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SODIUM TECHNOLOGY QUARTERLY REPORT

October—December 1970

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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 activities 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.

Starting with the next quarterly report, Sodium Technology Quarterly Report for January, February, March 1971, the reports in this series will be issued as regular ANL reports and will not carry the special designation of the previous reports.

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SODIUM TECHNOLOGY QUARTERLY REPORT

OCTOBER, NOVEMBER, DECEMBER 1970

ABSTRACT

The research, development, and management efforts of Argonne National Laboratory's Sodium Technology Program for the period October, November, December 1970 comprised activities in the following areas: (1) Work in the national meter program was continued to characterize instrumentation for on-line monitoring of oxygen, carbon, and hydrogen impurities in sodium and for detecting leaks in steam generators, and to establish commercial availability of the on-line meters, which will be built to RDT standards. (2) In the analytical standards program, the management effort involved formulation of interim standard analytical and sampling methods and the establishment of sample interchange programs to test these methods. (3) Work continued on the development of a method for detecting fuel-cladding failures by monitoring the $^{135\text{m}}\text{Xe}$ daughter of ^{135}I . (4) Studies of the chemistry of sodium included investigation of the nature of nitrogen-bearing species and elucidation of phase relations in the sodium-rich corner of the Na-O-H ternary system. (5) Work on the purification of sodium continued with construction of an apparatus for characterizing the impurity content of cold-trapped sodium. (6) Studies of materials-coolant compatibility included investigation of the transport of carbon in sodium-steel systems and development of methods for determining activities of nonmetallic impurities in sodium by equilibration of metal specimens.

SUMMARY

ON-LINE IMPURITY MONITORS

Oxygen Meter Development. A program has been established that is expected to result in the commercial availability of improved electrochemical oxygen meters by July 1971. ANL is coordinating efforts at WADCO and Zircoa to produce improved solid electrolyte tubes (isostatically pressed thoria-7.5 wt % yttria) for the meters and at Westinghouse and BNL to evaluate the material by performance tests in sodium. The work is showing encouraging results: two cells with electrolyte tubes produced at WADCO have been operated for more than 1000 hr at 370 to 485°C.

A pumped sodium apparatus has been constructed to proof-test up to four oxygen meters, and operation of the apparatus has begun.

A test of the effect of radiation on oxygen meters is being planned for initiation at EBR-II early in 1971. Design of equipment and fabrication of piping is complete. Delivery of the oxygen meter, with a special WADCO isostatically pressed electrolyte tube, is now scheduled for February 1971.

Apparatus is being designed to provide for an extended characterization of the performance of ten standard oxygen meters. These will be connected in series with a specimen-equilibration module, which will be used to calibrate the oxygen meters by the vanadium-wire equilibration method, and with a cold trap to control the oxygen content of the sodium.

Hydrogen Meter Development. Development work on an equilibrium-type hydrogen-activity meter is being continued. Studies were carried out during this period to evaluate a capacitance manometer as a potential pressure gauge for the meter. With this device, the hydrogen meter gives accurate results when carefully operated. However, the capacitance manometer is sensitive to vibration and temperature fluctuations, a disadvantage that may prevent its use as a component of the hydrogen meter except for laboratory applications.

Studies were also carried out to test the response of the hydrogen-activity meter at 372°C to changes in hydrogen concentration; this information is needed because it may be necessary to operate the meter at such temperature in the oxygen-hydrogen meter modules. The capacitance manometer was used as the pressure sensing device. The time required for the meter to reach a new steady output after a step change in the hydrogen level of the sodium was 40-60 min at 372°C as compared with 10-20 min at 500°C. The response time at 372°C should be adequate for reactor applications.

Low-level gamma radiation studies with ⁶⁰Co indicated that neither the capacitance manometer nor the Varian Millitorr pressure sensing device is affected by an exposure of ~15 min to low-level gamma radiation (surface dosage rate, ~200 R/hr). Tests at higher radiation levels are planned.

Nickel bellows-shaped membranes are currently being evaluated for applications in which the membranes will be subjected to high pressure differentials. The results to date indicate that some of the membranes produced by an electrodeposition process developed small blisters during hydrogen annealing. Moreover, tests in sodium indicated that these membranes do not diffuse hydrogen adequately. Electrodeposited membranes have, therefore, been dropped from further consideration. Bellows-shaped membranes formed both from tube and sheet nickel, currently being obtained, will also be evaluated.

Carbon Meter Development. Studies of the effects of various operating parameters of the carbon meter are being carried out to optimize the response of the carbon meter to low carbon levels. These studies will also provide a comparison of the response of the UNC carbon probe (stainless steel housing) with that of an ANL-modified probe (molybdenum liner in the high-temperature housing and all internal parts of the carbon probe copper-plated).

The effect of sodium flow, probe temperature, water content of decarburizing gas, and gamma radiation on the carbon flux are being investigated. A three-fold increase in the sodium flow (0.02 gpm to 0.06 gpm) produced a small (10 to 15%) increase in the flux of the ANL version of the meter; similar flow effects had been noted earlier with the UNC meter. An increase in temperature produced a small increase in the carbon flux from both meters. An increase in the water content of the decarburizing gas also increased the carbon flux of both meters.

Low-level gamma radiation from a ^{60}Co source (20-min exposure at a surface dose rate of 89 R/hr) had no effect on the carbon flux. Exposures at higher radiation levels are planned.

Design of Meter Modules for FFTF. A detailed design has been completed for an on-line monitoring module containing two oxygen meters and one hydrogen meter and the associated hardware and electronics. Comments from EBR-II and FFTF on the conceptual design have been incorporated in the detailed design. Procurement of materials, equipment and electronic components has been initiated. Two modules are being fabricated. The first module to be completed will be tested on a pumped loop at ANL-Illinois to establish the performance of the provisions for control of temperature and flow. The second module will be installed and proof-tested at EBR-II.

A detailed design has been completed for an on-line carbon meter module. By substitution of a specimen holder for the carbon meter probe, this unit can also serve for equilibrating metal specimens to be used in calibration of the oxygen and carbon meters. Fabrication of two modules has been started. One module will be tested at ANL-Illinois; the other will be installed and proof-tested at EBR-II.

Detection of Leaks in Steam Generators. The ion-current stability of a special ion pump was evaluated during this period to determine its potential as the detector component of the hydrogen meter leak detector. The pump is specially designed to

pump hydrogen and should, therefore, possess a longer pumping life than standard pumps. The results of the studies with the special ion pump (pumping speed, 20 liters/sec) indicated a stability of $\pm 0.53\%$, as compared with $\pm 0.06\%$ for the D-I ion pump (pumping speed, 11 liters/sec) presently being used. The larger deviation for the special pump is thought to result from its larger size. Similar tests will, therefore, be carried out on 11 liter/sec hydrogen pumps, which are now available.

ANL has agreed to supply a hydrogen meter leak detector to LMEC by April 1, 1971, for their Sodium Components Test Installation (SCTI). A design description was supplied to LMEC for review, the design was approved, and fabrication of the unit has been started. The leak detector alarm system has been designed and ordered. Orders have been placed for all of the instrumentation, and the project appears to be on schedule.

ANALYTICAL STANDARDS PROGRAM

Administrative Activities. A meeting of the National Standards Working Group was held in November 1970. A draft of the methods manual was discussed in detail and agreement was achieved on the interim sampling and analytical methods and on the procedural details to be used and, hence, to be included in the manual. Subsequently, the manual was revised and will be issued early in 1971 as ANL/ST-6, "Interim Methods for the Analysis of Sodium and Cover Gas." Prepublication copies of the manual have been distributed to the laboratories participating in the analytical standards program.

Samples of EBR-II primary and secondary sodium to be used in the sample interchange program between ANL-Ill., EBR-II, LMEC, and WADCO have been sent to each of the participants. Analyses will be performed for hydrogen, carbon, oxygen, and trace metals. Plans have been made for future interchange programs, which will also include AI, GE, and Westinghouse.

A meeting was held in December 1970 at ANL with representatives from E. I. duPont de Nemours, a major supplier of sodium, for the purpose of obtaining information which will be useful in revising an RDT Standard on purchase specifications. Meetings are also planned with Ethyl Corp. and U.S.I. Chemicals Co. for the same purpose.

Laboratory Activities. Preparations are being made to perform a set of experiments for the purpose of determining the affect of line length on the trace impurity content of sampled sodium. In these experiments, a sudden change in impurity content will be

produced at one end of a 100-ft-long section of tubing in a bypass loop. The magnitude of the change in concentration at both ends of the bypass loop will be measured as well as the time required for detection of the change. Initial experiments will be with oxygen as an added impurity. Modification of an existing loop is nearly complete.

A preliminary design of an overflow sampler for use in the remote sampling facility at FFTF is complete. Fabrication will begin after FFTF personnel review and comment on the device and the operational procedure.

A standard procedure for the analysis of particulates in sodium is needed. A primary concern is the recovery of the particulate matter unchanged from the sodium. Separations from sodium involving distillation, dissolution in mercury, and dissolution in liquid ammonia are being investigated.

High temperature gas chromatography is being investigated as a means of separating fission product gases and vapors from each other and from sodium vapor and aerosol. Construction of gas-chromatographic equipment for this investigation is complete, and experiments to establish conditions for the separations have been started.

FISSION PRODUCT AND COVER GAS TECHNOLOGY

Development of Radioisotope Monitoring Methods. Fission product cesium, rubidium, iodine, and tellurium should be easily leached from oxide fuel by coolant sodium contacting the oxide at cladding defects. The concentration level of certain isotopes of these fission products in the coolant should provide the means for characterizing a failure and indicating the magnitude of the cladding defect. Therefore, monitoring methods for measuring concentration levels of these isotopes are being investigated. At present, a monitoring concept for measuring the ^{135}I content of reactor sodium is of primary interest. In this concept, the concentration of ^{135}I is determined by (1) separating its daughter $^{135\text{m}}\text{Xe}$ from the sodium (by stripping it into a carrier gas) so that it can be gamma counted and (2) calculating the amount of parent from the count rate of the daughter.

The method of application of this monitoring concept is dependent on the kinetics of the transfer of xenon from sodium to the carrier gas. Accordingly, mass transfer in gas-sodium contactors is under investigation. An experimental apparatus is being built that will permit testing of gas-sodium contactors of various designs. The first contactor to be tested is one in which helium is bubbled through sodium to strip out the xenon. Apparatus design, except for the sparger, has been completed, and the components are being built or procured.

SODIUM CHEMISTRY

Characterization of Nitrogen-Bearing Species in Sodium. Information on the existence, identification and behavior of nitrogenous species in liquid sodium is needed to further the development of methods for analyzing reactor sodium for nonmetallic species. Current experiments in this study have involved nitrogen absorption by sodium, sodium-calcium solutions, and sodium-calcium-phosphorus solutions at 590°C. These experiments have shown that calcium added to sodium inhibits the nitridation of Type 304 stainless steel that is submerged in the sodium. The possibility is suggested that this inhibition results from the removal of nitrogen carriers by reaction between calcium and the carriers to form compounds that are insoluble in sodium or are inactive as nitriding agents. Carbon in the form of cyanide is advanced as a possible nitrogen carrier. Speculation is offered that the mechanism for carrier removal involves the formation of CaC_2 (calcium carbide) and/or CaCN_2 (calcium cyanamide).

Within the framework of certain assumptions and reasonable extrapolations, the conclusion is reached that of the nitrogen that reacts with impurities in sodium, only about one-fourth reacts with carbon. The nature of the other impurities is unknown. The addition of phosphorus (a possible reactive impurity) to a calcium-sodium solution produced no significant increase in nitrogen uptake.

Studies of the Sodium-Sodium Oxide-Sodium Hydroxide-Sodium Hydride System. The objective of this program is an understanding of the behavior of oxygen- and hydrogen-bearing species in liquid sodium. This knowledge will be useful in developing and evaluating analytical methods for oxygen and hydrogen impurities in sodium. Current effort has been directed toward elucidating the phase relationships in the sodium-rich corner of the sodium-oxygen-hydrogen diagram. In this connection, heat treated and/or quenched samples composed of selected mixtures of $\text{Na-Na}_2\text{O-NaH}$, Na-NaOH , and $\text{Na}_2\text{O-NaOH-NaH}$ are being studied by X-ray diffraction methods. Preliminary findings suggest that NaOH is stable at temperatures above $\sim 500^\circ\text{C}$.

PURIFICATION OF SODIUM

Characterization of Cold-Trapped Sodium. Tests to determine the effect of cold trapping on nonmetallic impurities (O, C, H, N) in sodium will be conducted in the Apparatus for Monitoring and Purifying Sodium (AMPS) and in the primary-coolant purification system at EBR-II. Current work is directed primarily toward

the design of AMPS, which is scheduled for completion by Nov. 1, 1971. Work on the conceptual design has been completed and preliminary specifications for fabrication of vessels have been prepared. The piping and equipment layout is essentially complete, a stress analysis has been performed, and detailed design is being started.

MATERIALS-COOLANT COMPATIBILITY

Studies of Carbon Transport in Sodium-Steel Systems. The objectives of this work are an understanding of the thermodynamics and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and a correlation of the compositional and microstructural changes with the mechanical-property behavior of these materials.

Previous equilibration experiments to determine the distribution of carbon between sodium and iron and iron-base alloys at 650 and 750°C have indicated that the carbon concentrations in sodium were in the sub-ppm range. In a recent experiment, foil specimens (2 mils thick) of Types 304 and 316 stainless steel, Fe-18 wt % Cr-8 wt % Ni, Fe-8 wt % Ni and iron were exposed to flowing sodium at 650 and 750°C. Iron and vanadium wires were also included at each of the temperatures. In order to increase the carbon concentration in sodium to a more readily measurable range, a carburized iron source was located downstream from the specimen.

Combustion analyses of the equilibrated foil specimens indicated a substantial increase in the carbon concentrations; for example, the carbon concentration in Types 304 and 316 SS increased from 0.045 wt % and 0.074 wt % to 0.64 wt % and 1.13 wt %, respectively, at 750°C. The iron, Fe-8 wt % Ni, and Fe-18 wt % Cr-8 wt % Ni foils also showed significant increases in carbon concentration. Analyses of the iron and vanadium wires and the sodium samples for carbon are being obtained. This experiment will yield information on the carbon activity in sodium and the distribution of carbon between sodium and the austenitic alloys.

Three austenitic stainless steels (Types 304, 316, and 347) were equilibrated with Fe-8 wt % Ni alloys at 600, 700, and 800°C in Vycor capsules at different carbon activities. The carbon activities corresponding to the carbon concentrations in the steels will be reported when the carbon activity studies in the Fe-8 wt % Ni alloys are completed. The experiments described above will provide a means for extending the results for the distribution of carbon between sodium and the stainless steels over a much wider range of carbon activities than can be achieved experimentally in loop systems over a reasonable time period.

Determination of Nonmetallic Impurities in Sodium by the Equilibration Method. The purpose of this work is to develop methods for accurately measuring the activity of nonmetallic elements, e.g., O, C, N, and H, in sodium at the low concentrations of interest for LMFBR applications.

A procedure for determining the oxygen activity in liquid sodium by the vanadium-wire equilibration method has been developed and the necessary distribution coefficient data obtained. The present effort in this area is directed toward (1) standardization and characterization of the method and (2) comparison of the results with other methods of oxygen analysis. Additional 4-hr exposures of vanadium wire to liquid sodium of known oxygen concentrations at 750°C have been made to establish the precision of the method.

Results of vanadium-wire equilibrations were compared with results obtained from four standard UNC electrochemical oxygen meters used consecutively on a pumped sodium system. Three important characteristics of cell operation were noted: (1) The curves of emf versus oxygen concentration for the four cells did not have the same slope or intercept. These differences may be due to variations in structure or impurities in the cell electrolyte. (2) The slopes were considerably greater than that of the calculated curve, thereby resulting in higher than theoretical voltages at high oxygen concentrations in sodium. (3) Linear plots of the cell emf versus the logarithm of the oxygen concentration in sodium were obtained for all of the cells. Three orders of magnitude in the oxygen concentration were investigated with one of the cells.

The effect of maximum temperature in the loop on the oxygen concentration in sodium is of interest for the following reasons: (1) the vanadium wire equilibration temperature has been set at 750°C, (2) electrochemical oxygen cells operate at temperatures between 300 and 500°C, and (3) the sodium temperature in a LMFBR will vary from the cold trap temperature to the maximum sodium temperature in the core. No effect of maximum loop temperature in the range 450 to 750°C on the cell emf was found for a range of oxygen concentrations in sodium between 0.34 and 30 ppm.

A UNC oxygen meter operating at 402°C has been calibrated using the standard vanadium-wire equilibration method over the range 0.8 to 11 ppm oxygen in sodium. All points were within 1 mV of the curve.

The equilibration method is being extended to the measurement of carbon activities in sodium. The properties of a suitable detector metal are the same as those specified previously for an oxygen detector, i.e., (1) a low solubility in liquid sodium, (2) a significant range of carbon solid solution in the metal, (3) relatively high diffusion rates for carbon in the solid, and (4) experimentally measurable distribution coefficients for carbon which are greater than unity. Both iron and vanadium appear to be acceptable detector metals for carbon, and work is in progress to establish the required distribution-coefficient data for carbon between these metals and liquid sodium. Further work will be required, however, to establish optimum exposure times and temperatures and the effects of other nonmetallic elements on the distribution coefficients and the carbon activity.

1. ON-LINE IMPURITY MONITORS
(J. T. Holmes)

Argonne has been given the responsibility of setting up and implementing a national meter program for developing, testing, and establishing commercial availability of meters for use in FFTF and in other LMFBR systems. The meters to be developed and characterized in this program are monitors for oxygen, carbon, and hydrogen and a leak detector for steam generators. Meter modules that provide flow and temperature control are being developed for FFTF. These modules will be tested at EBR-II.

1.1 Oxygen Meter Development (J. M. McKee, V. M. Kolba, L. J. Marek, P. J. Mack)

The objective of this work is to characterize and proof-test a meter for monitoring oxygen activity in the sodium coolant of FFTF and other LMFBRs. For FFTF application, two oxygen meters and one hydrogen meter will be incorporated into a single meter module (see Section 1.4).

Electrolyte Development. ANL is coordinating the joint efforts of WADCO, Zircoa, BNL, and Westinghouse to standardize an improved version of the electrochemical oxygen meter, which utilizes an improved solid electrolyte tube and a gas reference electrode. A meeting of these contractors was held at ANL on October 14, 1970, at which it was reported that the first batch of improved-purity electrolyte tubes produced by Zircoa exhibited unacceptably short service life in sodium, apparently due to contamination during firing of the electrolyte. It was concluded that (1) emphasis on high purity should be retained, (2) the isostatic pressing method of tube manufacture should be continued, (3) cell performance at 370 to 430°C should be characterized before exploring higher temperatures, and (4) the oxygen-gas reference electrode should be retained for use at these temperatures. The yttria content of the thorium-yttria electrolyte is to be kept at 7.5 wt %. Tests of linearity of cell emf vs. oxygen at low oxygen levels are to be performed at BNL.

Progress made since the meeting has been encouraging. Within two weeks of the meeting, five tubes which met the specifications that will be given to Zircoa were produced at WADCO by isostatic pressing. These were immediately sent to Westinghouse and BNL.

and incorporated into cells, and testing was begun. The tubes have performed very well. Their electrical performance is distinctly superior to that of commercial-purity tubes and their life appears to be satisfactory. Two cells have operated more than 1000 hr at 370 to 485°C. WADCO has ordered 200 tubes from Zircoa, where an electric, refractory-metal furnace is being installed to eliminate contamination during firing. ANL has arranged for WADCO to produce a few more tubes for use in the characterization program until Zircoa has qualified their process. WADCO sent four more tubes to Westinghouse in December 1970, and these will be incorporated in standard probes and delivered to ANL in January 1971. Three of these are slated for use in early tests at EBR-II. An additional 10 tubes are being produced at WADCO.

Oxygen Meter Characterization. Westinghouse meters with gas reference electrodes have been selected for standardization. These meters will be tested on two sodium systems. One system, now being constructed, will be used to determine the calibration stability of the meters; the other will be used to test reference gases, evaluate electronic equipment for measuring cell emf, and for other short-term tests.

To provide a statistically significant measure of the calibration stability of the oxygen meter, 20 standard meters will be tested: 10 at ANL and 10 at Westinghouse. Initial calibration curves at oxygen levels from <1 to 15 ppm will be determined for all meters at 430°C by the vanadium-wire equilibration method, which measures the oxygen activity in sodium. These calibrations will be repeated after three months of continuous operation at 430°C to determine calibration stability. The temperature coefficients of the meters will be measured at intervals during this period. Testing will continue for at least a year, under conditions determined by results obtained during the first three months. The first three-month test period is expected to be completed in July 1971, provided that the meters are delivered to ANL early in March 1971.

In the system under construction at ANL, ten standard meters will be connected in series with the laboratory prototype specimen-equilibration module and with a cold trap used to control the oxygen content of the sodium.

The apparatus for the short-term tests provides for testing up to four oxygen meters and for determining their stability as a function of operating life in a sodium system having sodium

flow rates up to 0.5 gpm at temperatures up to 485°C. A cold trap is also provided in this system for controlling the oxygen level.

During this period, the construction, assembly, and leak-testing of the apparatus was completed; sodium was added to the loop; and flow was initiated.

To gain experience with the apparatus and to compare two voltage-measuring devices, two UNC cells having Cu-Cu₂O reference electrodes and standard 15 wt % Y₂O₃-ThO₂ slip-cast electrolyte tubes were installed in the apparatus. The emf of the two cells was monitored at several sodium temperatures and at various oxygen levels, which were attained by cold-trapping. During the course of loop operation, vacuum distillation samples were taken at various cold-trap temperature settings, and the residues analyzed for oxygen to verify the oxygen level in the sodium.

The two UNC cells, once calibrated, were used to follow the changes in oxygen levels as the levels were varied by cold-trap temperature changes. The two cell voltages differed at a constant oxygen level by ~4 mV.

Radiation Test at EBR-II. An oxygen meter will be operated on an existing sampling line at EBR-II to permit a rapid evaluation of the effects of direct beta and gamma radiation on the oxygen meter. A proposed experimental test procedure has been prepared and submitted to EBR-II, Idaho, for review, comments and approval. Design of equipment and fabrication of piping is complete. Delivery of the oxygen meter, which has a special electrolyte tube produced at WADCO by isostatic pressing, is scheduled for February 1971.

1.2 Hydrogen Meter Development (D. R. Vissers, L. G. Bartholme)

The design, development, and prooftesting of an on-line hydrogen meter for measuring hydrogen dissolved in the primary and secondary LMFBR sodium systems are the goals of this program. An equilibrium-type hydrogen-activity meter developed at ANL is being evaluated for the on-line hydrogen-meter component of the oxygen-hydrogen meter module (see Section 1.4). Appropriate response-test and on-line calibration procedures are being developed for the monitoring station where required.

Design, Construction, and Evaluation of Meter. The ANL hydrogen-activity meter is an equilibrium diffusion-type monitor with a direct pressure readout of the hydrogen activity; its principal components are a nickel diffusion membrane, a pressure sensing device, and a high-vacuum system (see ANL/ST-2, p. 1-10). Previous tests of the prototype hydrogen-activity meter have utilized a Varian Millitorr hot-triode ion gauge for the direct hydrogen pressure measurement. These studies have indicated that the Millitorr gauge, when calibrated for hydrogen, has the potential of serving as the sensor component of the hydrogen meter. However, as a possible means of eliminating the need for calibration or frequent recalibration, a new pressure sensor, a MKS baratron capacitance manometer, is being tested. The MKS unit, which was partially damaged in shipment, as reported earlier (ANL/ST-4, p. 13), has been repaired and is now functional over its complete pressure range (5×10^{-4} to 1 Torr). The unit was installed into the prototype hydrogen meter, and evaluated in a gas-flow apparatus with standard argon-hydrogen gas mixtures. The results of this study (see Table 1-1) clearly indicate that the MKS unit requires no calibration. During the course of these studies, however, the readout pressure was found to be very sensitive to temperature changes and to vibration in the sensor portion of the device. These disadvantages may prevent the use of the MKS gauge in the hydrogen meter; however, this device has potential application for the calibration of other gauges, such as the Millitorr ion gauge.

Most of the earlier tests with the hydrogen meter were carried out at 500°C. Since it may be desirable to operate the meters at lower temperatures in the oxygen-hydrogen meter module, the response characteristics of the prototype hydrogen meter were tested in the gas-flow apparatus with standard argon-hydrogen gas mixtures at 372°C. The results of this study, which was conducted with the MKS gauge, indicate that the time required to reach the approximate equilibrium pressure, after a step change in the hydrogen level of the system, is ~40-60 min (see Fig. 1-1). Although this time is longer than the time required at 500°C (10-20 min), it appears to be an acceptable time for a hydrogen-activity monitor for FFTF or EBR-II.

Table 1-1. Calibration of MKS Capacitance Manometer (500°C)

Hydrogen Content of the Argon ^{a,b} (Torr)	Equilibrium Hydrogen Pressure Measured by MKS Gauge (Torr)
0.095 ± 0.003	0.093
0.078 ± 0.003	0.072
0.057 ± 0.003	0.053
0.036 ± 0.003	0.034
0.016 ± 0.002	0.017
0.014 ± 0.001	0.013
0.0075 ± 0.0005	0.009
0.013 ± 0.002	0.014
0.016 ± 0.001	0.014

^aHydrogen pressure calculated from gas-chromatographic analysis of hydrogen-argon gas mixtures.

^bThe "±" values indicate the normal scatter of the data.

Tests in Sodium. A prototype of the ANL hydrogen-activity meter has been installed on the Sodium Analytical Loop (SAL). This meter utilizes a Varian Millitorr ion gauge for direct pressure readout, and is currently being operated at 400°C. During preliminary studies to determine how the meter functions in a pumped sodium system, the equilibrium hydrogen pressure of the sodium system was measured with the meter and found to be 1.3×10^{-1} Torr, which corresponds to a hydrogen level in the sodium of 1.68 ppm. Equilibrium hydrogen gas samples taken from above a second nickel membrane and analyzed by gas chromatography gave a calculated average pressure of $1.3 \pm 0.2 \times 10^{-1}$ Torr, which is in good agreement with the hydrogen-activity meter value.

Efforts are currently being made to improve the equilibrium gas-sampling procedures to eliminate the variability present in the gas-chromatographic analyses of hydrogen.

Gamma Radiation Studies. The components of the potential pressure sensing devices (Millitorr ion gauge and MKS baratron) were exposed to a 37-Ci ^{60}Co source to determine whether a low-level gamma radiation field would affect the pressure readings of the gauges. The results indicated that exposure for 10-20 min to a radiation field equivalent to a surface dosage rate of 200 R/hr had no effect on the devices. Similar studies in high-level radiation fields (10^4 to 10^6 R/hr) are planned.

Nickel-Membrane Studies. The application of the ANL hydrogen meters to LMFER sodium systems will require that the nickel membranes of these meters operate under high pressure differentials (up to 150 psi at 500°C). Accordingly, bellows-shaped nickel membranes are being evaluated for this application. Initial tests of bellows-shaped membranes formed by electrodeposition, in which the membranes were exposed to $\text{H}_2\text{-H}_2\text{O}$ vapors at 800°C, showed that the membranes contained voids and had a tendency to blister. Further tests of the membranes in sodium showed inadequate diffusion of hydrogen. Electrodeposited membranes have, therefore, been dropped from further consideration. Bellows-shaped membranes formed both from nickel tube and sheet, which are currently being obtained, will be evaluated next.

1.3 Carbon Meter Development (C. Luner, D. J. Raue, P. J. Mack)

The objective of this work is a commercially available on-line carbon meter that will indicate the probability of significant carbon transfer taking place in EBR-II, FFTF, and later in demonstration and commercial LMFBRs. The immediate objectives

Fig. 1-1. Time to Equilibrium for Hydrogen-Activity Meter

are the testing and improvement of the UNC diffusion-type carbon meter, which will be incorporated into a prototype module containing the necessary flow and temperature control devices (see Section 1.4). During this reporting period, molybdenum-lined chambers for housing the carbon-meter probe and for exposing iron or Fe-C alloys to flowing sodium at temperatures up to 650°C were installed on the Test and Evaluation Apparatus (TEA). All hot surfaces of the ANL-modified probe in contact with collected carbon-bearing gases were copper-plated to minimize carbon transfer within the meter. Studies with the new system have begun.

Recent work has been directed toward comparing the responses of the UNC probe (stainless steel housing) and the ANL-modified probe (molybdenum-lined and internal parts copper-plated) to important operating parameters and to the addition of low levels of carbon to the sodium.

Parameters which are most likely to affect the carbon flux, such as probe temperature, sodium flow, water vapor content of the decarburizing gas, and gamma radiation are being investigated. In the experiments described below, sodium was circulated continuously through a cold trap maintained at 275°C while the remainder of the loop was operated at temperatures between 325 and 360°C. The two carbon probes were operated in parallel.

Probe Temperature. Preliminary experiments previously reported (ANL/ST-2, p. 1-7) have indicated that the carbon flux of the UNC probe has a small temperature dependence. Further measurements have now been made at 630 and 750°C with both the UNC probe and ANL modification. Both probes were at the same operating temperature during each experiment. The results confirmed previous studies and showed that with both the UNC probe and the ANL probe the carbon flux has a small temperature dependence. Experiments are now in progress to determine the effect of small additions of carbon on the carbon flux of the two probes at various temperatures. The results of these experiments will be used to determine the standard operating temperature of the carbon probe.

Sodium Flow. A small (~10%) increase has been previously observed in the carbon flux of the UNC probe with a twofold increase in the sodium flow. Tests of this effect have now been extended to include the ANL-modified probe. Recent data for both meters qualitatively confirm previous observations made on the UNC probe, namely, that about a 10-15% increase in carbon flux was observed with a threefold increase in the sodium flow (0.02 to 0.06 gpm). This increase was observed at both 630 and 710°C. Quantitative data will be presented in a later report.

Water-Vapor Content of Decarburizing Gas. Experiments now in progress appear to confirm previous data (ANL/ST-2, p. 1-7), which indicated that increasing the water vapor content of the decarburizing gas significantly increases the carbon flux.

After completion and confirmation of the series of experiments described above, the standard operating conditions of the probe will be determined.

Gamma Radiation. Under field conditions, the carbon probe will be exposed to intense gamma radiation arising primarily from ^{24}Na . Although gamma radiation would not be expected to affect the structural components markedly, a possibility exists that radiation-induced reactions of gases (CO , H_2O) in the probe could affect the carbon flux. Indeed, carbon monoxide, the gas that is formed within the carbon probe, has been shown to undergo decomposition when exposed to gamma radiation. To determine the effect, if any, of gamma radiation of the gases in the carbon probe, the UNC probe was exposed for 20 min to a ^{60}Co source to give a surface exposure rate of about 89 R/hr. The carbon flux was continuously monitored during exposure; no change was observed. It appears that, for low carbon fluxes at least, this level of gamma radiation does not affect the flux. Further experiments will be conducted at higher radiation levels.

Stirred-Pot Experiments. The objectives of these experiments are (1) to relate carbon-meter readings to the carbon activities of standard metal specimens and (2) to determine the response of the carbon probe to various additives such as hydrogen, oxygen, lubricating oil, etc. Materials and equipment are being obtained for these experiments. The carbon activity of the sodium will be fixed by equilibrating the sodium in containers whose activity is known or can be determined. The carbon flux obtained from sodium contained in Type 304 stainless steel and 2 1/4 Cr-1 Mo crucibles will be measured first.

In a preliminary experiment, the effect of added hydrogen on low-level values of the carbon flux was investigated. Increasing increments of hydrogen gas were added to the cover gas of a molybdenum pot containing sodium, which was stirred during the experiment. No significant change in the flux was observed after any of the additions.

1.4 Design of Meter Modules for FFTF (V. M. Kolba, J. M. McKee, P. J. Mack)

The objective of this work is to design, proof test, and establish commercial availability for on-line meter modules to be installed at FFTF. These modules include flow and temperature controls as well as the meters for monitoring impurities. The proof testing will be carried out on laboratory sodium systems and on the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II. Two modules are now being designed¹ and fabricated: (1) an oxygen-hydrogen meter module containing two oxygen meters (in case one should fail) and a hydrogen meter; and (2) a carbon-meter module, which, by substitution of a specimen holder for the carbon probe, will also serve as a module for equilibrating metal specimens.

Oxygen-Hydrogen Meter Module. Two modules are being fabricated: one will be tested at ANL-Illinois, the second will be installed for proof testing at EBR-II in April 1971.

During this period, a detailed design of the module and components has been completed. A sketch of the module is shown in Fig. 1-2. A preliminary flexibility analysis of the module piping has been completed. Procurement of materials such as fittings, valves, vacuum components, and instrumentation has begun.

Control and instrumentation schematics for operation of the module and the control console have been completed. A preliminary operational plan covering the power, control, and instrumentation system for the modules has been prepared and submitted to EBR-II, Idaho and FFTF for comments.

Specimen Equilibration-Carbon Meter Module. This module will provide a housing for the carbon meter and a means for equilibrating metal specimens with flowing sodium to provide on-line calibration of oxygen and carbon meters. Two modules are being fabricated: one will be tested at ANL-Illinois, the other will be installed and proof tested at EBR-II. The module is sketched in Fig. 1-3.

¹M. A. Slawicki, Chemical Engineering Division, is preparing the electrical packages for both modules. E. C. Filewicz, EBR-II Project, is preparing the mechanical and structural packages for both modules.

Fig. 1-2. Oxygen-Hydrogen Meter Module

Fig. 1-3. Specimen Equilibration-Carbon Meter Module

Detailed design drawings of the specimen holder and the piping have been completed. A flexibility analysis of the module piping has been started.

Two modules will ultimately be installed in Cell C of the RSCL at EBR-II. Installation of the modules has been planned so that access for removal of wire specimens will be through the existing cell wall and the cell door. Details of piping for this layout are now being developed.

1.5 Detection of Leaks in Steam Generators (D. R. Vissers, C. C. McPheeters, L. G. Bartholme)

This program involves the evaluation of requirements for a leak-detection system for LMFBR steam generators and the development and prooftesting of a detection system to meet these requirements. This system will use on-line impurity monitors for detecting the products of the sodium-water reaction. Hydrogen monitors are being given first consideration for leak detection because they appear to be durable and sensitive to small changes in the hydrogen level in sodium. However, other means of detection (i.e., oxygen meters) are not being excluded from consideration. A signal analysis and alarm system will be developed to accommodate normal temperature and hydrogen fluctuations in the sodium without generating false alarms.

The requirements for the leak-detection system and a description of the ANL detector were presented previously (ANL/ST-2, p. 1-14). The principal requirements are that it be sensitive, rapid, and precise. The sensitivity required to detect leaks that would lead to rapid perforation of adjacent tubes in a large generator (10^6 lb sodium/hr) is the capability of detecting a 4% change in the hydrogen level at a concentration of 0.1 ppm hydrogen dissolved in sodium.

An in-sodium hydrogen monitor is presently being developed at ANL for leak detection. This device is based on measurement of the diffusion rate of hydrogen through a nickel membrane operated under a dynamic vacuum. A vacuum (10^{-6} to 10^{-8} Torr) is drawn at a steady rate by an ion pump; thus, a hydrogen-activity gradient develops from the sodium side to the vacuum side of the membrane and results in the diffusion of hydrogen through the membrane. The rate of hydrogen diffusion through the membrane, a direct measure of the hydrogen concentration in the sodium, is determined by monitoring the current through an ion pump.

For reactor application, the operating life of the ion pump is an important consideration. An evaluation was, therefore, made of an ion pump that may have a longer operating life than the unit presently in use. The pump, which was built especially for pumping hydrogen (pumping speed, 20 liters/sec), has cathode plates constructed of 125-mil titanium sheet with special reenforcing brackets on the cathode plate to prevent plate warpage and subsequent shorting of the ion-pump grid system. The D-I pump presently in use (pumping speed, 11 liters/sec) has cathode plates (~90 mils thick) of two different metals; one is titanium sheet and the other tantalum sheet.

In this study, the stability of the ion-pump current of the special unit was compared with the stability of the ion-pump current of the D-I ion pump. Ion-pump current readings were taken at 1-sec intervals while the ion pumps were being operated as the detector components of prototype hydrogen-meter leak detectors. The tests were conducted on the Sodium Analytical Loop (SAL) at ~433°C. The results of this study indicated a stability of $\pm 0.53\%$ for the special unit, as compared with $\pm 0.06\%$ for the D-I unit; however, the stability of the special unit may still be adequate for use in the ANL hydrogen-meter leak detector. A possible reason for the difference in ion-pump current stability of the two ion pumps is the larger number of cells in the discharge chamber of the 20 liter/sec ion pump. Accordingly, hydrogen-type ion pumps with pumping speeds of 11 liters/sec are being obtained, and their ion-current stabilities will be evaluated in a similar manner.

LMEC Leak Detection System. A hydrogen-meter leak detector is being built for installation on the Sodium Components Test Installation (SCTI) at LMEC. The leak detector will be used in their tests of the AI-designed steam generator. Performance of the leak detector in terms of long-term stability, reliability of the alarm system, and response to changes in hydrogen concentration will be determined.

ANL is to supply all of the device except for the pump, flowmeter, isolation valves, and power and instrumentation cables. Delivery of the unit to LMEC is scheduled for April 1, 1971, and delivery of the instrumentation package is scheduled for April 15, 1971.

A design description of the leak detector was completed and sent to LMEC in November 1970. The design was approved with minor changes in the list of applicable standards.

The leak detector consists of a heat exchanger, a nickel membrane and its housing, a vacuum system, and connecting piping. Sodium flows through the heat exchanger, through a heated section to the membrane housing, and back through the heat exchanger. The sodium temperature at the nickel membrane is maintained within $\pm 0.5^{\circ}\text{C}$ with a controller that varies the power to the heated section. A vacuum is maintained on the inside of the nickel membrane with a differential ion pump. The ion-pump current is proportional to the flow rate of hydrogen through the nickel membrane, which in turn is proportional to the hydrogen concentration in the sodium. Changes in the ion-pump current signal indicate changes in hydrogen concentration in the sodium.

The leak detector alarm system is designed to alarm on either a rapid increase in the pump-current signal or on a high current signal. The actual alarm levels used will depend somewhat on the operating conditions of the SCTI during tests.

Fabrication of the unit has been started and is proceeding on schedule. Certifications are being obtained on all materials of construction. Orders have been placed for all of the instrumentation.

Plans have been made to evaluate nickel membranes in the form of helical bellows. Thin-wall nickel tubes are to be swaged to 1/2-in. OD and then magnetically formed on a helical mandrel to provide a convoluted membrane of increased strength. Electro-deposited bellows-type membranes were found to contain voids and blisters and were inadequate for diffusing hydrogen. A mechanical forming process is expected to provide membranes of higher integrity.

2. ANALYTICAL STANDARDS PROGRAM (R. J. Meyer, M. H. Barsky)

The long-term objective of the Analytical Standards Program is a set of sampling and analytical methods which, when combined with corrosion and purification data, will constitute the basis for a final set of purity specifications for the operation of reactor and large non-reactor sodium systems. To achieve this objective, ANL has established an Analytical Standards Laboratory to handle the administrative and laboratory aspects of this program. The administrative aspect involves coordination of contractor activities in the Analytical Standards Program. The laboratory aspect involves (1) participation in the testing of interim sampling and analytical methods to satisfy the near-term needs of EBR-II, FFTF, and contractor laboratories and (2) the development of reference and standard methods that fully satisfy the long-range needs of the sodium technology effort.

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

2.1.1 National Standards Working Group

Two working groups were originally established to assist ANL in its standardization program. One group (the Reactor Standards Working Group) was concerned with the immediate requirements and problems related to reactor operations; the other group (the National Standards Working Group), with the national R & D program in sodium technology. The Reactor Standards Working Group has now satisfied its objective and its membership (WADCO and EBR-II) has been officially incorporated into the National Analytical Standards Working Group. This advisory group met at ANL on Nov. 23-24, 1970. Representatives from AI, ANL-Illinois, EBR-II, LMEC, RDT, Westinghouse (ARD), and WADCO were present.

Approximately two weeks prior to the meeting, the representatives reviewed a draft of a methods manual and forwarded comments to ANL. Pertinent comments were discussed at the meeting and in some cases revisions of the manual were agreed upon. ANL presented its assessment of the vanadium-wire equilibration method as an interim procedure for the determination of oxygen activity in sodium, and agreement was reached on the inclusion of this method in the manual. At the meeting it was also decided that the needs of the entire sodium technology community (reactor and R & D contractors) could be satisfied by a single methods manual.

2.1.2 Interim Methods Manual

During this quarter, a third draft of the methods manual was prepared for the meeting discussed above. Following the meeting, a prepublication copy of the manual titled "Interim Methods for the Analysis of Sodium and Cover Gas," was completed and sent to members of the National Standards Working Group. Final editing and publication in printed form (as ANL/ST-6) should be completed early in 1971. Every three months, ANL will assess the need for updating the manual and will publish new editions when warranted by advances in the National Analytical Standards Program.

2.1.3 Interim Methods Test Program

A sample interchange program (previously described in ANL/ST-4, p. 20) was initiated by the Reactor Standards Working Group to provide an interlaboratory test of the interim methods detailed in the methods manual. Samples of EBR-II sodium were taken by EBR-II personnel and sent to WADCO, LMEC, and ANL-Illinois; samples were also reserved for EBR-II. Samples for oxygen, carbon, and hydrogen analysis were taken from the secondary sodium system, and samples for trace-metal analysis from the primary sodium system. Analysis of these samples was scheduled to begin upon receipt of the prepublication copy of the methods manual. Plans were also made to start a second sample interchange, which will include AI, G.E., and WARD as well as those already involved. This program is scheduled to begin by the end of the fiscal year.

The initial sample interchange utilizing EBR-II sodium constitutes for the most part a test with "low" levels of impurities. A source of sodium with "high" nonmetallic impurity levels for future sample interchange is apparently not immediately available. Consideration will be given (when funding permits) to the preparation of standard sodium samples with suitably "high" impurity levels.

2.1.4 Purchase Specifications for Sodium

ANL has been given the responsibility for generating all RDT standards related to purity specifications for sodium systems. At present, ANL is revising RDT-M13-IT, the official document for sodium purchase specifications. This revision is expected to be completed early in 1971.

As a major supplier of sodium, E. I. duPont de Nemours contacted ANL regarding proposed changes in purchase specifications. As a result of this interest, a meeting was held at ANL in December

1970 with representatives of duPont. The tendency toward more rigid purchase specifications is of concern to duPont because these specifications might increase the production cost of reactor-grade sodium. ANL presented its position that impurity limits would be set only for elements that could lead to detrimental or undesirable effects, such as increased corrosion, production of tritium, production of fission products, absorption of neutrons, reduction in sensitivity of FEDAL systems, or inducement of positive reactivity. It was also pointed out that a method of analysis would be specified for each element and that this method would be included in the manual "Interim Methods for the Analysis of Sodium and Cover Gas."

The Sodium Analytical Standards Laboratory agreed to analyze, by interim methods, a few samples of currently produced sodium to be submitted by duPont.

ANL has also invited the Ethyl Corp. and U.S.I. Chemicals Co., as major sodium suppliers, to discuss proposed changes in purchase specifications.

2.2 Laboratory Activities

Effort during this quarter has been devoted to setting up the sodium analytical facilities, including installation of inert atmosphere gloveboxes and procurement of apparatus for the interim methods. Additional activities are discussed in the sections below.

2.2.1 Effects of Line Length on Sample Validity (S. B. Skladzien, W. E. Ruther¹)

One of the ANL lead assignments related to FFTF needs is the determination of the effect of sampling line length on sample validity. Of principal interest is the effect of line length on the determination of (1) nonmetallic impurities, mainly oxygen, hydrogen, and carbon, (2) metals and halides, and (3) radioactive species.

Work has started on setting up the necessary equipment to determine line-length effects on oxygen. An existing high-temperature sodium loop is being modified by the addition of a bypass loop, which will contain two oxygen-monitoring cells and

¹EBR-II Project.

two sampling sites separated by a 100-ft coil of 5/8-in. stainless steel tubing. The main loop and the bypass loop can be pumped independently.

Experiments to investigate line-length effects will be conducted as follows: (1) the oxygen content of the main loop will be brought to a high level while the isolated bypass loop is maintained at a low oxygen level; (2) the sodium from the main system will be diverted into the bypass loop; (3) the time between the responses of the two oxygen meters will be compared with response times calculated on the basis of flow rates, and the magnitude of the responses of the two meters will be compared with previously established calibration curves; and (4) if necessary, sodium samples taken from the sampling sites at the ends of the bypass loop will be used to establish equilibrium impurity concentrations.

Modification work on the loop has been progressing and completion is expected by the end of January 1971. Experiments will be started shortly thereafter.

2.2.2 Prototype FFTF Overflow Sampler (S. B. Skladzien)

The objective of this work is an overflow sampler that will be suitable for obtaining sodium samples, for trace metal and halide determinations and for radioactivity assays, from the sampling sites available within the proposed FFTF sampling cell. This work includes (1) modification of an existing EBR-II sampler design to meet FFTF requirements, (2) construction of the sampler, and (3) testing on an existing ANL loop.

Appropriate design modifications of the EBR-II sampler have been made.² A schematic of the preliminary design is shown in Fig. 2-1. This design and a tentative operating procedure will be submitted to FFTF for review. One of the main design objectives was to provide a single sampler which could be attached to any one of the five pairs of in-cell sampling lines with a minimum of cross-contamination between the systems. For this reason, a separate sodium inlet line (designated as 3 on Fig. 2-1) is provided for each of the five sampling stations.

After agreement is reached between ANL and FFTF on the final sampler design, a working sampler will be constructed and tested.

²After consultation with L. F. Lust and J. J. McCown of WADCO and W. H. Olson of EBR-II.

Fig. 2-1. Prototype Overflow Sampler

1. Quick-disconnect coupling	6. Coupling and hollow metal O-ring
2. Vacuum-inert gas line	7. Sheathed heating elements
3. Sodium inlet line	8. Conoseal fittings
4. Sample cup (50-g capacity)	9. Adjustable support
5. Sodium outlet line	

2.2.3 Particulate Analysis (M. D. Adams)

As a part of the Analytical Standards Program, ANL will specify a method of particulate analysis for use in sodium technology programs. Most of the aspects of such a procedure have been reasonably well established; however, the recovery of the particulates unchanged from a filter device and their examination in an inert atmosphere are unsettled procedural problems.

Particulate recovery by the common practice of using a polar solvent such as alcohol or water is not considered satisfactory. An effective separation of excess sodium from the filter by distillation was demonstrated in tests reported in ANL/ST-4, p. 23. However, alternative separations based on dissolution of sodium in an inert solvent followed by filtration of the solution are also attractive recovery techniques and are being investigated. The use of mercury as an inert solvent for sodium seemed to be a simple approach; accordingly, an experiment was performed in which the residual sodium on a filter was amalgamated with mercury and the amalgam forced through the filter by pressurizing with helium. However, small droplets of mercury which could not be removed by further pressurization remained on the filter. Liquid ammonia is another inert solvent that has been used to separate sodium from impurities. Moreover, there are no problems associated with its removal from the filter. Accordingly, an apparatus is being assembled that will allow dissolution of sodium from the filter and subsequent transfer of the filter to an inert atmosphere box for examination of particulates collected.

Modifications have been completed to convert a glove-box microscope to a petrographic instrument. An additional light source, a substage condenser, and a body tube with a polarized light analyzer were added. The microscope can now be used with either vertical light or transmitted light. Petrographic examination inside an inert atmosphere will allow determination of optical properties of some of the particulates without exposure to air.

Small filter assemblies (1-in. dia, 4 in. long) containing a cup-shaped stainless steel filter of 7 μ m nominal pore size and 10 cm² area have been used to collect particulate from two different loops at flow rates of $\sim$ 0.1 gpm. The material collected on these filters is being used for methods investigations. The information on flow restriction by this type of filter is being used to design filter assemblies for large operating sodium systems at higher flow rates (<1 gpm).

2.2.4 Determination of Metal and Halide Impurities in Sodium (H. S. Edwards)

A survey method is needed for the rapid and routine determination of changes in metallic impurity levels in sodium. The method selected for initial evaluation was emission spectrography utilizing induction-coupled plasma excitation of a metal-dust aerosol generated by ultrasonic nebulization of molten sodium. This approach has the potential for in-line applications.

In preliminary experiments, the ultrasonic nebulizer system was tested by generating an aerosol from a tin-bismuth eutectic alloy (mp, 138.5°C). Further work on this method has been deferred because of a reallocation of funds.

2.2.5 Development of Reference Methods for Total Oxygen, Carbon, and Nitrogen in Sodium (M. F. Roche)

Work has been in progress on the development of proton activation as a reference method for the determination of total oxygen, carbon, and nitrogen in sodium. The validity of this approach for the determination of oxygen was demonstrated with two proton irradiations of sodium containing ~15 ppm oxygen (described in ANL/ST-4, p. 25). A further experiment was started with sodium containing about 50 ppm oxygen. However, after equilibration of the sampling/irradiation cell with sodium at 450°C for two days, a valve diaphragm failed and the experiment was terminated. After removing the sodium and the diaphragm, the cell interior was examined to determine how effectively the 450°C equilibration cleaned the cell wall. The metal surfaces in this case were bright and shiny. Cleaning the cell with 450°C sodium thus appears to effectively remove contaminants which might interfere in the proton-activation analysis.

Further work on this project has been deferred because of reallocation of funds.

2.2.6 Sampling and Analysis for Fission Products in Cover Gas (M. H. Barsky, A. F. Panek)

The objective of this work is to develop an apparatus for determining the types and levels of radioactive fission products in reactor cover gas. This information is expected to be useful in the detection and characterization of fuel failures.

The major fission products released to the cover gas are the noble gases xenon and krypton, which are formed directly in fission or by fission-product decay. Also present are radioactive cesium, rubidium, iodine, bromine, tritium, argon, neon, and their associated decay products. Sodium vapor is present, and sodium

aerosols may or may not be present depending upon the conditions prevailing at the time and location a sample is taken. The detection and characterization of fuel failures requires discrimination of short-lived isotopes in the presence of (1) a high level of radioactivity and (2) sodium as vapor and possibly as aerosol. Sampling of the cover gas is complicated by the presence of the high ^{24}Na activity, as well as by the aerosol.

As discussed in ANL/ST-3 (pp. 2-6, 2-7), we believe that the technique of high-temperature gas chromatography will provide a simple approach to the separation of metal vapor and aerosol from the noble gases and the permanent gases. After the initial vapor-gas separation on a high temperature column, a further separation of the gases (e.g., the separation of ^{23}Ne and ^{41}Ar from the krypton and xenon isotopes) can be made on a second column at room temperature. A further separation of the vapors (e.g., the separation of sodium isotopes from rubidium and cesium isotopes) can be made on a third column, which is also operated at high temperature.

Construction of a gas-chromatographic system to demonstrate vapor-gas separations has been completed. Experimental work to establish conditions for these separations is now in progress.

3. FISSION PRODUCT AND COVER GAS TECHNOLOGY (W. E. Miller)

3.1 Development of Radioisotope-Monitoring Methods (N. R. Chellew, C. C. Honesty)

The goal of this work is the development and testing of monitoring methods for characterizing fuel failures in LMFBR systems. In the event of a serious cladding failure, certain fission products, e.g., cesium, rubidium, iodine, and tellurium, should be easily leached from oxide fuel by sodium entering the fuel pin, and these isotopes should appear in the sodium coolant prior to extensive washout of oxide fuel from the cladding. Various techniques for monitoring fission product isotopes in the sodium coolant have been considered (see ANL/ST-4, pp. 29-32). These techniques all involve the separation of radioactive fission products from the high level of ^{24}Na present in the sodium, followed by gamma-spectrometric assay.

Current emphasis is on the development of a method for monitoring the concentration of iodine in reactor sodium by gamma assay of the xenon daughter. The iodine and xenon isotopes of primary interest for reactor application are ^{135}I (6.7 hr) and $^{135\text{m}}\text{Xe}$ (15.6 min). The advantages of these isotopes over other iodine-xenon pairs have been previously discussed (ANL/ST-4, p. 30).

The present approach to monitoring iodine involves (1) sampling of reactor sodium in a special cell, (2) sparging of the sample with inert gas to strip the sodium of xenon, (3) allowing xenon daughters of iodine retained in the sodium to build up for a predetermined time, (4) restripping the sample with inert gas and trapping the xenon produced from iodine decay, and (5) gamma assay of the trapped xenon for $^{135\text{m}}\text{Xe}$ and calculation of the concentration of ^{135}I from this assay.

In the development of the iodine-monitoring concept, information is needed on the time required for inert gas sparging of xenon from a coolant sample and the efficiency of devices for separating sodium aerosols produced by sample sparging. The former is important in evaluating the overall time interval for sampling and analyses, and the latter is important for accurate assay of trapped xenon by gamma counting.

An experimental apparatus for obtaining this information is being fabricated. The apparatus, schematically shown in Fig. 3-1, consists of (1) a small-scale ($\sim 750\text{ cm}^3$ capacity) pumped sodium circuit for introducing xenon activity into a combination sampling-stripping vessel ($\sim 500\text{ cm}^3$ capacity) at a preselected temperature and pressure, (2) controls and equipment for purifying and feeding inert sparge gas to the stripping vessel, (3) an aerosol trap, gas flowmeter, and

Fig. 3-1. Apparatus for Xenon-Stripping Tests

two xenon traps through which stripper effluent gases can be directed, (4) a detachable drain-feed vessel to permit introduction of sodium to the system and to allow for removal of sodium contaminated with added trace isotopes, and (5) suitable piping, valves, pressure gauges, and vacuum for control of gases and sodium during experimental operations. Components of the system in contact with liquid sodium will be constructed of Type 304 or 316 stainless steel and will be designed for operation at a maximum temperature of 500°C. Xenon released from the stripping vessel during sparging will be trapped on Type 5A Molecular Sieves or on silica gel cooled to -196°C.

Because of the short half-life (15.6 min) of ^{135m}Xe , the isotope of interest for reactor application, 5.3-day ^{133}Xe will be utilized in the laboratory experiments to obtain the requisite data on xenon sparging. In subsequent experiments, ^{22}Na or ^{24}Na will be charged to the apparatus to assist in evaluation of the efficiency of the aerosol trap. For an initial test, a gas mixture consisting of 1 Ci ^{133}Xe , 0.1 vol % carrier xenon, and the remainder helium will be added to the gas zone of the gas-sodium contacting vessel at 1 atm pressure. The xenon will be dissolved in 450°C sodium recirculated between the contacting and stripping vessel.

Calculations based on the solubility data of Veleckis (see ANL/ST-4, pp. 44-48) indicate that at equilibrium about 10^{13} atoms of total xenon containing 4×10^{10} atoms of ^{133}Xe will be present in the 500 cc of sodium in the stripping vessel. The activity present ($\sim 6 \times 10^4$ dps) is believed adequate to permit its release to be followed by gamma counting. The total number of xenon atoms in the stripper can be controlled by variation of the initial xenon concentration in the gas phase or variation of the sodium temperature.

After a suitable contacting period, the stripping vessel will be isolated from the sodium system and valves of the gas-control system will be adjusted to permit stripping of the xenon from the sodium with pure helium. As indicated in Fig. 3-1, helium and xenon leaving the vessel will be directed through an expansion chamber above the power-activated valve, a sodium aerosol trap, then through the primary trap, where xenon is separated from the helium by selective adsorption. Present plans are to monitor both the stripping vessel and primary xenon trap for xenon activity during the sparging operation to determine the removal rate and assist in evaluation of activity-holdup problems in the system tested. If desired, activity collected in the primary trap during the experiment can be transferred to a detachable secondary trap either for disposal or for external analysis of the specific activity of ^{133}Xe . These data will be used to determine mass transfer coefficients.

A multichannel gamma spectrometer, designed for performing single- or dual-parameter counting under either internal or computer control, is being procured for general use in the development of radioisotope monitoring methods, and this instrument will be used in the studies of the iodine-monitoring concept. Delivery is scheduled for January 1971.

Fabrication and procurement of other equipment for the iodine-monitoring studies are proceeding. Components of the sodium recirculation system, including the gas-contacting vessel and manifold, the sodium drain-feed vessel, and a magnetic pump have been fabricated or are on hand. The following items have been ordered: (1) two lithium-drifted germanium detector systems and associated electronics for use with the multichannel gamma spectrometer and (2) filter, valves, flowmeter, and pressure gauges for the gas-control system. Delivery of these items is expected by March 1971. Design of the piping layout, including heaters and insulation, has been started.

3.2 Evaluation and Control of Sodium Aerosol Problems

This program, which has been directed toward determining sodium aerosol properties, investigating the mechanism of aerosol formation, and studying methods of aerosol control, has been deferred because of budgetary limitations.

4. SODIUM CHEMISTRY (F. A. Cafasso)

4.1 Characterization of Nitrogen-Bearing Species in Liquid Sodium (A. K. Fischer)

The experimental study of the chemistry of nitrogen in liquid sodium is connected with the mission of developing methods for analyzing reactor sodium for nonmetallic species. In this study, information is sought on the existence, identification and behavior of nitrogenous species in sodium. In previous quarterlies (ANL/ST-2, -3, and -4) the approach, experimental procedures and some early findings on the role of calcium as a nitrogen-interacting element in sodium at 590°C have been presented. Current work has focused on the interactions between nitrogen, calcium, and phosphorus in sodium.

Briefly, the experiments have involved (1) measurement of nitrogen absorption at 590°C by sodium, Na-1 at. % Ca, and Na-1 at. % Ca-1 at. % P; (2) determination of the degree of nitridation of stainless steel tabs submerged in these solutions; (3) assay of the sodium for calcium and for selected carbon- and nitrogen- bearing species; and (4) deduction of the probable nitrogen carrier from the findings.

The absorption experiments which were done at 590°C and under pure nitrogen at 720 Torr are as follows:

- Expt. 1. The melt was 0.01 g-atom Ca in 0.99 g-atom Na.
- Expt. 3. This experiment was a "dry" blank with no melt.
- Expt. 4. The melt was nominally pure sodium (no calcium added).
- Expt. 6. This experiment was a duplicate of Expt. 1.
- Expt. 7. The melt was initially of the same composition as in Expt. 1.

Experiment 7 differed from the others in that it was done in three parts. The system was initially heated at 590°C in helium for two days and then cooled to room temperature. The helium was replaced with nitrogen and a five-day absorption experiment (7A) was performed at 590°C. After cooling, the nitrogen in the vessel was replaced with a fresh charge, and absorption measurements were made over a period of fourteen days (Expt. 7B). The system was cooled again and 0.01 g-atom of phosphorus was added to the sodium-calcium mixture (Expt. 7C). The reactions between sodium, calcium, and phosphorus were allowed to proceed at 590°C in a helium atmosphere for about 2 hr. After cooling the system to room temperature once again, the helium was replaced with nitrogen, and standard absorption measurements were made at 590°C.

The results of these experiments are discussed below.

Nitridation of Tabs. Tabs immersed in nominally pure, calcium-free sodium (Expt. 4) experienced considerable nitridation¹ (initial level, 375 ppm; final level, 1800 ppm). Tabs submerged in experiments with added calcium (1 and 6) were not significantly nitrided (330 and 440 ppm, initial and final levels, respectively). Apparently, nominally pure sodium promoted nitridation, whereas the addition of calcium had an inhibiting effect. This finding contradicts a frequently cited² conjecture that calcium functions as a nitrogen carrier and thereby promotes nitridation.

Analysis of Sodium. Accumulated evidence^{3,4} indicates that cyanide may form in sodium containing carbonaceous impurities when the sodium is maintained under a nitrogen atmosphere. Moreover, stainless steel tabs immersed in solutions of cyanide in sodium have been found to undergo nitridation.⁵ This information suggested the possible involvement of cyanide in nitridation phenomena. Accordingly, samples of sodium were taken from selected experiments, after their completion, and analyzed for cyanide.

In Expt. 4, in which no calcium had been added, the cyanide content of the sodium was 244 ppm. This corresponds to a total of 2.15×10^{-4} g-atom C in the melt. In Expt. 6, in which calcium had been added, the cyanide level was below the detection limit (<7.4 ppm), which is equivalent to $<6.5 \times 10^{-6}$ g-atom C in the melt. Although these results suggest the formation of cyanide, the exact nature of the Ca-N-C interaction in sodium is probably more complex and is difficult to define. For example, in Expt. 6 some "slushy" sodium adhering to test tabs was analyzed for calcium and for nitrogen by the Kjeldahl method. The resulting overall atom ratio (Ca:N = 1.51:1) suggested that Ca_3N_2 had formed and precipitated. However, it also was noted that when the white calcium-containing residue from the Kjeldahl dissolution was treated with acid, it behaved like a carbonate. This suggests that perhaps part of the original material in the sodium might have been calcium cyanamide, CaCN_2 , because the hydrolysis of CaCN_2 (in the Kjeldahl dissolution) would lead to the formation of carbonate:

¹No concomitant increase in the carbon content of the tabs was observed.

²L. F. Epstein, Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, Argonne, Ill., Nov. 7-9, 1968, ANL-7520, Part I, p. 36 (1969).

³E. W. Hobart, R. G. Bjork, Nucl. Appl. 1, 490 (1965).

⁴"Chemical Engineering Division Semiannual Report July-December 1965," ANL-7125, pp. 140-141 (1966).

⁵"Chemical Engineering Division Research Highlights," ANL-7550, p. 69 (1969).

It is conceivable that in the presence of calcium, carbon in sodium reacts with nitrogen at the gas-sodium interface to form calcium cyanamide. There are three conceivable routes for the formation of cyanamide. First, it may form by the reaction between CaC_2 and N_2 .⁶ Second, it may form via the thermodynamically feasible reaction

We believe that Ca_3N_2 already is present from reaction between calcium and nitrogen, and further reaction to yield CaCN_2 might be possible. Third, cyanide itself can be a cyanamide precursor: it is known that $\text{Ca}(\text{CN})_2$ and CaCN_2 interconvert reversibly according to the following reaction:⁷

These considerations suggest that either cyanide or cyanamide or both may form in a calcium-containing sodium solution. The precipitation of either calcium cyanide or calcium cyanamide from a calcium-sodium solution would account for the absence of cyanide in these calcium experiments. Moreover, either of these precipitation reactions would effectively remove carbon as a possible nitrogen carrier and might, in part, account for the results observed in the calcium-sodium systems.

Nitrogen Uptake. Figure 4-1 shows the variation of uptake of nitrogen with time for each of the experiments except 3. No curve is plotted for this "dry", blank experiment because no nitrogen was absorbed; hence the curve, if it were shown, would be identical to the X-axis of the figure.

The interpretation given to the curves is that (1) the linear portions represent nitrogen absorbed by the stainless steel and (2) the intercepts obtained by linear extrapolation (dashed line) to time zero represent nitrogen consumed by processes other than nitridation of stainless steel, i.e., by reaction in sodium and by absorption on surfaces. The nitrogen uptake by stainless steel is believed to occur mainly at the ring of intersection of the liquid surface with the container wall. (The submerged tab, even when nitrided as in the calcium-free experiment, made only a small contribution to the overall nitrogen uptake.) This belief is supported by the finding of 5000 ppm nitrogen in filings taken from a reaction-vessel⁸ section in this region. No attempt will be made to

⁶ Calcium cyanamide is produced commercially by this reaction.

⁷ The melting point of $\text{Ca}(\text{CN})_2$ has not been observed because the compound converts to CaCN_2 above 350°C.

⁸ See ANL/ST-2, p. 6-4 for description of vessel.

interpret differences in slope among the curves. Differences in the wetting of the Type 304 stainless steel vessel walls by sodium refluxing above the melt surface could account for the differences in nitridation rate and no way is available to assess this possibility. The interpretive emphasis, then, will be on the intercepts.

Information on the amount of nitrogen reacting with calcium and/or impurities is extractable from the intercepts provided that a measure of the nitrogen uptake due to surface absorption is available. Experiment 7B was done to obtain the requisite information. This experiment involved replacing the nitrogen atmosphere that had been present in the first part of the experiment (7A) with fresh nitrogen, reheating, measuring nitrogen uptake as a function of time, and then extrapolating the curve to time zero. As shown in Fig. 4-1, this curve (7B) intercepts the Y-axis at 1.0×10^{-4} mol N_2 .⁹ This value, which is believed to be the amount of nitrogen uptake due to absorption only, must be subtracted from the intercepts of the other curves to obtain the nitrogen absorbed due to reactions with calcium and/or impurities. Table 4-1 summarizes the results of this calculation for the various experiments.

A semi-quantitative analysis of the absorption curves is now possible within the framework of our limited understanding of the pertinent chemistry. In Expt. 4, no calcium was present to form $CaCN_2$. The carbon that was present in the sodium as cyanide (244 ppm)² at the end of the experiment represented 2.15×10^{-4} g-atom N. The corrected zero-time intercept in Expt. 4 was 9.0×10^{-4} g-atom N. If one makes the admittedly questionable assumption that the cyanide content at the end of the experiment corresponds to cyanide that formed at time zero, then the amount of nitrogen that was consumed in reaction with impurities other than carbon (to form cyanide) may be estimated to be $9.0 \times 10^{-4} - 2.15 \times 10^{-4} = 6.8 \times 10^{-4}$ g-atom N. In other words, we estimate (with some reservations) that of the total amount of nitrogen reacting with impurities, about one-fourth reacted with carbon.

In Expt. 7A, the conditions were such that calcium could getter carbon (to form CaC_2 , perhaps) and other getterable impurities before nitrogen was admitted. The difference between the corrected zero-time intercepts for Expts. 6 and 7A is $6.46 \times 10^{-3} - 5.68 \times 10^{-3} = 7.8 \times 10^{-4}$ g-atom N. This amount of nitrogen is in fairly good agreement with the 9.0×10^{-4} g-atom N estimated to have been consumed in impurity reactions in Expt. 4 and, therefore, provides some support for the estimate given above.

⁹Other experiments, not described here, have also yielded this value.

Fig. 4-1. Nitrogen-Absorption Experiments at 590°C and 720 Torr

Table 4-1. Calculated Amounts of Nitrogen Reacting
with Impurities in Sodium

<u>Expt. No.</u>	<u>Intercept (mol N₂)</u>	<u>Correction (mol N₂)</u>	<u>Nitrogen Reacting with Impurities</u>	
			<u>(mol)</u>	<u>(g-atom)</u>
4	5.5×10^{-4}	1.0×10^{-4}	4.5×10^{-4}	9.0×10^{-4}
6	3.33×10^{-4}	1.0×10^{-4}	3.23×10^{-3}	6.46×10^{-3}
7A	2.94×10^{-3}	1.0×10^{-4}	2.84×10^{-3}	5.68×10^{-3}
7C	3.50×10^{-4}	1.0×10^{-4}	2.50×10^{-3}	5.00×10^{-4}

Experiment 7C was performed to determine the effects of phosphorus addition on nitrogen uptake. The slope of the linear part of the curve for 7C is similar to the slope of the other curves. Although no attempt has been made to interpret differences in slopes between the various curves, it probably is justified to state that there appears to be no gross effect on the nitridation rate when phosphorus is added to the system. In regard to the intercept, the corrected value of 5.0×10^{-4} g-atom nitrogen indicates that very little nitrogen was consumed in reactions with phosphorus or impurities--less, in fact, than in the case of nominally pure sodium (Expt. 4). This is surprising since one would expect a reaction between nitrogen and phosphorus, for example, via the following reaction:

Apparently, the bulk of the phosphorus was not available for reaction with nitrogen. It may have been tied up as Ca_3P_2 , Na_3P , or Na_2P_5 .

Conclusions. Nitrogen absorption experiments show that calcium added to sodium inhibits the nitridation of Type 304 stainless steel that is submerged under sodium. These data suggest that this inhibition may result from the removal of nitrogen carriers by virtue of reaction between calcium and the carriers to form compounds that are insoluble or are inactive as nitriding agents. A conceivable carrier for nitrogen is carbon in the form of cyanide, and the removal process with calcium could be the formation of CaC_2 (calcium carbide) and/or $CaCN_2$ (calcium cyanamide). On the basis of certain assumptions and reasonable extrapolations, one can estimate from the curves for the nitrogen-absorption experiments that of the total amount of nitrogen that reacts with impurities in the sodium perhaps one-fourth reacts with carbon. The nature of these other impurities is unknown. The addition of 1 at. % phosphorus (a possible reactive impurity) to a calcium-sodium solution produced no significant increase in nitrogen uptake. This finding suggests that phosphorus was not one of the unknown reactive impurities in such a solution.

Work on this project has terminated due to reallocation of funding.

4.2 The Sodium-Sodium Oxide-Sodium Hydroxide-Sodium Hydride System (K. M. Myles, R. D. Wolson)

Investigation of the nature and behavior of oxygen- and hydrogen-bearing species in liquid sodium is continuing. The effort at present is directed toward the elucidation of the phase

relations that exist between Na, Na₂O, NaOH, and NaH at room temperature. When complete, this information will provide a foundation for determining which one of two potential phase diagrams of the Na-Na₂O-NaH-NaOH system (see ANL/ST-3, pp. 4-4 to 4-13) is more correct, i.e., which of the two diagrams should be used to guide further work in this area.

The experimental technique involves welding mixtures of Na, Na₂O, NaOH, and NaH in nickel capsules, subjecting the mixtures to various heat treatments, cooling gradually to room temperature, and examining the products with an X-ray diffractometer. In recent experiments, various mixtures of Na-Na₂O-NaH, Na-NaOH, and Na₂O-NaOH-NaH were heated to 500-600°C and slowly cooled in an attempt to achieve room-temperature equilibrium. Thus far, caking and consequent separation of the reaction products has inhibited further reactions from occurring as the samples were cooled. Efforts are currently being directed toward circumventing this difficulty by modifying the experimental procedure.

In other experiments, capsules at 500°C were quenched rapidly in an attempt to retain the high-temperature phases at room temperature. These preliminary experiments have indicated that NaOH is an equilibrium phase near 500°C.

5. PURIFICATION OF SODIUM (J. T. Holmes)

5.1 Characterization of Cold-Trapped Sodium (C. C. McPheeters)

The purpose of this work is to determine the effect of cold trapping on nonmetallic impurities (O, C, H, N) in sodium. The Apparatus for Monitoring and Purifying Sodium (AMPS) as well as the EBR-II primary-coolant purification system will be utilized for the experimental work. AMPS, which will provide sodium having stable but adjustable impurity levels for cold trapping and monitoring tests, will permit testing under controlled conditions. Tests in the EBR-II installation will permit testing under reactor-operating conditions. This information will provide insight into the effect of cold-trapping parameters on impurities.

A meeting was held¹ in October 1970 to discuss the process diagram and the conceptual design description of AMPS. The design was approved with no major changes. Preliminary specifications for fabrication of major vessels and the sodium-level indicator have been prepared. The piping and equipment layout is essentially complete. A stress analysis of the system has been made, pipe hanger locations have been chosen, and detailed design of components is being started. The scheduled date of completion for AMPS is Nov. 1, 1971.

¹With personnel of the Engineering and Technology Division of ANL, who are doing the design work for AMPS.

6. MATERIALS-COOLANT COMPATIBILITY (T. F. Kassner)

6.1 Studies of Carbon Transport in Sodium-Steel Systems (K. Natesan, T. F. Kassner, C. A. Youngdahl)

The objectives of this work are an understanding of the thermodynamics and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and a correlation of the compositional and microstructural changes with mechanical behavior of these materials. These studies will allow predictions to be made regarding the structural integrity of these steels in a reactor system.

6.1.1 Distribution of Carbon Between Austenitic Iron-Base Alloys and Liquid Sodium

Additional experiments to determine the distribution of carbon between sodium and iron or iron-base alloys (viz., Types 304 and 316 stainless steel, Fe-18 wt % Cr-8 wt % Ni, Fe-8 wt % Ni) are in progress. Results of previous equilibration experiments with iron and austenitic alloys in the temperature range 600 to 750°C in flowing sodium^{1,2} suggest that the carbon concentration in sodium was in the sub-ppm range. In an attempt to confirm our result, sodium samples were taken during these experiments and were analyzed for carbon via the oxyacidic flux method.³ Considering the problems attending analyses in the sub-ppm range and the unresolved question concerning the detection limit of the oxyacidic flux method, the limited agreement between our result and the analytical data was acceptable.

Because analyses for carbon in sodium can be performed with a higher degree of confidence at the ppm level and above, an attempt is being made to increase the carbon content in our sodium system. This is being done by locating a carburized iron source downstream from the specimens in the molybdenum test section. Before equilibrating the austenitic alloys in sodium, iron foils and vanadium and iron wires were exposed in the specimen positions to determine the effect of the carbon source on the carbon potential in sodium. Internal friction analyses of iron and vanadium wires as well as combustion analyses of iron foils indicated that the carbon concentrations in sodium were significantly raised by the presence of the carbon source.

¹K. Natesan, T. F. Kassner, J. Nucl. Mater. 37, 223-235 (1970).

²"Sodium Technology Quarterly Report, July, August, September, 1970," ANL/ST-4, pp. 50-52 (December 1970).

³C. C. Miles, Anal. Chem. 41, 1041-1048 (1969).

The austenitic alloy samples (of 2-mil thickness) were exposed to the flowing sodium in the presence of the carbon source at 650 and 750°C with a cold trap temperature of 125°C for a period of 340 hr. Iron and vanadium wires and iron foils were also included in the experiment. Two sodium samples were obtained in flow-through samplers during the course of the experiment. Combustion analyses of the equilibrated foil specimens indicated a substantial increase in the carbon concentrations; for example, the carbon concentration in Types 304 and 316 stainless steel increased from 0.045 wt % and 0.074 wt % to 0.64 wt % and 1.13 wt %, respectively, at 750°C. The iron, Fe-8 wt % Ni, and Fe-18 wt % Cr-8 wt % Ni foils also showed significant increases in carbon concentration. The internal friction analyses of vanadium and iron wires and the carbon analyses of sodium samples are being obtained. This experiment will yield information on the carbon activity in sodium, the sensitivity of the oxyacidic-flux method for carbon, and the carbon distribution values between sodium and the austenitic alloys. A similar experiment with a carbon source is in progress. To obtain additional data, experiments will also be conducted in a molybdenum test section attached to the Core Component Test Loop at the prevailing carbon level in sodium.

6.1.2 Measurements of Carbon Activities in Fe-Ni and Fe-Cr-Ni Alloys

Measurements of carbon activities over a wide range have been undertaken in Fe-Cr-8 wt % Ni alloys, with chromium contents ranging from 0 to 22 wt %. The experiments involve equilibration of the Fe-Cr-Ni alloys with carburized Fe-8 wt % Ni alloys whose carbon activities are known or are being determined. The experimental procedure was described in quarterly report ANL/ST-2, p. 4-1; also reported were isoactivity lines for carbon at 900°C. Data at 800°C were reported in ANL/ST-3, p. 6-2. Similar data at 725, 660, and 600°C have been obtained for the carbon concentrations in Fe-Cr-8 wt % Ni alloys as a function of chromium content; however, carbon activities cannot be assigned to the curves until measurements of carbon activities (with graphite as the standard state) are completed for Fe-8 wt % Ni alloys at these temperatures. This work, described in ANL/ST-4, pp. 52-55, is still in progress.

Three austenitic stainless steels (Types 304, 316, and 347), whose compositions are given in Table 6-1, were equilibrated in Vycor capsules at 800°C and 700°C with Fe-8 wt % Ni alloys at several carbon activities. The metal specimens used in these experiments were 2 to 3 mils thick. The carbon concentrations in these alloys after equilibration are given in Tables 6-2 and 6-3;

Table 6-1. Composition of Austenitic Stainless Steels
 (Concentrations are given in wt %; the remainder is iron)

<u>Type</u>	<u>C</u>	<u>N</u>	<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>Mo</u>	<u>Si</u>	<u>Nb</u>	<u>Ti</u>	<u>Zr</u>	<u>V</u>	<u>Co</u>	<u>Cu</u>
304	0.047	0.045	19.28	9.23	1.69	0.44	0.42	0.015	0.001	<0.001	0.2	0.05	0.2
316	0.074	0.033	17.04	12.92	1.46	2.26	0.37	0.08	0.004	<0.001	0.1	0.05	0.2
347	0.064	0.049	19.21	11.09	0.94	0.09	0.62	0.68	0.015	0.12	0.2	0.05	0.1

Table 6-2. Carbon Analyses of Commercial Alloy
Samples Equilibrated at 800°C

<u>Capsule Number</u>	<u>Fe-8 wt % Ni</u>	<u>Carbon Concentration (ppm)</u>		
		<u>Type 304 SS</u>	<u>Type 316 SS</u>	<u>Type 347 SS</u>
1	27.9	541	863	960
2	40.5	670	1098	1135
3	57.0	935	1590	1510
4	58.3	930	1710	1760
5	78.3	1210	1980	1920
6	111.0	1520	2500	2210

Table 6-3. Carbon Analyses of Commercial Alloy
Samples Equilibrated at 700°C

<u>Capsule Number</u>	<u>Fe-8 wt % Ni</u>	<u>Carbon Concentration (ppm)</u>		
		<u>Type 304 SS</u>	<u>Type 316 SS</u>	<u>Type 347 SS</u>
1	17.7	1045	705	675
2	26.3	1260	930	885
3	33.5	1460	1245	1085
4	49.5	1850	--	1380
5	58.8	2000	1510	1470

each value is an average of duplicate determinations. Similar equilibrations at 600°C are in progress.

The carbon activities corresponding to the carbon concentrations in these steels will be reported when the carbon activity studies in Fe-8 wt % Ni alloys are completed. The above results will provide a means of extending the results for distribution of carbon between sodium and iron-base alloys (Fe, Fe-8 wt % Ni, Fe-Cr-8 wt % Ni, and commercial austenitic stainless steels) over a much wider range of carbon activities than can be achieved experimentally in loop systems in a reasonable time period.

6.1.3 Diffusivity of Carbon in Ferritic Fe-Cr-Mo Alloys and Austenitic Fe-Cr-Ni Alloys

An experiment to determine the diffusivity of carbon in ferritic Fe-Cr-Mo and austenitic Fe-Cr-Ni alloys by a steady-state method was described in ANL/ST-4, pp. 56-57. The first assembly consisting of four Fe-2.25 wt % Cr-1 wt % Mo alloy specimens was exposed to various $\text{CH}_4\text{-H}_2$ carburizing gas mixtures at 700°C. The flux of carbon through the samples was obtained by collecting the methane in decarburizing gas mixtures at temperatures between -218 and -238°C and analyzing the condensate by gas chromatography. The cylindrical samples are being sectioned to determine the carbon concentration profile across the wall. This experiment will give data on the diffusion coefficient as a function of carbon level in the alloy. A second assembly with Fe-2.25 wt % Cr-1 wt % Mo alloy and Armco iron samples is being constructed; this assembly will be exposed to $\text{CH}_4\text{-H}_2$ mixtures at 800°C.

6.2 Determination of Nonmetallic Impurities in Sodium by the Equilibration Method (D. L. Smith)

The purpose of this work is to develop methods for accurately measuring the activity of nonmetallic elements, e.g., O, C, N, and H, in sodium at the low concentrations of interest for LMFBR applications.

6.2.1 Development of the Vanadium-Wire Equilibration Method for Determination of Oxygen in Sodium

The procedure for determining the oxygen activity in liquid sodium by the vanadium-wire equilibration method has been

reported,⁴ as has the required distribution coefficient data.⁵ The present effort in this area is directed toward 1) standardization and characterization of the method and 2) comparison of the results with other methods of oxygen analysis.

Standardization and Characterization. The equilibration method can be used satisfactorily under a variety of conditions of sample geometry and equilibration temperature. For LMFBR-related applications, a standard procedure has been recommended (0.25-mm-dia vanadium wire equilibrated in 750°C sodium for 4 hr) to facilitate interlaboratory comparison of analyses. Additional measurements have been made under these standard conditions of exposure to demonstrate the precision of the method.

After exposure to sodium cold-trapped at various temperatures, the vanadium wires (250 mg) were analyzed for oxygen by the inert gas fusion technique.⁶ The results are presented in Table 6-4. Where duplicate analyses are given, they represent analyses of vanadium wires equilibrated simultaneously in the same sodium. The results in column 3 were obtained from equilibrations subsequent to those in column 2 while the conditions (sodium temperature and oxygen content) were maintained constant within experimental capability. The results in column 4 were obtained after the oxygen concentration in sodium had been changed for a period of time and then returned to the initial level. The agreement of duplicate analyses is an indication of the good precision of the equilibration method. Comparison of the results in column 2 with those of columns 3 and 4 also gives an indication of the experimental capability of controlling the oxygen concentration in sodium and the equilibration temperature in the system used for the distribution coefficient measurements.

Comparison of the Wire-Equilibration Method with Other Methods of Oxygen Analysis. The wire-equilibration method was compared with other methods of oxygen analysis in a flowing sodium system, in which the oxygen content was controlled by cold trapping at various temperatures. The system performance was examined by means of vanadium wires and vacuum distillation analyses, and the oxygen content was related to the cold trap temperatures by the following

⁴D. L. Smith, "An Equilibration Method for Measuring Low Oxygen Activities in Liquid Sodium," to be published in Nucl. Appl. Technol., May 1971.

⁵D. L. Smith, "Investigation of the Thermodynamics of V-O Solid Solutions by Distribution Coefficient Measurements in the V-O-Na System," Met. Trans. 2, 579-583 (February 1971).

⁶Analyses performed in the Chemistry Division, ANL.

Table 6-4. Typical Analyses of Oxygen in Equilibrated Vanadium Wires (Exposure Conditions: 750°C, 4 hr)

Test No.	Oxygen Concentration in Vanadium (wt %)		
	Initial Exposure	Subsequent Exposure	
		Constant Conditions ^a	Varied Conditions ^b
1	0.638, 0.635	0.608, 0.618	
2	0.865, 0.865	0.877, 0.878	
3	0.995, 0.987		
4	1.14, 1.139		1.12, 1.13
5	1.40, 1.39		
6 ^c	1.22		1.22
7 ^c	1.39	1.36	
8 ^c	0.48	0.51	

^aOxygen concentration of sodium maintained at the initial level.

^bOxygen concentration of sodium changed and then returned to initial level.

^cNon-standard equilibration conditions; lower equilibration temperatures and correspondingly longer equilibration times.

equation for the solubility of oxygen in sodium⁷

$$\log \frac{O}{Na} \text{ (ppm)} = 6.940 - 2801 (1/T)$$

The vacuum distillation analyses confirmed that the Na-Na₂O equilibrium was established in the cold trap for the temperature range 115 to 240°C (0.5 to 30 ppm oxygen in sodium). Titration of the residue from the vacuum distillation indicated no Na₂CO₃ present; therefore, the total sodium titrated was attributed to Na₂O. No effect of sampling temperature on the vacuum distillation analyses was detected in the range 500 to 750°C.

The equilibration results were also compared with results obtained from four UNC electrochemical oxygen meters, which were used consecutively on the sodium system. Figure 6-1 is a plot of the cell voltages as a function of oxygen concentration, as determined from the solubility equation at the cold trap temperature. All the data were obtained at a cell temperature of 352°C (625°K). Also shown on the figure is the curve calculated from available free energy and solubility data on the basis of an ionic transference number of unity for the ThO₂-15 wt % Y₂O₃ electrolyte. In most cases, the plotted points were recorded after the voltage remained constant for a period of 25 hr. In general, the data were not obtained in the order of successive increases or decreases in the oxygen level. In several cases, the cell temperatures were varied between ambient temperature and ~450°C during the period in which the data were obtained. Three important characteristics of cell operation are noted from these curves. First, the curves for the different cells do not have the same slope or intercept. These differences are attributed to variations in structure or impurities in the electrolyte, which affect the conductivity.⁸ Second, the slopes are considerably greater than that of the calculated curve resulting in cell voltages that are higher than theoretical at high oxygen concentrations. Third, linear curves of $\log \frac{O}{Na}$ vs emf were obtained for all of the cells. (The curve for cell 4 covers three orders of magnitude in oxygen concentrations.) This result is in contrast to non-linear curves obtained by H. Isaacs at BNL⁹ for similar cells tested in pots containing sodium. A different method of oxygen analysis of the sodium (i.e., the uranium-tab method) was used at BNL.

⁷ D. L. Smith, T. F. Kassner, Corrosion by Liquid Metals, pp. 137-149, Plenum Press (1970).

⁸ A commercial oxygen meter is presently under investigation (see Section 1.1) that makes use of a newly developed high-purity electrolyte.

⁹ H. Isaacs, Brookhaven National Laboratory, private communication (1970).

Fig. 6-1. Cell Emf versus Oxygen Concentration in Sodium for Four UNC Oxygen Meters

Cells 2 and 4, which were operated for 2 months and 1 month, respectively, followed the curves in Fig. 6-1 for their total operational period while they were at 352°C. Cell 3 showed an increase in emf of ~ 12 mV after 10 days of operation and then followed the curve shown in the figure for its operational period of 2 months. Cell 1, which had previously been used on another apparatus, operated for 5 months in these experiments before it was replaced with a new cell.

All of the cells have been operated at different cell temperatures in the range 302 to 452°C. A period of approximately 8 hr was required to obtain a constant voltage from the cells after changing the cell temperature 25 to 50°C at a rate $\sim 1^\circ\text{C}$ per min.

In Fig. 6-2, the temperature coefficient of Cell 2 is compared with the calculated value at two oxygen levels. The agreement in slope is good at both concentrations. Better agreement between the calculated and experimental curves at 4.9 ppm oxygen is due to the fact that the calculated and experimental curves in Fig. 6-1 intersect near 4.9 ppm for Cell 2.

The sodium temperature in an LMFBR will vary from the cold-trap temperature to the maximum sodium temperature in the core. Moreover, electrochemical oxygen meters will be operated at temperatures between 300 and 500°C and their outputs must be correlated with results of vanadium-wire equilibrations, which will be conducted at 750°C. It is, therefore, important to determine whether the oxygen content of sodium, and thus the cell emf, is affected by contact of the sodium with materials of construction at the high temperatures. Accordingly, measurements of cell emf were made while the maximum temperature of the loop was varied between 450 and 750°C. In this range of maximum loop temperatures, no effect on the emf of Cell 2 was noted for oxygen concentrations in sodium between 0.34 and 30 ppm (Fig. 6-3): all data points fall on the same curve. Similar results were observed for the other cells.

The emf of Cell 3 has been compared with the oxygen concentration in sodium measured by the vanadium-wire equilibration method. The results are shown in Fig. 6-4. This cell was operated at a temperature of 402°C and the wires were equilibrated at 750°C. All points except two are within 1 mV of the curve. These two points (2.1 and 0.87 ppm) were the first taken after the cell temperature was changed to 402°C. This small discrepancy may be attributed to transient conditions in the cell-sodium system.

Fig. 6-2. Variation of Cell Emf with Temperature at 2.1 and 4.9 ppm Oxygen in Sodium

Fig. 6-3. Effect of System Temperature (500-750°C) on the Operating Characteristics of UNC Oxygen Meter

Fig. 6-4. Cell Emf versus Oxygen Concentration in Sodium Determined by the Vanadium-Wire Equilibration at 750°C

6.2.2 Application of the Equilibration Method to the Measurement of Carbon Activity in Sodium

An attempt is being made to apply the equilibration method to the measurement of carbon activities in sodium. Present work is aimed at selection of an appropriate detector metal for carbon. The properties of a suitable detector are similar to those specified previously for an oxygen detector, i.e., 1) a low solubility in liquid sodium, 2) a significant range of carbon solid solution in the metal, 3) relatively high diffusion rates for carbon in the solid, and 4) experimentally measurable distribution coefficients for carbon which are greater than unity.

Iron and vanadium both appear to be acceptable as detector metals for carbon. Vanadium has a higher carbon solubility and a larger distribution coefficient than iron; however, there is concern that the activity of carbon in vanadium, and hence the distribution coefficient, $N(C_v)/N(C_{Na})$, may be affected by the relatively high oxygen concentrations which will also be present in the vanadium as a result of equilibration in sodium. The primary disadvantage of iron results from the relatively low solubility of carbon and the low distribution coefficient. A sensitive method of carbon analysis is, therefore, required to measure the low carbon activities expected in LMFBR sodium. An advantage of iron is the available data for directly relating the carbon concentration to activity since this is the reference commonly used when considering carbon transport and carbon equilibria in stainless steel reactor components.

The major problem in developing an equilibration method for measuring carbon activities in sodium is the difficulty in varying and controlling the carbon concentration in sodium. Although carbon can be added and removed from sodium by inserting carburized tabs or carbon getters, quantitative measurements are difficult because of lack of understanding of interactions between carbon and the sodium containment material or other dissolved species in the sodium.

Some preliminary measurements have been made using vanadium and iron detectors. Several vanadium wires, which were equilibrated in various sodium systems for oxygen analyses, have also been analyzed for carbon. Carbon concentrations in these wires in the range 40 to 400 ppm have been obtained by the combustion method of analysis. In one sodium loop, a value of 180 ppm carbon in vanadium was obtained after equilibration in sodium which contained 0.4 ± 0.2 ppm total carbon as determined by C. C. Miles (ANL-ID) using the oxyacidic flux method.³ After adding carbon source (carburized Fe-8 wt % Ni alloy tab) to the sodium, a value

of 380 ppm carbon was measured in a vanadium wire. Another sodium sample obtained after the wire exposure has been sent to ANL-ID for a total carbon analysis.

Results to date indicate that vanadium can be used as a detector for carbon in sodium at the levels expected in LMFBRs. Carbon concentrations in equilibrated vanadium wires can be determined with a sufficient degree of accuracy by the combustion technique. Further work is required, however, to determine optimum exposure times and temperatures and any effects of other interstitial elements in vanadium on the distribution coefficient and the activity of carbon in vanadium.

Both combustion and internal friction techniques (see ANL/ST-4, pp. 52-55) are being used to measure carbon in the iron wires since the concentrations expected are near the limit of detection by the combustion techniques. A value of 31 ppm carbon was measured in iron samples equilibrated at 750°C in a sodium loop that contained a carburized Fe-8 wt % Ni alloy source at 650°C; this concentration can be measured with sufficient accuracy by the combustion technique. Present indications are that measurable carbon concentrations will be obtained in iron detectors equilibrated at the low activities expected in LMFBR sodium; however, further work is required to determine if iron is a satisfactory detector at the levels of interest.

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