

2.2.1 CEL-1

CEL-1 was filled with sodium and began operation in August 1971. Various operating problems were subsequently encountered and solved by modifying the system. Operating procedures were developed for specimen loading and unloading and the operation of the various meters.

The principal operating problem was identified as the introduction of hydrogen from the UNC carbon meter into the system.

During the last reporting period, 12 runs were performed and further modifications were identified.

1. It was decided to replace the carbon source with one of a new design incorporating sealed mild steel capsules filled with sodium and powdered graphite.
2. The BNL meter was to be removed and installed on CEL-2.
3. A standard tab exposure chamber (STEC) was designed and partially fabricated.

The system was purged of hydrogen by using an external cold trapping device.

2.2.2 CEL-2

Fabrication and installation of this system were completed during the last reporting period leaving only minor additions to the cover gas system, installation of the smoke detectors, and the carbon source to be finished.

CEL-2 incorporates two BNL meter housings and is scheduled to have a standard tab exposure chamber installed. Additional control equipment for the second BNL meter and the STEC were ordered.

2.2.3 ITF

A conceptual design for the Interstitial Transfer Facility has been completed. The facility will be a simulation of the FFTF primary system. The ITF is a forced circulation ΔT loop consisting basically of two hot-leg regions, a cold-leg region, an electromagnetic pump, three flow meters, and a heat exchanger. The hot legs, cold leg, heat exchanger, and certain lengths of connecting piping are all used as specimen test sections. Test section locations are chosen to represent critical regions of the FFTF system. The oxygen concentration is controlled by varying the temperature in a by-pass cold-trap line and measured using an electrolytic oxygen meter. The carbon activity is measured using a suitably calibrated carbon meter and/or standard tabs. The nitrogen activity is measured using standard tabs. The meter and tab exposure station will be located in separate by-pass lines with suitable temperature control.

Access to specimens located through the test sections will be accomplished by removing welded end caps located at each end of the test sections.

A Conceptual System Design Description was written and submitted to the AEC for approval.

The available FFTF design data were analyzed to determine the surface areas and temperature profiles.

The system was broken down into 17 components or groups of components, and each was considered individually. Results of the analysis were presented as axial temperature distribution curves with the accumulated surface area represented by each curve indicated on the figure.

The analysis was conducted on the basis of the FFTF improved core design, which stipulates an approximate 800°F inlet sodium temperature and a 1050°F outlet sodium temperature (mixed mean). All surface area data were calculated from the most current design data. In several instances, however, the temperature distribution data were taken as representative of the present FFTF design.

2.3 On-Line Metering

2.3.1 UNC Diffusion Carbon Meter

Modifications were made to the system to reduce the amount of hydrogen diffusing into the CEL-1 sodium. An argon supply was provided which could be used to replace the decarburizing gas supply when the meter was not in use. Meter readings did not generally correlate with measured carbon levels. The background reading limited the sensitivity of the readings. An investigation of the system suggested that it was severely contaminated with carbon during its prior use. Steps were taken to eliminate the sources of contamination.

2.3.2 BNL Carbon Meter

Work continued with the BNL meters but was hampered by the hydrogen content of the CEL-1 sodium.

Difficulties with intermittent shorting of the meters were encountered even with the new, mild steel housing.

The effect of hydrogen on the meter was significant, a 400°F saturation temperature (one ppm H_2 in Na) producing a 5 mv depression. At a 360°F saturation temperature (1/2 ppm H_2 in Na), the effect was negligible.

2.3.3 Westinghouse Oxygen Meter

Operation of the Westinghouse Oxygen meter on CEL-1 was generally successful. Oxygen meter behavior is reported in Section 4 of this document, "On-line Meter Characterization."

2.4 Experimental Work

Twelve loop runs were completed up to the end of the last reporting period. After several proving runs, it was shown that:

1. The containment material had a surface value in excess of 500 ppm carbon as expected.

2. Hot trapping above 1200°F dramatically lowers the carbon activity of the sodium.
3. There is little or no activity difference between locations in the sample tank.
4. The new carbon source is very effective in raising the carbon activity of the system.
5. Cold trapping effectively reduces the carbon activity of the sodium.

Using Type 304 L stainless steel as a reference material at 1300°F, C values were measured for the various materials at 1300°F between values of 70 and 4000 ppm. It was shown that Incoloy 800 and Type 321 stainless steel equilibrated at carbon values much higher than Types 304 and 316. The 1300°F C_e curves were essentially completed during the reporting period.

3.0 Current Progress

3.1 Facility Design and Installation

3.1.1 CEL-1

Five runs were completed during the reporting period under various operating conditions. Details of the runs are given in Section 3.2.1.

CEL-1 was shut down in mid-August in order to perform maintenance and scheduled modifications. These included:

1. Replacement of the hot trap valve
2. Removal of the vacuum distillation side loop
3. Installation of the Standard Tab Exposure Chamber (STEC) side loop
4. Removal of the BNL meter side loop
5. Installation of the second UNC carbon meter side-arm

All welding work is now complete together with the installation of the additional control equipment.

The next series of runs will be at 1400°F.

3.1.2 CEL-2

CEL-2 was filled and brought into operation on July 7, 1971. Over a period

of three weeks minor operating problems were identified and rectified. The loop ran for short periods of time up to 1200°F.

Difficulties were experienced in raising the loop temperature above 1200°F. The loop was dumped, modifications were made to the loop insulation, and additional heaters were added. Temperatures in excess of 1300°F are now easily achieved.

The STEC was installed, a failed oxygen meter probe was replaced, and the loop was returned to operation.

New sample bobbins have been prepared and will be used in the first CEL-2 run at 1300°F.

3.1.3 ITF

Work continued on the ITF design during the current reporting period. The decision that the ITF shall 'mock up' FFTF interstitial transfer conditions means several assumptions must be made during the design stage. This is due to a lack of sound theoretical understanding of the mechanisms involved in interstitial transfer in a polythermal, sodium/stainless steel and, consequently a lack of knowledge of the relative importance of the many system parameters involved. As a result, there is no established parameter that may be used in the scaling down process.

Experimental observation suggests that different mechanisms are involved in the hot and cold legs of a polythermal loop. In the hot leg regions, the process involves the removal of interstitials from the exposed metal surface. Experimental data indicate that this is limited by solid state diffusion. In the cold leg, the mass transfer process involves deposition, nucleation, and growth phenomena. This process must involve liquid state diffusion, and the material has to be brought into contact with containment walls before depositing. Hence, turbulence levels and residence times are assumed to be rate limiting steps in the cold region. Therefore, two types of parameter rather than one must be used in the scaling process.

For the experimental facility to successfully duplicate the reactor system and yield valid carbon transfer rates, carbon concentrations in the sodium hot leg regions of the loop must be the same as they are adjacent to the corresponding reactor component. The carbon concentration of the sodium at any point in hot leg areas of the loop can be expressed as follows:

$$C_x = C_i + \frac{FA}{Q} \quad (1)$$

where: C_x = Carbon concentration of the sodium at any downstream point in the hot leg region

C_i = Carbon concentration of the sodium at inlet to hot leg region

F = Average carbon flux from the wall to the sodium

A = Wetted surface area

Q = Volumetric flow rate of the sodium

The inlet carbon concentration, C_i , will be controlled by the cold leg scaling parameter. If at this point it is assumed that a valid mock up is achieved in the cold leg; then for the carbon concentration to be the same in the experimental loop as it is in the reactor, the second term in the above equation must be a constant; i.e.,

$$\left(\frac{FA}{Q}\right)_{\text{loop}} = \left(\frac{FA}{Q}\right)_{\text{reactor}} = K_1, \text{ constant} \quad (2)$$

Following this argument one step further, if the loop and reactor carbon concentrations and temperature levels are identical, the carbon fluxes from the walls must be the same; i.e., $F_l = F_r$.

Hence, Equation 2 reduces to:

$$\left(\frac{A}{Q}\right)_{\text{loop}} = \left(\frac{A}{Q}\right)_{\text{reactor}} = K_2, \text{ constant}$$

For a simple pipe, A/Q can be written as $4L/DV$, where L is the length of the pipe, D is the diameter, and V is the sodium velocity. Values of (A/Q) have been developed for the various components of the FFTF and will be duplicated in the loop system.

In the deposition, or cold-leg regions, the scaling parameter that will be used is $(N_{Re})^{0.8} \Delta T$, where N_{Re} is the Reynold's number, and ΔT is the residence time. The Reynold's number to the 0.8 power determines the thickness of the laminar boundary layer at the wall, which in turn determines the rate at which carbon bearing species can diffuse across this barrier and subsequently deposit. The residence time is included in the scaling parameter to insure sufficient time for this liquid phase diffusion to occur. Again, values of the parameter $(N_{Re})^{0.8} \Delta T$ have been calculated for the reactor; and an attempt will be made to duplicate these values in the loop system.

Superimposed on the scaling-down process described above is the requirement that correct temperature profiles and surface area ratios of the various alloys be maintained in the loop system.

3.2 Experimental Data

Apart from the CEL data, some measurements of the effective diffusion rate of nitrogen in Types 304 and 316 stainless steel were performed in a static pot system. Also, the possibility of using ion probe mass spectrometry to determine carbon and nitrogen gradients was investigated in cooperation with Westinghouse Research Laboratories.

3.2.1 CEL-1 Experimental Data

Five further loop test runs at 1300°F were completed during this report period. Experimental data and carbon analyses are given in Table 3-1.

During Run 12, it was noted that Type 321 stainless steel gained significantly in carbon while all other materials tested showed a decarburizing trend. Run 13 was designed to study foil behavior under carburizing conditions. Carbon increases in the austenite materials were excessive, as seen in Table 3-1. However, the two ferritic alloys continued to show a carbon loss.

Carbon concentration data in Type 304 stainless steel plotted against equilibrium concentration of carbon in other structural materials given in Figure 3-7 of the last report[3] showed an absence of data in the very low (<80 ppm) and middle (200 - 700 ppm) concentration ranges. Runs 14 through 18 were designed to fill these gaps.

Run 14 was allowed to proceed with no carbon source, hot trap, or cold trap operating under the assumption that the high carbon concentration of the previous run would be moderated by diffusion into the containment walls. Data within the required middle range were obtained.

The next two Runs (15 and 16) were aimed at the low end of the concentration scale, first by cold trapping and then by hot trapping. Both methods were successful, yielding 38 ppm carbon in Type 304 stainless steel for both runs. Some discrepancy was noted in the Incoloy 800 and Type 321 stainless steel data; the former being higher and the latter lower in Run 15 than in Run 16.

Run 18 was designed as a preliminary investigation of the effects of time on these experiments. The data given in Table 3-1 were the result of several duplicate analyses for Types 304 L and 316 L stainless steel. As shown, there was no change with time on the carbon content of the Type 304 L stainless steel while the Type 316 L stainless steel material showed a slight decrease in carbon concentration after the 30 hour run.

The complete set of carbon data for the 1300°F experiments has been plotted in Figure 3-1 with scatter bands shown for each material, rather than individual data points. These bands do not represent analytical error, but reflect inconsistencies in the experiments themselves that are not yet understood. The figure, however, does illustrate some definite trends, and the following points should be noted:

1. Data for ARMCO Iron are almost random within the 0-100 ppm range, and no directional change or correlation can be observed with Type 304L stainless steel data increasing from 30 to 3000 ppm.
2. With the exception of one data point, good correlation is shown for Type 304L stainless steel versus 2-1/4 Cr-1Mo. The three other data points are in each decade and lie on a straight line. Even under severe carburizing conditions for Type 304 L stainless steel, the ferritic alloy still decarburizes by an order of magnitude from

Table 3-1. Operational Data and Carbon Analyses from CEL-1 Runs 12, 13, 14, 15, 16, 18

Carbon Analyses							
Run Number	12(a)	13	14	15	16	18	
Foil Material	304L SS, 316 SS, 1800, 321 SS, 2 1/4 Cr-1Mo ARMCO Iron	304 SS, 316 SS, 1800, 321 SS, 2 1/4 Cr-1Mo ARMCO Iron	304 SS, 316 SS, 1800, 321 SS, 2 1/4 Cr-1Mo ARMCO Iron	304 SS, 316 SS, 1800, 321 SS, 2 1/4 Cr-1Mo ARMCO Iron	304 SS, 316 SS 1800, 321 SS 2 1/4 Cr-1Mo ARMCO Iron	304 SS, 316 SS	
Temperature (°F)	1300	1300	1300	1300	1300	1300	
Duration (hrs)	97	119	121	121	120.5	314	
Carbon Source	Not Operating	Continuous at 1300°F	Not Operating	Not Operating	Not Operating	Not Operating	
Cold Trap	Continuous at 310°F	Not Operating	Not Operating	Continuous at 300°F	Not Operating	Continuous at 300°F	
Hot Trap	Not Operating	Not Operating	Not Operating	Not Operating	Continuous at 1300°F	Not Operating	
Operational Data							
Foil Material	As Received (ppm)	After Run #12	After Run #13	After Run #14	After Run #15	After Run #16	After Run #18
304 SS	340 ± 30	117 ± 0 ^(b)	2030 ± 117	267 ± 27	38 ± 1	38 ± 1	40 ± 7
316 SS	204 ± 14	156 ± 1	2375 ± 103	269 ± 25	42 ± 12	48 ± 1	25 ± 9
ARMCO Iron	110 ± 2	26 ^(c)	35 ^(c)	50 ± 12	42 ^(c)	64 ^(c)	- - -
321 SS	696 ± 19	823 ± 20	3262 ± 314	1319 ± 31	810 ± 1	648 ± 8	- - -
Incoloy 800	485 ± 9	240 ± 7	3572 ± 536	803 ± 30	253 ^(c)	338 ^(c)	- - -
2 1/4 Cr-1Mo	1080 ± 53	- - -	93 ± 1	68 ± 2	54 ± 3	53 ^(c)	- - -
(a) Data from previous report period							
(b) Two identical analyses for Type 304L stainless steel specimens							
(c) One analysis only

Figure 3-1. Carbon Equilibrium Values, C_e , of Structural Materials at 1300°F

4500-2

approximately 1200 ppm nominal to 100 ppm after exposure.

3. The rather wide scatter band for Type 304 L stainless steel versus Type 316 L stainless steel may be due in part to a slight non-uniformity in the duration of experiments.
4. It was hypothesized in the last report that the presence of titanium in Incoloy 800 and Type 321 stainless steel would cause these alloys to carburize to a level sufficient to tie up all the stabilizing element. The data obtained to date for these alloys show rather that they will not decarburize below a given level. It is also likely that nitrogen is playing a part in determining this lower level.

Although the planned equilibrium measurement work at 1300°F is now completed, the first series of runs planned for CEL-2 will be at 1300°F at conditions comparable to several of the CEL-1 runs to ensure that CEL-2 will provide data comparable to that obtained for CEL-1.

Run 18 was also used to expose a nine-inch length of annealed 12-mil wall, Type 316 stainless steel cladding for tensile testing. A similar length was placed in an evacuated tube in the sample tank thermocouple well so that physical and chemical data could be compared between these two exposure environments and the as-received annealed condition. Foil analysis for Type 316 stainless steel (Table 3-2) may be used to predict the mean carbon concentration expected in the sodium-exposed tubing after exposure.

Table 3-2. Analytical Data Obtained From Type 316 Stainless Steel Cladding Exposed in CEL-1 During Run 18		
Conditions	Carbon	Nitrogen
As-Received	540 $\pm$ 2	498
Vacuum Aged	651 $\pm$ 33	1090
Sodium Exposed	501 $\pm$ 6	367

The mean carbon concentration ($\bar{C}$) after time (t) is given by:

$$\bar{C}(t) = C_e + \frac{8(C_o - C_e)}{\pi^2} \sum_{n=1}^{\infty} \exp\left(\frac{-(n-1)^2 \pi^2 D t}{(2n-1)^2 a/2}\right) \quad (3)$$

where: $a/2$ = thickness across which diffusion is taking place; in this case, since the cladding is exposed to sodium on both tube surfaces, $a/2 = 6$ mils

C_o = initial concentration = 558 ppm;

C_e = surface equilibrium concentration; 25 ppm.

Equation 3 may be simplified if all but the first term in the exponential series are neglected.

$$(\bar{C})_t = C_e + 8 \frac{(C_o - C_e)}{\pi^2} \exp \frac{-\pi^2 D t}{a^2} \quad (4)$$

This is a good approximation when $\bar{C} \leq 0.8 (C_o - C_e)$.

Taking the diffusivity of carbon at 1300°F to be $0.9 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$ [2], and adjusting for appropriate units, Equation 4 gives:

$$\bar{C} = 25 + \frac{8}{\pi^2} (540 - 25) \times 0.340 = 167 \text{ ppm} \quad (5)$$

Comparison of this number with the data given in Table 3-2 for bulk analyses of the tube after sodium exposure is not good.

It appears that little or no carbon has been lost by the tube material, even though foils exposed in the same run decarburized to levels <50 ppm.

Some earlier work at ARD involving this same tubing also produced anomalous results. After 5000 hour exposure in the Pre-Exposure Loop (PEL), the tubing and some 0.018 mil sheet located in an isothermal section of the hot leg yielded the data shown in Table 3-3.

Table 3-3. Interstitial Analyses of PEL-1-1 Samples (Summarized)			
Sample	Condition	Carbon (ppm)	Nitrogen (ppm)
0.018 inch sheet	As-Received	608	46
	5000 hr/1200°F	644	326
	5000 hr/1325°F	679	132
0.012 inch wall tube	As-Received	558	500-560
	5000 hr/1200°F	532	452
	5000 hr/1325°F	466	106
Loop operated with 300°F ΔT and continuous cold trapping at 200-300°F			

It will be noted that even after 5000 hours at 1325°F, the tubing lost only 100 ppm carbon. Furthermore, in spite of the expected decarburizing environment at the specimen location, the sheet carburized by 70 ppm at 1325°F. Although the nitrogen data, particularly for the as-received material, are not good, it is evident that the tubing has at least lost about 80% of its nitrogen content after exposure of the higher temperature.

Further investigation of this material to determine either the chemical or physical reasons for the anomalous behavior is indicated.

3.2.2 Metallography

Examination of the foils exposed to sodium was initiated during the current report period. The work concentrated on an initial metallographic study of each material to determine the range of physical changes that could be observed after the various exposure conditions experienced at 1300°F in Runs 9 through 16. It is intended to complement the data presented in Figure 3-1 with descriptive metallography over the complete range of carbon concentration illustrated for each alloy.

3.2.2.1 Comparison of Type 304 L and Type 316 L Stainless Steel

Although the data in Figure 3-1 indicate little difference between carbon concentrations in the two alloys after equilibration treatment in sodium, there are several structural differences to be noted.

Figure 3-2 shows the appearance of Type 304 L stainless steel after one vacuum aging treatment and three different sodium exposures. There is very little structural difference between the vacuum aged specimen (carbon content assumed to be that of the as-received material, 340 ppm) and the two sodium-exposed samples containing 139 and 654 ppm carbon. The primary precipitation location is at grain boundaries, although scattered spherical intragranular particles can be observed located in many instances on partially coherent twin boundaries. The grains are predominantly equiaxed, but have a wide variation in size with many curved and unstable boundaries. It is evident that this alloy does not reach an equilibrium structure after 120 hours at 1300°F.

Figure 3-2d shows the effects of carburizing to a level of 3025 ppm carbon. Precipitation has been so intense and so fast that much of the as-received nature of the structure has been preserved; twinning and angular grains typical of an annealed structure are much in evidence. The precipitation at incoherent twin boundaries is a marked feature, together with the dense spherical carbides appearing within the grains.

Figure 3-3 compares a vacuum aging treatment with sodium exposure for Type 316 stainless steel both at a low carbon concentration. A few intermetallic particles and some inclusions are visible, but there is little to be observed in the way of carbide precipitation either inter- or intergranularly. A non-equilibrium structure is again noted with considerable variation in grain size.

a. VACUUM AGED FOR 116 HOURS, (Run No. 10) C = 340 ppm 20 μm

b. SODIUM EXPOSED FOR 116 HOURS, (Run No. 10) C = 139 ppm 20 μm

c. SODIUM EXPOSED FOR 120 HOURS, (Run No. 11) C = 654 ppm 20 μm

d. SODIUM EXPOSED FOR 140 HOURS, (Run No. 9) C = 3025 ppm 20 μm

Figure 3-2. Type 304L Stainless Steel After Exposure at 1300°F (Etch: Chromic Acid)

4500-8

a. VACUUM AGED FOR 121 HOURS (Run No. 14) C = 204 ppm

b. SODIUM EXPOSED FOR 121 HOURS (Run No. 14) C = 269 ppm

Figure 3-3. Type 316L Stainless Steel After Exposure at 1300°F (Etch: Glycerol/HCl/HNO₃)

4500-9

Figure 3-4 shows Type 304 and Type 316 stainless steel specimens taken from Run 9. Figure 3-4a may be compared directly with Figure 3-2d; only the etching treatment is different. The glycerol-base reagent attacks austenite and grain boundaries vigorously, but leaves carbides, ferrite, and sigma in relief; chromic acid is preferred for Type 304 stainless steel as a rule, because of its more moderate reaction with austenite and grain boundaries. The same etchant was used in this figure not only so that a direct comparison could be made between the two austenitic steels, but also to illustrate the changes in appearance that can result from using different etches on the same material. The most notable features of Figures 3-4a and 3-4b are:

1. Figure 3-4a has lost much of the as-received character of Figure 3-2d with the more severe etch attack at grain boundaries; otherwise the main features of the two micrographs are comparable.
2. There is no twin boundary decoration in Type 316 stainless steel specimen in Figure 3-4b.
3. Intragranular precipitation is spherical in Type 304 stainless steel, but appears as needles in Type 316 stainless steel. This is the most significant single difference noted between the two alloys. The nucleation of needles apparently along specific crystallographic directions may possibly be due to the presence of molybdenum in Type 316 stainless steel.

3.2.2.2 Type 321 Stainless Steel

Figure 3-5 compares a vacuum aged specimen with a sodium-exposed sample from Run 12 that experienced slight carburization. Little difference was observed between the two specimens; both have very small grain size ($\sim$ ASTM 10), and both show precipitation of large (carbide) particles at triple points together with the more massive characteristic yellow and grey titanium nitride and carbide cuboids. Some change, however, has occurred at the grain boundaries of the sodium-exposed sample. Despite repeated polishing, they remained difficult to etch and gave a "ghosting" appearance. Further specimens must be examined before valid significance can be placed on this observation.

3.2.2.3 ARMCO Iron

Figure 3-6 compares vacuum aged and sodium exposed structures. They are only notable for their absence of features. The heavily-worked as-received structure has undergone recrystallization and considerable grain growth. Small chains of spherical particles are observable at certain grain boundary locations in Figure 3-6b. This is unlikely to be any form of carbide precipitation, but may be oxide forming from traces of sodium seeping out at occasional boundaries.

3.2.2.4 2-1/4 Cr-1Mo Alloy

Again a very small grain size is noted for the vacuum aged structure. Figures

a. TYPE 304L STAINLESS STEEL, SODIUM EXPOSED FOR 140 HOURS
(Run No. 9) C = 3025 ppm

b. TYPE 316L STAINLESS STEEL, SODIUM EXPOSED FOR 140 HOURS
(Run No. 9) C = 4070 ppm

Figure 3-4. Type 304L Stainless Steel and Type 316 Stainless Steel After Exposure at 1300°F (Etch: Glycerol/HCl/HNO₃)

4500-10

a. VACUUM AGED FOR 97 HOURS (Run No. 12) C = 696 ppm

b. SODIUM EXPOSED FOR 97 HOURS (Run No. 12) C = 823 ppm

Figure 3-5. Type 321 Stainless Steel After Exposure at 1300°F (Etch: Chromic Acid)

4500-11

(NOMARSKI)

20 μm

a. VACUUM AGED FOR 120 HOURS (Run No. 16) C = 110 ppm

(NOMARSKI)

20 μm

b. SODIUM EXPOSED FOR 120 HOURS (Run No. 16) C = 64 ppm

Figure 3-6. ARMCO Iron After Exposure at 1300°F (Etch: Nital)

4500-12

3-7a and 3-7b show a similar grain size to that observed in the Type 321 stainless steel material. Although good thermal stability is noted for the alloy at 1300°F (the as-received structure of Figure 3-8b), the change after sodium exposure is dramatic. As noted earlier, even under severe carburizing conditions for the austenitic alloys, the 2-1/4Cr-1Mo material decarburized by an order of magnitude. The result is massive grain growth with the structure assuming the appearance of a single-phase alloy, not unlike that of ARMCO Iron. The only sign of prior precipitation is the presence of marks within the grains where the matrix has offered a different resistance to the polishing and etching procedure.

3.2.2.5 Incoloy 800

The as-received material (Figure 3-8a) was difficult to etch through lack of precipitation at grain boundaries. The micrograph shows a twinned equiaxed structure with only the large titanium carbide/nitride particles to break the appearance of a single-phase structure. The foil surfaces (not shown in Figure 3-8a) appeared to be heavily worked, probably due to a final cold-rolling operation. Depth of this worked layer was approximately 0.3 to 0.6 mils.

Figure 3-8b shows heavy carbide precipitation at grain boundaries as a result of the heat treatment of 1300°F. The middle zone of the sodium exposed foil is very similar in appearance to the vacuum aged specimen, in spite of the order of magnitude increase in carbon content. It may well be that the carbon is concentrated in the foil surface region where the broken-down structure provides a very large grain boundary surface area.

3.2.3 Measurement of Effective Diffusion Coefficients of Sodium in Type 304L and Type 316 Stainless Steel in Sodium and Cover Gas

The main objectives of the experiment are:

1. To determine the nitrogen diffusion coefficients and equilibrium nitrogen contents in Types 304 and 316 stainless steel foil specimens as a function of temperature and nitrogen partial pressure (nitrogen concentrations from 50 to 500 ppm in the argon carrier gas).
2. To obtain physical property data for Types 304 and 316 stainless steels as a function of nitrogen content.

Three-inch long foil tabs were exposed in the apparatus shown schematically in Figure 3-9. The chamber, approximately half filled with sodium, provided accommodation for numerous specimens in both the gas and liquid phases. Arrangement was made to allow the gas mixture to flow through the system at a controlled rate so that any pre-determined nitrogen level was maintained throughout the experiment regardless of reactions occurring within the test chamber.

(NOMARSKI)

10 μ m

a. AS-RECEIVED MATERIAL, C = 1080 ppm

(NOMARSKI)

10 μ m

b. VACUUM AGED FOR 121 HOURS (Run No. 15)
C = 1080 ppm

(NOMARSKI)

10 μ m

c. SODIUM EXPOSED FOR 121 HOURS (Run No. 15)
C = 54 ppm

Figure 3-7. Fe-2-1/4Cr-1Mo Before and After Exposure at 1300°F (Etch: Nital)

4500-13

(NOMARSKI)
a. AS-RECEIVED MATERIAL, C = 485 ppm 20μm

b. VACUUM AGED FOR 119 HOURS (Run No. 13)
C = 485 ppm 20μm

FOIL SURFACE
STRUCTURE

c. SODIUM EXPOSED FOR 119 HOURS (Run No. 13)
C = 3527 ppm 20μm

Figure 3-8. Incoloy 800 Before and After Exposure at 1300°F (Etch: Chromic Acid)

4500-14

Figure 3-9. Schematic of Gas Control System for Nitrogen D_{eff} Measurements

The initial test parameter matrix is given in Table 3-4.

Table 3-4. Preliminary Test Matrix For Cover-Gas Nitriding			
Test No.	Liquid Sodium Temperature (°F)	Approximate Gas Temperature (°F)	N ₂ Concentration in Cover Gas (ppm) Helium
1	1100	850	50
2	1200	1000	500
3	1200	1000	5000

Each test lasted for approximately 300 hours during which time specimens of Types 304 and 306 stainless steel were removed from both liquid and gas phases after seven different exposure periods. A subsequent analysis of mean nitrogen concentration as a function of time provided data for determining nitrogen diffusivities and the relative concentration changes brought about by the various cover gas compositions.

Tests 1 and 2 were completed. The changes observed with time at 1100°F and with 50 ppm nitrogen in the cover gas were insignificant; the only notable feature being that Type 304 stainless steel lost approximately 200 ppm nitrogen from liquid-phase specimens during the first exposure period.

At 1200°F with 500 ppm nitrogen in the cover gas, definite changes with exposure time were observed. Types 304 and 316 stainless steel picked up 200 ppm in the gas phase, but the more significant changes were observed in the liquid sodium where nitrogen concentrations dropped by 300 to 400 ppm. Data were fed into a computer program, and the following diffusivity results were obtained.

At 1200°F in liquid sodium:

Type 304 stainless steel $D = 0.676 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ $C_e = 152 \text{ ppm N}_2$

Type 316 stainless steel $D = 0.749 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ $C_e = 356 \text{ ppm N}_2$

Earlier data^[6] indicate that Diffusivity of N₂ in Type 316 stainless steel at this temperature is $0.2 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$.

[6] GMAD-3643-8, "Investigation of Bimetallic Liquid Metal System," Final Report, September 1966.

The computer program is based on the following theory:

Mean concentration after time, t , is given by the expression,

$$\bar{C}(t) = C_e + 8 \frac{(C_o - C_e)}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{(2n-1)^2 \pi^2 D t}{a^2}\right)}{(2n-1)^2} \quad (6)$$

where: C_e = Surface equilibrium concentration

C_o = Initial concentration

D = Diffusion coefficient

$a/2$ = Distance across which diffusion takes place

If it is assumed that Equation 6 may be simplified by neglecting all but the first term in the series, then

$$\bar{C}(t) = C_e + 8 \frac{(C_o - C_e)}{\pi^2} \exp \frac{-\pi^2 D t}{a^2} \quad (7)$$

Differentiating with respect to time (t),

$$\frac{d\bar{C}}{dt} = - \left[\frac{8D (C_o - C_e)}{a^2} \right] \exp \frac{-\pi^2 D t}{a^2}$$

This may be written as,

$$\ln \frac{d\bar{C}}{dt} = \ln \left[\frac{-8D (C_o - C_e)}{a^2} \right] - \frac{\pi^2 D t}{a^2} \quad (8)$$

It can be seen that Equation 8 is linear in form, and that D may be obtained from the slope of a plot of $\ln (d\bar{C}/dt)$ vs t . It should also be noted that the surface equilibrium concentration can be evaluated from the intercept on the ordinate axis.

3.2.4 Carbon and Nitrogen Profiling in Type 304L Stainless Steel by Ion Probe Mass Spectrometry

3.2.4.1 Introduction

Ion probe mass spectrometry is a recently developed microanalytical technique for the surface and interior bulk analysis of all classes of solids. Preliminary work has now been completed utilizing this technique to establish the carbon and nitrogen gradients in a series of Type 304 L stainless steel foils in the following conditions: as-received, thermally aged in vacuum, and sodium-exposed. Because the technique is relatively new, a brief description of its capabilities is in order before discussing the results.

The instrument employed, the Cameca Ion Analyzer, is capable of detecting every element and isotope from H to U at sensitivities in the parts per million range. This unique analytical ability is particularly important for such elements as H, C, N, and O which are ordinarily difficult or impossible to characterize on a microscale. The technique utilizes a primary ion beam of either A^+ or O_2^+ to bombard a 4-500 μm diameter region on the sample surface and sputter off layer-by-layer the constituent atoms.

A portion of these atoms is ionized in the process, and the resulting secondary ions can then be mass analyzed to determine their identity.

Continuous sputtering and recording in a given region permits depth profiles of any desired element to be achieved. The material removal rate can be controlled from less than one $\text{\AA}$ per second to several hundred $\text{\AA}$ per second, depending on the total distance over which information is desired and the time available for the analysis.

In addition to electrical recording of the mass-resolved secondary ion signal from the surface of the sample, the Cameca Ion Analyzer also has the ability to form ion images from these secondary ions which reveal the spatial distribution of any selected element within a 200 μm diameter circular region on the sample to a resolution of about 1 μm^2 . The ion optics of the instrument are specially designed to maintain a one-to-one correspondence between the point of origin of a secondary ion on the sample and its location in the final ion image. By recording the ion images of several observed elements, some insights can be gained into possible compound or alloy formation.

The sensitivity with which secondary ions are generated varies from element to element and is a function of the bombarding gas, the chemical state of the surface, and its crystallographic orientation. Thus, with all the variables it is difficult at this stage of the technique's development to achieve quantitative analyses without the use of standards, and it is also difficult to produce relevant standards which are characterized on the required scale. Nevertheless, qualitative data are readily produced, although considerable care must be taken in its interpretation because of the number of variables involved.

3.2.4.2 Experimental Procedure

The samples used were Type 304L stainless steel foils from the CEL program in the as-received, thermally-aged, and sodium-exposed conditions (Table 3-5).

Table 3-5. Samples Used For Ion Mass Spectroscopy Study		
Sample	Carbon (ppm)	Nitrogen (ppm)
1	340 $\pm$ 30	929 $\pm$ 64
2	340 $\pm$ 30	929 $\pm$ 64
3	189 $\pm$ 14	906 $\pm$ 78
Material: Type 304 L Stainless Steel Foil		
Sample 1: As-Received		
2: Thermally-aged in vacuum (251 hr at 1200°F)		
3: Sodium-exposed in CEL-1 (251 hr at 1200°F)		
Size - : 3 mils thick, approximately 3/8 x 1/2 inch		

The samples were cleaned in alcohol after being lightly abraded to remove any mass transfer deposits. They were then subjected to a low temperature ashing treatment to remove any surface carbon contamination that may have occurred during cleaning.

A series of depth profiles for C and N extending beyond 10 μ m in distance were performed on each sample. The C_2^- secondary ion was monitored for the carbon analysis while NO^- was used for nitrogen. Several ion images showing the carbon distribution were recorded from the surface and are shown in Figure 3-10. The carbon is non-uniform and concentrated into discrete localized regions.

Typical recorded carbon profiles are shown in Figure 3-11. No quantitative interpretation can be made at this time, however, some generalized qualitative statements can be made.

The variation in surface carbon concentration leads to some differences in the observed carbon profile from run-to-run. There were even significant variations in the carbon level from the bulk of the material. Nevertheless, there are some notable distinctions which can be drawn between the nature of the carbon profiles recorded from each of the three types of foils, and Figure 3-10 presents typical results in this regard. Both the as-received and the sodium-exposed foils exhibit high surface carbon concentrations compared with their interiors. Their carbon gradient is particularly steep within 1/2 micron of the surface, but even to depths of 1-1/2 microns the

REGION A

100 μm

REGION B

100 μm

REGION C

100 μm

Figure 3-10. Ion Images Showing the Carbon Distribution on Three Regions of Surface of Type 304L Stainless Steel Foil After Sodium Exposure (251 hours at 1200°F)

4500-15

Figure 3-11. Typical Carbon Profiles in Type 304L Stainless Steel Foils Exposed to Different Environments

4500-19

carbon level appears enhanced. Whereas the gradient for the as-received material is typically smooth as indicated in the figure, the gradient of the sodium-exposed sample shows some internal variation, indicating localized concentrations of carbon precipitating at grain boundaries (as Cr_{23}C_6 because of sensitization) or from some other cause associated with the decarburization process. However, this concentration at least is not as great qualitatively as that observed in the thermally-aged material. This is consistent with the reduced carbon level after sodium exposure. The thermally aged material does not show a large surface carbon concentration. Instead, the sample showed a surface carbon depletion relative to the interior, possibly resulting from the combustion of surface carbon in the ashing process. The nature of this gradient is good evidence for the reality of the gradients observed in the other two samples. The thermally aged sample produced the most consistent profiles, and they each contained considerable fine structure in the bulk as shown in the figure. This is evidence of carbon segregation within the material.

Figure 3-12 presents typical nitrogen profiles for the samples, and these indicate that the element is fairly uniform in the material except within the outer 1/3 micron. The as-received and thermally-aged samples show some nitrogen depletion over this distance, while the sodium-exposed sample shows a definite surface enhancement. Because of the irregular nature of the surface, however, these conclusions are tentative. The apparent restriction of any effects to a thin, localized region correlates well with the bulk nitrogen analyses that showed little difference between the samples.

Further investigation is required before the practical significance of these results can be assessed. It must be remembered that the analyses were made on a very fine scale, to a total depth of 1-2 microns. These thin surface layers may or may not be due to surface contamination during preparation or to the rough abraided nature of the surface.

Traces to much greater depths are required before any statement can be made as to whether equilibrium has been achieved or not. The ability of the instrument to identify the low mass elements and to detect segregation on a fine scale does, however, make the instrument a tool with great potential in the study of carbon and nitrogen behavior in structural materials.

3.3 On-Line Metering

3.3.1 UNC Diffusion Carbon Meter

Based on previously reported work with this meter, the following modifications to the gas supply and analysis console have been made:

1. Because of the large carbon background (10 x that of an equivalent system at ANL) deriving from the console, certain parts of the copper piping have been replaced and a new catalytic converter purchased from UNC. In addition, a new supply of decarburizing gas has been

Figure 3-12. Typical Nitrogen Profiles in Type 304L Stainless Steel Foils Exposed to Different Environments

4500-18

obtained to a specification of total carbon content <0.2 ppm rather than hydrocarbon content <0.2 ppm.

2. Some piping changes have been made to include the catalytic converter in the "zero FID" mode of operation, which allows the zero to be set to compensate for all likely residual carbon sources.
3. New needle valves have been installed to provide improved ability to set a required flow.
4. The components for readout of a second carbon meter probe have been installed. This is in anticipation of installation of the second meter on CEL-1.
5. Provision is made for flowing pure argon through the meter probes in place of the decarburizing gas. This was an earlier change made to reduce exposure of the loop to the hydrogen in the decarburizing gas.
6. Another earlier change was insertion of a Matheson Linear Mass Flow-meter before the flame ionization detector. This provides accurate flow measurement, and the rotameters are now used only to confirm that there is flow in the correct circuits. Figure 3-13 is a schematic of the carbon meter gas supply and analysis console showing the changes.

3.3.2 BNL Carbon Meter

Housings for two meters are installed on CEL-2 but no work with meters has been performed during the shakedown operations on this new loop.

3.3.3 Westinghouse Oxygen Meter

Details of some preliminary tests of meters incorporating the initial batch of electrolyte tubes made by Zircoa to a WADCO specification are given in Section 4, "On-Line Meter Characterization."

3.4 Thermodynamic Modeling

Temperature surface area data for the FFTF were collected and reduced to a single temperature-surface area function for the entire primary circuit of the reactor [7] system. This function was then used in a computer program described previously to determine the equilibrium carbon distribution for the FFTF reactor. The carbon balance necessary for the calculation was made by assuming that an infinitesimal thickness of stainless steel was involved. With this assumption, the integral determining the total amount of carbon became a surface integral rather than a volume integral.

[7] WARD-4210T1-1, "Sodium Technology Program Progress Report for the Period Ending November 30, 1970," January 1971.

Figure 3-13. Modified Carbon Meter Gas Supply and Analysis Console

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The results of this analysis are shown in Table 3-6 for initial bulk carbon concentrations of 200 and 550 ppm. The results are presented graphically on a simple flow schematic of the reactor system in Figure 3-14 for the 500 ppm initial carbon concentration. It should be remembered when considering the results that the model used is a purely thermodynamic one and assumes that all of the carbon released in the hot leg goes into solid solution in the cold leg material. The calculated figures also assume that the carbon is in solution in the austenite. This of course, is only true in the high temperature regions.

Table 3-6. Carbon Concentrations as a Function of Temperature for the FFTF		
Temperature (°F)	Equilibrium Carbon Concentration (ppm) (initial Concentration 200 ppm)	Equilibrium Carbon Concentration (ppm) (ini- tial Concentration 500 ppm)
800-850	400	987
850-900	232	580
900-950	140	349
950-1000	87	217
1000-1050	56	139
1050-1100	37	92
1250-1300	9	23

A key factor in the model is a mass balance requirement, and this is reflected by the data; the lower the starting carbon level, the lower the final level.

The principal value of the modeling work is that it indicates the feasibility of predicted carbon transfer on a purely thermodynamic basis and the importance of taking the entire system into consideration. The carbon levels predicted by this method are not unreasonable and are probably of the right order of magnitude. Values as low as those in Table 3-6 have not been observed unless the carbon activity of the system is artificially lowered through the use of a hot trap, and it is suspected that the model is predicting sodium carbon activities which are somewhat too low.

Observations have also shown that the carbon in the cold leg is not absorbed by solid state diffusion, but is deposited either as a compound, for example with chromium, or as elemental carbon.

A second, much simpler approach is currently being formulated which takes into account the existence of cold-leg carbon and carbide deposition and the formation of carbides within the austenitic steels. This model makes use

LOCATION	TEMPERATURE (°F)	Ce (ppm)
A	1250-1300	14
B	1150-1200	22
C	1050-1100	92
D	850-900	580
E	800-850	1000
F	1050-1100	92
G	800-850	1000
H	1050-1100	92

Figure 3-14. Predicted Equilibrium Carbon Distribution in FFTF Primary Circuit

of the thermodynamic data used in the earlier model, and preliminary calculations indicate that the predicted hot-leg carbon levels are not unreasonable. The approach will be detailed in later reports.

3.5 Exposure of Brookhaven National Laboratory Mechanical Property Specimens to Sodium

For FY-1972, an additional sub-task was added to the Component Materials Computability portion of the contract. Specifically, the work to be performed under this subtask is the pre-exposure of 30 mechanical property specimens from BNL to sodium in a presently available, non-isothermal, high purity loop system. Fifteen of these specimens will be exposed at 1200°F in a corrosion area of the system while the remaining 15 will be exposed at 1000°F in a deposition or weight gain region. All specimens will be exposed for 5000 hours, and an operating history of the loop run will be provided to BNL after the exposure is complete. In addition, detailed chemical and metallurgical analyses will be performed on corrosion samples located at the entrance and exit of the two test legs. The results of these analyses will also be provided to BNL.

During this period, all specimens were received from BNL and are presently being dimensionally characterized. Holders were designed to position the specimens in the test legs, and all necessary materials were ordered and received. The test facility, in which the BNL specimens will be pre-exposed, is presently engaged in a test run. However, when the fabrication and assembly of the new test legs is completed, the test run will be interrupted and the BNL specimens section added. This will occur early in the next reporting period.

SECTION 4

ON-LINE METER CHARACTERIZATION

E. Berkey, B. R. Grundy, G. R. Taylor

1.0 OBJECTIVES

The program will provide needed information on the performance characteristics of a standard electrochemical oxygen meter for the FFTF and subsequent LMFBR applications. A standard meter is currently manufactured by Westinghouse Nuclear Instrumentation and Control Department.

A key component of the meter is the solid electrolyte. The process for producing a high-quality electrolyte has been developed at WADCO, and ZIRCOA, the commercial supplier, has adopted this process. Therefore, verification of adequacy of quality of the commercially available electrolyte is an essential part of the program.

Performance of the standard meter is to be tested by operating ten meters on a newly built subloop added to an existing ARD facility. The primary calibration method will be the standard vanadium wire equilibration method developed at ANL. A similar ten meter test is to be run at ANL. The number of meters tested will enable a statistically valid assessment to be made.

2.0 PRIOR WORK

In the last quarter, design and fabrication of a ten oxygen meter (TOM) subloop for the existing Fission Product Loop Number Two (FPL-2) was initiated. Preliminary meter tests on existing facilities of the initial batches of Zircoa isopressed electrolyte were started. Materials characterization of this electrolyte was initiated at Westinghouse Research Laboratory (WRL).

3.0 CURRENT PROGRESS

3.1 TOM Subloop

Work proceeded on the ten oxygen meter (TOM) subloop of FPL-2. Drafting of the subloop and initial changes to ANL drawings of the vanadium wire equilibration module have been completed; drafting of electrical systems schematics is completed but a shortage of checkers has delayed final signing-off for some drawings.

Purchase of necessary equipment for TOM is completed and virtually all items have now been received.

Construction of the subloop is underway. It became apparent that the critical item affecting scheduling would be delivery of oxygen meters. These

were received in mid-August. Construction of components of the subloop and electrical systems were rescheduled to keep ahead of the meter delivery date. The most important component other than the meters is the vanadium wire equilibration module, and this was completed at the time the meters were delivered. As construction of the vanadium wire module proceeded from ANL drawings, certain simplifications were made after consultation with ANL. These were in addition to changes made and drafted before construction started, and additional drafting will be required to properly document them.

Dialogue continued with ANL to coordinate the two, ten meter tests. Agreement on detailed operational procedures was reached; this was officially documented by ANL using ARD contributions where appropriate.

3.2 Characterization of Electrolyte Tubes

The analytical characterization of oxygen meter electrolyte tubes using scanning electron microscopy (SEM) and an associated energy dispersive X-ray detector was continued at Westinghouse Research Laboratories. The work was concentrated in four major areas:

1. Characterizing failed WADCO tubes from previous oxygen meter tests at both Westinghouse ARD and ANL
2. Comparing the phosphoric acid etch resistance of WADCO and commercially produced ZIRCOA tubes
3. Determining the relative purity of the inside and outside surfaces of WADCO and ZIRCOA tubes
4. Characterizing the effect of the platinizing process on the ceramic material during formation of the gaseous reference electrode

3.2.1 Failure Analysis on WADCO Tubes

Samples of isotatically pressed yttria-doped thoria electrolyte tubes produced by WADCO were examined by SEM following their use in oxygen meters at Westinghouse ARD and ANL. The objective was to study the sodium attack resistance of the ceramic material and to determine possible failure mechanisms for the tubes. Table 4-1 identifies the tubes studied and their sodium exposure history.

Table 4-1. History of WADCO Tubes Examined			
WADCO Tube	Loop	Lifetime (hrs)	Temperature (°F)
42-2-D	CEL-1, ARD	1011	700-800
42-1-B	FPL-2, ARD	2591	700-900
42-2-B	FPL-2, ARD	2059	700-900
72-2-2	Module, ANL	< 50	800

Figure 4-1 presents a selection of scanning electron micrographs illustrating the excellent sodium attack resistance of the 42-series tubes which attained the longest lifetimes in sodium of any WADCO tubes tested in meters. The typical appearance of the OD surface of these tubes in the as-received condition is shown in Figure 4-1a where the absence of appreciable amounts of second phase material can be noted. Figure 4-1b shows the surface of tube 42-2-D after its removal from sodium, and visible corrosion effects are limited to slight grain boundary grooving and attack at many of the triple points.

The surface of tube 42-2-B shows these same effects more clearly in Figure 4-1c where the results of chemical attack on grain sized surface regions is also evident. X-ray analysis of these regions reveals the presence of Ca at the locations where material removal is most pronounced. The effects of sodium corrosion can also extend over areas covering many grains in size as indicated by Figure 4-1d for tube 42-1-B, where even whole grain removal has taken place. In summary, the yttria-thoria ceramic material appears to resist sodium corrosion quite well for the most part except in regions such as grain boundaries, triple points, or other areas likely to contain impurities.

Since the overall chemical attack resistance of the tubes appears good, there are no strong indications that sodium interactions led to the failure of the tubes; although the reaction products and impurities could have affected meter performance. Changes in the thermal or mechanical shock resistance of the material with exposure time are other possible means by which the tubes can fail, and in fact, they may be the most important ones. Figure 4-1e shows a crack that developed on the surface of tube 42-1-B during sodium exposure causing its failure. Close inspection reveals that the crack propagated in a mostly trans-granular fashion. The development of tubes which retain mechanical strength and resist cracking appears to be one way to add lifetime to an oxygen meter.

The failure analysis for tube 72-2-2 which failed by having its tip fracture into small pieces within two days of start-up at ANL was conducted by viewing the fracture face of several pieces. Fractographic analysis of tubes has proven to be a valuable way to assess possible failure modes. Figure 4-2 contains a set of micrographs comparing the nature of the fracture in tube 72-2-2 with those from mechanically induced breakages in both a WADCO tube (42-1-V) and a ZIRCOA tube (5-0-10-17-5) from the second commercial production run. Some closed pores can be seen in each picture, but the overriding features are the predominantly transgranular fracture morphology of both the 42-series WADCO tube and the ZIRCOA tube and the predominantly inter-granular type of fracture in tube 72-2-2. Moreover, the grain size of this latter tube is seen to be considerably larger, arising from the tube's higher sintering temperature during fabrication (1950-2000°C versus about 1800-1850°C for the 42-series WADCO tubes). The increased grain size and the consequent decreased strength at the grain boundaries in tube 72-2-2 appear to account for the nature of its intergranular fracture and its short in-sodium lifetime. Similar problems plagued the Z-4 batch of improved slip-cast tubes produced previously by ZIRCOA which also showed exclusive inter-granular fracture. It is also interesting to note that the isostatically-pressed ZIRCOA tube, Figure 4-2c, shows somewhat less transgranular fracture and more intergranular fracture than the 42-series WADCO tube (Figure 4-2b).

LIFETIME: 1011 HOURS
b. WADCO 42-2-D
5 μ m

LIFETIME: 2059 HOURS
c. WADCO 42-2-B
5 μ m

LIFETIME: 2591 HOURS
d. WADCO 42-1-B
20 μ m

LIFETIME: 2591 HOURS
e. WADCO 42-1-B
20 μ m

AS-RECEIVED
a. WADCO 42-1-V
5 μ m

NOTE:
THE SURFACE CRACK IN (e) LED TO
TUBE FAILURE

Figure 4-1. Scanning Electron Micrographs
Comparing the As-Received Sur-
face of a WADCO Tube with the
Sodium Exposed Surface of Three
WADCO Tubes After Their Use in
Oxygen Meters

LIFETIME: < 50 HOURS

20 μ m

a. WADCO 72-2-2

10 μ m

b. WADCO 42-1-V

10 μ m

c. ZIRCOA 5-0-10-17-5

Figure 4-2. Scanning Electron Micrographs of Fracture Faces Showing the Intergranular Type of Fracture in WADCO Tube 72-2-2 Which Failed Shortly After Start-up and the Largely Transgranular Fractures Characteristic of Good WADCO and ZIRCOA Tubes

4500-23

3.2.2 Phosphoric Acid Etch Resistance

Figure 4-3 contains information regarding the comparative phosphoric acid etch resistance of WADCO and ZIRCOA tubes. Figure 4-3a confirms that the OD surface of the 42-series WADCO tubes was not etched by H_3PO_4 (90 min. @ $90^\circ C$). This is explained by the single phase grain structure of these tubes that indicates complete solid solution and the lack of second phase material on the surface. Figure 4-3b indicates that ZIRCOA tube 4-08-6 from the first commercial production run of twenty tubes did undergo slight etching by the acid, particularly at those triple point locations where second phase material rich in Y, Al, and Si was visible in the as-received condition. Subsequent batches of ZIRCOA tubes no longer show any etching on the OD surface, thus having achieved good single phase structure. However, the ID surface of these tubes continues to reveal the presence of second phase material that is etched by the acid as shown in Figure 4-3c, where the material at the triple points is seen to have been consistently removed during etching.

3.2.3 Purity of the Inside Surface

While it appears that the fabrication process for the manufacture of isostatically-pressed tubes is capable of producing material which is essentially single-phase on the OD surface, investigation has revealed that all tubes have contained significant amounts of second phase material on the ID surface at triple points and grain boundaries. This is illustrated in Figure 4-4 which shows micrographs of the ID surface from a WADCO tube (42-1-V), a ZIRCOA tube from the first production run (4-10-1), and a ZIRCOA tube from the second production run (5-0-10-14-5). The origin of these phases is believed to be associated with the lack of gas flow along the ID surface compared with the OD during sintering of the tubes.

While it has not been established how far away from the ID surface these second phases continue to exist, it is known that they have a number of different compositions and that they appear to concentrate some of the major impurities present in the ceramic material. Figure 4-5 gives a representative sampling of the X-ray spectra obtained from analyzing several of the second phase regions in one of the most recent ZIRCOA tubes (5-0-10-14-5) and compares them with the spectrum of the bulk material. While only characteristic X-rays from Y and Th are visible from the bulk (Figure 4-5a), some regions are observed to be quite Y-rich (or Zr-rich) by comparison (Figure 4-5b) or to contain Al, Ca, and extra Y (Figure 4-5c) or to have Mg, Al, and extra Y (Figure 4-5d). From a large number of these analyses, it is possible to conclude that Al is the most predominant ID impurity in the ZIRCOA tubes slated for use in the oxygen meter characterization program.

3.2.4 Effects of the Platinizing Process on the Ceramic

The presence of these impurities on the ID (plus Si which has also been observed) can lead to chemical reactions with the Pt during the platinizing process for formation of the gaseous reference electrode. During the combustion process to remove the organic binder in the Pt paste, locally reducing conditions can be produced which reduce Al_2O_3 and SiO_2 (for example)

AS-RECEIVED

5 μm

a. WADCO 42-1-V, OD

H₃PO₄ ETCHED (90 min at 90°C)

5 μm

10 μm

b. ZIRCOA 4-08-6, OD

10 μm

AS-RECEIVED

5 μm

c. ZIRCOA 5-0-10-14-5, ID

H₃PO₄ ETCHED (90 min at 90°C)

5 μm

Figure 4-3. Scanning Electron Micrographs Comparing the Phosphoric Acid Etch Resistance of the OD Surface of a WADCO Tube (no etching), the OD Surface of an Early ZIRCOA Tube (slight etching), and the ID Surface of a Recent ZIRCOA Tube (slight etching)

4500-24

a. WADCO 42-1-V

10 μm

b. ZIRCOA 4-10-1

10 μm

c. ZIRCOA 5-0-10-14-5

10 μm

Figure 4-4. Scanning Electron Micrographs of the ID Surface of WADCO and ZIRCOA Tubes Showing the Presence of Second Phase Material at Triple Points and Grain Boundaries

4500-25

a. BULK MATERIAL

b. REGION 1

c. REGION 2

d. REGION 3

Figure 4-5. Comparison of X-Ray Spectra Recorded From Bulk Material of ZIRCOA Tube 5-0-10-14-5 and Various Second Phase Regions of ID Surface
4500-3

and make it possible for Pt-Al and Pt-Si reactions to occur. Since these impurities exist at grain boundaries, the possibility of deleterious effects cannot be excluded.

Fractographic analysis of WADCO and ZIRCOA tubes which have been platinized with the standard Westinghouse process used over the past few years has revealed that the tubes fracture intergranularly over 20-25% of the wall thickness nearest the ID, with the remainder of the tube fracturing in the normal transgranular fashion. This is illustrated in Figures 4-6a and 4-6b. As shown, the transition between the two fracture modes is quite abrupt. Although no conclusive analytical evidence has proven that Pt penetration along the grain boundaries from the ID surface accounts for the intergranular portion of the fracture, it is undesirable for this effect to exist in the tubes. Some evidence points to the loss of grain boundary material from the wall of the tubes by gas phase reactions as a cause of the fracture mode. In addition, definite visible evidence has been obtained indicating that the second phase material at the ID is consumed during the platinizing process. Nevertheless, because of its implications on the ultimate mechanical strength of the tubes, it was felt desirable by all people in the program to have the amount of potential intergranular fracture in the tubes limited as much as possible. A new platinizing process was developed at Westinghouse Research designed to limit any reactions with the second phase impurities and any intergranular fracture effects. Figure 4-6c shows a micrograph of a ZIRCOA tube platinized with this new process and indicates that 90% of the previous intergranular fracture distance has now been eliminated. The small remaining intergranular fracture depth, now only about six to eight grains wide, is of little or no consequence to the overall strength of the tube. Moreover, some slight penetration of Pt into the ceramic, if it occurs, is probably desirable for the gaseous reference electrode. Loop tests at Westinghouse ARD with tubes platinized with the new process are proceeding as described in Section 3.3.

3.3 Tests of Initial Batch Zircoa Tubes in Meters

The preliminary meter tests continued on ZIRCOA 4-series and some later 5-series tubes as shown in Table 4-2.

Table 4-2. Summary of Meter Operations With Zircoa Isopressed Electrolyte			
Tube Number	Sodium Loop	Total Operational Time (Hours)	Meter Failed
4-08-6	CEL-1	2500, continuing	No
4-19-2	FPL-2	838, discontinued	No
4-20-2	FPL-2	646, discontinued	No
5-0-10-14-5	FPL-2	196, discontinued	No
5-N-11-15-5	CEL-2	80, discontinued	No
5-0-12-6-8	CEL-2	6	Yes

NOTE:

(a) AND (b) SHOW THAT TUBES FIRED WITH THE OLD PLATINIZING PROCESS YIELD INTERGRANULAR FRACTURE OVER 20-25% OF THE WALL THICKNESS, WHILE (c) SHOWS THAT THE NEW PROCESS RESTRICTS THIS TO ONLY ABOUT 2%

Figure 4-6. Scanning Electron Micrographs of Tube Fracture Faces Revealing the Presence of Intergranular Fracture Near the ID Edge of the Tubes

As shown in the table, operation of certain cells was discontinued to allow substitution of another test cell or to allow loop modifications in the case of FPL-2. Meters have been operated at 700°F. As described previously, meters generally showed some drift of EMF during initial operation. When stable operation was achieved, the calibration correlations covered a wider band than previously observed for meters with WADCO electrolyte.^[8]

In agreement with WADCO, the first five meters listed in Table 4-2 were subjected to a 920-950°F temperature excursion, the aim being to accelerate any changes which might be occurring slowly at the lower temperature. After returning to 700°F, a permanent shift in calibration was noted for all the 4-series tubes, as illustrated in Figure 4-7. No further drift has been observed over a 55-day period for tube 4-08-6. The figure also shows for reference purposes, the combined WADCO tube correlation. The later 5-series tubes showed poorest behavior in that the EMF drifted at 700°F and also during and after the high-temperature excursion. Consequently no calibration points are shown.

Electrolyte examinations at Westinghouse Research Laboratory and WADCO have revealed grain boundary impurities at the ID of ZIRCOA tubes and also grain boundary penetration by the Pt coating of the reference electrode, sometimes to the extent of 1/4 the wall thickness (see Section 3.2). Since some micro-cracks have been observed to originate in this region (although no ZIRCOA tube had failed in service at this point), an effort has been made to change the Pt firing process to eliminate the penetration. It has also been speculated that this might remove some of the meter to meter variability which has been noted in these preliminary tests. This appears to be originating at the reference electrode, the grain boundary impurities causing deviation from "ideal" behavior. The changed Pt firing process has reduced penetration to about six to eight grains in depth, as described in detail in Section 3.2.

A new test electrode using the changes Pt firing process was placed in CEL-2. It incorporated tube 5-0-12-6-8 that was selected after consultation and agreement with WADCO and ANL. It failed after only six hours operation and during a period of slowly rising temperature which had only reached 550°F. The EMF behavior was observed to be typical of a normal startup, although full temperature was never reached; no significant change in electrical behavior appears to have resulted from the changed reference electrode processing. Subsequent examination of the cell showed the failure to be the result of lack of quality assurance procedures which had been bypassed for this experimental situation. A circumferential crack in the electrolyte tube was well above the platinized region. It was caused by severe lack of concentricity on the guard sheath which consequently applied side pressure to the tube. A repeat test was started in CEL-2 using a second tube 5-N-13-6-8 that was made available. Appropriate precautions were taken to avoid a similar failure, particularly since the available tubes were outside WADCO dimensional specifications. The cell has operated for about 100 hours and behavior has been similar to 4-series cells. Drift of EMF was observed for the first 50-60 hours since when operation has been stable.

[8] B. R. Grundy, E. Berkey, E. T. Weber, W. A. Ross, "Performance of the Improved Electrochemical Oxygen Meter Using High-Purity Electrolytes," Trans. Am. Nucl. Soc., 14 (1), pp 186-188, 1971.

Figure 4-7. Effect of High-Temperature Excursion on Westinghouse Oxygen Meter Calibrations (ZIRCOA Isopressed Tubes; Air Reference)

4500-21