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SODIUM TECHNOLOGY QUARTERLY REPORT

January—March 1972

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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SODIUM TECHNOLOGY QUARTERLY REPORT
January-March 1972

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FOREWORD

The Sodium Technology Quarterly Report describes the current activities of the Sodium Technology Program at Argonne National Laboratory, sponsored by the Coolant Chemistry Branch of the USAEC Division of Reactor Development and Technology. In the areas of sampling and analysis and on-line monitoring of impurity elements, Argonne is involved in research and development as well as in the coordination of national efforts to meet the near-term needs of sodium technology, particularly those of FFTF. Argonne's program also includes research and development work on fission-product behavior and control, sodium chemistry, and materials-coolant compatibility. The program is a coordinated effort between two Argonne Divisions--Chemical Engineering and Materials Science--with assistance being given on specific problems by the EBR-II Project and the Idaho Facilities.

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SODIUM TECHNOLOGY QUARTERLY REPORT
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ABSTRACT

The research, development, and management efforts of Argonne National Laboratory's Sodium Technology Program for the period January-March 1972 comprised activities in the following areas: (1) In the national meter program, performance-characterization tests of an improved electrochemical oxygen meter have continued, with emphasis on meter calibration by the vanadium-wire equilibration method for determining oxygen activity; other work has included testing of on-line monitors for hydrogen and leak detectors for steam generators, development of a method for relating the outputs of carbon meters to the carbon activity of sodium, and testing of modules for these meters. (2) In the analytical standards program, efforts continued on the preparation of RDT standards relating to specifications for measuring and controlling the purity of sodium and cover gas; laboratory work included characterization of particulates filtered from various sodium systems and development of methods for determining oxygen activity in sodium by the equilibration of niobium wires and for determining hydrogen activity in sodium by the equilibration of vanadium and niobium. (3) Design work was started on a cover-gas analysis system for separating ^{23}Ne from noble-gas fission products in cover gas, fabrication was started on a laboratory prototype of a system for monitoring the ^{135}I content of reactor primary sodium, and development work continued on an on-line diffusion meter for monitoring tritium in sodium. (4) Studies of the chemistry of liquid sodium have been directed toward investigations of oxygen-hydrogen interactions in sodium using deuterium as a stand-in for hydrogen, and construction of an apparatus for determining the effects of oxygen-hydrogen interactions on oxygen and hydrogen meters. (5) Work has continued on the program to determine the integrated effects of fast-neutron and sodium environments on the properties of stainless steel, to develop postexposure testing methods for the stainless steel specimens, and to correlate the results from experimental and reactor sodium systems; in the study of carbon transport in sodium-steel systems, additional data have been obtained on carbon activities in Fe-Ni and Fe-Ni-Cr alloys.

SUMMARY

On-Line Impurity Monitors

Oxygen Meter Characterization. Performance evaluation of the oxygen meters on the Oxygen Meter Rig at ANL is continuing. The meters are being calibrated by the vanadium-wire equilibration method. During the fourth month of operation, the voltage stability of the meters at 700°F improved and the drift changed from that of a generally downward movement

to small fluctuations (noise) at a constant oxygen level. The calibration curves for the meters are described by the equation

$$\text{Meter emf (volts)} = K_1 - K_2 \log (\text{ppm O})$$

The 2σ deviation in K_1 (an indication of meter stability) averaged about 10 mV (equivalent to a factor of 1.6 uncertainty in the oxygen activity) for a 30-day period. The K_2 value of the meters at 700°F during the same period was 0.048 ± 0.003 (2σ) V, which is in good agreement with the previously obtained value.

On February 8, 1972, after 2782 hr of operation at 700°F, the meter operating temperature was increased to 900°F in an effort to improve the voltage stability. A performance evaluation of the meters at 900°F indicated a 2σ deviation in K_1 of 6.7 mV for the last 25 days of operation. A K_2 value of 0.065 ± 0.001 (2σ) V was determined experimentally for the 11 meters. This compares with a theoretical value of 0.075 V. The 2σ values of K_1 include the error in the determination of oxygen in sodium ($\pm 10\%$ or 3 mV) and possibly an error resulting from variation in fin temperature. The meters at ANL have been operated, as of March 31, 1972, for approximately 24 weeks without a meter failure.

The performance of the oxygen meters at EBR-II at ~700°F has been characterized by significant voltage drifting. Plans are being made to increase the temperature to 900°F to improve the voltage stability. A total of 2827 and 2393 hr of operating time has been accumulated for the two meters in the primary sodium system at EBR-II.

Hydrogen Meter Development. Studies were carried out to determine the operating life of a special 11-liter/sec ion pump with titanium cathodes, which will be used as a detector and vacuum-generating component in the hydrogen-meter leak detector and in the hydrogen-activity meters. The results indicated that the life of this pump is greater than 16 months when operated at hydrogen pressures of 2.8×10^{-6} Torr. The life of the pump is dependent upon the hydrogen pressure at which it is operated; hence, at lower pressures ($< 3 \times 10^{-7}$ Torr), at which the ion pump will operate during service as a steam-generator leak detector, this life may be extended by as much as a factor of five or ten. Ion pumps with cathodes constructed of tantalum are also being tested.

Studies to improve the operating characteristics of the hydrogen meter in the equilibrium mode have indicated that the hydrogen-activity meter must be operated (preconditioned) in a hydrogen-rich system before it will function properly in the equilibrium mode. The source of the problem is believed to be a thin oxide film which forms on the vacuum side of the nickel membrane at room temperature when the membrane is exposed to air. This oxide film gives rise to species other than hydrogen in the equilibrium gas system. Mass spectrometer studies have indicated that these species include carbon monoxide and water, which are formed directly, and methane, which is probably formed indirectly. Hydrogen conditioning of the system removes this oxide film. The presence of an oxide film is believed to be the source of difficulty in performing equilibrium-mode measurements with the hydrogen meter at EBR-II. Methods

are being explored for conditioning the nickel membrane with hydrogen so that meaningful equilibrium measurements can be made.

Carbon Meter Development. A method of measuring the chemical activity of carbon in sodium, based on the equilibrium distribution of carbon between 700°C sodium and a tab of Fe-8Ni or Fe-12Mn, has been developed. The method has been used to (1) obtain data on carbon activity vs. carbon concentration at 700°C for Types 304 and 321 stainless steels, (2) measure the chemical activity of carbon in two sodium loops, the Test and Evaluation Apparatus and the Oxygen Meter Rig, and (3) calibrate the United Nuclear Corporation (UNC) carbon meter.

Meter Modules. The oxygen-hydrogen meter (O-H) module in Cell B of the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II was shut down at the end of March 1972 for maintenance work that will provide for on-line purging of the oxygen-meter reference gas. The meter operating temperature is expected to be raised to 900°F by mid-June 1972.

Because of previous problems with the equilibration of vanadium metal specimens in the carbon meter-equilibration (C-E) module on the RSCL, screens are being installed in the inlet and outlet piping to prevent the possible loss of vanadium-wire specimens.

Detectors for Leaks in Steam Generators. The mechanical components and electrical console of a steam generator leak detector have been completed and sent to the Liquid Metal Engineering Center (LMEC). This unit is a smaller, more compact unit than the first leak-detector unit built for LMEC.

Bids are being received and evaluated at EBR-II for 10 steam-generator leak-detector modules that were designed at ANL-Illinois. The hydrogen meter in the module is based on RDT Standard C 8-6, "Hydrogen Meter for Service in Liquid Sodium."

Apparatus for Monitoring and Purifying Sodium, AMPS. Construction of AMPS is progressing; it is expected that the system will be filled with sodium in August 1972. The piping layout is being modified to include tritium monitors in the sodium and cover gas. A test plan for developing methods of tritium control has been sent to RDT.

Analytical Standards Program

RDT Standards. ANL has the responsibility for generating all RDT standards related to purity specifications for sodium and gases used in reactors and other sodium systems. The status of the following standards is described: RDT A 1-5, "Purity Specifications for Operating Sodium Systems;" RDT F 3-40, "Interim Methods for the Analysis of Sodium and Cover Gas;" RDT M 13-1 Rev. 1, "Reactor Grade Sodium--Purchase Specifications;" and RDT M 14-1, "Sodium Cover Gas--Purchase Specifications."

Analysis of Particulates in Sodium. Work has continued on the testing of various designs of filters for isolating particulates from flowing sodium systems. Two types of filters are being tested: one with bolted flanges and the other of all-welded construction. Both designs utilize

the same type of filter--namely, one of pressed-and-sintered Type 304 stainless steel having a nominal porosity of 10 μ m.

The data on particulates collected from various sodium systems are being used to evaluate criteria for establishing permissible levels of particulates in sodium. Results from all systems examined to date indicate that an amount of particulates corresponding to ~ 1 ppm in sodium is a high concentration (the level of particulates in EBR-II is $\sim 3 \times 10^{-3}$ ppm).

Analysis of Nonmetallic Impurities in Sodium by the Equilibration Method. Work is continuing on the development of equilibration methods for determining oxygen and hydrogen activities in sodium. A large number of vanadium and niobium specimens have been equilibrated in sodium over a range of cold-trap and system temperatures. These samples have been submitted for hydrogen and oxygen analyses. Data on these equilibrations will be presented when the analytical results are available.

Fission Product and Cover Gas Technology

Development of FEDAL Methods for FFTF. Methods for detection and characterization of fuel-element cladding failures in sodium-cooled reactors are being developed. Two types of systems have been designed: a cover-gas analysis system for detecting noble fission gas releases and a system for analysis of sodium by a sparging technique to detect ^{135}I release.

The cover-gas analysis system samples the reactor cover gas, discriminates against interferences from ^{23}Ne and ^{41}Ar by high-speed chromatography, and analyzes for xenon and krypton by Ge(Li) detection techniques.

The activities of xenon and krypton isotopes expected in the FFTF cover gas were estimated by extrapolating data from EBR-II to the conditions of FFTF by means of the ratio of sodium turnover times between FFTF and EBR-II. The important conclusions drawn from these calculations are as follows: (1) the background activities of FFTF are not very different from those found in EBR-II, (2) most of the xenon and krypton isotopes of interest, except for ^{138}Xe and ^{135m}Xe , are detectable even for a small leak (1% of plenum gas per hour), and (3) all isotopes of interest are detectable in a large burst release (10% of plenum gas).

The design layout of the cover-gas analysis system is essentially complete and a design description and specifications are being prepared for the hardware portion of the system using the draft version of RDT C 12-1, "Gas Chromatograph for Sodium Cover Gas Service," as a base standard. Specifications are being prepared for the spectrometer/computer portion of the cover-gas analysis system using RDT C 14-3, "Gamma-Ray Spectrometer-Computer System," as a base standard. The latter standard has been reviewed, comments have been incorporated, and the standard has been submitted to RDT for approval.

Work has proceeded in the design and fabrication of two similar systems for detecting fuel element failure by monitoring reactor sodium for dissolved gases and ^{135}I . The method involves sparging samples of

reactor sodium with inert gas to strip out dissolved fission gases, which are analyzed with a Ge(Li) detector. Proof-testing will be carried out on a laboratory system with nonradioactive sodium. Construction and assembly of sodium-containment components for the laboratory system have been started. A prototype sparger and sparge-gas analysis system will be tested on the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II. Detail design drawings for the sodium-containment components of the EBR-II system are nearly complete and procurement of required components to meet applicable RDT standards is under way.

On-Line Tritium Monitor. Calculations have demonstrated that a diffusion-type meter with an iron membrane would serve as a tritium monitor. The tritium in the sweep gas from the diffusion probe would be measured in an ionization counter. At low hydrogen concentrations in the sweep gas ($<0.01\%$) and low flow rates ($<1 \text{ cm}^3/\text{sec}$), the tritium concentration in the sweep gas, mainly as HT molecules, would reach equilibrium with the sodium. However, the HT concentration would be sensitive to changes in the hydrogen concentration in the sodium. At high hydrogen concentrations in the sweep gas ($>1\%$) and high flow rates ($>1 \text{ cm}^3/\text{sec}$), the HT concentration in the sweep gas would be high and unaffected by the hydrogen content of the sodium or small changes in hydrogen concentration in the sweep gas. This appears to be the most useful mode of operation of the meter. A laboratory apparatus now being tested will be used to define conditions for counting tritium with a proportional counter. Later, the apparatus will be used to evaluate components for the Apparatus for Monitoring and Purifying Sodium (AMPS), where the tritium monitor will be proof-tested.

Sodium Chemistry

Studies of Oxygen-Hydrogen Interactions in Sodium. The kinetics of the decomposition of hydroxide dissolved in sodium at 500°C is being studied by means of an isotope-exchange technique in which NaOD is used as a stand-in for NaOH. Data obtained from mass-spectrometric monitoring of the D_2 evolved upon heating a Na-NaOD mixture, combined with a measurement of residual NaOD (upon quenching) by an alcoholysis exchange technique, have provided information on the rate of decomposition of NaOD. The decomposition reaction was found to be first order in OD^- and to have a half-time of about 150 min.

A program has been started to determine the effects of oxygen-hydrogen interactions in sodium on oxygen and hydrogen activities. Simultaneous measurements of activities, by means of oxygen and hydrogen meters, will be made as functions of oxygen and hydrogen content of the sodium. The apparatus for these studies is described.

Materials-Coolant Interactions and Mechanical-Property Evaluations

Development of Test-Specimen Characterization Methods and Procedures. Methods for the characterization of mechanical-property and corrosion specimens prior to and after exposure to high-temperature sodium are being developed. Information on the chemical composition and composition gradients in the materials and on the amount, distribution,

and morphology of the various phases that result from thermal aging is required in order to interpret and correlate mechanical-property data.

Type 316 stainless steel from heat V-87210 in the annealed and 20%-cold-worked condition has been thermally aged for various times between thirty and several thousand hours at temperatures of 550, 650, and 750°C to provide representative specimen materials for the characterization studies. Type 304 stainless steel from a sodium heat exchanger that operated at temperatures between 400 and 750°C for up to 8 years is also being examined. Characterization is being accomplished by optical metallography, scanning electron microscopy, and X-ray diffraction techniques, as well as extraction and analysis of the carbide and intermetallic phases in the materials. An early objective of this work is to define the extent to which these various specimen-characterization methods must be employed and the usefulness of the information in establishing quantitative relationships between microstructural results and mechanical-property data.

Development of Specimen-Exposure Facilities and Postexposure Mechanical-Property Testing Capability. The relocation and modification of the nine uniaxial creep machines to be used in this program has been completed. Temperature profiles on the furnaces are being adjusted and temperature calibrations are being obtained.

A special heat of Type 316 stainless steel with low nonmetallic-element concentrations has been successfully cast, and tube blanks and rectangular bars have been extruded from the material. Some difficulty has been encountered in producing a homogeneous heat of this material with higher than normal nonmetallic-element concentrations; however, further attempts will be made. Mechanical property data on test specimens from these special heats will be used for comparison with specimens that have undergone decarburization and carburization to similar levels in liquid sodium at high temperatures.

Studies of Carbon Transfer in Sodium-Steel Systems. Previously reported information on the distribution of carbon between sodium and various iron-base alloys was based, in part, on high-temperature data for the solubility and activity of carbon in these materials that was extrapolated to temperatures below 800°C. To decrease the uncertainty in the calculated carbon-distribution results, measurements of carbon activities in Fe-Ni and Fe-Cr-Ni alloys at temperatures of interest in LMFBR sodium systems were made, and the results are reported. This information will be used in the monitoring of carbon activity in sodium by foil-equilibration methods and will also establish surface and equilibrium carbon levels in austenitic stainless steel loop materials when the carbon concentration of the sodium and temperature are specified.

An interaction-parameter relationship is being used to correlate the carbon activity data for the Fe-Cr-Ni-C alloys in terms of temperature and alloy composition. Mathematical relations for the temperature dependence of the carbon solubility and previously obtained data on austenite-carbide phase equilibria are being used in the development of a model for carburization and decarburization of austenitic stainless steel in sodium.

The input information for this model consists of system-independent materials data and system-dependent operating parameters. Carbon concentration profiles in austenitic stainless steels generated by numerical solutions to the diffusion equation, in which the carbide-sink term is properly taken into account, are being compared with available experimental data.

I. ON-LINE IMPURITY MONITORS (J. M. McKee)

Argonne National Laboratory is coordinating, as well as participating in, a national program for development, testing, and establishing commercial availability of impurity meters for use in LMFBR sodium systems. The meters being developed and characterized in this program are monitors for oxygen, carbon, and hydrogen impurities in sodium; the hydrogen meter can also be used as a leak detector for steam generators. Standardized modules for these meters that provide flow and temperature control are being developed.

A. Oxygen Meter Characterization

1. ANL-Westinghouse Joint Test Program (D. R. Vissers, J. M. McKee, L. J. Marek, L. G. Bartholme)

To provide a statistically significant measure of the calibration stability of the oxygen meter, twenty meters are being evaluated--ten at ANL and ten at the Westinghouse Advanced Reactors Division (WARD). The meters being evaluated are Westinghouse meters with $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolytes and gas reference electrodes. An eleventh meter, adapted to fit a United Nuclear Corporation (UNC) meter housing is also being tested at ANL. At both sites, the oxygen meters are being calibrated at various oxygen levels in sodium by the vanadium-wire equilibration method, which is used to determine the oxygen content of the sodium.

At ANL, the ten meters are being evaluated in a system [the Oxygen Meter Rig (OMR)] in which the meters are connected in series with a cold trap and a prototype carbon meter-equilibration (C-E) module.

During the fourth month of operation of OMR, the stability of oxygen meter emf at 700°F improved for all meters and the downward drift in voltage (ANL-7916, p. 10) changed to small fluctuations (noise) at a constant oxygen level. The calibration curve for this type of electrochemical cell has the general form

$$\text{emf (volts)} = K_1 - K_2 \log (\text{ppm O}) \quad (1)$$

During the 30-day period, the value of K_2 was found to be 0.048 ± 0.003 (2 σ) V, which is within the uncertainty in the previously determined value, 0.049 ± 0.003 (2 σ) V. The theoretical value at 700°F is 0.064 V. The deviation (2 σ) in K_1 (an indication of meter stability) averaged about 10 mV (equivalent to a factor of 1.6 uncertainty in the oxygen activity) for this period, as compared with the previous value of about 16 mV during the initial calibration period. Similar performance was observed at WARD.

When it became clear that further improvement in meter stability was unlikely to occur, a decision was made to increase the operating temperature of the ANL meters to 900°F, while continuing to test the WARD meters at 700°F. On February 8, 1972, after 2782 hr of operation at 700°F, the temperature of the 11 oxygen meters on the OMR was increased to 900°F in an effort to further improve the voltage stability.

After several preliminary vanadium-wire equilibrations, 18.7 g of sodium oxide (~500 ppm oxygen in the sodium with the reservoir isolated) was added to the sodium via a perforated stainless steel "tea bag" in the expansion tank. During the addition, the cold-trap temperature was raised to 625°F. The purpose of this oxygen addition was to replenish the oxygen supply of the sodium which had been removed by the vanadium-wire equilibrations. The oxygen meter readings indicated that solution of the oxide through the perforated sheet (9 mils thick, 14-mil holes on 27-mil centers, square array) was complete in 5 hr at 900°F.

The change in emf exhibited by the eleven oxygen meters as a result of these additions was 153.4 ± 1.89 (2 σ) mV. The excellent agreement observed in the changes of emf by the eleven meters supports previous indications that the slope of the meter calibration curve (K_2 in Eq. 1) is the same for all eleven meters, and very probably does not change with time.

After the oxygen level in the sodium system was returned to its former level, a nine-point calibration series was then performed at 7 different concentrations of oxygen in sodium (0.7 to 15 ppm) over a period of 25 days. The emf of Meter OM-8 became erratic during this series and was excluded in calculating meter performance. The average slope of the calibration curve, K_2 , at 900°F was found to be 0.065 ± 0.001 (2 σ) V, which is significantly higher than at 700°F. The theoretical value of K_2 at 900°F is 0.075 V.

At 900°F, the average 2 σ deviation in K_1 for the ten remaining meters was 5.6 mV. This means that 95 percent of the time, the oxygen activity indicated by the meter will agree with that determined by vanadium equilibration within a factor of 1.2 or less.

The second calibration sequence at 700°F for the nine¹ oxygen meters being operated at WARD indicated an average 2 σ deviation of about 10 mV during the 15-day calibration period. This confirms our earlier conclusion that the stability of the oxygen meters at 700°F over a 30-day period is about 10 mV. Thus, the uncertainty in the indicated oxygen activity for the oxygen meters appears to be about 3 times greater at 700°F than at 900°F.

It should be noted that individual determinations of oxygen in sodium by the vanadium-wire equilibration method have an uncertainty of ± 10 -20%. A 10% error in the oxygen content measured for a given calibration point creates an apparent variation in K_1 for all the meters of 3 mV. Thus, the actual stability of the meters may be better than the above calculations indicate.

Part of the meter emf instability reported above is probably also due to variations in the temperature gradient from the electrode tip to the cooled top end of the finned housing. The temperature at the base of the top fin is recorded with each meter reading. These

¹Oxygen Meter 5 at Westinghouse failed after 2068 hr of operation at 700°F.

data indicate a fin temperature coefficient of 0.35 ± 0.25 (2σ) mV/°F at 900°F. (Variations in emf with fin temperature were also observed at 700°F.) This sensitivity of emf to fin temperature suggests that the effective area of the reference electrode extends upward from the tip of the tube into the annulus of static sodium (or gas). Although there are several possible mechanisms for the observed effect, insertion of the electrolyte tube farther down into the sodium stream would probably eliminate all of them. Significantly, Meter OM-11, in which the tip of the tube is placed lower than in the other 10 meters, has a fin temperature coefficient of about 0.17 mV/°F.

The 11 meters on the OMR have operated for 4000 hr, as of March 31, 1972, without failure of an electrolyte tube. The problem recently encountered with Meter OM-8 may be in the external circuitry.

The oxygen-meter program at WARD was terminated on March 6, 1972, because of a sodium fire in the system. The second oxygen-meter calibration sequence had been completed prior to that time.

2. Oxygen Meter Performance on Other Facilities

a. Radioactive Sodium Chemistry Loop (RSCL) at EBR-II (J. T. Holmes)

Two Westinghouse oxygen meters are also being tested in a prototype oxygen-hydrogen meter (O-H) module in Cell B of the RSCL of EBR-II. Two vanadium-wire equilibrations, conducted during December 1971, were described in the preceding report (ANL-7916, p. 15). Results of the second equilibration, which were not available at that time, showed an oxygen content of 0.74 ± 0.02 (2σ) ppm for EBR-II primary sodium. [The previously reported value was 0.85 ± 0.06 (2σ) ppm.]

The two meters in EBR-II were operated at 702 to 712°F during the period January-March 1972 and have accumulated total operating times of 2827 and 2393 hr, respectively; however, they have exhibited a somewhat greater voltage drift than is considered acceptable. The drift does not correlate with the several temperature excursions encountered on the RSCL during the 3-month period. Plans are being made to increase the operating temperature of these meters to 900°F; this is expected to result in improved voltage stability of the meters, similar to that of the meters on the OMR.

b. Test and Evaluation Apparatus (TEA) (V. M. Kolba, P. J. Mack)

Both Westinghouse oxygen meters on TEA continued in operation during the quarter and as of March 31, 1972, had accumulated total times of 7690 and 7162 hr for HEDL tubes 73-1-2 and 72-2-1, respectively. A breakdown of the times at various temperatures is shown below:

Module No.	Meter Westinghouse Meter No.	HEDL Tube No.	Time, hr. at Temperature			Total Time hr
			700°F	800°F	900°F	
0-1	II-E-2	73-1-2	3432	2818	1440	7690
0-2	II-E-1	72-2-1	3240	2482	1440	7162

c. Recirculating Sodium Equilibration Apparatus No. 2 (RSEA-2)
(D. L. Smith)

The sodium apparatus used for the vanadium-wire equilibration investigations is equipped with electrochemical oxygen meters as an alternative method of monitoring the oxygen concentration in sodium. Interpretation of the oxygen-meter emfs measured during the distribution-coefficient measurements provides additional confidence in the results obtained. Commercial United Nuclear Corporation (UNC) and Westinghouse meters have been used in addition to modified meters of both types, in which the conventional reference electrode has been replaced by a Na-Na₂O reference electrode. Cells with Na-Na₂O reference electrodes possess several advantages for measurements to provide data which will resolve the discrepancies between measured cell emfs and values calculated from thermodynamic data on the basis of ideal cell operation.

In view of the significant drift problems that were observed (ANL-7916, p. 10) the initial calibration tests of the Westinghouse (air reference electrode) oxygen meters, experience with another recently installed UNC (Cu-Cu₂O reference electrode) oxygen meter is of particular interest. Our previous experience² with the UNC meters did not indicate extensive drift problems; however, this aspect of meter operation was not as severely scrutinized as in the present work.

Meter 5C was installed in a previously used housing on a bypass leg of RSEA-2 while the main loop flow was maintained at 0.1 gpm with the cold trap at 150°C (2.1 ppm, estimated oxygen concentration in sodium). Within a period of 3 hr, the cell was heated to near the operating temperature, flow was initiated through the oxygen meter section, the loop temperatures were stabilized, and the desired cell operating temperature (400°C) was attained. At this time, the meter voltage was 1.183 V; a leveling-off value of 1.189 V was recorded after weekend operation. Subsequent operating history of this meter is summarized in Table I-1.

The following conclusions are drawn from this test:

(1) The initial response of the meter was rapid. A meter reading within 6 mV of the final value was reached in a period of less than 3 hr after installation. Most of this time was required to heat the cell to operating temperature and establish a steady sodium flowrate through the meter section.

²D. L. Smith and R. H. Lee, ANL-7891 (January 1972).

TABLE I-1. Operating History of UNC Oxygen Meter 5C
(Cu-Cu₂O reference electrode at 400°C)

Cold-Trap Temp., °C	Oxygen Concentration in Sodium, ppm		Oxygen Meter Emf, V	Period of Stable Loop Operation, days
	From Solubility at Cold-Trap Temp.	From V-Wire Equilibration		
150 ± 1	2.1 ± 0.1	1.95	1.189 ± 0.002	21
200 ± 1	10.7 ± 0.3	a	1.155 ± 0.001	28
150 ± 1	2.1 ± 0.1	a	1.188 ± 0.002	10
175 ± 1	5.1 ± 0.2	a	1.168 ± 0.002 ^b	28

^aAnalyses incomplete.

^bAfter 8 days at these conditions, cell voltage began a steady downward drift of ~0.5 mV/day.

(2) Constant meter voltages were recorded for periods of stable loop operation up to four weeks. In general, the slight variations in cell voltage corresponded to small fluctuations in the cold-trap temperature ($\pm 1^\circ\text{C}$) or cell temperature ($\pm 2^\circ\text{C}$).

(3) Reproducible meter voltages were obtained when the cold-trap temperature was returned to 150°C after extended operation (28 days) at a higher temperature (200°C).

(4) A linear plot with a slope of 48 mV/decade was obtained for emf versus the logarithm of the oxygen concentration in sodium. This slope is somewhat less than that obtained from similar meters operated previously at low temperatures. Reasons for the difference are being investigated. One possibility is an upgrading of the electrolyte purity by Zircoa in the process of development of the high-purity tubes manufactured for the Westinghouse meters.

(5) Stable emfs were obtained from the meter for a period of more than two months, after which a steady decrease in voltage, of the order of 0.5 mV/day, was observed. Much longer periods of stable meter operation have been attained with similar meters operated at 352°C and with modified meters with Na-Na₂O reference electrodes. The decrease in voltage after extended operation is probably the result of current leakage caused by sodium penetration into the electrolyte. This type of meter response suggests that the unpredictable drift observed with the Westinghouse meters is likely associated with the air reference electrode.

B. Hydrogen Meter Development

The ANL diffusion-type hydrogen activity meter can be operated in two modes.³ In the equilibrium mode, the hydrogen level of the sodium is determined from a direct measurement of the hydrogen pressure in equilibrium with the sodium. In the dynamic mode, the hydrogen activity in sodium is determined from the rate of hydrogen diffusion through a nickel membrane immersed in the sodium. A vacuum is maintained on the membrane by an ion pump. The meter is normally operated in the dynamic mode; periodic calibrations are made by operating the meter in the equilibrium mode. The hydrogen meter used to detect steam-generator leaks to the sodium systems of LMFBRs is also operated in the dynamic mode.

1. Studies of Ion-Pump Stability (D. R. Vissers, L. G. Bartholme)

The useful life of these meters will be determined in large measure by the stability of the ion pump, which serves as the vacuum source and hydrogen sensor. Consequently, stability studies of the ion pumps have been initiated.

The studies are being carried out on a vacuum system in which hydrogen is supplied to the pump at a fixed rate by an all-metal valve with a variable orifice. The valve is connected to a 2-liter reservoir of hydrogen gas at a pressure of about 2 atm. The current of the ion pump is monitored over a period of time to determine the pump stability and the quantity of hydrogen that the pump will accept before it becomes unstable.

The results of these studies indicate that the useful life of an 11 liter/sec ion pump with titanium cathodes, built by the Ultek Division of Perkin-Elmer, is greater than 16 months when operated at hydrogen pressures of 2.8×10^{-6} Torr. The life of the pump is dependent upon the hydrogen pressure at which it is operated; hence, at pressures below 3×10^{-7} Torr (the pressures at which the pump will operate during service as a steam-generator leak detector), this life may be extended by as much as a factor of five or ten.

Three second-generation ion pumps having cathodes constructed of tantalum have been obtained. Preliminary studies performed by J. Singleton⁴ indicate that this type of pump may exhibit a pumping speed which does not change with time or with changes in hydrogen flux. One of these pumps is now being tested.

2. Characterization Studies of Hydrogen Meter (D. R. Vissers, L. G. Bartholme)

Efforts to improve the operating characteristics of the hydrogen meter in the equilibrium mode have been continued. Although no problems have been encountered with the laboratory version of the hydrogen-activity

³ D. R. Vissers, J. T. Holmes, and P. A. Nelson, A Hydrogen Activity Meter for LMFBRs, Trans. Amer. Nucl. Soc. 14(2), 610 (1971).

⁴ Westinghouse Research Laboratories.

meter during operation at hydrogen levels in sodium of 50-100 ppb, attainment of equilibrium at these levels with the meters in the oxygen-hydrogen meter (O-H) modules has been very difficult. Recent work has been directed toward investigating the possibility that preconditioning of the nickel membrane with hydrogen is necessary for proper meter operation. Two meters were used in the present work. The first was a standard ANL hydrogen-activity meter; the second was a hydrogen-activity meter in which the standard sensor, a Varian Millitorr ion gauge, was replaced with a quadrupole mass spectrometer. The mass spectrometer was added to determine the composition of the gases present in the vacuum system of the meter while an equilibrium pressure measurement was being made and to determine whether this gas composition was affected by hydrogen conditioning.

The results showed that the hydrogen-activity meter must be operated or preconditioned with a hydrogen flux of 2×10^{-5} (liter)(Torr)/sec or more at $\sim 900^\circ\text{F}$ before it will function properly in the equilibrium mode. The source of this problem is believed to be a thin oxide film which forms on the vacuum side of the nickel membrane at room temperature when the membrane is exposed to air. This oxide film gives rise to a continuous generation of gaseous species other than hydrogen, which prevent attainment of an equilibrium pressure. The species include carbon monoxide and water, which are formed directly, and methane, which is probably formed indirectly. Hydrogen conditioning of the system removes this oxide film.

Hydrogen conditioning is not necessary for operation of the meter in the dynamic mode. This fact was established in earlier work and was verified during the present studies.

3. Hydrogen Meter Performance at EBR-II (J. T. Holmes)

The hydrogen meter at EBR-II has not operated satisfactorily in the equilibrium mode (see ANL-7916, p. 20) because the nickel membrane had become oxidized by air in-leakage through polyimide valves, which have since been replaced with stainless steel valves. Methods are being explored for providing a means of conditioning the nickel membrane with hydrogen so that meaningful measurements in the equilibrium mode can be made. These measurements can then be used to calibrate the continuous readings obtained in the dynamic mode.

Operation of the hydrogen meter in the dynamic mode indicates that the hydrogen content of EBR-II sodium is <100 ppb.

C. Carbon Meter Development (M. F. Roche, J. W. Allen, R. J. Meyer)

A method of measuring the chemical activity of carbon in sodium has been developed. The method is based on the equilibrium distribution of carbon between sodium and a tab of Fe-8Ni or Fe-12Mn immersed in the sodium. With graphite chosen as the standard state, the chemical activity of carbon in the tab and in sodium is the same at equilibrium. The carbon activity of the metal, and consequently, that of the sodium can then be derived from carbon analysis of the metal tab and from the established relationship between carbon concentration and carbon activity in the tab

alloy. This method is analogous to the vanadium-wire method that is used to measure the oxygen activity in sodium.⁵

The primary use of the tab-equilibration method will be in determining the chemical activity of carbon in sodium systems. These measurements and measurements of the activity vs carbon concentration for sodium-system materials of construction, such as Type 304 stainless steel, are needed for predicting the direction and rate of carbon transport in sodium systems.⁶ If carbon meters are present in the sodium systems, the tab-equilibration method would also serve to evaluate and calibrate the on-line meters.

1. Tab Experiments

The tab experiments are performed in an inert-atmosphere box equipped with two furnace wells. Each well holds a pot containing about 2 liters of stirred sodium at 700°C. One of the pots, made of 200 nickel, has a high carbon activity; the other pot, made of Type 304 stainless steel, has a low carbon activity. These pots control the carbon activity in the sodium and thus control the carbon concentrations in the equilibrated tabs.

Survey experiments with a number of tab materials led to the choice of Fe-8Ni and Fe-12Mn as monitors of carbon activity. Some of these experiments, which involved simultaneous equilibration of up to eleven tabs in each pot and comparison of the carbon concentrations of the tabs with the output of carbon meters, have been reported previously (ANL-7916, pp. 21-25). At that time, sufficient data had been accumulated to eliminate cobalt, nickel, titanium, tantalum, and zirconium from further consideration. A limited number of experiments with vanadium and molybdenum have indicated that these materials are also unsatisfactory. They getter considerable amounts of carbon at all activities, behaving in a manner similar to titanium.

Figure I-1 presents the data accumulated to date from Fe-12Mn and Fe-8Ni tabs equilibrated in sodium at 700°C for various lengths of time. The line labelled "Fe-8Ni" represents the relationship between carbon activity and $N_C/(1 - 5 N_C)$ for Fe-8Ni, where N_C is the mole fraction of carbon in the alloy.⁷ The carbon activity in Fe-12Mn was taken to be equal to that in the simultaneously equilibrated Fe-8Ni, whereas the value of $N_C/(1 - 5 N_C)$ for Fe-12Mn was calculated from the equilibrium carbon concentration in the tabs. It is evident that both Fe-8Ni and Fe-12Mn respond in the same manner to changes in carbon activity in the sodium. At a given activity, the equilibrium carbon content of Fe-12Mn is about three times that of Fe-8Ni; thus, Fe-12Mn is a more useful monitor in systems having low activities. The expected limit of a measurement of carbon activity in Fe-12Mn is about 5×10^{-4} (corresponding to approximately 10 ppm C in the tab).

⁵D. L. Smith, Nucl. Technol. 11, 115 (1971).

⁶K. Natesan and T. F. Kassner, J. Nucl. Mater. 37, 223 (1970).

⁷C. Bodsworth, I. M. Davidson, and D. Atkinson, Trans. Met. Soc. AIME 242, 1135 (1968).

Fig. I-1

Carbon Activity vs $N_c / (1 - 5N_c)$
for Fe-8Ni and Fe-12Mn at
700°C

The results of carbon activity measurements in two sodium loops, the Test and Evaluation Apparatus (TEA) and the Oxygen Meter Rig (OMR), are also given in Fig. I-1. The loop studies, which were performed in preparation for a measurement of the carbon activity in EBR-II, included both Fe-8Ni and Fe-12Mn tabs. As in the other experiments, the activity was calculated from the equilibrium carbon contents of the Fe-8Ni tabs, and the carbon contents of the Fe-12Mn tabs, expressed as $N_c / (1 - 5N_c)$, were simply plotted at this calculated activity. Clearly, the activity could have been calculated from the line already established for the Fe-12Mn in pot experiments. The carbon concentrations in the sodium in TEA and in OMR were calculated from the measured activities to be 0.3 ppm and 0.08 ppm, respectively, taking the solubility of graphite in sodium at 700°C (the equilibration temperature) as 39 ppm⁸ and assuming that the carbon concentration in the sodium is the product of the activity and solubility.

Shiels and Bagnall⁹ of WARD have been using Type 304 stainless steel tabs of 3-mil thickness as carbon monitors in their loops, and have

⁸B. Longson and A. W. Thorley, J. Appl. Chem. 20, 372 (1970).

⁹S. Shiels and C. Bagnall, WARD, unpublished work.

compared the carbon concentration in these monitor tabs with the carbon concentration in other alloys such as Type 321 stainless steel. We have completed a series of intercalibration experiments to relate the carbon concentration in their alloys to carbon activity. Types 304 and 321 stainless steel tabs, both obtained from WARD, were exposed along with Fe-12Mn tabs to well-stirred 700°C sodium for one week in either the stainless steel pot or nickel pot. Figure I-2 is a plot of the measured carbon concentration in the Types 304 and 321 stainless steel tabs vs carbon activity calculated from the Fe-12Mn tab analyses.

2. Experiments with UNC Carbon Meter

Initial calibration experiments with a UNC carbon meter have been described previously (ANL-7916, p. 25). The flame ionization detector (FID) readings¹⁰ produced by the meter during Fe-8Ni and Fe-12Mn tab equilibration experiments were plotted against the carbon activity as determined from the tab analyses. The resulting linear curve, which was obtained from data in the activity range from 0.1 through 0.3, passed through the origin and was in good agreement with the theoretical curve based on a simple diffusion model. Experimentation at activities below 0.1 has now shown, however, that the carbon-meter reading at low carbon activities deviates from the previously reported linear relationship. These data are plotted in Fig. I-3. The cause of the deviation has not yet been determined, but is under investigation.

3. Experiments with BNL Electrochemical Meter

Previous calibration of the Brookhaven National Laboratory (BNL) electrochemical carbon meter (ANL-7916, p. 27) showed that the cell potential approached a limit in the region of lower carbon activities (below 0.1). An effort to improve the performance of this meter by isolation of the anode and cathode compartments was unsuccessful. Isolation was achieved by enclosing the graphite reference electrode within a beryllia tube-and-crucible arrangement that limited ionic transport between compartments to a thin electrolyte film. Although initially the cell gave higher voltages, its performance quickly deteriorated (within a few weeks) to about the same limiting potential (~40 mV) as was observed in the unmodified cell. A survey of other electrochemical methods of measuring carbon activity in sodium has been started.

¹⁰The operation of the UNC meter is based on diffusion of carbon through the membrane and reaction of the carbon with a flowing, moist, hydrogen-argon gas mixture to form CO. The CO is then catalytically converted to CH₄, which is measured with a flame ionization detector. A background flame-ionization detector reading of about 170 FID units, due to contaminants in the gas mixture, is subtracted from the observed reading.

Fig. I-3

Calibration Curve for UNC Carbon Meter (sodium temperature, 700°C)

- D. Meter Modules (V. M. Kolba, J. T. Holmes, J. M. McKee, D. R. Vissers, M. A. Slawewski,¹¹ P. J. Mack, L. G. Bartholme)

The objective of this work is to design, proof-test, and establish commercial availability of on-line meter modules. These modules include impurity meters and the flow and temperature controls required for proper meter operation.

1. Oxygen-Hydrogen Meter (O-H) Modules

Two O-H modules, each containing two oxygen meters and one hydrogen meter, are currently being tested: one at ANL-Illinois in the Test and Evaluation Apparatus (TEA) and the other in radioactive primary sodium at EBR-II. A third O-H module is presently under construction for use on the Apparatus for Monitoring and Purifying Sodium (AMPS).

The O-H module at EBR-II has been operated in primary sodium for a total of 2827 hr. During the period from January through March 1972, the O-H module was in operation 86% of the time. The module was shut down on March 28, 1972, to perform maintenance work on the sodium and instrument systems. The tasks included (1) replacing the thermocouple for measuring the sodium temperature for oxygen meter No. 1; (2) providing a vent line for sampling the reference gas for radioactivity during periodic flushing of the oxygen-meter reference gas; (3) providing a pressure relief valve (5 psi) on the reference gas line to prevent the possibility of excessive pressure on the ceramic electrolyte tube; (4) replacing the reference gas rotameter (0 to 0.08 scfh) with one having a range from 0 to 0.2 scfh; and (5) replacing the chopper circuits in the silicon control rectifier (SCR) temperature controllers with choppers of an improved design for better reliability.

2. Carbon Meter-Equilibration (C-E) Modules

The C-E module contains a preheater and an isothermal zone (for the carbon-meter probe or for equilibration of metal specimens) in series with a regenerative heat exchanger, flow control valve, and flow indicator. Three of these modules have been built at ANL; one is in use at ANL on the Oxygen Meter Rig (OMR), one is in operation at EBR-II in Cell C of the RSCL, and one has now been installed on AMPS. These three modules are being used initially for calibrating oxygen meters by the equilibration of vanadium metal specimens. A fourth module was built at WARD and is used for calibrating oxygen meters there.

As reported in ANL-7916, p. 30, difficulties were encountered in the removal of vanadium-wire specimens from the second equilibration of vanadium wires in the RSCL. When the specimen holder was removed, two wires were lost. Consequently, a holder that provides positive containment of the specimens will be built and tested on OMR and this type of specimen holder will be used in the RSCL module. However, for equilibrations conducted in the near future, the module at EBR-II will be operated with 100-mesh screen strainers in the inlet and outlet

¹¹ Design Group, Chemical Engineering Division, ANL.

Conoseal unions, and larger diameter (20-mil versus the previous 10-mil) wires, which are less fragile after exposure to sodium, will be used.

The strainers, which will fit into the module Conoseal unions, have been designed, fabricated, and mechanically tested. The 100-mesh stainless steel screen was spotwelded between two 0.008-in.-thick stainless steel rings at eight to ten places around the periphery. (This assembly is contained in the gap between the Conoseal flanges.) Five strainer assemblies were tested to the destruction point. In all tests, the screens broke away from only half of the spotwelds but were retained to the rings by the remaining welds, and the strainers all remained within the Conoseal unions. The loads required to cause breakage of the screens from the spotwelds were 40, 38, 40, 23, and 67 lb for the five tests. An operating temperature of $\sim 750^{\circ}\text{F}$ is calculated to reduce the load required for breakage by about 17%. The maximum load on the screens from the available pump head at EBR-II is calculated to be ~ 3.2 lb. The screen-strainer assembly has a high natural frequency, calculated to be >1900 Hz, and hence is not expected to undergo resonant vibration. These tests and calculations demonstrate that the screen assembly has sufficiently high integrity for use in the EBR-II system.

Strainers of the design described above have been fabricated and sent, together with the quality assurance documentation, to EBR-II.

Active use of the C-E module on OMR for vanadium-wire equilibrations is continuing in support of the oxygen-meter characterization program (see Section I.A.1 above). Six batches of vanadium wires have been equilibrated that included both 10- and 20-mil diameter wires. The oxygen content of the standard 10-mil wire was found to be slightly but consistently higher (about 4%) than that of the 20-mil wire. Preliminary tests indicate that this was due to pickup of oxygen during cooling from 1382°F , rather than to incomplete equilibration. The pickup of oxygen can be eliminated by faster cooling or by displacing the sodium with argon before cooling. The 20-mil wire provides more metal for analysis, shows better precision in oxygen content, and is much less likely to break during handling. Tests¹² have indicated that 16 hr at 1382°F is adequate for equilibration of 20-mil wires.

A modified specimen holder is being built for testing in the C-E module. The specimens will be contained in a basket 3 in. long by 7/16 in. ID with 60-mesh screens at each end. The basket can be used to hold sheet specimens for determination of carbon, hydrogen, and oxygen in addition to vanadium wires. The specimens are entirely contained and hence cannot be lost to the sodium stream. The power input to the specimen guard heater has been adjusted so that the sodium temperature is constant within $\pm 0.4^{\circ}\text{F}$ over the 4 1/2-in. length from the bottom tip of the basket to the top end of the platinum resistance winding. It is expected that this modified holder will be used at EBR-II after proof-testing on the OMR.

¹²Performed by D. L. Smith.

E. Detectors for Leaks in Steam Generators (J. T. Holmes, V. M. Kolba, P. J. Mack, L. G. Bartholme)

When operated in the dynamic mode, the hydrogen meter (see Section I.B above) can serve as a detector for leaks in LMFBR steam generators.

Purchase specifications have been prepared by the EBR-II Project for 10 steam-to-sodium or water-to-sodium leak-detector modules. The specifications are based on RDT Standard C 8-6, "Hydrogen Meter for Service in Liquid Sodium." Bids are currently being received and evaluated.

Recently, a second leak-detector module was fabricated, assembled, checked for operability, and shipped to the Liquid Metal Engineering Center (LMEC) for use on their Sodium Components Test Installation. This unit differs from the earlier module supplied to LMEC in that it is a smaller, more compact unit having only a high-hydrogen-level alarm. The package consists of a sodium piping system with a regenerative heat exchanger, a linear induction pump, a nickel membrane and housing, a vacuum system, and an electrical console.

Sodium enters the leak-detector module through a 1-in. pipe and flows into the shell side of the regenerative heat exchanger to the pump tube entrance, through the pump tube and down the shell side of the heat exchanger where it is heated to 950°F. It exits through holes into the tube side of the heat exchanger, past the nickel membrane, and out through the center tube, which protrudes slightly into the main sodium stream. The heat exchanger shell is made from 1-in. schedule 40 pipe; the 7/8-in. center tube is anchored solidly at one end and is slip-fit at the other end to prevent thermal stresses. Figure I-4 shows the leak detector with the heaters and thermocouples removed.

The main heat input to the leak detector is provided by clam-shell heaters located along the region of the heat exchanger between the pump and membrane. These heaters are controlled by a temperature controller which senses the temperature at the nickel membrane housing. Other heaters on the unit are used for preheating or, under some conditions, for trace heating to reduce heat losses. The heaters are located so that preheating can proceed from the inlet-outlet end progressively to the membrane end of the module.

Thermocouples are placed on the piping in locations which allow control of system operation and preheating, namely, one each at the inlet, the outlet, the end of the pump tube, and on the linear induction pump, two at the membrane housing, and two on the vacuum system. Figure I-5 shows the new leak detector as shipped to LMEC.

An operating manual was prepared for this leak detector. This manual and the quality-assurance documentation for the fabrication of the detector piping system were also sent to LMEC.

Fig. I-4. Modified Leak Detector for LMEC with Heaters, Thermocouples, and Insulation Removed. ANL Neg. No. 308-2818A

Fig. I-5. Leak Detector as Shipped to LMEC. ANL Neg. No. 308-2823A

F. Characterization of Impurity Meters and Meter Response to Impurity Species (J. M. McKee, D. J. Raue)

Construction of the Apparatus for Monitoring and Purifying Sodium (AMPS) is continuing on a schedule intended to permit filling the system with sodium in August 1972. Assembly and installation of the two cold traps, the getter trap, and the C-E module have been completed. Installation of the sodium containment system is essentially complete. Most of the trace heaters and leak-detection windings are in place. One O-H module and two in-line samplers are nearly ready for installation. A second O-H module will be transferred from TEA after sodium circulation in AMPS has been started.

The AMPS piping layout has been modified to include a tritium monitor, which is arranged so that it can measure the tritium content of the sodium either entering or leaving the experimental cold trap. The modified schematic piping diagram was included in a document entitled "Plan for Development of Tritium Monitoring and Removal Methods for LMFBRs," recently sent to the AEC's Division of Reactor Development and Technology for approval. The location of the tritium monitor within the AMPS enclosure has been selected, and detailed drawings of the additional piping are being prepared. The probe to be used initially for monitoring tritium in AMPS is identical with the carbon-meter diffusion probe and can be used in the low-cost equilibration device recently developed (ANL-7916, p. 31). One of these units is being fabricated for use on AMPS.

Design of the cover gas system for AMPS has been completed. Two vapor traps will be installed for removal of argon from the dump tank and from the expansion tank. The system provides for continuous recirculation of argon from the cover gas in the expansion tank, through the vapor trap, a tritium monitor, a sampling manifold, and back into the expansion tank.

II. ANALYTICAL STANDARDS PROGRAM (R. J. Meyer)

A. Administrative Activities (F. A. Cafasso, R. J. Meyer, M. H. Barsky)

Argonne National Laboratory has the responsibility for generating all RDT standards related to purity specifications for sodium and gases used in reactors or other sodium systems. These documents will specify (1) acceptable impurity levels for the purchase of sodium and cover gas and for the operation of sodium and cover-gas systems and (2) the sampling and analytical methods for monitoring all impurities and for demonstrating that certain impurities (for which methods of control exist) are at or below the acceptable level.

The current status of each of the standards presently being prepared on sodium and cover-gas purity is given in Table II-1. These standards were discussed at a meeting of the National Analytical Standards Working Group, held on February 1-3, 1972, at the Liquid Metal Engineering Center (LMEC).

The manual of analytical methods, previously published as ANL/ST-6, will become RDT Standard F 3-40. This document was reviewed by the Working Group for possible changes and additions. ANL's methods for determining oxygen, carbon, and hydrogen activities in sodium by equilibration of metal specimens were discussed. It was agreed that the oxygen

TABLE II-1. Status of RDT Standards

Standard Designation	Title	Status	Next Action
RDT A 1-5	Purity Specifications for Operating Sodium Systems	Revision in progress	Submission for approval (July 1972)
RDT F 3-40	Interim Methods for the Analysis of Sodium and Cover Gas	Revision in progress	Submission for approval (May 1972)
RDT M 13-1 Rev. 1 ^a	Reactor Grade Sodium-- Purchase Specifications	Revision nearly complete	Submission for approval (May 1972)
RDT M 14-1	Sodium Cover Gas-- Purchase Specifications	Submitted for approval (Feb. 1972)	

^aThis document will supersede RDT M 13-1T.

method is now fully accepted by the analytical community and that the carbon and hydrogen methods are accepted as tentative methods. The oxygen method, which was included in ANL/ST-6, will be incorporated into the main body of RDT F 3-40, and the carbon and hydrogen methods will be added to the appendix.

The Working Group agreed that the provisions in RDT Standard A 1-5, "Purity Specifications for Operating Sodium Systems," were generally acceptable to the analytical community, with a few revisions, which are currently being made. The most significant revision is the incorporation of the use of the plugging indicator into the standard.

B. Laboratory Activities

1. Analysis for Particulates in Sodium (M. D. Adams)

a. Analysis of EBR-II Primary Sodium

The results of examination of particulates from the first filter installed on the primary sodium system of EBR-II were presented in a previous report (ANL-7916). A second filter has now been shipped to EBR-II for sampling of the primary sodium. In the test previously reported, ~1100 gal of sodium flowed through the filter; in the second test, approximately twice that amount will be filtered.

b. Analysis of Sodium in TEA

The sodium in TEA has been filtered several times to provide experience for evaluation of the particle-analysis procedure and to test filter designs. The filters have been operated for longer-than-normal sampling periods to determine if problems of design exist.

A rather large amount of particulate material has been isolated from TEA on the first two filters. (A third filter has been removed from the system, but has not yet been examined.) The bulk of the material on the first two filters was a fine black powder. Carbon analysis on ~0.4 mg of the material indicated 14 wt % carbon. X-ray diffraction has shown no evidence of carbides, but gamma-iron, alpha-iron, and a sigma-phase structure common to a number of binary and ternary iron alloys have been identified. These are structures typical of (1) stainless steel fragments and (2) iron dissolved and recrystallized from sodium. A small amount of the black powder was also examined with the ion microprobe. The major elements present were Na, Ca, Al, and the stainless steel components, Fe, Cr, and Ni. Significant peaks were also found for C, Mg, Si, Ti, and V. On the basis of this information, there is apparently some mass transfer taking place as iron is being dissolved and reprecipitated.

Two types of filter cartridges have been tested on TEA, one with bolted flanges and one of an all-welded construction; the latter is shown in Fig. II-1. The same type of filter element is used in each, namely, a filter of pressed-and-sintered Type 304 stainless steel having a nominal porosity of 10 μ m, welded to a gasket of nickel which is held

Fig. II-1

Design of All-Welded Filter Cartridge for Use with High Temperature Sodium

either in the bolted flange or with a bayonet locking ring in the welded model.

Both models have been operated at 400°C for periods of several weeks. Filter cartridges of the bolted-flange design presented no disassembly problems after periods of operation up to one week. However, after longer periods, disassembly was difficult. The nickel gasket appeared to be bonded, or welded, firmly to the stainless steel flanges, and it was necessary to force a steel wedge between the flanges to separate them. Changes in the bolted-flange design to eliminate the disassembly problem are being considered. Although disassembly of the welded model requires cutting of the cartridge with a large pipe cutter (an awkward task in a glovebox), no serious problems have been encountered.

c. Analysis of Sodium from the Core Components Test Loop (CCTL)

A sodium filter installed on CCTL has been disassembled for examination. The filter was the same all-welded design previously shown to be satisfactory for use at 400°C on TEA.

During the 42.5 hr of operation on CCTL at 600°C, a small hole developed at the weld between the nickel gasket and the stainless steel filter. Thus, quantitative measurements of the amount of particulate

would be of doubtful value. However, a few of the particles have been identified. Of the transparent particles, which can usually be identified by petrography, Al_2O_3 was the most common. One unusual particle not seen in previous systems has been identified by petrographic methods as $\text{Ca}_5\text{Al}_6\text{O}_{14}$. Of the opaque particles, alpha-iron and fragments of stainless steel have been identified. Other materials have been submitted for X-ray diffraction identification.

The hole at the nickel gasket-filter interface was apparently a welding problem, possibly a small crack eroded to visible dimensions by the passage of sodium through it. A bubble test has, therefore, been devised to check future filters before use. The filter is submerged in water and compressed air is forced through it. If the first breakthrough of bubbles is at the welded joint, it indicates a questionable spot which should be rewelded.

A second filter of the same design, which showed no leak in the weld region during the bubble test, has been placed in operation on CCTL.

d. Criteria for Evaluating Results of Particulate Analysis

The single property of particulates that gives the most information on the purity of a sodium system and one that is easily measured is the total weight of particulates collected.

Identification of particles can be informative as to the nature of processes occurring in the loop or reactor and is sometimes necessary. However, identification of all particles is expensive because of the time involved in performing the analyses and in the training of personnel, and also because of equipment costs.

Determination of the weight of particulates is a simple procedure which does not interfere with identification, if this is required. Particulates are removed from the filter routinely by ultrasonic cleaning, first in dry xylene, then in water. The cleaning solution is passed through a 25-mm-dia, preweighed membrane filter of 1.2- μm porosity to isolate the particles. The weight of particles is determined from the weight change of the filter after drying. A blank membrane filter is carried through the procedure to correct for the weight change of the membrane filter. The only significant problem with this procedure occurred when atmospheric contamination at an inert-atmosphere box during disassembly of a filter cartridge added some Na_2O to the material collected during xylene treatment.

To establish criteria for evaluating permissible amounts of particulates in a sodium system, the amounts found in each of the ANL systems examined thus far have been correlated with the amount of sodium passed through the filter, or with the amount of sodium in the system when the total volume of sodium was filtered. The information obtained to date is summarized in Table II-2.

TABLE II-2. Summary of Data on Filtration and Identification of Particulates in Sodium Systems

Date	Loop ^a	Amount of Na Filtered	Amount of Particulate Isolated, ^b mg	Identification and Remarks
9-9-70	CORMET (18 gal)	Total	10-20 (0.2-0.5 ppm)	Na ₂ O, probably sodium chromite, SiO ₂ and complex silicates.
1-12-71	SAL (15 gal)	Total	50-100 (1-2 ppm)	Na ₂ O, UO ₂ .
9-21-71	EBR-II (86,000 gal)	1085 gal	~10 (3 x 10 ⁻³ ppm)	Largely reduced metallic particles; SS, Al, Mg, Fe, and Ca identified by electron microprobe and chemical tests; Cs, Mn, Co, Ta, Sn, and Ba, identified by gamma spectrometry.
11-24-71	TEA (5 gal)	Total	10-20 (0.5-1 ppm)	Large amounts of black particles (~14 wt % C) isolated; Na, Ca, Al, Fe, Cr, and Ni identified by X-ray; Mg, Ti, Si, V identified by ion microprobe.
12-27-71	TEA (5 gal)	Total	13 (0.7 ppm)	Same type of particles as in first filtration of TEA sodium; some SS particles and possibly chromite-type particles.

^aNumbers in parentheses are the sodium capacities of the loops.

^bNumbers in parentheses are the estimated concentrations in sodium.

The concentration of particulates in a sodium system would serve primarily as a warning. If the concentration is high--and on the basis of present experience concentrations in excess of one ppm are high--identification of the particulates would aid in finding their source.

2. Analysis for Nonmetallic Impurities in Sodium by the Equilibration Method (D. L. Smith)

The purpose of this work is to develop equilibration methods for accurately measuring the activity of the nonmetallic elements, oxygen, carbon, hydrogen, and nitrogen in liquid sodium at the low concentrations of interest for LMFBR applications.

a. Vanadium-Wire Equilibration Method for Analysis of Oxygen in Sodium

A topical report entitled, "Characterization of the Vanadium-Wire Equilibration Method for Measurement of Oxygen Activity in Liquid Sodium" has been published as ANL-7891.

b. Niobium Equilibration Method for Analysis of Oxygen in Sodium

The base technology required for the application of niobium as a detector for measurement of oxygen activity in sodium by the equilibration method is being developed. The primary advantage of niobium as a detector compared to vanadium is the capability of measuring oxygen concentrations in the range of interest, i.e., ≤ 20 ppm oxygen in sodium, with lower equilibration temperatures. This advantage is achieved at the expense of a decrease in sensitivity of the analysis since the oxygen distribution coefficient in the Nb-O-Na system is considerably lower than that in the V-O-Na system. Internal friction and inert-gas fusion techniques are being used for the determination of oxygen in the niobium. The sodium exposures have been completed and the samples are awaiting analysis.

c. Application of the Equilibration Method to the Measurement of Hydrogen Activity in Liquid Sodium

An investigation is in progress to determine the feasibility of using an equilibration method to measure the hydrogen activity in liquid sodium. The objective of this work is to extend the capability for measurement of hydrogen activities to lower levels than is possible with existing hydrogen-activity meters, and to provide a method for comparing results of the meters at higher levels where both techniques are believed to be reliable.

It has been demonstrated that the hydrogen pickup by niobium exposed to sodium is dependent upon the hydrogen concentration in sodium.^{1,2} Additional measurements have been conducted with niobium and

¹Sodium Technology Quarterly Report, October-December 1971, ANL-7916, pp. 45-47 (1972).

²A. Thorley and C. Tyzak, Proc. Symp. Thermodynamics of Nuclear Materials, pp. 365-397, IAEA, Vienna (1962).

vanadium specimens to investigate effects of quenching rate of the detector after exposure and to obtain additional distribution coefficient data. The use of a semipermeable nickel membrane in the equilibration analysis for hydrogen has been suggested.³ This is accomplished by encapsulating the detector metal in a thin-walled nickel capsule which is then immersed in the sodium. The hydrogen diffuses through the nickel wall until equilibrium with the detector specimen is achieved. This procedure permits a wider selection of detector metals since compatibility with sodium and the other nonmetallic elements in sodium is no longer a requirement for the detector metal. Tests have been conducted with niobium and vanadium in nickel capsules for comparison with results obtained from wires exposed directly to sodium. Possible redistribution of hydrogen between the samples and their environment during quenching will also be examined in these tests. Samples from both types of tests have been prepared for analyses and the results will be reported when the analytical results are available.

³D. R. Vissers, ANL, private communication.

III. FISSION PRODUCT AND COVER GAS TECHNOLOGY (C. C. McPheeters)

A. Development of FEDAL Methods for FFTF

Two types of systems for detection and characterization of fuel-element failure in liquid-metal-cooled fast reactors are under development for FFTF application: a cover-gas analysis system and a sparger and sparge-gas analysis system. These systems will be incorporated in the Reference Fuel Failure Monitoring System for FFTF.

In the cover-gas analysis system, a sample of cover gas is passed through a high-speed chromatographic column. Neon-23 and ^{41}Ar are rapidly eluted while xenon and krypton isotopes are retained and counted with a lithium-drifted germanium $[\text{Ge}(\text{Li})]$ detector and spectrometer. In the sparger and sparge-gas analysis system, the primary coolant sodium is sampled and the soluble gases are stripped from the sample; the gases are separated by gas chromatography and counted by $\text{Ge}(\text{Li})$ spectrometry, as in the cover-gas analysis. Subsequent sparging and analysis for $^{135\text{m}}\text{Xe}$ which grows in from decay of ^{135}I provides a measurement of ^{135}I in the coolant. This combination of systems is expected to provide rapid detection and characterization of fuel-element failures in sodium-cooled fast breeder reactors.

1. Analysis of Cover Gas (C. C. McPheeters, M. S. Foster,¹
R. W. Kessie,¹ R. D. Wolson)

The cover-gas analysis system is designed to sample the reactor cover gas, collect the sample on a chromatographic column, elute the ^{23}Ne and ^{41}Ar , and analyze for the xenon and krypton isotopes of interest. Samples sizes of 1 ml and 100 ml may be taken, and the cycle time, including sampling, elution, and counting, is approximately 4 min.

To aid in the design of the cover-gas analysis system, calculations were made to estimate the fission-product activity levels expected in the cover gas of FFTF. Data from EBR-II on the ratio of cover gas activity to fission-product production rate were extrapolated to the conditions of FFTF. The basis of extrapolation was simply the ratio of sodium turnover time for FFTF to that in EBR-II and the effect of cover-gas recirculation and cleanup in FFTF which will effectively decrease the activity of the longer lived isotopes. In addition, data on the release fraction of the isotopes of interest from the fuel to the fuel-pin plenum² were used to determine the quantities of the respective fission gases expected to be present in the plenum.

Five situations were considered in these calculations to include the range of activity levels that might be expected at FFTF. These situations were (1) the background level due to tramp uranium; (2) a steady leakage of 1% per hour of the gas-plenum inventory of a fuel pin; (3) a

¹Computer Applications Group, Chemical Engineering Division.

²R. Capana, Pressure Equalization System for Gas-Cooled Fast Breeder Reactor Fuel Elements, Nucl. Technol. 12, 185 (October 1971).

steady leakage of 10% per hour of the gas-plenum inventory of a fuel pin; (4) a burst release of 1% of the gas plenum inventory; and (5) a 10% burst release. For these calculations, a burnup of 6000 MWd/metric ton was assumed.

The results of the calculations are presented in Table III-1. The important features of these results are (1) the background activities are not very different from those found in EBR-II; (2) most of the isotopes of interest are detectable even for the 1% per hour leak, except for the short half-life ^{138}Xe and $^{135\text{m}}\text{Xe}$; and (3) for a larger leak or a burst release, all the isotopes considered are detectable.

The conceptual design of the cover-gas analysis system is complete, and detailed design work is in progress. A design description and specification for the hardware portion are being written for the system to be used on FFTF. The specification is based on RDT Standard C 12-1, "Gas Chromatograph for Sodium Cover Gas Service," currently in draft form.

The specification for the spectrometer/computer section of the cover-gas analysis system is being written based on RDT Standard C 14-3, "Gamma-Ray Spectrometer-Computer System," also currently in draft form. This standard was written and distributed to personnel of Oak Ridge National Laboratory, Hanford Engineering Development Laboratory, Liquid Metals Engineering Center, and Argonne National Laboratory for comments and recommendations. These comments and recommendations were incorporated into the standard, and the standard has been submitted to RDT for approval.

2. Analysis of Sodium by Sparging (N. R. Chellew, C. C. Honesty, R. D. Wolson)

A sparger and sparge-gas analysis system is being fabricated for testing with nonradioactive sodium. The piping layout, valving, and component arrangement and the gas-handling system will simulate a system to be installed at EBR-II.

An apparatus that will supply sodium containing dissolved gaseous activity to the prototype sparger system is being fabricated. The apparatus consists of a small (2.5-gal) pumped sodium circuit designed to supply a controlled flow of sodium to the prototype sparger. Construction of the sodium supply system has been completed except for minor modification of an electrical control system and installation of an inert-gas feed system. Installation of a ventilated steel enclosure around the sodium vessels and piping has been completed and final check-out of heaters and thermocouples is under way.

Construction of the prototype sparger has also been started. Heaters, valves, thermocouples, and materials for fabrication are on hand or have been ordered. The conceptual design of the sparge-gas analysis system has been completed and procurement documents for flowmeters and valves are being prepared.

TABLE III-1. Calculated Activities of Isotopes in FFTF Cover Gas

Isotope	λ , hr ⁻¹	r x Yield, dps	Fractional Release (f) From Fuel	Gas Plenum Inventory, atoms	Production Rate (R _p), atoms/sec	Background, dps/cm ³	1%/hr Leak		10%/hr Leak		1% Burst Release		10% Burst Release	
							dps/cm ³	S/B ^a	dps/cm ³	S/B ^a	dps/cm ³	S/B ^a	dps/cm ³	S/B ^a
¹³³ Xe	0.00348	3.7 x 10 ¹³	0.2	4.86 x 10 ¹⁸	4.3 x 10 ⁹	5.2	16,300	3,140	163,000	31,400	4,930	948	49,300	9,480
¹³⁵ Xe	0.0753	4.42 x 10 ¹³	0.012	2.53 x 10 ¹⁶	4.2 x 10 ⁹	28.8	500	17.4	5,000	174	352	12.2	3,520	122
^{85m} Kr	0.158	4.48 x 10 ¹²	0.03	2.96 x 10 ¹⁵	9.7 x 10 ⁸	7.5	65.5	8.7	655	87	86.5	11.5	865	115
⁸⁸ Kr	0.248	9.1 x 10 ¹²	0.007	9.29 x 10 ¹⁴	2.3 x 10 ⁹	15.9	18.2	1.15	182	11.5	42.6	2.68	426	26.8
⁸⁷ Kr	0.545	7.41 x 10 ¹²	0.004	1.98 x 10 ¹⁴	1.7 x 10 ⁹	11.1	3.7	0.333	37	3.33	20	1.8	200	18
¹³⁸ Xe	2.45	3.25 x 10 ¹³	0.0001	4.77 x 10 ¹²	4.3 x 10 ⁹	2.8	0.008 ^b	0.0029	0.08 ^b	0.029	2.17	0.77	21.7	7.7
^{135m} Xe	2.67	1.1 x 10 ¹³	0.0001	1.48 x 10 ¹²	1.3 x 10 ⁹	1.4	0.005 ^b	0.0036	0.05 ^b	0.036	0.7	0.5	7.0	5
²³ Ne	66.6	-	-	-	7 x 10 ¹⁵ ^c	27,900	-	-	-	-	-	-	-	-

^aS/B = signal/background.^bGiven only for reference. These would not be detected.^cAssumed to be 10 times EBR-II rate.

3. Installation of Prototype Detection System on EBR-II
(C. C. McPheeters, N. R. Chellew, R. D. Wolson, C. C. Honesty)

Current plans are to install prototypes of a sparger and sparge-gas analysis system and a cover-gas analysis system on EBR-II for testing. The sparger module will be located in Cell B of the Radioactive Sodium Chemistry Loop (RSCL) and the sparge-gas analysis system will be located outside Cell B. The cover-gas analysis system will be installed in a small building outside the primary containment building.

The design and procurement of materials for the sparger module are continuing. The basic component package of the module, without instrumentation, will include piping, fittings, valves, flow indicators, and a liquid-level sensor. The present approach is to comply with Class II Code (ASME 1971 Boiler and Pressure Vessel Code, Section III) requirements in design and to attempt to procure basic components in accordance with applicable RDT standards.

Specifications have been written and submitted to suppliers for fabrication of valves to RDT Standard E 1-19T, a flow indicator to RDT Standard C 4-5T, an inductive liquid-level sensor to RDT Standard C 5-1T, piping to RDT Standard M 3-3T, and forging to RDT Standard M 2-2T. Quotations have been received on the valves, piping, and forgings and purchase orders have been placed for the piping and forgings. Bids for the valves are still under consideration. However, design work for the module has continued with the following assumptions: (a) valves for the module will not exceed a height of 20 in. and will have a maximum distance between inlet-outlet pipe ends of 8.5 in., and (b) the size requirements for the liquid-level sensor and flowmeters can be met by the suppliers. The present, nearly complete assembly drawing of the module and framework indicate that a rectangular area of Cell B amounting to 41 by 21 in. will be required. The overall height of the module about 74 in., including 10 in. of space under the module. The time schedule for completion of module fabrication depends on the delivery times required for long-lead items. Quotations for the valves have indicated that at least six months will be required for their fabrication. Detailed design work on the sparge-gas analysis system for the reactor installation will be started in May 1972.

B. On-Line Tritium Monitor (P. A. Nelson, M. S. Foster,¹ A. F. Panek)

The objective of this work is the development of on-line tritium monitors for LMFBR sodium and cover gas. These monitors will be proof-tested in the laboratory and at EBR-II for service at FFTF. Such monitoring devices are needed to control tritium levels in the sodium and cover gas and the resulting releases of tritium to the environment. Tritium, which is generated in the fuel by ternary fission and in tetraboron carbide control rods (to be used in FFTF) by the reaction $^{10}\text{B}(n,2\alpha)\text{T}$, diffuses rapidly through most metals and alloys, resulting in transport through the entire reactor system. Tritium along with hydrogen is removed from the sodium by cold trapping.

It has been concluded that the tritium level in sodium can be continuously monitored with a diffusion-type meter. In the operation of the tritium monitor, an iron or nickel membrane would act as a diffusion medium, allowing tritium and hydrogen to diffuse. A carrier gas would sweep the tritium to an ionization-type counter for the measurement of its concentration.

1. Calculational Results

The iron membrane in the standard carbon-meter probe (RDT Standard C 8-7T), which could be used as a tritium diffusion probe, is a tube 3/8-in. OD by 3 1/2 in. long with a 0.018-in.-thick wall. This membrane is supported by a tube having a helical groove machined on the outer surface for gas flow. The tritium concentration in the sweep gas leaving the probe has been calculated by computer. For this calculation, the iron membrane is considered to be a series of 1000 cylindrical sections. In each of these sections, T_2 , H_2 , and HT enter the section in the gas from the preceding section. Tritium diffuses through the wall of the tube section as a result of the difference in concentration of tritium outside the tube (considered to be in equilibrium with the sodium), and that inside the tube (considered to be in equilibrium with the gas entering the tube section). The concentrations of gas leaving a tube section and entering the next section were calculated from the equilibrium constant for the reaction

The volumetric flow rate to each tube section was adjusted to the operating temperature from STP conditions and for gains and losses resulting from diffusion through the probe wall.

The rate of diffusion into each section was calculated for hydrogen and tritium from the following diffusion relationship:

$$\left(\frac{dV}{dt}\right)_n = \frac{KA}{\theta} \left(\pi^{1/2} - P_{n-1}^{1/2} \right) \quad (2)$$

where

$$\left(\frac{dV}{dt}\right)_n = \text{volume of } T_2 \text{ or } H_2 \text{ transferred per unit time into section } n, \text{ cm}^3/\text{sec},$$

$$K = \text{permeation coefficient, cm}^3/(\text{cm})(\text{sec})(\text{atm})^{1/2},$$

$$A = \text{permeation area per section, cm}^2,$$

$$\theta = \text{thickness of membrane, cm},$$

$$\pi = T_2 \text{ or } H_2 \text{ partial pressure in equilibrium with sodium, atm},$$

$$P_{n-1} = \text{partial pressure of } H_2 \text{ or } T_2 \text{ in gas entering from section } n-1.$$

The above calculations were carried out for all combinations of the following set of parameters:

Tritium (T_2) pressure in equilibrium with sodium, 10^{-15} atm
 Hydrogen pressure in equilibrium with sodium, 10^{-4} , 10^{-7} , 10^{-10} atm
 Gas flow rate, 0.01, 0.1, 1.0, 10.0 cm^3/sec
 Hydrogen concentration in sweep gas (balance argon), 0, 0.001, 0.01, 0.1, 1.0, 10.0, 100%
 Temperature, 500, 600, 700, 750°C

In all cases, the T_2 concentration leaving the probe was negligible compared with the H_2 and HT concentrations. Therefore, the results could be applied to any tritium concentration in the sodium for high hydrogen-to-tritium ratios by use of the ratio:

$$R' = \frac{HT}{T_{Na}} \quad (3)$$

where

HT = the HT concentration in atm in the gas leaving the probe

T_{Na} = the tritium concentration in ppm in the sodium.

The Sieverts' law constant for hydrogen in equilibrium with sodium at 450°C has been determined³ to be 5.73 $\text{ppm/Torr}^{1/2}$. The value is almost unaffected by temperature. If the solubilities of hydrogen and tritium, expressed in moles, are assumed to be the same in sodium, the Sieverts' law constant for T_2 in equilibrium with sodium is 17.2 $\text{ppm/Torr}^{1/2}$. For this value, a partial pressure of T_2 in equilibrium with the sodium of 10^{-15} atm, which was assumed in the computer calculations, would correspond to a tritium concentration in the sodium of 1.5×10^{-5} ppm. This concentration, T_{Na} , was used to calculate values of R' from the calculated HT concentrations.

Typical results obtained in this study are shown in Fig. III-1. At 700°C, a flow rate of 1.0 cm^3/sec (STP), and low hydrogen concentrations (<0.01%) in the gas to the diffusion probe, equilibrium is reached for both hydrogen and tritium. In this mode of operation, the tritium content of the gas counted by the tritium monitor would be the same as that in the cover gas contacting the sodium. This tritium concentration is a function of the hydrogen content of the sodium. At high hydrogen concentrations (>1%) in the sweep gas and flow rates greater than about 0.1 cm^3/sec to the diffusion probe, the tritium content of the gas side of the iron membrane, T_{Fe} , is maintained near zero by the reaction

For this condition, the rate of tritium transferred to the sweep gas is near the maximum. It is unaffected by small changes in the hydrogen concentration in the sodium or the sweep gas. Therefore, this operating mode appears to be the most useful for determining the tritium content of the sodium.

³D. R. Vissers, J. T. Holmes, and P. A. Nelson, A Hydrogen Activity Meter for LMFBRs, Trans. Amer. Nucl. Soc. 14(2), 610 (1971).

Fig. III-1. Effect of H_2 Concentration in Sweep Gas to Monitor on HT Concentration in Gas Leaving Monitor [temperature, 700°C ; flowrate, $1.0 \text{ cm}^3/\text{sec}$ (STP)]

A summary of the calculations showing the regions of parameter values that result in equilibrium-mode operation of the monitor are shown in Fig. III-2. In Table III-2, data are summarized for operation with hydrogen-containing sweep gas at 500 and 700°C . To minimize the rate of hydrogen addition to the sodium, the probe should be operated at low temperatures and moderate hydrogen concentrations of about 1%.

The rate of disintegration of tritium in the gas from the probe is adequate for counting purposes. Typical tritium concentrations at EBR-II are about 5×10^{-6} ppm (1×10^{15} atoms/kg) in the primary sodium and 1×10^{-6} ppm (2×10^{14} atoms/kg) in the secondary sodium. From the values of R' in Table III-2 at $0.1 \text{ cm}^3/\text{sec}$ flow rate and 500°C , the activity of the gas from the monitor would be about $70 \text{ d}/(\text{sec})(\text{cm}^3)$ for primary sodium and $14 \text{ d}/(\text{sec})(\text{cm}^3)$ for secondary sodium. For ionization counting tubes of 10 to 100 ml volume, this count rate will be sufficient for precise analysis.

2. Laboratory Testing of Monitor

The initial tritium-meter proof-testing will be done on the Apparatus for Monitoring and Purifying Sodium, AMPS (see Section I.F). The standard carbon-meter probe will be used in the testing.

TABLE III-2. Calculated Tritium Concentration in Hydrogen-containing Sweep Gas from a Diffusion Probe
(probe membrane: iron tube, 3/8-in. OD by 3.5 in. long with 0.018-in.-thick wall)

Temp., °C	Flow Rate, cm ³ /sec (STP)	H ₂ Conc. to Monitor, %	H ₂ Conc. from Monitor, %	Tritium Ratio, HT from Monitor/T _{Na}	
				R', atm/ppm	R, d/(sec)(cm ³ gas)(ppm)
500	0.1	10	8.04	2.70×10^{-4}	1.31×10^7
		100	100.0	3.11×10^{-4}	1.50×10^7
	1.0	0.1	0.079	2.65×10^{-5}	1.28×10^6
		1.0	0.931	2.89×10^{-5}	1.40×10^6
		5.0	4.85	2.96×10^{-5}	1.43×10^6
		10.0	9.80	2.97×10^{-5}	1.44×10^6
		100.0	100.0	2.99×10^{-5}	1.46×10^6
700	1.0	1.0	0.795	8.22×10^{-5}	3.97×10^6
		5.0	4.54	8.82×10^{-5}	4.27×10^6
		10.0	9.38	8.97×10^{-5}	4.33×10^6
		100.0	100.0	9.34×10^{-5}	4.50×10^6

Fig. III-2. Operating Modes of Tritium Monitor

Prior to the installation on AMPS, however, several aspects of the counting scheme must be investigated. The first is the selection of an appropriate size of counting tube. As noted above, the tritium concentration in the gas to be counted is expected to be high, and, therefore, a small counting-tube volume should be sufficient. Also, a small tube volume will reduce the background level. The characteristics of the available counting tubes, which range in size from 10 to 100 ml, will be determined in laboratory tests with hydrogen-tritium mixtures and one of suitable volume will be selected. Following this, the major factors that affect the accuracy, reproducibility, and efficiency of the counting system will be examined. These include possible coincidence losses, the effect of changes in gas composition and flow rate through the counter, the quenching effect of carrier-gas impurities (such as moisture), and the shielding required.

Figure III-3 illustrates the laboratory apparatus for testing the tritium monitor. The electronics package has been built to our specifications and is now under test. The gas handling system has been designed not only to perform the tests outlined above but to evaluate the various components likely to be used on AMPS.

Fig. III-3. Laboratory Apparatus for Testing Tritium Monitor

IV. SODIUM CHEMISTRY (F. A. Cafasso)

A. Studies of Oxygen-Hydrogen Interactions in Sodium

1. Isotope-Exchange Studies (A. K. Fischer)

This program addresses the questions of (1) whether or not hydroxide can form in liquid sodium under conditions (temperature and concentrations of oxygen and hydrogen) of interest in reactor technology and (2) how rapidly and under what circumstances hydroxide will decompose in reactor sodium.

An isotope-exchange method, in which sodium deuterioxide (NaOD) is used as a stand-in for NaOH, is being employed in these studies. Details of the isotope-exchange procedure were described in a preceding quarterly report (ANL-7868, pp. 46-48). Briefly, the method involves (1) preparing a solution of NaOD in liquid sodium, which is sealed in a decarburized nickel tube; (2) heating the tube at 500°C in a Knudsen chamber attached to a mass spectrometer; (3) monitoring with a mass spectrometer the hydrogen species that diffuse through the nickel tube as a function of time; (4) quenching the sample to room temperature at some desired time; and (5) performing an alcoholysis exchange reaction on the quenched sample. The isotope-exchange process that occurs during the alcoholysis makes it possible to measure the amount of unreacted OD⁻ remaining in solution in the sodium.

Previous work (ANL-7868, pp. 46-49; ANL-7916, pp. 55-56) was directed to establishing the experimental details and conditions under which the monitoring of deuterium diffusion through the nickel capsule was an effective means for determining the kinetics of decomposition of NaOD. Recent work, which emphasized the application of the devised experimental procedures and the collection of kinetic and exchange data, is described below.

The reactants (2.34 g sodium and 0.0051 g NaOD) were heated at 500°C under vacuum for about 4 hr and the heights of the mass peaks for H, H₂, HD, and D₂ were monitored as a function of time. The source of the H₂ and HD is believed to be moisture from the air, absorbed on the outside of the nickel tube and the inside of the Knudsen chamber during connection of the apparatus to the mass spectrometer. During the experiment, this moisture desorbs and undergoes exchange reactions in the gas phase of the Knudsen chamber with the D₂ that has diffused through the nickel tube. These reactions are

With these processes occurring, the sum of the H_2 , HD, and D_2 peaks is a measure of the rate of liberation of D_2 by the reaction between Na and NaOD inside the nickel tube. This follows because each molecule of HD and H_2 has a molecule of D_2 as a precursor. (The mass peak for H, which was negligible, probably resulted from fragmentation of H_2O desorbed from the wall.) Analysis of the various instrumental factors affecting the sensitivity for determining H_2 , HD, and D_2 revealed that the peak heights were an accurate measure of the relative amounts of each species.

After the Na-NaOD system had been monitored mass spectrometrically for about 4 hr at $500^\circ C$, the system was cooled and an alcoholysis was performed on the contents of the nickel tube to measure residual NaOD. The alcoholysis exchange measurement showed that 27% of the original NaOD remained in the sodium. It follows that 73% of the original amount of NaOD in sodium (0.0051 g NaOD in 2.34 g Na) had decomposed (i.e., reacted with sodium). The integrated area under a plotted curve of summed, instantaneous peak heights vs. time reflects the course of this reaction. Graphical integration was used to determine, for various periods, the amount of NaOD that had reacted since the start of the experiment. This information then yielded values for the amount of NaOD remaining at any time, as shown in Fig. IV-1.

An analysis to determine the kinetics order of the reaction was undertaken, using the data from Fig. IV-1. It was assumed that the rate of transit of deuterium through the nickel tube and the rate of effusion through the Knudsen orifice were high compared with the rate of liberation of deuterium. In other words, the rate-determining step was taken to be the Na-NaOD reaction. Data for the analysis were taken with time zero at 45 min (the time at which the reaction system reached temperature). The general rate expression for a first order reaction is $kt = \ln a_0 / (a_0 - x)$ where a_0 is the amount of the species of interest at time zero, $a_0 - x$ is the amount of the species remaining at a given time, k is the rate constant, and t is time. A plot of $\lg a_0 / (a_0 - x)$ against time is given in Fig. IV-2. There appear to be two fairly linear portions of the data. A possible explanation is that the short, early portion, which lasted about 30 min after the system reached temperature, represents the time during which the NaOD was going into the solution. The long, second portion, then, represents the reaction in solution. The data from this portion of the curve indicate that the observed reaction between NaOD and Na is a first-order process. This is reasonable because the large excess of one reactant (sodium, in this case) would cause even a bimolecular reaction to follow a first-order rate equation. From the slope of the second linear portion of Fig. IV-2, a rate constant of $k = 4.5 \times 10^{-3} \text{ min}^{-1}$ was obtained. In turn, the half-time ($t_{1/2} = \ln 2/k$) for the reaction under the described conditions was calculated to be 150 min.

The initial reaction mixture of sodium and NaOD corresponds to 2200 ppm NaOD in Na. This quantity of NaOD, if totally decomposed, would yield 860 ppm O and 107 ppm D in Na. (This deuterium can be regarded as equivalent to 54 ppm H.) At the end of the reaction, with 27% of the NaOD remaining, the system contained 595 ppm NaOD. Since the oxide that formed as a reaction product could not escape, the system contained 630 ppm O as oxide, and 230 ppm O still combined in NaOD. The remaining

Fig. IV-1

NaOD Remaining in Sodium
vs Time

Fig. IV-2
Test for First Order
Kinetics

28 ppm D (14 ppm H) would have been present as unreacted NaOD plus whatever deuterium had not yet diffused out through the tube. Thus, the reaction proceeded in the presence of accumulating oxide reaction product. The first order behavior in deuterioxide then implies that the oxide has no significant effect on the Na-NaOD reaction, at least in the specified concentration range. This concentration range may be expected to have relevance to a reactor situation in which a water leak into a secondary sodium loop results in a local, high concentration of hydroxide. The information being developed here will enable judgments to be made, if a leak occurs, on how long hydroxide, as such, must be contended with, and how soon the decomposition products become possible factors in reactor operation.

2. Effects of Oxygen-Hydrogen Interactions on Meter Readings (K. M. Myles)

This program seeks to determine and evaluate the influence of oxygen-hydrogen interactions in sodium, at low impurity concentrations, on oxygen- and hydrogen-meter readings. The approach that will be used involves the simultaneous measurement of hydrogen and oxygen activities (by means of hydrogen and oxygen meters immersed in a sodium bath) as functions of oxygen and hydrogen content of the sodium. The apparatus that has been assembled and tested for this purpose is shown schematically in Fig. IV-3.

The sodium container consists of a 2-liter nickel crucible that has a stainless steel secondary. The secondary is fastened to the underside of a helium-atmosphere drybox and surrounded by a wire-wound furnace. The crucible opens into the drybox, but is sealed from the box atmosphere by a stainless steel flange. A 1-in.-dia sample access port cuts through

Fig. IV-3

Schematic Diagram of Apparatus
for Studying Oxygen-Hydrogen
Interactions in Sodium

the flange. Beneath the flange and extending into the crucible is a series of nickel radiation shields; the shields are welded to the sample-port projection. Also extending from the flange are a nickel stirrer and a nickel thermocouple well. Two Conoseal fittings are welded into the flange to accommodate a hydrogen meter and an oxygen meter. All of the welds and seals have been helium leak-tested and the system is regarded as being leak tight to a pressure of about 10^{-6} Torr. The nickel parts were decarburized with flowing moist hydrogen gas at 650°C for 7 days. The temperature of the sodium is maintained to about $\pm 0.25^{\circ}\text{C}$ and the system is essentially isothermal.

The hydrogen meter is of the ANL design and is being operated in the equilibrium mode. The permeation membrane is a 0.270-in.-OD by 0.008-in.-wall nickel tube that extends into the sodium. The equilibrium hydrogen pressure is determined by a C.G.S. Datametrics Barocel pressure-transducer system that has a sensitivity of about 10^{-5} Torr. Preliminary tests have indicated that the meter is quite stable down to at least 0.1 ppm hydrogen in sodium.

A Westinghouse oxygen meter was tested initially in this apparatus. However, excessive noise and the inability to calibrate this type of meter accurately in pot-type experiments prompted a conversion to an oxygen meter with a Sn-SnO_2 reference electrode, which was developed at Argonne. The electrolyte tube that is being used is from the current batch of tubes procured by Zircoa for the Westinghouse meters. A Hewlett-Packard differential voltmeter is used to measure the cell emf. Work is now in progress to determine the temperature coefficient of the cell. As soon as this is done, experimentation to determine the extent of oxygen and hydrogen interactions and their influence on meters will begin.

V. MATERIALS-COOLANT INTERACTIONS AND MECHANICAL-PROPERTY EVALUATIONS (T. F. Kassner, R. W. Weeks)

The objective of this program is to provide a sound technical basis for determining the effect of the LMFBR sodium environment on the performance of fuel cladding, core structure, and out-of-core components. The required technology will be established according to the following plan: (1) determine the integrated effects of fast-neutron and sodium environments on the properties of stainless steel, (2) correlate mechanical-property and corrosion data obtained in reactor (EBR-II) and experimental sodium systems, (3) establish specifications for test specimens for sodium environmental tests, (4) develop postexposure testing methods and demonstrate their validity by correlation with in-sodium test data, and (5) develop a sufficient understanding of nonmetallic element transfer to predict compositional changes of materials in reactor sodium systems and ultimately relate these changes to the mechanical properties.

A. Development of Test-Specimen Characterization Methods and Procedures (J. Y. N. Wang)

Methods are under development for the characterization of mechanical property and corrosion specimens prior to and after exposure to high-temperature sodium in loop systems and in EBR-II for both in-core and out-of-core conditions. Information on the chemical composition and composition gradients in materials exposed to high-temperature sodium for long periods of time, as well as the amount, distribution, morphology and composition of the various phases that form as a result of thermal aging in a reactor environment, is required for interpretation and correlation of the mechanical property data. Techniques that have been found to be useful in this work are transmission and scanning electron microscopy, optical metallographic methods, and chemical and X-ray diffraction analyses of phases extracted from the specimens by anodic dissolution of the materials. In situ analyses of the phases by electron microprobe and mass analyses by ion microprobe coupled with quantitative metallography techniques are also being evaluated for use in this program. An early objective of this work is to define the extent to which these various specimen characterization methods must be employed and the usefulness of the information in establishing quantitative relationships between microstructural results and mechanical property data.

Phase instabilities in Types 316 and 304 stainless steels as a function of time, temperature, degree of cold work, and carbon and nitrogen content of the materials are being investigated to obtain a direct knowledge of the capabilities of the various specimen characterization methods and to provide base line microstructural information on thermal aging effects in the materials to be used in this program. Sheet specimens of Type 316 stainless steel (heat No. V-87210) were solution annealed for 0.5 hr at 1050°C and water quenched. Some of the specimens were subjected to a 20% cold-work reduction prior to thermal aging at 550, 650, and 750°C for times of 30, 300, 1000 hr and beyond.

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A scanning electron microscope (MAC-700) equipped with accessories for energy dispersive X-ray spectrometry is being used to determine the phases present in the thermally aged specimens. Typical scanning-electron micrographs of selectively etched specimens, shown in Fig. V-1, reveal carbide and sigma phase protruding from the specimen surface. The X-ray intensity spectra for Fe, Cr, and Mo were determined at grain boundaries, in precipitated particles, and in the surrounding matrix. The Cr/Fe and Cr/Mo intensity ratios, corrected for background, were used to identify the presence of the $M_{23}C_6$ carbide and sigma phase which were located primarily in the grain boundary regions. To quantitatively determine the amount of these phases present after thermal aging, the materials are being dissolved electrolytically in a HCl-methanol solution at low current densities and the residues are being recovered, weighed, and then analyzed by standard X-ray techniques.

To obtain additional information on the microstructural and compositional changes that occur during long exposure of austenitic stainless steel to flowing sodium at high temperatures, a small heat exchanger constructed from Type 304 stainless steel was removed from a low-velocity sodium loop after ~8 yr of operation.

Fig. V-1. Scanning Electron Micrographs (original magnification 1000X) and Characteristic X-ray Spectra of Sigma Phase, $M_{23}C_6$ Carbide, and Austenite Matrix of Type 316 Stainless Steel after Thermal Aging at 650°C for 1000 hr. Neg. No. MSD-57134

A schematic drawing of the heat exchanger and representative microstructures of the material in contact with the sodium at temperatures between 750 and 400°C are shown in Fig. V-2. The sodium was pumped upward through the 1.75-in.-OD outer pipe, around the baffle, and through a high-temperature test section before returning to the lower temperature part of the system through the 0.5-in.-OD inner tube. The test section and outer portion of the heat exchanger were in operation for ~8 yr, whereas the baffle and inner pipe were in contact with the sodium for ~5 yr. During most of the operational history, the temperature along the heat exchanger ranged from ~400°C at the bottom to ~700 to 750°C at the top. The oxygen concentration in the sodium was maintained at levels between 0.3 and 10 ppm during most of the operating history; however, occasionally the oxygen level was increased to the 30 to 100 ppm range for short periods (i.e., a few days) to calibrate oxygen meters present on the system.

Fig. V-2. Microstructures of Type 304 Stainless Steel Heat-Exchanger Material after 8 yr of Exposure to Low-Velocity Sodium at Temperatures between 400 and 750°C ("a" Murakami etched, all others electroetched in 10% oxalic acid. Original Magnification 350X). Neg No. MSD-57133

The microstructures shown in Fig. V-2 are consistent with expectations for the above operating conditions. A small chromium-depleted zone, resulting in a discontinuous ferrite surface layer ~1.6 mils in thickness, was observed at the highest temperatures (Fig. V-2a to 2d). In the 650 to 500°C intermediate temperature region (Fig. V-2e to 2h), no metallic element mass-transfer effects were observed as a result of the low-velocity sodium; however, grain boundary carbides are present. The material is being sectioned for carbon analyses and specimens for determining the amount of carbide and intermetallic phases are being obtained by electrolytic dissolution in HCl-methanol solution and analyses of the residues.

No unusual surface effects were observed following sodium exposure for long times at high temperatures that would suggest that serious problems may be encountered in postexposure mechanical testing of materials from a similar sodium system.

B. Development of Specimen-Exposure Facilities and Postexposure Mechanical-Property Testing Capability (J. J. Weins, R. W. Weeks, R. R. Schlueter, W. E. Ruther, and T. F. Kassner)

The objective of this work is to develop the capability for (1) exposing standard uniaxial and biaxial test specimens to sodium of controlled nonmetallic element concentrations and (2) performing the postexposure property measurements in accordance with test conditions that provide design verification and operational support data to the FFTF. The information will also be compared with property data obtained in flowing sodium to establish the equivalence of in-sodium versus post-exposure test results for alloys of the same composition and thermal history.

The relocation and modification of nine uniaxial creep-rupture machines for use in this program has been completed. The heaters on the three zone furnaces are being balanced, and temperature calibrations for the furnaces are being obtained. All of the furnaces and instrumentation have been operated for a short check-out period and minor problems are being corrected.

Type 316 stainless steel from heat V-87210 is being rolled into sheet stock of 15-, 50-, and 120-mil thickness for the fabrication of uniaxial test specimens. Some of the material has been supplied to a vendor for fabrication of test specimens.

A special heat of Type 316 stainless steel with low nonmetallic element concentrations has been successfully cast and both tube blanks and rectangular bars have been extruded from the material. Mechanical property data on test specimens from this heat, whose composition is given in Table V-1, will be compared with results from Type 316 stainless steel that has lost carbon and nitrogen to similar levels upon exposure to flowing sodium at high temperature. Some difficulty has been experienced in producing a high-carbon heat of Type 316 stainless steel for property comparisons with material that has undergone carburization in flowing sodium. Further attempts to obtain a homogeneous material will be made.

TABLE V-1. Composition of Modified Type 316 Stainless Steel with Low Carbon and Nitrogen Contents

Element	wt %	Element	wt %
C	0.0107	Ni	13.8
N	0.0030	Cr	17.0
Mn	1.5	Fe	Balance ^a
Mo	2.0		

^aTrace element concentrations are being determined.

A small sodium loop, described in the preceding quarterly report (ANL-7916, pp. 59-60), is under construction. The loop will be used for the exposure of standard mechanical-property test specimens to low-velocity sodium in order to produce a range of carbon and nitrogen concentrations in the alloys prior to testing in inert gas. An existing loop is also being modified to include a high-velocity test section for exposing FTR fuel cladding to sodium at a temperature above 700°C and a sodium velocity greater than 20 ft/sec. The test section has been designed and is also being fabricated.

C. Studies of Carbon Transfer in Sodium-Steel Systems
(K. Natesan, R. B. Snyder, T. F. Kassner, C. A. Youngdahl)

Information on the thermodynamics and kinetics of carbon transfer in sodium-steel systems, under conditions where temperature gradients and materials of different composition are present in the system, is required for predicting the magnitude and rate of carbon migration in FFTF and LMFBR systems and for relating these effects to mechanical property changes in the materials.

1. Activity of Carbon in Fe-Ni and Fe-Ni-Cr Alloys

Information on the distribution of carbon between sodium and various iron-base alloys at temperatures between 500 and 800°C has been reported;^{1,2} this information was based, in part, upon the extrapolation of high-temperature data for the activity and solubility of carbon in these materials. Since carbon activities in these alloys do not conform to ideal behavior, simple thermodynamic concepts of solid solutions are not sufficiently accurate to extrapolate the results with the degree of

¹K. Natesan and T. F. Kassner, J. Nucl. Mater. 37, 223 (1970).

²Sodium Technology Quarterly Report, July-September 1971, ANL-7868, pp. 53-68 (1972).

confidence required for predicting surface and equilibrium carbon concentrations in sodium loop materials. Measurements of carbon activities in Fe-Ni and Fe-Cr-Ni alloys at temperatures of interest in LMFBR systems have been made to decrease the uncertainty in the calculated carbon distribution results.

Foil specimens of Fe-8 wt % Ni and Fe-16 wt % Ni alloys were equilibrated in $\text{CH}_4\text{-H}_2$ gas mixtures of fixed compositions at temperatures of 700, 800, and 900°C. Since moisture contamination of the $\text{CH}_4\text{-H}_2$ gas mixtures can lead to errors in directly determining the carbon activities from the gas composition, the carbon activity was determined from the carbon content of nickel foils included in the experiments and from application of Henry's law to the carbon solubility at the various temperatures.

The solubility of carbon in nickel was also redetermined by equilibrating pure nickel with $\text{CH}_4\text{-H}_2$ gas mixtures in the presence of graphite at temperatures between 500² and 1000°C. The carbon concentrations in the foil specimens were determined by the combustion method using a Leco Low-carbon Analyzer and a range of standards. The average values of duplicate analyses are plotted in Fig. V-3 along with the results of other investigators.³⁻⁹

The present data are in good agreement with the results of Wada *et al.*⁶ and Smith⁷ and the combined data are represented by the relation:

$$C_{\text{Ni}} (\text{wt } \%) = 12.4 \exp \{-5160/T\}$$

The relation between carbon activity and carbon concentration in the Fe-8 wt % Ni alloy at temperatures of 700, 800, and 900°C is shown in Figs. V-4 and -5. The information in Fig. V-5 encompasses a wider range of carbon activities than is required for use in typical sodium-steel systems. The carbon activity-concentration relationship for the Fe-16 wt % Ni alloy at 700, 800, and 900°C is shown in Fig. V-6. These results are particularly useful for determining the activity of carbon in sodium by equilibration methods at temperatures below 800°C, because in contrast to the

³W. W. Dunn, R. B. McLellan and W. A. Oates, Trans. AIME 242, 2129 (1968).

⁴H. Schenck, M. G. Froberg and E. Jaspert, Arch. Eisenhüttenw. 36, 683 (1965).

⁵J. J. Lander, H. E. Kern and A. L. Beach, J. Appl. Phys. 23, 1305 (1952).

⁶T. Wada, H. Wada, J. F. Elliott and J. Chipman, Met. Trans. 2, 2199 (1971).

⁷R. P. Smith, Trans. AIME 218, 62 (1960).

⁸K. K. Rao and M. E. Nicholson, Trans. AIME 227, 1029 (1963).

⁹C. B. Alcock and G. P. Stavropoulos, Trans. Inst. Mining Met., Section C, 77, 232 (1968).

Fig. V-3. Temperature Dependence of the Solubility of Carbon in Nickel.
Neg. No. MSD-57127

Fig. V-4. Carbon Activity-Concentration Relationship for Fe-8 wt % Ni Alloy at 700, 800, and 900°C at Low Carbon Concentrations.
Neg. No. MSD-57122

Fig. V-5. Carbon Activity-Concentration Relationship for Fe-8 wt % Ni Alloy at 700, 800, and 900°C up to the Solubility Limit.
Neg. No. MSD-57124

Fig. V-6. Carbon Activity-Concentration Relationship for Fe-16 wt % Ni Alloy at 700, 800, and 900°C at Low Carbon Concentrations.
Neg. No. MSD-57123

Fe-8 wt % Ni alloy, the higher nickel content insures that the alloy is fully austenitic at lower temperatures. Figures V-7 and -8 indicate that the present results for the Fe-8 wt % Ni alloy, obtained over a wide range of carbon activities, are in good agreement with the available data¹⁰⁻¹³ at temperatures between 800 and 925°C. The effect of nickel on the activity of carbon in Fe-Ni-C alloys was determined from the data using first order free-energy interaction parameters. The carbon activity in the ternary alloys, as a function of temperature (°K) and composition (i.e., mole fraction of carbon, N_C , and nickel, N_{Ni}), can be determined from the relation:

$$\ln a_C^{\text{Fe-Ni-C}} = \ln \left\{ \frac{N_C}{1 - N_C} \right\} + \left(11.92 - \frac{6330}{T} \right) \frac{N_C}{1 - N_C} - 1.845 + \frac{5100}{T} - \left(2.2 - \frac{7600}{T} \right) N_{Ni}$$

The dashed lines in Figs. V-7 and -8 were computed using the above relation.

The carbon activity-concentration relationships for the Fe-8 wt % Ni and Fe-16 wt % Ni alloys were used to establish carbon activities in Fe-Cr-8 wt % Ni alloys whose chromium content ranged between 2 and 22 wt %. In these experiments, the iron-nickel alloys were equilibrated with a series of the Fe-Cr-8 wt % Ni alloys in Vycor and quartz capsules under partial vacuum. The relation between the carbon and chromium concentration in these alloys for a range of carbon activities is given by the isoactivity lines in Figs. V-9 to V-13 for temperatures of 600, 660, 725, 800, and 900°C.

The experimental data on carbon activities in Fe-Ni and Fe-Cr-Ni alloys are being used with similar data for the Fe-C system to obtain a generalized, mathematical interaction-parameter relationship for carbon activity as a function of composition for the Fe-Cr-Ni-C austenitic steels at temperatures between 600 and 900°C. This relationship will be used in the selection of a material for monitoring the carbon activity in sodium by foil equilibration methods and will also establish surface and equilibrium carbon levels in sodium loop materials when the carbon concentration of the sodium and temperatures are specified.

A number of the Fe-Cr-8 wt % Ni alloy specimens from the carbon activity studies are being used to obtain information on austenite-carbide phase equilibria that is required for the analysis of carburization-decarburization phenomena described in a preceding quarterly report (ANL-7868, pp. 53-68). The composition of the austenite matrix and the $M_{23}C_6$ carbide (i.e., Cr/Fe ratios) are being determined from X-ray intensity data generated by scanning electron microscopy.

¹⁰C. Bodsworth, I. M. Davidson and D. Atkinson, Trans. AIME 242, 1135 (1968).

¹¹J. C. Greenbank, J. Iron Steel Inst. 209, 819 (1971).

¹²A. J. Heckler and P. G. Winchell, Trans. AIME 227, 732 (1963).

¹³S. Ban-ya, J. F. Elliott, and J. Chipman, Met. Trans. 1, 1313 (1970).

Fig. V-7. Comparison of Carbon-Activity Data for Fe-8 wt % Ni Alloy at 800°C with Literature Data. Neg. No. MSD-57119

Fig. V-8. Comparison of Carbon-Activity Data for Fe-8 wt % Ni Alloy at 900°C with Literature Data. Neg. No. MSD-57117

Fig. V-9. Isoactivity Lines for Carbon in Fe-Cr-8 wt % Ni Alloys at 600°C from Equilibrations in Vycor Capsules under Partial Vacuum.
Neg. No. MSD-57126

Fig. V-10. Isoactivity Lines for Carbon in Fe-Cr-8 wt % Ni Alloys at 660°C from Equilibrations in Vycor Capsules under Partial Vacuum.
Neg. No. MSD-57131

Fig. V-11. Isoactivity Lines for Carbon in Fe-Cr-8 wt % Ni Alloys at 725°C from Equilibrations in Vycor Capsules under Partial Vacuum. Neg. No. MSD-57130

Fig. V-12. Isoactivity Lines for Carbon in Fe-Cr-8 wt % Ni Alloys at 800°C from Equilibrations in Quartz Capsules under Partial Vacuum. Neg. No. MSD-57128

Fig. V-13. Isoactivity Lines for Carbon in Fe-Cr-8 wt % Ni Alloys at 900°C from Equilibrations in Quartz Capsules under Partial Vacuum. Neg. No. MSD-57132

Carbon-activity and phase-equilibria data are also being obtained for commercial grades of austenitic stainless steels (e.g., Types 304, 316, 321, and 347) and will be used with the present information to take into consideration the effect of minor alloying constituents and carbide stabilizing elements.

2. Development of a Mathematical Model for the Carburization and Decarburization Kinetics of Austenitic Stainless Steels in Sodium

The phenomenological aspects of carburization of austenitic stainless steels in flowing sodium have been established from numerous experimental observations. When a stainless steel is exposed to liquid sodium having a carbon activity greater than that in the alloy, carbon from the sodium diffuses into the material and precipitates some fraction of the chromium, molybdenum, niobium or titanium present in the alloy as a finely dispersed carbide. In the initial stages of the process, carbides with high Cr/Fe ratios are precipitated and as the process continues, the carbides become richer in iron and the austenite becomes leaner in chromium and richer in carbon as the amount of carbide increases. This process continues until an equilibrium between the austenite and carbide is established, in which the total carbon concentration in the alloy is dependent upon the carbon concentration in sodium. A thermodynamic analysis of the carburization-decarburization process involving austenitic stainless steels, described in a preceding report (ANL-7868, pp. 53-58), showed that, in the presence of sodium with carbon contents in the range of interest for LMFBR and experimental loop systems, a significant amount of carbon transfer can occur at very low carbon activities and small activity gradients.

A mathematical model that will yield surface or equilibrium carbon concentrations and concentration-penetration profiles in austenitic stainless steels as a function of time, temperature, and sodium purity (i.e., carbon concentration in sodium) is being developed. The input information for the model consists of system-independent materials data and system-dependent operating parameters. The materials data consist of analytical equations for the solubility and activity of carbon in Fe-Cr-Ni alloys and in sodium, austenite-carbide phase equilibria relations, and the diffusion coefficient of carbon in austenite as a function of temperature. Mathematical relations for use in the model were obtained for these parameters from the graphical data given in ANL-7868. This information is being modified to include the results from our carbon solubility and activity measurements for the austenitic alloys.

The system input parameters include the material composition, time, temperature, carbon concentration in the sodium, and thickness of the material. In the present computer program, the sodium loop is considered to be an "open system" with regard to carbon, i.e., the carbon levels can be specified and are considered to be independent of time. A program will also be written for a "closed system" in which the total amount of carbon in the sodium and loop materials are specified, along with the temperature gradients and relative surface areas of materials at various temperatures, so that a carbon mass balance and time-dependent carbon levels in the sodium can be factored into the carbon-transfer model. Depending upon the size of the sodium system and the operating conditions, both types of systems must be considered.

Carbon concentration profiles in austenitic stainless steels generated by numerical solutions to the diffusion equation, in which the carbide-sink term is properly taken into account, are being compared with available experimental data.