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ARGONNE NATIONAL LABORATORY

SODIUM TECHNOLOGY QUARTERLY REPORT

JULY, AUGUST, SEPTEMBER 1970

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Compiled and Edited by
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December 1970

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SODIUM TECHNOLOGY QUARTERLY REPORT

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ABSTRACT

The research, development, and management efforts of Argonne National Laboratory's Sodium Technology Program for the period July, August, September 1970 comprised work in the following areas: (1) A national meter program was implemented 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 continued, with the goal of formulating standard analytical and sampling methods to be uniformly applied throughout the national sodium technology program; development work proceeded on methods for determining oxygen, carbon, nitrogen, and trace metals in sodium. (3) Work continued on the definition of radioactivity problems associated with the repair and maintenance of LMFBRs, the development of methods for detecting and characterizing fuel failures, and the evaluation of problems created by sodium aerosol in cover gas. (4) Studies of the chemistry of sodium included investigation of the nature of nitrogen-bearing species in sodium, elucidation of phase relations in the sodium-rich region of the Na-O-H ternary system, and measurement of the solubility of xenon in sodium. (5) Work on the purification of sodium continued with development of methods for characterization of cold-trapped sodium. (6) Studies of materials-coolant compatibility included investigations of the transport of carbon in sodium-steel systems and of the adequacy of vanadium alloys as cladding for LMFBR fuels.

FOREWORD

The major objectives of the sodium technology program at Argonne National Laboratory are to (1) provide base sodium technology support to EBR-II and other ANL-operated national test facilities, (2) demonstrate selected processes and equipment using EBR-II as a test facility, and (3) advance sodium technology in selected fundamental areas of sodium chemistry and materials compatibility. The ANL program strongly utilizes EBR-II as a test facility for the advanced equipment and procedures that are being developed for subsequent Liquid Metal Fast Breeder Reactors (LMFBRs)--the Fast Flux Test Facility (FFTF) including

the FFTF test loops, demonstration LMFBRs, and finally commercial LMFBRs.

The Coolant Chemistry Branch of the AEC Division of Reactor Development and Technology has assigned ANL the lead role in the area of sodium quality control and measurement. Also assigned to ANL are supporting roles in the areas of fission product behavior and control, cover gas technology, and materials-coolant compatibility. The lead and supporting roles are designed to provide cross linkages between contractors and thus promote close working relationships. The program is highly mission-oriented, being directed mainly to filling the urgent needs of FFTF, although some work is directed beyond FFTF to the early demonstration LMFBRs.

In the areas of sampling and analysis and on-line monitoring of impurity elements, ANL not only has a research and development role, but also has been assigned a management role associated with the coordination of national efforts needed to meet near-term needs in these areas. In the sampling and analysis area, the management program is called the Analytical Standards Program. The purpose of this program is to standardize sampling and analytical methods in current use within the LMFBR community. In the on-line monitoring area, the program is called the National Meter Program. The purpose of this program is to have available design specifications for meters of proven capability so that they can be manufactured to fill needs as they arise.

This report presents the results of research and development work performed in two ANL divisions--Chemical Engineering and Materials Science. Since the Sodium Technology Program was established at ANL to achieve program coordination between divisions, further reports will present, as appropriate, work of the divisions involved.

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SUMMARY

ON-LINE IMPURITY MONITORS

Oxygen Meter Modules. A program has been established that is expected to result in the commercial availability of improved electrochemical oxygen meters by July 1971. In support of this program, a pumped sodium apparatus has been constructed to proof-test up to four oxygen meters, and operation of the apparatus is beginning.

An important test of the effect of radiation on currently available oxygen meters is being planned for initiation at EBR-II early in 1971. Design of equipment is complete and fabrication of components for this test has begun.

A preliminary conceptual design has been developed 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 concept are being incorporated in the detailed design which has begun.

A preliminary conceptual design has been completed for an on-line module that will be used for oxygen-meter calibration; the calibration method to be used is the equilibration and analysis of vanadium metal specimens.

Apparatus is being designed to provide for the characterization of ten oxygen meters as part of the national meter program. The apparatus will have provisions for up to ten meters and an on-line calibration device.

Carbon Meter Module. A new carbon meter housing with a relatively inert (molybdenum) liner, a device for exposing metal specimens, and a bypass sampler have been added to the Test and Evaluation Apparatus (TEA). The system has been tested and is now being filled with sodium. Work will proceed to (1) establish a standard probe and housing design, (2) establish recommended operating temperature, decarburizing gas composition, and sodium flow rate. Attempts will be made to correlate carbon meter readings with activities determined from metal specimens equilibrated with the carbon contained in the sodium in TEA.

Hydrogen Meter. Development work on the ANL diffusion-type hydrogen-activity meter is being continued. Either this meter, which is being given prime consideration, or the UNC electrochemical

meter will serve as the on-line meter component of an oxygen-hydrogen meter module. Earlier studies with the ANL hydrogen-activity meter showed that equilibrium hydrogen pressures measured in a gas-flow system with standardized hydrogen-argon gas mixtures were approximately 25% lower than the values calculated from gas-chromatographic analyses. Recent information has indicated that the discrepancy resulted from an incorrect factor for calibrating the ion gauge for use with hydrogen. This factor has been revised, and our measured pressures are now in good agreement with results of gas-chromatographic analyses.

Tritium data reported by EBR-II for the secondary and primary sodium systems have been used to calculate the in-sodium level of hydrogen in these systems. The technique assumes that tritium is a radioactive tracer for hydrogen, and utilizes the tritium data to calculate the distribution coefficient of hydrogen between the sodium and the cover gas. Since the distribution coefficient varies with the level of hydrogen dissolved in the sodium (Sievert's law), one can determine the level of hydrogen present in the sodium from the distribution coefficient and the Sievert's law constant for the hydrogen-sodium system. The results of this analytical technique indicate the secondary sodium at EBR-II contains 0.2-0.3 ppm of dissolved hydrogen as hydride, whereas the primary sodium contains about 0.4 ppm of hydrogen as hydride.

Detection of Leaks in Steam Generators. Plans are being made to supply an ANL hydrogen-meter leak detector for the Sodium Component Test Installation (SCTI) at IMEC for use in their test of the AI "hockey stick" steam generator, which is scheduled for spring of 1971. Design work is also underway for a leak detection system to be installed on the secondary systems at EBR-II.

ANALYTICAL STANDARDS PROGRAM

Analytical Standards Laboratory. The operation of the Analytical Standards Laboratory is a combination of laboratory and administrative work. The experimental activities result from ANL participation in the methods-testing programs; the administrative activities, from coordination of the Analytical Standards Program. Within the Analytical Standards Program, two advisory working groups have been formed: A Reactor Standards Working Group and a National Standards Working Group.

Plans are proceeding for a sample-interchange program among participants in the Reactor Standards Working Group. Arrangements have been made with EBR-II to supply samples of sodium for oxygen, carbon, hydrogen, and trace-metal analyses for the sample-interchange tests. An updated methods manual to be used in these tests is nearly complete.

At a planning meeting of analytical chemists from laboratories participating in the National Standards Working Group, agreement was reached concerning the methods to be used by this group. A meeting of the group is scheduled for mid-November, and ANL is now preparing a methods manual to be used by the group.

Recent laboratory work has been directed primarily toward procurement and assembly of apparatus for determining oxygen, hydrogen, carbon, and trace metals. The procedure for trace-metal analysis involves distillation of a sample of sodium and emission spectrographic analysis of the residue. A test of the procedure using a sample of EBR-II sodium showed good agreement between the emission spectrographic analysis and results of atomic-absorption spectrographic analyses reported by EBR-II. Work has begun to establish a procedure for characterizing particulate matter in sodium.

Development of Reference Methods for the Determination of Total Oxygen, Carbon, and Nitrogen in Sodium. Experiments are in progress to provide data for further evaluation of proton-activation analysis for the determination of total oxygen in sodium. A combined sampling and irradiation cell has been used to obtain two samples from a sodium loop and to irradiate them in a well-stirred molten state. Results indicated that interference from other induced activities could be either adequately controlled or circumvented and that the sensitivity for oxygen attainable in this cell approaches 1 ppm. The design of a new cell, which provides an improvement in the signal-to-background ratio and in the counting geometry, is expected to increase the sensitivity of the oxygen analysis to 0.1 ppm.

Method for the Determination of Metal and Halide Impurities in Sodium. A survey method is being developed for the rapid and routine determination of changes in metallic impurity levels in sodium. The method selected for further evaluation is emission spectroscopy utilizing induction-coupled plasma excitation of a metal-dust aerosol formed by ultrasonic nebulization of molten sodium. Work is in progress on testing of components and assembly of an integrated set-up for performing the necessary experimental measurements.

FISSION PRODUCT AND COVER GAS TECHNOLOGY

Radioisotope Problem Areas. Program plans have been issued by Atomics International, General Electric, and Westinghouse for developing technology required to solve the radioactivity problems associated with maintenance of LMFBRs. ANL is formulating a similar program plan; the ANL plan will emphasize utilization of EBR-II. As a first step in the program, means must be found for measuring system contamination. This can probably best be done by insertion in the primary sodium system of removable surfaces, e.g., tabs, which would be examined for activity buildup during experiments in which activity is released.

Development of Radioisotope Monitoring Methods. Work is underway on three new concepts for monitoring the primary coolant of an LMFBR to yield information regarding the condition of fuel failures. These concepts are (1) on-line distillation of sodium to permit analysis of volatilized cesium and rubidium isotopes, (2) determination of ^{135}I in sodium by separating and counting its daughter $^{135\text{m}}\text{Xe}$, and (3) determination of nonvolatile activities in sodium by assaying them after they are extracted into a lithium phase from which the sodium is continuously removed by distillation. The current effort is directed primarily at obtaining information important to the successful operation of the second monitoring method. Equipment is being designed to obtain kinetic data on the removal of xenon activity (in this test, ^{133}Xe) from molten sodium. The key problem in all three monitoring concepts is the separation of the activities to be monitored from the sodium activation product ^{24}Na , which is present at high levels in reactor sodium.

Evaluation and Control of Sodium Aerosol Problems. Preliminary measurements have been made of the particle-size distribution of sodium aerosol in argon cover gas over sodium at 400°C . The mass mean diameter was $\sim 4\text{ }\mu\text{m}$. A calculational study has also been performed, in which the theory of nucleation has been applied to the tendency of sodium vapor to condense on non-sodium nuclei and ions, and to homogeneous nucleation.

SODIUM CHEMISTRY

Characterization of the Nitrogen-Bearing Species in Sodium. Information on the existence, identification, and behavior of nitrogenuous species in liquid sodium is needed to further the development of methods for analyzing reactor sodium for nonmetallic species. The current experiments in this study are involved with nitrogen absorption by sodium and by Na-Ca solutions at 590°C

and the results, so far, may be interpreted to indicate that the rate of nitrogen uptake by Type 304 stainless steel at the intersection of the liquid surface with the container wall is the same whether or not a large amount of calcium is initially present in the sodium. The stoichiometry of the interaction of nitrogen with calcium is $\text{Ca}_{1.78}\text{N}$.

The Sodium-Sodium Oxide-Sodium Hydroxide-Sodium Hydride System.

This investigation seeks to understand the behavior of oxygen- and hydrogen-bearing species in liquid sodium. The results will be useful in developing and evaluating analytical methods for oxygen and hydrogen impurities in sodium. The effort to date has been directed toward the elucidation of the phase relations in the $\text{Na-Na}_2\text{O-NaOH-NaH}$ system. Two tentative phase diagrams have been constructed. Experimental verification and refinement of the actual diagram is underway. Room-temperature X-ray studies of carefully heat-treated alloys may reveal the basic construction of the diagram. A high-temperature Knudsen cell is being designed for the investigation at elevated temperatures.

Determination of the Solubility of Gases in Liquid Sodium.

Work is continuing on a study to determine the solubility of xenon in liquid sodium as a function of both temperature (350-600°C) and pressure (2-10 atm). This information is aiding the implementation of current programs for the detection and location of fuel element failures in future LMFBR systems. A total of 47 solubility determinations have been made at six temperatures. The mean Henry's law constants for the xenon solubility, expressed in ppb/atm (grams of gas dissolved in 10^9 grams of sodium per atmosphere of gas pressure), are 90.9 (600°C), 37.9 (550°C), 17.4 (500°C), 6.56 (450°C), 3.06 (400°C), and 0.799 (350°C). The value calculated for the heat of solution of xenon in liquid sodium is 19.4 ± 0.8 kcal/mol. The results are in good agreement with those predicted by a theoretical model developed at ANL.

PURIFICATION OF SODIUM

Characterization of Cold-Trapped Sodium. The work plan has been approved and is being implemented for the design and construction of the Apparatus for Monitoring and Purifying Sodium (AMPS). AMPS will be used to characterize cold-trap operations by utilizing continuous reading on-line impurity monitors. Target date for startup is mid FY 1972.

A detailed equipment layout has been prepared for installing two oxygen meters and one hydrogen meter on the outlet of the EBR-II primary cold trap. These meters will be used in conjunction with meters to be installed on the Radioactive Sodium Chemistry Loop of EBR-II (RSCL) for characterizing the operation and efficiency of the primary cold trap.

MATERIALS-COOLANT COMPATIBILITY

Carbon Transport in Sodium-Steel Systems. An experimental program to elucidate reactions involving carbon transfer in ferritic and austenitic steels has proceeded in a number of areas. Additional information has been obtained on the distribution of carbon between sodium and iron-base alloy (viz., Type 304 SS, Fe-18 wt % Cr-8 wt % Ni, Fe-8 wt % Ni and Fe-16 wt % Ni) foil specimens at 650 and 750°C. The results showed that the concentration of carbon in Type 304 SS is about a factor of ten greater than that in the Fe-18 wt % Cr-8 wt % Ni alloy. The order of magnitude difference between the carbon concentrations in the two alloys has also been observed in equilibration studies conducted in Vycor capsules at 800°C. Minor alloying elements (e.g., Mn) and metallic impurities (e.g., Si, Ti, Zr) in the commercial alloy apparently have an important effect on the total carbon content of these alloys at low carbon activities.

The activity of carbon in liquid sodium is being determined by equilibrating carbon in sodium with α -iron at temperatures below 723°C. Since carbon activity values in sodium-steel systems generally range between 0.01 and 0.1 (with graphite as the standard state), the carbon concentrations in α -iron are typically below 10 ppm. Internal-friction methods have been shown to be useful in determining the carbon concentration of iron-wire specimens at these low carbon levels.

Successful prediction of carburization-decarburization rates of materials in a reactor system will require the development of calculational methods as well as the determination of diffusion coefficients of carbon as a function of alloy composition and temperature. An experiment to determine the diffusivity of carbon in an Fe-2.25 wt % Cr-1 wt % Mo alloy at 700°C by a steady-state method is in progress to obtain data on the diffusion coefficient as a function of carbon level in the alloy.

An investigation of the carburization and nitridation of steels by cyanide in sodium at 800°C has been completed. The distribution of carbon and nitrogen between an Fe-18 wt % Cr-8 wt % Ni alloy and sodium containing cyanide concentrations up to 37 ppm was determined. The results indicate that the nitridation potential of cyanide in sodium is about a factor of ten greater than that for carburization at 800°C.

Candidacy of Vanadium-Base Alloys for Cladding LMFBR Fuels.

The corrosion of vanadium in liquid sodium has been investigated under the well-defined hydrodynamic conditions produced by the rotating disk sample geometry at temperatures between 450 and 700°C. Corrosion-rate data obtained under conditions where the linear corrosion rate is a function of both velocity and oxygen concentration in sodium were used in the convective-diffusion model for mass transport to a disk to obtain values for the diffusion coefficient of oxygen in liquid sodium. The vanadium corrosion rates were related to the diffusional flux of oxygen to the disk by the stoichiometric relation $V + \frac{1}{2}O_{Na} = VO$ for the vanadium monoxide corrosion product. The diffusion coefficient of oxygen in liquid sodium from these measurements ranged from 1×10^{-6} cm²/sec at 500°C to 1×10^{-5} cm²/sec at 700°C. Although the data are encompassed by the lower limit of the range of values commonly observed in liquid-metal systems, an extrapolation to lower temperatures results in unreasonably low values. Further interpretation may resolve the problem; the results will be given in a topical report that is now in preparation.

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

Argonne has been given the responsibility of implementing a national meter program for developing, testing, and establishing commercial availability of meters for use on FFTF and in other LMFBR systems. The meters to be developed and characterized in this program consist of monitors for oxygen, carbon, and hydrogen and a leak detector for steam generators. The FFTF schedule requires commercial availability of the oxygen and carbon meters by July 1971.

1.1 Oxygen Meter Modules (V. M. Kolba, L. J. Marek, R. R. Schlueter)

Electrochemical Oxygen Meters. Electrochemical oxygen meters having an improved ThO_2 -7.5 wt % Y_2O_3 ceramic electrolyte and an oxygen gas reference electrode promise long-time, high-temperature operation for monitoring LMFBR coolant sodium. A program has been set up between ANL, WADCO, BNL, and Zircoa that is expected to result in improved electrolyte tubes; these should be commercially available by early 1971. The electrolyte tubes will be of the size (1/4-in. dia) that is currently used in the Westinghouse version of the oxygen meter.

Prior to the availability of the final electrolyte material, meters having electrolytes produced by a slip-cast or isostatic pressing process will be obtained from BNL and Westinghouse. One of these meters will be installed at EBR-II for evaluating the effects of radiation from the activated primary sodium.

Apparatus for Oxygen-Meter Calibration. The object of this work is to provide a system that can be used to proof-test oxygen meters, evaluate electrolyte tubes and various reference electrode gases, provide a calibration facility, and permit evaluation of electronic equipment for readout of meter emfs.

The apparatus provides for testing up to four oxygen meters and determining their stability as a function of operating life in a sodium system having sodium flow rates of 0 to 0.5 gpm at temperatures up to 900°F. A cold trap is provided for controlling the oxygen level of the system.

Construction of the apparatus is complete and most of the instrumentation has been received and installed. Two UNC (BNL-type) housings are presently installed on the apparatus. Six

Westinghouse meters are on order; however, delivery may be held up pending receipt of improved electrolyte tubes. Six BNL electrode assemblies, which fit into the UNC housings have been received and will be used in the shakedown operations.

Radiation Test at EBR-II. The object of this work is to conduct an oxygen meter test at EBR-II using an existing sampling line; the test will permit a rapid evaluation of the effects of direct beta and gamma radiation on the operation of the oxygen meter.

Drawings have been prepared and a service request submitted for fabrication of the piping. One of the Westinghouse oxygen meters now on order is scheduled to be installed with this piping. Base line data prior to reactor start-up will be obtained on this meter so that the effects of the radiation can be evaluated.

Oxygen-Hydrogen Meter Module. The objective of this work is to develop, proof test, and establish commercial availability for an on-line module for monitoring oxygen and hydrogen activity in sodium systems.

During this period, a preliminary layout of a module containing two oxygen meters and one hydrogen meter was completed. The layout was primarily aimed at FFTF requirements. Comments have been received from EBR-II and WADCO and are being considered in the detailed design. The heat exchanger design is complete. Specifications for procurement of oxygen meters for the modules have been prepared.

The module incorporates two Westinghouse oxygen meters and one ANL hydrogen meter (discussed in Section 1.3, below) in a stepped array (see Fig. 1-1). The following components are also provided: (1) a cooler to accommodate FFTF inlet-sodium temperatures up to 1200°F, (2) a regenerative heat exchanger and line heaters to meet temperature-control requirements, (3) a control valve and flow meter to regulate and monitor sodium flow, and (4) an ion pump, vacuum valve, and ionization-type pressure gauge for the hydrogen meter.

Preliminary layouts of the electrical and instrumentation packages for the modules have been made and reviewed. These also are aimed at FFTF requirements.

It is planned to pre-test a prototype module at ANL-Illinois prior to proof testing it at EBR-II. A detailed schedule and job assignment chart has been developed with the aid of EBR-II for installation of the modules at EBR-II on the Radioactive Sodium Chemistry Loop (RSCL), Cell B.

Fig. 1-1. Schematic Diagram of Oxygen-Hydrogen Meter Module.

On-Line Calibration Module. The objective of this work is to develop, proof test, and establish commercial availability for an on-line module for equilibrating refractory metal specimens with flowing sodium to provide on-line calibration of oxygen and carbon meters.

During this period, the preliminary design layout of a module has been completed. The module contains a flow control valve, a flow meter, a regenerative heat exchanger and a molybdenum-lined heater section which will heat sodium up to 1400°F. This conceptual design, with slight modifications, is to be used for two separate purposes, namely, as a device for specimen equilibration (on-line calibration) and as a housing for a carbon meter probe (see Section 1.2, below). Fabrication has begun on the heater and isothermal test sections of this module.

Preliminary layout of the electrical and instrument packages is scheduled to begin shortly.

Meter Characterization Test. The objective of this work is to characterize oxygen meters at temperatures from 700 to 900°F. Planning for the testing of ten Westinghouse meters in a series assembly has begun. The test apparatus, which will have provisions for up to ten meters and an on-line calibration device and capabilities for heating sodium up to 1200°F, will be used in the following programs: (1) ANL tests of the oxygen-hydrogen meter module, (2) ten meter characterization tests, and (3) test of the on-line calibration module (required in conjunction with items 1 and 2).

A conceptual plan for this apparatus has been developed. A design layout to determine space requirements and the preliminary design of a regenerative heat exchanger, heater, and cooler have been started.

1.2 Carbon Meter Module (C. Luner, D. J. Raue, P. J. Mack)

The objective of this work is a commercially available on-line carbon-meter module 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 are the testing and improvement of the UNC diffusion-type carbon meter, which will be incorporated into a prototype module containing necessary flow and temperature control devices. Proof testing of the prototype module will be conducted on the RSCL at EBR-II.

Carbon-Diffusion Meter. Previous testing of the carbon probe at ANL has shown that in stirred-pot experiments using a noncarburizing container (copper), a significant response was

obtained on the addition of approximately 1 ppm C added as sodium carbide or sodium cyanide. The insertion of a carburized iron rod into the melt also increased the flux significantly (ANL/ST-2, p. 1-5). However, no significant response was observed when ~1 ppm C (as Na_2C_2) was added to the Test and Evaluation Apparatus (TEA), a small pumped sodium loop of stainless steel construction. In this test, the main loop was at 500°C and that of the side loop, where the carbon meter probe was located, 750°C (ANL/ST-3, p. 1-3).

One possible reason for the lack of response of the probe was that, at the elevated temperature of the side loop, the added Na_2C_2 may have been removed by the stainless steel before it reached the carbon probe. To test this hypothesis, another probe housed in a molybdenum-lined, heated section (which would not be expected to remove significant amounts of carbon from the flowing sodium) has been installed on TEA in a parallel side loop. The response to carbon additives of the two meters will be compared, and if the flux from the molybdenum-lined housing is significantly higher, a molybdenum lining may be incorporated in future housing designs.

A molybdenum-lined chamber for exposing Fe or Fe-Ni alloys to flowing sodium has also been installed. Startup of these new additions to TEA is now in progress. Work will proceed to (1) establish a standard probe and housing design and (2) establish recommended operating temperature, decarburizing gas compositions, and sodium flow rate. Attempts will be made to correlate carbon meter readings with activities determined from metal specimens equilibrated with the carbon contained in the sodium in TEA.

An instrument system and gas console for operating the new carbon meter probe has been constructed and calibrated.

1.3 Hydrogen Meter (D. R. Vissers, L. B. Bartholme)

The goals of this program are the design, development, and prooftesting of an on-line hydrogen meter for measuring the hydrogen activity in primary and secondary LMFBR sodium systems. The diffusion-type hydrogen activity meter being developed at ANL and the UNC electrochemical hydrogen meter will be evaluated for the on-line meter component of this station. Appropriate response-test procedures and on-line calibration procedures are being developed for the meter when required.

Design, Construction, and Evaluation of Meter. The ANL hydrogen activity meter is a diffusion-type monitor with a direct pressure readout of the equilibrium pressure above the sodium. This

pressure is related to the activity of hydrogen in the sodium,¹ since the solubility of hydrogen in sodium obeys Sievert's law. The principal components of the meter are a nickel diffusion membrane, a pressure sensing device, and a high-vacuum system for periodic pumpdown; the meter has been described in detail previously (see ANL/ST-2, p. 1-10).

Previous studies (ANL/ST-2 and -3) utilized a prototype of the ANL hydrogen-activity meter, and were carried out in a gas-flow system at 500°C with standard hydrogen-argon mixtures. In these tests, the pressures indicated by the Varian Millitorr ionization gauge were approximately 25% less than the values calculated from gas-chromatographic analyses for hydrogen. As reported in ANL/ST-3, p. 1-4, the Millitorr gauges are originally calibrated with nitrogen, and the pressure readout of the gauge must be corrected when the gauge is used to measure hydrogen (ion gauges are less sensitive to hydrogen). Varian recommends, on the basis of the data of Dushman,² that the gauge readout (calibrated for nitrogen) must be multiplied by two when measuring hydrogen. However, recent studies³ on the relative sensitivities of the ion gauge toward hydrogen and nitrogen have indicated that the meter reading should be multiplied by 2.78 rather than 2. When we use a factor of 2.78, we find excellent agreement between the measured hydrogen pressure, as indicated by the Millitorr gauge, and that determined by gas chromatography. These data, which are shown in Fig. 1-2, indicate that the Millitorr gauge, when calibrated for hydrogen, possesses the potential to serve as the sensor component of the ANL hydrogen activity meter.

Another pressure sensor, a MKS baratron capacitance manometer, is also being tested for the ANL meter. This device will be evaluated as a possible means of eliminating the need for calibration or frequent recalibration of the pressure sensor. The MKS baratron has been received, but due to damage resulting from shipment, its evaluation as a potential pressure sensor for the ANL meter has been delayed. Replacement of the damaged gauge is expected by mid-October 1970.

Hydrogen-Tritium Studies. The levels of hydrogen in the primary and secondary systems of EBR-II are important parameters, not only because of installations to be made at EBR-II, but because

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¹S. A. Meacham, E. F. Hill, and A. A. Gordus, "Quarterly Technical Progress Report on AEC-Sponsored Activities," APDA-228 (1968).

²S. Dushman and J. M. Lafferty, Scientific Foundations of Vacuum Technique, J. Wiley and Sons, Inc., New York, N. Y. (1962).

³K. B. Das, Boeing Development Center, Seattle, Wash., personal communication (September 1970).

Fig. 1-2. Hydrogen-Activity Meter Calibration.

EBR-II must be considered to be the best source of knowledge, at present, on the level of hydrogen in future LMFBR sodium systems. Earlier calculations of hydrogen production rate due to aqueous corrosion in an LMFBR steam generator⁴ (9 mils/30 years) indicated that the hydrogen content of the sodium in the secondary loop would be about 0.2 ppm when this sodium is in equilibrium with the hydrogen present on the steam side of the generator.

Recently, Pacific Northwest Laboratory (now WADCO) analyzed a sodium sample taken from the secondary sodium of EBR-II. The sample was taken on March 10, 1970 and analyzed for hydrogen by the amalgam-reflux method. The results⁵ of two determinations indicated 0.21 and 0.29 ppm hydrogen as hydroxide, and 0.05 and 0.07 ppm as hydride plus free hydrogen. It is believed that the hydrogen determined by analysis as hydroxide may be present at the system operating temperature as hydride. Cover gas analyses⁶ for the month of March indicated a hydrogen level of 4 ppm in the secondary cover-gas system. This level of hydrogen⁷ in the cover gas indicates that, on the basis of the Sievert's law relationship,¹ the concentration of hydride hydrogen in the secondary sodium should be about 0.26 ppm.

Tritium analyses⁸ of samples of EBR-II secondary sodium and cover gas taken on March 24, 1970, indicate a tritium level in the sodium of 2.27×10^{14} atoms per liter and a tritium level in the cover gas of 1.55×10^{11} atoms per liter. If one assumes the tritium is a hydrogen tracer and obeys Sievert's law in the sodium system, as has been shown for hydrogen, it is possible to calculate the level of hydrogen in the secondary sodium and in its cover gas from the tritium data and from Sievert's law, which is given by

$$KP^{1/2} = S \quad (1)$$

where K is Sievert's constant, P is the pressure of hydrogen, and S is the hydrogen concentration in the sodium. Since the relationship between the hydrogen pressure above the sodium and the

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⁴"ANL 1000-MWe LMFBR Follow-On Study Task I Report," Vol. 1, AI-68-Memo-37 (1968).

⁵Reactor Development Program Progress Report, July 1970, ANL-7726, p. 45.

⁶Reactor Development Program Progress Report, April-May 1970, ANL-7688, p. 90.

⁷The assumption is made that little or no hydrogen is lost during the chromatographic cover gas sampling procedure.

⁸W. H. Olson, EBR-II, personal communication (September 1970).

concentration of hydrogen dissolved in the sodium is a square root relationship, the distribution coefficient of hydrogen between the sodium and the cover gas will vary with the concentration of hydrogen in the sodium. Thus, for a given distribution coefficient, the level of hydrogen in the sodium is fixed. This relationship is illustrated in Fig. 3-3, where distribution coefficients for hydrogen, calculated from the work of Meacham et al,¹ are plotted against concentration of hydrogen in sodium. In this analysis, the hydrogen distribution coefficients are calculated as concentration per liter of sodium/concentration per liter of cover gas. A knowledge of the distribution coefficient would thus provide the information for calculating the concentration of hydrogen present in the sodium and the cover gas.

The tritium data cited above for samples taken on March 24, 1970 indicated a distribution coefficient of 1465 at 300°C (atoms per liter of sodium/atoms per liter of cover gas). From this value, the concentration of hydride hydrogen in the secondary sodium is calculated to be 0.23 ppm and the concentration of hydrogen in the cover gas, 3 ppm. These results are in good agreement with the cover gas analysis of 4 ppm reported for hydrogen during this period. A similar treatment of the tritium data for the primary system indicates the primary sodium on March 24, 1970 contained 0.4 ppm of hydride hydrogen.

The results of this study strongly indicate that the hydride hydrogen concentration of EBR-II primary and secondary sodium is 0.2-0.4 ppm. These results also suggest that determinations of hydrogen by the amalgam-reflux method be reported as total hydrogen, rather than as hydride and hydroxide hydrogen.

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

The evaluation of requirements for a leak detection system for LMFBR steam generators and the development and proof testing of a detection system to meet these requirements will be carried out in this program. On-line impurity monitors will be used for detecting the products of the sodium-water reaction. Other means of detection, however, are not being excluded from consideration.

Monitors for hydrogen are being given first consideration for leak detection because they appear to be durable and are sensitive to small changes in the hydrogen level of the sodium. A detailed description of the ANL hydrogen-meter leak detector and the requirements for the leak detection system have been presented in detail previously (ANL/ST-2, p. 1-14).

Fig. 1-3. Distribution Coefficient of Hydrogen
Between Sodium and Its Cover Gas.

The presentation of a paper on the ANL hydrogen-meter leak detector at the 16th Annual Meeting of the American Nuclear Society and to the staff of the Liquid Metal Engineering Center (LMEC) has generated requests for additional information on the meter from Westinghouse, Atomic Power Development Associates (APDA), and LMEC, and discussions have been held with the respective organizations during the past months. Westinghouse has decided, from these discussions, to install a hydrogen-meter leak detector on their Fission Product Loop Number Two. This loop is used to study the behavior of fission products in sodium-stainless steel systems. The long-range plans at Westinghouse call for evaporators, reheaters and superheaters to be constructed of Incoloy 800; therefore, their requirements for a leak detector are much less stringent because the wastage rates of Incoloy 800 are much less than those of Croloy-2 1/4 or of Type 304 stainless steel. Consequently, the Westinghouse leak detector will be operated under conditions which require less rapid response times than called for by other systems. Nickel membranes are currently being fabricated here at ANL for Westinghouse.

Plans are being made to supply an ANL hydrogen-meter leak detector for the Sodium Component Test Installation (SCTI) at LMEC for use in their test of the AI "hockey stick" steam generator, which is scheduled for spring of 1971.

A leak detector system for the secondary sodium system at EBR-II is also being developed.

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 sodium systems. To achieve this objective, ANL has established an Analytical Standards Laboratory and an Analytical Development Group. The function of the Laboratory is the management and coordination of the interlaboratory aspects of the Analytical Standards Program. Present efforts in this area are directed toward establishing a set of interim methods to meet immediate needs. The efforts of the Development Group are being directed toward producing reference and analytical methods that fully satisfy the long-range needs of the sodium technology effort.

2.1 Analytical Standards Laboratory

The operation of the Analytical Standards Laboratory is a combination of administrative and laboratory work. The administrative activities involve the coordination of the Analytical Standards Program; the laboratory work includes participation in this program and the satisfaction of near-term FFTF needs.

2.1.1 Administrative Activities (F. A. Cafasso, R. J. Meyer, M. H. Barsky, H. S. Edwards, L. E. Ross, S. B. Skladzien, R. C. Haglund)

Two advisory working groups, a Reactor Standards Working Group and a National Standards Working Group, have been formed to assist ANL in coordinating the Analytical Standards Program. Recent activities centered around these groups are described in the sections below.

Reactor Standards Working Group. This group, composed of representatives from RDT, LMEC, EBR-II, and ANL-Illinois met at ANL-Illinois on July 31, 1970. The purposes of the meeting were as follows:

1. To establish formal agreement on interim sampling and analytical methods.
2. To receive comments on and gain acceptance of the manual of procedures, Interim Methods for the Analyses of Reactor Sodium and Cover Gases.

3. To review the Purity Specifications for Large Operating Sodium Systems, recently compiled by ANL, and establish their acceptability.
4. To review ANL's assessment of the vanadium-wire equilibration method of measuring oxygen activity in sodium and evaluate ANL's recommendation that this method be included in the interim methods test program.
5. To establish a starting date for the interim methods test program.

Documents presented by ANL at the meeting were the following:

1. ANL Plan for the Selection of Interim Sampling and Analytical Methods for EBR-II and FFTF
2. A list of Selected Interim Sampling and Analytical Methods
3. Interim Methods for the Analysis of Reactor Sodium and Cover Gases
4. Purity Specifications for Large Operating Sodium Systems
5. The Vanadium-Wire Method for Measuring Oxygen Activity in Sodium--An Evaluation
6. The Vanadium-Wire Method for Measuring Oxygen Activity in Sodium--Recommended Procedure

All of the above documents except the procedure manual were discussed in detail and approved by the group. A detailed discussion of the procedure manual was not attempted because of its volume; however, expansion and minor revisions of the manual in a few areas were recommended. These changes are in progress, and the manual is expected to be completed by November 1, 1970.

The group agreed to start sample interchange tests on November 1, 1970 using EBR-II primary and secondary sodium as a source of samples. Accordingly, arrangements have been made with EBR-II personnel to provide samples for oxygen, carbon, hydrogen, and trace-metal determinations. The oxygen and carbon samples will be supplied in back-to-back extrusion samplers, the hydrogen samples in stainless steel tubes, and the trace-metal samples in tantalum cups.

National Standards Working Group. A meeting of this group, composed of representatives from RDT, AI, LMEC, GE, WADCO, Westinghouse, and ANL-Illinois, is scheduled for mid-November 1970. In mid-September, a planning meeting of analytical chemists from the participating laboratories was held; at this meeting tentative agreement was reached on the methods to be used, and ANL is preparing a manual of procedures for these methods, which are listed in Table 2-1. Completion of the manual is expected by mid-October.

Summary of EBR-II Analytical Data on Primary and Secondary Sodium. As a part of the development of Purity Specifications for Large Operating Sodium Systems, mentioned above, EBR-II analytical data on primary and secondary sodium was accumulated and converted to graphic form. This graphic representation proved to be very useful for recognizing trends and changes in impurity concentrations, and it evoked considerable interest from personnel of other laboratories. Consequently, the data will be published as a part of an EBR-II publication. An in-house computer program has been modified to provide the data to EBR-II in a form suitable for publication.

2.1.2 Laboratory Activities (R. J. Meyer, M. H. Barsky, A. F. Panek, S. B. Skladzien, L. E. Ross, H. S. Edwards, M. D. Adams)

Most of the laboratory effort during this quarter has been devoted to setting up and checking out the methods to be used in the sample interchange of the Reactor Standards Working Group. Some effort has also been made to establish a procedure for particulate analysis. Important developments in these areas are discussed in the sections below.

Hydrogen Determination. The amalgam-reflux method to be used as an interim method for the determination of hydrogen in sodium originally called for extrusion aliquoting. This aliquoting method must be replaced because of recent evidence of radial segregation of hydrogen in the solid sodium. An approach that involved remelting and pouring the sodium from the sample (ANL/ST-3, p. 2-3) was investigated at EBR-II using primary sodium, which contains tritium. After remelting and pouring of the sodium, analyses showed that more than 75% of the tritium remained in the container, thus demonstrating that this approach will not eliminate the segregation problem. Therefore, the sample must be introduced in a section of the bypass sampler. Specific details of the procedure are yet to be established. Previous experience

Table 2-1

Interim Analytical Methods for the National Standards Working Group

<u>Element</u>	<u>Method</u>	<u>Sampler</u>	<u>Aliquoting Method</u>
H	Amalgamation-Reflux	Bypass	Section
C	Oxyacidic Flux	Bypass	Extrusion
N	Kjehldahl-Colorimetric	Bypass	Section
O	Amalgamation	Bypass	Section
Metals (Survey)	Distillation-Spectrographic	Overflow	None
Non-volatile Metals (Indiv.)	Distillation-Atomic Absorption	Overflow	None
Alkali Metals	Dissolution-Flame Photometric	Overflow	None
Zn-Cd	Dissolution-Atomic Absorption	Overflow	None
Halides	Dissolution-Colorimetric	Overflow	None

with this approach¹ has indicated that hydrogen in a stainless steel sampler contributes hydrogen to the analysis. However, modifications of this approach used at LMEC² and Westinghouse³ show promise for overcoming this problem. LMEC performs the entire reflux procedure without removing the section of sampler. Correction for hydrogen contributed by the section is made by running a blank on an adjacent section of the sampler after removal of the sodium. Westinghouse removes the section of sampler after the amalgamation is complete but before refluxing is begun. The merits of both approaches will be evaluated.

Determination of Trace Metals in Distillation Residues.

The survey method to be used for the determination of trace metals in sodium utilizes emission spectrographic analysis of a distillation residue of the sodium. A sample of EBR-II sodium has been used to check out this procedure in our laboratory. The results of the spectrographic analysis of the residue are given in Table 2-2. Included in the table, for comparison, are EBR-II atomic-absorption analyses,⁴ for individual elements, of a sample taken within the same week. The agreement between these two sets of results is considered excellent.

Particulate Analysis. As a part of the Analytical Standards Program, ANL has agreed to 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; more attractive recovery techniques are distillation of sodium from the filter, or dissolution of sodium in an inert solvent followed by filtration of the solution. Distillation has been selected as the technique to be used for removal of sodium. This procedure will involve (1) forcing the excess sodium from the filter housing by heating to 125°C and establishing a helium pressure of about 4 psi on the entrance tube, (2) evacuating and heating to 300°C for 24 hr to distill the residual sodium and collect it in the cold end tubes, (3) opening the filter housing and separating and weighing the residue, and (4) mounting portions of the residue for microscopic or X-ray examination.

¹S. A. Meacham, E. F. Hill, "The Determination of Hydrogen in Sodium," APDA-183 (1966).

²H. E. Johnson, LMEC, private communication.

³S. A. Meacham, Westinghouse, private communication.

⁴"Reactor Development Program Progress Report July 1970," ANL-7726, p. 44.

Table 2-2

Comparison of Spectrographic and Atomic-Absorption
Analyses of EBR-II Primary Sodium

<u>Element</u>	<u>Survey Method^a</u>	<u>Atomic Absorption Method^b</u>
Ag	0.05	0.06
Al	0.17	<0.6
B	<0.2	--
Ba	<0.2	--
Bi	2.4	2.0
Ca	<0.2	<0.02
Co	<0.2	<0.02
Cr	0.19	0.1
Cu	0.12	<0.02
Fe	1.0	0.15
Mg	0.19	<0.005
Mn	0.02	<0.005
Mo	0.04	<0.07
Ni	0.04	<0.04
Pb	9	9.4
Sn	--	21.6
Sr	<2	--
Ti	<0.2	--
V	<0.2	--

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^aAnalyses performed at ANL-Illinois.

^bAnalyses for individual elements performed at EBR-II.

This procedure was checked using a filter from an EBR-II Project sodium loop, the Mechanical Properties and Corrosion Loop. Microscopic observation showed that sodium removal had not been complete. Other than metallic sodium, a major constituent of the residue was a white, polycrystalline material of soft, white plates which were agglomerates of particles generally less than 10 μm on an edge. This material reacted with normal immersion oils and mounting materials. Particles of the polycrystalline material are being examined by X-ray diffraction.

Attention is also being given to the design of filters for large sodium systems. For this purpose, information is needed on the restriction of the sodium flow offered by filters of various porosities and areas. In this connection, a compact filter unit, consisting of a small-diameter, cup-shaped filter cartridge, has been installed in a bypass sampling location in the Sodium Analytical Loop (SAL). The nominal pore size of the filter is 7 μm and the area is about 10 cm^2 . Upon removal of this filter from the loop, its performance will be evaluated.

2.2 Analytical Development

Analytical development activities are being coordinated with the analytical standards effort to produce reference and analytical methods that fully satisfy the long-range needs of sodium technology. Recent effort has been devoted to continued evaluation of (1) a proton-activation method for determining oxygen, carbon, and nitrogen, and (2) a spectrographic method for determining metallic impurities.

2.2.1 Development of Reference Analytical Methods for Total Oxygen, Carbon, and Nitrogen in Sodium (M. D. Roche, L. E. Ross, R. J. Meyer)

Reference methods are needed for the determination of oxygen, carbon, and nitrogen in sodium to establish the accuracy of other analytical methods. These reference methods must be specific, accurate ($\pm 10\%$), capable of determining concentrations of 0.1 ppm in sodium, and free from contamination and segregation during sampling. Because proton activation is judged to have the potential for best satisfying these criteria, the Analytical Development Group is evaluating this approach.

The concept of determining oxygen, carbon, and nitrogen in sodium by proton activation is based on the following reactions: $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$, $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$, and $^{14}\text{N}(\text{p},\alpha)^{11}\text{C}$. The procedure currently being investigated involves (1) bypass sampling of the sodium system by means of a specially designed cell, (2) proton activation of the molten, well-stirred sodium in the same cell, (3) transfer of the sodium to a counting cell, and (4) assay of the induced activities.

Preliminary investigations of the feasibility of the method were performed by bombarding nickel-foil-covered NaF pellets spiked with known amounts of Al_2O_3 , C, and AlN. The results of these bombardments (ANL/ST-2, p. 2-3) indicated that adequate sensitivity could be obtained and that interferences from other induced activities could be either circumvented or adequately controlled.

The design of the sampling/irradiation cell for the proton bombardment of sodium samples was described in detail in the preceding report (ANL/ST-3, pp. 2-7 to 2-10). This cell permits irradiation of molten and well-stirred sodium and thereby circumvents the two major problems of proton activation, viz., surface activation rather than volume activation (due to the short range of the protons) and vaporization of sodium (caused by the heat generated in stopping the energetic proton beam).

Present effort is being directed toward testing of the cell and evaluating the problems involved in the determination of oxygen in sodium. Accordingly, two samples obtained from a sodium loop were bombarded with protons. Findings from these experiments indicated that (1) the cell functioned satisfactorily, (2) a detection limit of 1 ppm oxygen is possible with this cell design, and (3) the induced activities other than ^{18}F were ^{24}Na , ^{56}Mn and several copper isotopes.

The copper activities are believed to have been induced in the nickel window and to have recoiled into sodium via a breach in the thin cobalt layer that had been vapor-deposited on the window (see ANL/ST-3, p. 2-8). The ^{56}Mn is believed to have been induced in the cobalt layer via the reaction $^{59}\text{Co}(n,\alpha)^{56}\text{Mn}$.

The production of the manganese and copper activities can be eliminated by the use of a window made from ^{58}Ni . A cell has been designed which incorporates such a window and which holds smaller samples. The smaller sample size (10 g rather than 70 g) will greatly reduce the ^{24}Na interference. These improvements should allow the detection limit to be lowered to 0.1 ppm of oxygen.

2.2.2 Method for the Determination of Metal and Halide Impurities in Sodium (H. S. Edwards)

A survey method is being developed for the rapid and routine determination of changes in metallic impurity levels in sodium. The method which has been selected for initial evaluation is emission spectroscopy utilizing induction-coupled

plasma excitation of a metal-dust aerosol which has been generated by ultrasonic nebulization of molten sodium. This approach has the potential for on-line application.

Work is in progress on assembly of an integrated set-up for performing the necessary experimental measurements. A Jarrell-Ash Half-meter Ebert scanning spectrometer is on hand. A 30-MHz induction generator has been received and is being installed. An all-quartz plasma torch has been fabricated and is ready for testing as soon as the power source is installed. A glass nebulizer was made and attached to the ultrasonic probe by an O-ring seal at the accoustical node of the probe. A water aerosol was produced for the first test of the nebulizer system. To gain further experience with the nebulizer system, particularly as applied to liquid metals, several low-melting alloys will be nebulized.

3. FISSION PRODUCT AND COVER GAS TECHNOLOGY

(W. E. Miller)

3.1 Radioactivity Behavior and Control

3.1.1 Radioisotope Problem Areas (W. J. Mecham, W. E. Miller)

The primary system of an LMFBR becomes radioactive from activation of structural materials and sodium and from fuel sources, and the spread of this radioactivity throughout the primary system is expected to cause serious maintenance problems. Plans for the research and development work required to evaluate these maintenance problems are being formulated at ANL. Atomics International, General Electric, and Westinghouse have also issued program plans for developing the technology required to solve the radioactivity problems associated with maintenance of LMFBRs. The major difference between these plans and the ANL plan is that the latter proposes extensive use of EBR-II.

There are two trends in design and proposed mode of operation of future LMFBRs that will lead to primary system contamination levels greater than those presently existing in EBR-II. (1) The temperature levels will be higher and as a result transport rates of activated corrosion products will increase. (2) Reactors will continue to operate with fuel elements that have lost hermetic seals; thus, some fission products normally contained within the cladding could distribute throughout the primary system. The higher levels of radiation are expected to cause increased difficulties in maintenance, and the severity of these maintenance problems is related to the specific radiation levels in existence in the area of maintenance work.

At present, the radiation levels that will be encountered in future reactors cannot be predicted with any degree of certainty because the transport and deposition processes are very complex and complete theories for prediction do not exist. This information can be gained only by reactor experience, in which the radiation levels are monitored as temperatures are increased and the reactor is operated with some failed fuel in the core. We believe that valuable insight into some of the problems can be gained by studying the spread of radioactivity in EBR-II. To use EBR-II for this purpose, certain plant changes would have to be made and experiments carried out. These activities are as follows: (1) develop and implement standard methods of analysis for examination of contaminated surfaces taken from the reactor (these surfaces may be on tabs inserted for this purpose or on components taken from the primary system or from the analytical cold trap), (2) gain access to the shell side of the intermediate heat exchanger for deposition measurements,

(3) develop and execute a plan for the use of tabs as a tool for measuring system contamination during periods of operation with failed fuel, (4) conduct experiments using reactor sodium to investigate transport of activated corrosion products, (5) remove and analyze circulating particulates or measure their effects indirectly, (6) investigate methods for moving fixed activity in the reactor, and (7) use the cold trap or the analytical cold trap to investigate activity removal from primary sodium.

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

The objective of this work is the development and testing of methods for characterizing fuel failures in LMFBR systems. The methods currently being investigated involve monitoring the sodium coolant for selected fission products. Direct measurements of the coolant by gamma spectrometry may not be successful because of interference from the high gamma-activity level of ^{24}Na . Therefore, for on-line monitoring devices utilizing gamma-spectrometric assay, techniques are being incorporated for separation from or enrichment of the selected fission products in sodium.

Methods of current interest for separating fission products are (1) multistage distillation to separate more volatile elements such as cesium and rubidium, (2) sparging with inert gas mixtures to separate the xenon activity resulting from iodine decay, and (3) accumulation of fission products in molten lithium, from which the sodium and more volatile fission products are removed by distillation.

The concept of separating cesium and rubidium from sodium by multistage distillation was described previously (ANL/ST-2, pp. 3-8 to 3-12 and ANL/ST-3, pp. 3-7 to 3-8). Recent effort has been directed primarily toward the xenon separation and its application to monitoring iodine; a lesser effort has been devoted to the extractive-distillation separation.

Method for Monitoring Iodine. This concept involves determining the iodine concentration in coolant sodium by separation and assay of its xenon daughter on a batch basis. Studies of irradiated oxide fuel¹ have shown that iodine migrates toward the oxide-cladding interface and, therefore, would be readily available for dissolution in sodium that enters the cladding. The present approach to monitoring iodine in the sodium involves (1) sampling of the reactor sodium in a special sampling cell, (2) sparging the sample with helium (containing a small amount of inactive xenon) in a gas recirculation loop to strip the sodium of most of the xenon that was present at the time of sampling, (3) trapping and discarding the xenon stripped in step 2, (4) allowing iodine in the sample

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¹C. E. Johnson, ANL, private communication.

to decay for a predetermined time to allow buildup of xenon daughters, (5) restripping the sodium of xenon with recirculating helium containing added inactive xenon, and (6) trapping and assaying the xenon produced from iodine decay. Assuming that the transfer of xenon from the sodium to the xenon trap is essentially complete, the concentration of iodine in the sodium phase is calculable from the measured xenon activity, decay constants of the isotopes in the mass chain selected, and the times involved in the various steps.

Of the xenon activities considered for assay in reactor application of the iodine-monitor concept, the 15.6-min ^{135m}Xe isotope is of primary interest. Its precursor, ^{135}I (6.7 hr), has a long enough half-life that its escape fraction to the coolant through a cladding leak should be significantly greater than that of delayed neutron precursors. At the same time, its half-life is not so long that the buildup of activity in the coolant would interfere with the detection of subsequent fuel failures. In addition, the half-lives of the ^{135}I precursors, 1.9-sec Sb and 29-sec Te, are short enough that they will not complicate the ^{135m}Xe assay.

Factors believed important to successful operation of the monitor are as follows: (1) The Ostwald coefficient for the xenon-sodium system must be small to effect nearly complete removal of xenon to the gas phase (data on the temperature dependence of the solubility of xenon in liquid sodium in Section 4.3 of this report indicate that this coefficient is $<10^{-5}$ at temperatures below 500°C). (2) The overall time interval for sampling and analysis must be short to minimize the number of equipment units required if rapid detection of iodine concentration changes in the coolant becomes important. (3) Losses of iodine to vessel walls during coolant sampling must be minimal, or predictable, to assure representative sampling. (4) Reproducible sparging techniques must be developed. (5) Transfer of iodine to the gas phase of the monitor must be negligible to permit accurate assay of xenon.

Preliminary tests were conducted to obtain information required for design of a combination sampling and sparging vessel for the iodine-monitor concept. The tests were performed in vertically mounted glass cylinders containing 500 cm^3 of water, a volume that duplicates the volume of sodium believed to be adequate for the iodine monitor. Gas bubbles were formed in the liquid by injecting air at various velocities through several types of gas-injection distributors. Spacing of bubbles in the liquid media, smoothness of sparging action, tendency of bubbles to coalesce, and approximate time of gas holdup in the vessel were observed. Several assemblies were tested and one appeared promising for monitor application. This assembly consisted of a 1.89-in.-ID sampling vessel with a capped, 0.19-in.-ID tube extending into the bottom of the vessel. Gas was injected into the bottom of the vessel

through four equally spaced 0.014-in.-dia holes drilled through the circumferential surface of the smaller tube. At gas injection rates between 1000 and 2000 cm³/min, small, ellipsoid-shaped bubbles (longer axis roughly 0.20 in.) were produced in the liquid and these did not appear to coalesce as they reached the top of the column. Distribution of the bubbles appeared most uniform at gas sparging rates of 1500 cm³/min or greater, and the sparging action appeared smooth at all throughputs to 2500 cm³/min. The average gas-holdup time in the liquid with a gas throughput rate of 1500 cm³/min was about 1.8 sec for the four-hole distributor. Increasing the number of injector holes to eight decreased the holdup time at the same gas throughput by approximately 40%, and increasing the diameter of the sparge vessel resulted in less uniform distribution of injected gas bubbles. The above tests suggest that a four-hole gas distributor as described above may be suitable for service in an iodine monitor if the diameter of the cylindrical sampling vessel is about 1.9 in.

Current work is aimed at obtaining kinetic data on the removal of xenon from molten sodium and information on the sorption-desorption characteristics of xenon traps designed for adaptability to an on-line iodine monitor. The sampling-sparging vessel will be of a design similar to the one described above but constructed of stainless steel. The experiments will utilize ¹³³Xe(5.3 days). The concentration of xenon in the sampling-sparging vessel and in a xenon trap for gases leaving the vessel will be measured by gamma spectrometry. Xenon removal from sodium will be examined as a function of composition of the helium-xenon sparge gas, sparge rate, and initial concentration of xenon in the sodium.

A gamma analyzer suitable for use in this work has been ordered and specifications are being written for gamma detectors compatible with the analyzer system. Drawings of the sparging vessel, xenon trap, and a sodium feed vessel for the experimental work are being prepared.

Method for Monitoring Nonvolatile Activities. An on-line method is also being considered for analyzing the coolant sodium for fission products and impurities that are less volatile than sodium. This method involves accumulation of these radioactive materials in a captive lithium phase, which is less volatile than sodium, and gamma analysis of their concentration after reducing the level of interfering ²⁴Na activity by vacuum distillation. In this concept, reactor sodium is fed at a low rate (about 5 g/min) to a distillation device with a reboiler containing captive lithium. The sodium and elements more volatile than lithium are vacuum distilled, condensed, and returned to the reactor. The lithium, which accumulates impurities less volatile than sodium, is recirculated between the reboiler and a counting cell in which the gamma activities are monitored. The lifetime of the device without additional recharging with fresh lithium would be dependent on the concentration of nonvolatile impurities (oxygen, for example) in

the reactor sodium. At the low sodium inlet rate envisioned for operation, the rate of nonvolatile impurity accumulation in the lithium would not be high [215 mg/(month) (ppm impurity in Na)]

3.2 Evaluation and Control Sodium Aerosol Problems (R. W. Kessie, E. H. Van Deventer)

The presence of sodium aerosol in the cover gas can create significant problems in reactor operations. A discussion of some of these problems, description of the experimental program and equipment to assess these problems, and a calculation study of the influence of heat transport on aerosol production were presented previously (ANL/ST-2, pp. 3-12 to 3-16). A comparison of measured aerosol concentrations and calculated vapor concentrations (ANL/ST-3, pp. 3-10 to 3-13) indicated that aerosol concentrations can exceed maximum vapor concentrations by factors as large as nine.

Experimental Studies. Preliminary measurements of the particle-size distribution of sodium aerosol in argon over sodium at 400°C have been made with a Casalla jet impactor. The experimental equipment was essentially the same as described previously (ANL/ST-2, p. 3-14) except that larger inlet and outlet tubes (1/4-in. OD rather than 3/16-in. OD) were used. Measurements at lower temperatures were masked by a high blank in the sodium analysis and at higher temperatures were prevented by plugging of the outlet tube. These problems are expected to be overcome in future experiments.

The amount of sodium collected in the individual stages of the jet impactor is given in Table 3-1 for two experiments at 400°C. For the collection time employed in Run NAF5 (6 min), some of the material was lost from the first stage, and this was visually apparent from the irregularity of the deposit. The final filter collected sodium aerosol that had passed through the four impactor stages in both runs. Also presented in Table 3-1 are the results of an experiment (Run NAF8) in which all of the aerosol was collected on a single filter. The close agreement of the total aerosol concentration with the average total from the jet impactor runs indicates that aerosol collection in the body of the impactor is not significant. The fact that these values are about 20% higher than a previous value obtained at 400°C (ANL/ST-3, p. 3-11 Run NAF4) indicates the improvement effected by the larger-diameter outlet line.

The calculated stage particle size for 50% collection (and 50% penetration) is given in Table 3-2 along with averaged aerosol data from Table 3-1. The data are also plotted in Fig. 3-1, where it can be seen that the mass mean diameter was $\sim 4 \mu\text{m}$, i.e., 50 wt % of the sodium aerosol was present as particles have diameters less than $4 \mu\text{m}$. The plot in Fig. 3-1 assumes a logarithmic normal

Table 3-1. Sodium Aerosol Concentrations in
Argon Cover Gas

Sodium temperature: 400°C
Aerosol flow rate: 100 ml/min (25°C)
Impactor flow rate: 10 liters/min (25°C)

Run	Stage	Collection Time (min)	Sodium (mg)	Concentration (g/m ³)
NAJ5	1	6	Partially Lost	
NAJ5	2	6	0.425	0.71
NAJ5	3	6	1.150	1.92
NAJ5	4	6	1.025	1.71
NAJ6	1	1	0.30	0.30
NAJ6	2	1	0.0875	0.88
NAJ6	3	1	0.230	2.30
NAJ6	4	1	0.1275	1.28
NAJ5+6	Final Filter	7	0.475	0.68
NAJ5+6	Average Total			5.4
NAF8	Filter	40	21.25	5.31

Table 3-2. Particle-Size Distribution of
Sodium Aerosol at 400°C

	Stage				Final Filter
	1	2	3	4	
Calibration constant ^a (μm)	15.4	6.5	3.3	2.2	
Avg. sodium concentration (g/m ³)	0.3	0.8	2.1	1.5	0.7
Cumulative wt % less than stated diameter	94	80	41	13	

^aCalculated stage particle size for 10 l/min flow rate from Report
UR-129, "The Modified Cascade Impactor" by Sidney Laskin (1960).

Fig. 3-1. Particle-Size Distribution of Sodium Aerosol above Sodium at 400°C.

distribution and a sharp cutoff of particle-size collection in the jet impactor stages, whereas the line actually has a steeper slope due to real width of the stage cutoff. Future experiments and impactor calibration measurements are expected to improve the accuracy of particle-size information.

Theoretical Studies. Sodium vapor that has evaporated from the sodium pool surface will be cooled by natural convection in the cover gas. Most of the sodium vapor will condense on existing sodium aerosol particles and cause them to grow. As the sodium aerosol particles are removed from the cover gas space, primarily by gravitational settling and cover-gas recirculation, new particles are created by at least one of three nucleation processes. The three nucleation processes, in order of increasing driving forces normally experienced with respect to the degree of supersaturation of the sodium vapor, are (1) nucleation on foreign or non-sodium nuclei, (2) nucleation on ions, and (3) homogeneous nucleation. Since no studies have been found for these processes with metal vapor and the most extensively studied system is water vapor, comparisons will be made for sodium vapor at several temperatures with water vapor at one temperature.

For the first process listed above, the vapor pressure p of a small sphere of radius r is given by the well known Thomas-Gibbs² equation

$$\ln \frac{p}{p_{\infty}} = \frac{2\sigma M}{RT\rho r}$$

where: p = vapor pressure over sphere (dyne/cm²)

p_{∞} = vapor pressure over plane surface (dyne/cm²)

σ = surface tension of the liquid (dyne/cm)

M = molecular weight of the liquid

R = gas constant (erg/°K mol)

T = temperature (°K)

ρ = density of the liquid (g/cm³)

r = radius of the sphere (cm)

The results of this relation for water and sodium are compared in the upper (neutral) curves of Fig. 3-2, where supersaturation (p/p_{∞})

²H. L. Green and W. R. Lane, Particulate Clouds: Dusts, Smokes, and Mists, D. Van Nostrand Co., Princeton, N. J. (1964).

Fig. 3-2. Supersaturation for Small Particles.

is plotted against the particle radius required for nucleation. There is a very close correspondence between the supersaturation of water at 20°C and sodium at 600°C. At lower sodium temperatures, larger supersaturations are required for a small particle to grow. This relation assumes that foreign nuclei of the indicated size are readily wet by sodium. If this is not the case, the foreign condensation nuclei must be larger than indicated by the above relation.

When the surface of the sphere is charged, the relation is

$$\ln \frac{p}{p_{\infty}} = \frac{M}{RT\rho} \left[\frac{2\sigma}{r} - \frac{q^2}{8\pi\epsilon_1 r^4} \right]$$

where: q = charge on sphere

ϵ_1 = dielectric constant of gas

A single central electron charge gives

$$\ln \frac{p}{p_{\infty}} = \frac{M}{RT\rho} \left[\frac{2\alpha}{r} - \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \frac{q}{8\pi r^4} \right]$$

where ϵ_2 = dielectric constant of liquid. For metals, $\epsilon_2 = \infty$ and both equations reduce to the same result. For water, $\epsilon_2 = 81.07$ and the results of the two relations are similar. The above equations are plotted in Fig. 3-2 as the lower curves (ions) using a single electronic charge for q . Sodium will require a larger supersaturation than water for ion nucleation.

The theory of homogeneous nucleation contains more approximations than the two previous processes. The expression derived by Becker and Doring² for the rate of formation of homogeneous nucleation may be written

$$J = \frac{\alpha N}{\rho} \left(\frac{p}{RT} \right)^2 \sqrt{\frac{2\alpha MN}{\pi}} \exp \left[- \frac{16\pi\alpha}{3kT} \left(\frac{M\alpha}{pRT \ln p/p_{\infty}} \right)^2 \right]$$

where: J = rate of formation ($\text{cm}^{-3} \text{sec}^{-1}$)

α = accommodation coefficient of droplet surface

N = number of molecules per mol

R = gas constant (erg/°K mol)

k = Boltzmann's constant

The results of this equation as applied to sodium are plotted in Fig. 3-3 for a selected value of the accommodation coefficient ($\alpha = 1$). Experimental data of Vollmer and Flood² and of Wilson and Powell² for water are included in the figure for comparison with this theory. The curves for sodium do not include any effect of the tendency for sodium vapor to dimerize, which would tend to further reduce the supersaturation.

A comparison of supersaturation at intermediate rates of formation (Fig. 3-3) with the peak values of supersaturation for ions (Fig. 3-2) indicates that sodium will have a stronger tendency to homogeneous nucleation than water, particularly at higher temperatures.

Fig. 3-3. Becker-Doring Theory of Homogeneous Nucleation Applied to Sodium and Water.

4. SODIUM CHEMISTRY (J. G. Eberhart)

4.1 Characterization of Nitrogen-Bearing Species in 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. Previous quarterly reports have outlined the approach and experimental procedures involved (ANL/ST-2, p. 6-4 and ANL/ST-3, p. 4-1). Briefly, the current study involves measurement of the extent of (1) nitrogen absorption by a Na-1 at.% Ca solution in contact with Type 304 stainless steel and (2) nitridation of the stainless steel.

Nitrogen absorption experiments performed to date at 590°C are shown in Fig. 4-1. The two upper curves represent duplicate experiments with solutions of 1 at.% Ca in Na and these show good agreement. The two lower curves represent nitrogen absorption by systems containing sodium but no added calcium. A previous experiment (ANL/ST-3, p. 4-2) in a system containing no sodium or calcium revealed no nitrogen uptake. The curve for this experiment is not shown in Fig. 4-1. At the present time, 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 reaction in the sodium. The two lower curves (no calcium added) differed by a factor of two in the amount of sodium used, but the curve for 0.50 mole of sodium has an intercept that is not as was first expected. Subsequently recognized geometrical factors in this experiment are believed to be the cause of the discrepancy; therefore, only the experiment with 1.00 mole of sodium has been taken as the blank experiment for comparison with the calcium-containing experiments.

The fact that all curves are found to have the same slope in the linear region makes it appear that the rate of nitrogen uptake by the steel is the same whether or not a considerable quantity of extra calcium is added. For the first experiment with 1 at.% Ca (previously described in ANL/ST-3), a stainless steel tab that had been submerged in the solution did not reveal any nitrogen or calcium pick-up. Analysis of a filtered sample of sodium from

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

the same experiment showed less than 10 ppm calcium. (Chemical analyses for the second experiment are not yet finished.) These facts are consistent with the hypothesis of the formation (in sodium) of an insoluble calcium-nitrogen compound, and with the removal, by calcium, of yet unidentified nitrogen carriers. These reactions are deemed relatively rapid, compared with nitridation of steel. The nitrogen uptake by steel is believed to occur mainly at the ring of intersection of the liquid surface with the container wall. This belief is supported by the finding of 5000 ppm nitrogen in filings taken from a reaction-vessel section in this region.

The amount of absorbed nitrogen that is ascribed to interactions with calcium and impurities in the experiments with 1 at.% calcium is 3.37×10^{-3} mole (average of the two intercepts). By subtracting the corresponding value for the blank experiment with 1.00 mole of sodium, we arrive at an overall reaction stoichiometry representable by $\text{Ca}_{1.78} \text{N}$. Work is in progress on determining the role of selected impurities in the observed nitridation process.

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

This investigation seeks a basis for understanding the behavior of oxygen- and hydrogen-bearing species in liquid sodium. The results will be useful in developing and evaluating analytical methods for the monitoring of oxygen and hydrogen impurities in sodium. The initial effort is being directed toward the elucidation of the phase relations in the $\text{Na-Na}_2\text{O-NaOH-NaH}$ system.

From a review of the available literature, two versions of the $\text{Na-Na}_2\text{O-NaOH-NaH}$ ternary diagram were constructed (see ANL/ST-3, pp. 4-4 to 4-13). An experimental program has been undertaken to (a) determine which of the diagrams is more fundamentally correct, (b) refine the selected diagram, and (c) study the kinetics of the interactions between hydrogen and oxygen with sodium at LMFBR temperatures.

To determine the correctness of the diagrams, Na-H-O mixtures are being prepared from known amounts of Na , Na_2O , NaOH , and NaH . The mixtures are placed inside of sealed nickel capsules and carefully heat-treated to produce the phases that are in equilibrium at room temperature. The phases are to be identified by X-ray powder and diffractometer methods. The required laboratory equipment has been set up and appropriate techniques have been developed.

The phase relations will be established at elevated temperatures by means of an apparatus that simultaneously measures (1) the activities of oxygen and hydrogen in the various phase fields by use of appropriate meters and (2) the nature and concentration of the species in the vapor over the liquid and solid ternary phases by means of a mass spectrometer. A correlation of the parameters with addition of Na_2O , NaOH , and NaH to liquid sodium should delineate the phases and phase-region boundaries of the ternary system. The apparatus is in the final stages of design and most of the components have been ordered and delivered. The mass spectrometer (Granville Phillips RGA750) has been attached to an apparatus mock-up and familiarization runs have been made.

4.3 Determination of the Solubility of Gases in Liquid Sodium (E. Veleckis, W. A. Kremsner)

Work is continuing on a study to determine the temperature (350-600°C) and pressure (2-10 atm) dependence of xenon solubility in liquid sodium. Such information is of considerable value in the implementation of two programs currently underway at Argonne for the detection and the location of fuel cladding failures in LMFBR systems. In one program¹ concerned with locating failed experimental fuel in EBR-II, each fuel element in a subassembly is tagged with a mixture of xenon isotopes that is unique for that subassembly. If a cladding failure is indicated by one of the existing monitoring instruments, a sample of the reactor cover gas will be analyzed mass spectrometrically to permit identification of the affected subassembly. In the second program (see Section 3.3, this report) the detection of fuel failures by monitoring the primary coolant of an LMFBR will be tested. In the approach under consideration, iodine-135 released through failed cladding into coolant sodium is determined by separation and counting of its daughter xenon-135m.

The method of determining xenon solubility is adapted from that used by Grimes et al.² for noble gases in eutectic mixtures

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¹Chemical Engineering Division Annual Report--1969, ANL-7675, pp. 110-115 (April 1970).

²W. R. Grimes, N. W. Smith, G. M. Watson, J. Phys. Chem. **62**, 862 (1958).

of fused fluorides. This method incorporates important features for determining very low solubilities of gases in liquids at elevated temperatures. Our adaptation of the method involves saturating liquid sodium with natural xenon at a preselected temperature and pressure, transferring a portion of the saturated sodium to another container where the dissolved gas is stripped from sodium by sparging with helium, separating the stripping gas from the gas mixture by selective adsorption, and, finally, analyzing the remaining gas for the xenon originally dissolved in sodium. Xenon analyses are made with a Beckman GC-5 gas chromatograph. In employing this procedure, special precautions are taken to ensure representative solubility measurements: (1) good contact of the saturating gas with sodium is provided by prolonged bubbling of gas through the sodium; (2) saturated sodium is allowed to sit undisturbed for a long period of time to promote the coalescence and escape of bubbles; (3) only the bottom portion of sodium is transferred to the stripper and the transfer is performed slowly to avoid the sodium-gas or sodium-container interfaces, which are expected to be richer in xenon; and (4) efficient stripping of the dissolved xenon from sodium is ascertained by first cooling the sodium to a temperature ($\sim 150^{\circ}\text{C}$) at which the gas solubility is negligible and then sparging for 2 hr with helium.

Measurements of the solubility of xenon in liquid sodium have been carried out at approximately 50-degree intervals between 350 and 600°C. The results are summarized in Table 4-1 where the mean solubilities of 47 determinations are listed. The mean solubilities were obtained by averaging each set of solubility results which had been corrected to their respective nearest rounded (to two significant figures) temperatures. Corrections were made using the temperature dependence obtained from the least squares analysis of complete data. The relative standard deviations and the number of determinations at each temperature are shown in columns 4 and 5 of the table.

The solubilities in Table 4-1 are expressed in two forms: (1) the Henry's law constant, K_H , in ppb/atm, i.e., in grams of gas dissolved in 10^9 grams of sodium per atmosphere of gas pressure and (2) the Ostwald coefficient, λ , in volume of gas dissolved per unit volume of sodium, both the solute and solvent being at the temperature and pressure of the experiment. The two constants, when expressed in these units, are related to one another by the formula

$$\lambda = (RTd_{\text{Na}}/10^9 M_{\text{Xe}})K_H$$

Table 4-1

Solubility of Xenon in Liquid Sodium

<u>Temperature</u>	<u>Henry's Law Constant, K_H (ppb/atm)</u>	<u>Ostwald Coefficient, λ</u>	<u>Relative Std. Deviation (%)</u>	<u>Number of Determinations</u>
600	90.9	4.00×10^{-5}	--	1
550	37.9	1.60×10^{-5}	9	6
500	17.4	6.98×10^{-6}	17	17
450	6.56	2.50×10^{-6}	18	9
400	3.06	1.10×10^{-6}	6	7
350	0.799	2.70×10^{-7}	17	7

where the gas constant $R = 82.05 \text{ (cm}^3\text{)(atm)/deg(mol)}$, T is the absolute temperature, $d_{\text{Na}} = 0.950 - 2.30 \times 10^{-4} t - 1.46 \times 10^{-8} t^2 + 5.64 \times 10^{-12} t^3$ is the density of liquid sodium³ in g/cm^3 , M_{Xe} is the atomic weight of xenon, and t is the temperature in $^{\circ}\text{C}$.

The complete solubility data (47 points) are shown in Fig. 4-2 as a plot of $\log K_{\text{H}}$ vs. $1/T$. The regression line can be represented by

$$(350\text{--}600^{\circ}\text{C}) \quad \log K_{\text{H}} = 6.74 - 4252 T^{-1}$$

where K_{H} is in ppb/atm . Error analysis showed that at the 95% confidence limit the deviation of the mean value of $\log K_{\text{H}}$ is ± 0.022 ; the corresponding error in K_{H} in ppb/atm is $\pm 5.2\%$. The heat of solution of xenon in liquid sodium calculated from the slope of the line in Fig. 4-2 is $19.4 \pm 0.8 \text{ kcal/mol}$.

A theoretical model that satisfactorily accounts for the measured solubilities of noble gases in liquid sodium is being developed at ANL.⁴ Application of this model to the xenon-sodium system shows that the predicted xenon solubilities are lower than those presently measured by a factor of only ~ 2.5 . Furthermore, the predicted heat of solution was found to be almost identical to that obtained in this study.

³J. P. Stone et al., NRL-6241, Naval Research Laboratory, Washington, D. C. (Sept. 24, 1965); G. H. Golden, J. V. Tokar, ANL-7323, Argonne National Laboratory, Argonne, Ill. (August 1967).

⁴H. Schnyders and H. M. Feder, Argonne National Laboratory, private communication.

Fig. 4-2. Temperature Dependence of Solubility of Xenon in Sodium.

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

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

The primary goal of this work is the determination and interpretation of nonmetallic impurity levels in cold-trapped sodium as a function of cold-trap operating parameters and procedures. The methods for determining the impurities (O, C, H, N) in the sodium will be on-line impurity monitoring, and sampling and analysis. Experimental work will be carried on in a pumped-sodium apparatus that will provide stable but adjustable impurity levels in the sodium fed to the test cold trap. The work plan has been approved and is being implemented for the design and construction of the Apparatus for Monitoring and Purifying Sodium (AMPS). Target date for startup of AMPS is mid FY 1972. Data for both transient and steady-state operation of the test trap will be correlated with cold-trap parameters and the feed composition.

A detailed equipment layout has been prepared for installing two oxygen meters and one hydrogen meter on the outlet of the EBR-II primary cold trap. These meters will be used in conjunction with meters to be installed on the Radioactive Sodium Chemistry Loop (RSCL) of EBR-II for characterizing the operation and efficiency of the primary cold trap.

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

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

The objectives of this work are an understanding of the mechanism and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and a correlation of experimental results with mechanical-property data being obtained at other laboratories. 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

To obtain experimental evidence on the distribution of carbon between sodium and iron-base alloys (viz., Type 304 SS, Fe-18 wt % Cr-8 wt % Ni, Fe-8 wt % Ni, and Fe-16 wt % Ni), foil samples of each material were exposed to flowing sodium in a molybdenum test section at temperatures of 650 and 750°C for a period of 3500 hr. Sodium samples were obtained in "flow-through" samplers and were analyzed for total carbon by C. C. Miles (ANL-ID) by the oxyacidic flux method.¹ The foil samples were analyzed for carbon by combustion. The results of the carbon analyses of the foil samples and the sodium are shown in Table 6-1.

The results show that the concentration of carbon in Type 304 SS is about a factor of ten greater than that in the Fe-18 wt % Cr-8 wt % Ni alloy. These carbon analyses are consistent with photomicrographs of the equilibrated alloys; in the former significant carbide precipitation was observed in the entire cross section, whereas in the latter no carbides were present. An order of magnitude difference in the carbon levels between the two alloys has been observed in equilibration studies conducted in Vycor capsules at 800°C. Minor alloying elements (e.g., Mn) and metallic impurities (e.g., Si, Ti, Zr) apparently have an important effect on the total carbon content of these alloys at low carbon activities. The steels are being analyzed for the latter constituents to determine the elements which may have a strong effect.

Using the carbon activity and solubility values in the Fe-18 wt % Cr-8 wt % Ni alloy² and the data in Table 6-1, the

¹C. C. Miles, Anal. Chem. 41, 1041-1048 (1969).

²K. Natesan and T. F. Kassner, "Calculations of the Thermodynamic Driving Force for Carbon Transport in Sodium-Steel Systems," ANL-7646 (December 1969).

Table 6-1

Carbon Analyses of Iron-Base Alloy Foils and Sodium from
Carbon Distribution Studies

<u>Temp. (°C)</u>	<u>Carbon Content of Foils^a (ppm)</u>				<u>Carbon Content of Sodium (ppm)</u>
	<u>Fe-8 wt % Ni</u>	<u>Fe-16 wt % Ni</u>	<u>Fe-8 wt % Ni- 18 wt % Cr</u>	<u>Type 304 SS</u>	
750	14.0	9.3	96	960	0.4 ± 0.2, 0.7 ± 0.2
650	8.2	6.6	126	1285	

^aAll foils were 10 mils thick with the exception of Type 304 SS foils which were 5 mils thick.

carbon concentration in sodium was calculated to be 0.18 ppm in this experiment. This value is in reasonable agreement with the carbon concentration determined analytically. A carbon concentration of 0.18 ppm corresponds to carbon activities of 0.011 and 0.002 at 650 and 750°C, respectively.

The carbon concentrations in the two Fe-Ni alloys will also be used to evaluate the carbon activities in this experiment; this evaluation will be made upon completion of the equilibration study involving α -iron at low carbon activities described below.

6.1.2 Analysis of Low Carbon Concentrations in α -Iron by the Internal-Friction Technique

Carbon activity values in the range of 0.01 to 0.1 are required for carburization-decarburization studies in sodium-steel systems.² Measurements of carbon activities in Fe-Ni alloys in the range 0.4 to 1.0 (with graphite as the standard state) have been reported in the literature.^{3,4} A determination of carbon activities in Fe-Ni alloys in the range 0.01 to 0.5 (with graphite standard state) is in progress. For this purpose, 1/2-in.-dia iron rod of high purity (purity given in Table 6-2) was drawn into 65- and 18-mil wire.⁵

These wires were equilibrated at 700°C in quartz capsules with carburized Fe-8 wt % Ni alloys to yield carbon activities in the above range. After the equilibration, the capsules were quenched in brine solution. The 18-mil wires from these capsules were analyzed for carbon by the internal-friction technique, and the 65-mil iron wires were analyzed by the combustion method. Typical internal-friction peaks for several carbon concentrations in the iron are shown in Fig. 6-1. The dashed line is the "background" internal friction for the 75-ppm wire, above which the peak height is measured. The combustion analyses of the iron samples were used to establish the relationship between the internal-friction peak height and the concentration; this relationship is shown in Fig. 6-2. Similar data⁶ obtained by equilibrating iron wires with various gas mixtures are also included in Fig. 6-2. These results indicate that the internal-friction technique will be useful in determining carbon activities in various iron-base alloys that may be used in sodium-reactor systems, i.e., as low as a few ppm carbon in iron.

³A. J. Heckler, P. G. Winchell, Trans. Met. Soc. AIME 227, 732-736 (1963).

⁴R. P. Smith, Trans. Met. Soc. AIME 218, 62-64 (1960).

⁵Wire specimens prepared by F. Karasek, Fabrication Group, Materials Science Division, ANL.

⁶J. C. Swartz, Trans. Met. Soc. AIME 245, 1083-1092 (1969).

Table 6-2

Impurity Content (in ppm) of α -Iron Used for the
Determination of Carbon Activity

<u>Mn</u>	<u>S</u>	<u>P</u>	<u>Si</u>	<u>Sn</u>	<u>Cu</u>	<u>Cr</u>
500	50	<10	<50	<30	30	<40
<u>Ni</u>	<u>Mo</u>	<u>Al</u>	<u>Zr</u>	<u>V</u>	<u>Nb</u>	
120	<20	<40	<50	10	20	

Fig. 6-1. Typical Internal-Friction Peaks for Carbon in α -Iron.

Fig. 6-2. Internal-Friction Peak Height vs. Carbon Concentration in α -Iron.

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

Successful prediction of carburization-decarburization rates of materials in a reactor system will require the development of calculational methods as well as the determination of diffusion coefficients of carbon as a function of alloy composition and temperature. The objective of this work is to determine the diffusivity of carbon in ferritic Fe-Cr-Mo and austenitic Fe-Cr-Ni alloys by a steady-state method.^{7,8} The method involves passing a carburizing gas, $\text{CH}_4\text{-H}_2$, inside of a cylindrical shell specimen and a decarburizing gas, H_2 , outside of the specimen, and allowing the process to attain a steady state. The flux of carbon, J , through the cylindrical surface is given by $q/2\pi r\ell t$ where q is the quantity of carbon passing through the cylindrical area of length ℓ in a given time, t . By applying Fick's Law,

$$J = -D \frac{dc}{dr} = \frac{q}{2\pi r\ell t}$$

the diffusion coefficient of carbon can be written as:

$$D = -q/(2\pi\ell t)(dc/d \ln r) \quad (1)$$

By measuring the diffusive flow rate of carbon, q/t , through a specimen of length, ℓ , and the slope of carbon concentration profile (plot of c vs. $\ln r$), the diffusion coefficient at any given carbon content can be determined from Eq. 1.

The assembly for the first experiment (see Fig. 6-3) consists of four Fe-2.25 wt % Cr-1 wt % Mo alloy specimens which are being exposed to the carburizing and decarburizing gases at 700°C. Steady-state conditions have been established, and the gases are being analyzed for methane by gas chromatography. This experiment will give data on the diffusion coefficient as a function of carbon level in the alloy.

Similar experiments at temperatures of 600 and 500°C will also be made. At a later stage, austenitic alloy specimens with different chromium contents will be used to determine the effect of chromium on the carbon diffusivity in these alloys. The kinetic parameters will be used to evaluate the rates of carburization of austenitic steels and decarburization of ferritic steels in sodium-reactor systems.

⁷C. Wells, "Atom Movements," Amer. Soc. Metals, 26-50 (1951).

⁸R. P. Smith, Acta Met. 1, 578-587 (1953).

Fig. 6-3. Assembly for Carbon-Diffusion Studies in Fe-2.25 wt % Cr-1.0 wt % Mo Alloy.

6.1.4 Carburization and Nitridation of Steels by Cyanide in Sodium

Additional results have been obtained for the series of capsule experiments in which the distribution of carbon and nitrogen between several iron-base alloys and liquid sodium is being investigated. As was discussed in the preceding quarterly report (ANL/ST-3, pp. 6-1 to 6-4), a large fraction of the carbon initially present in the system could not be accounted for on the basis of a carbon mass balance after the equilibration.

Samples of the inner surface of two of the molybdenum capsules used in the experiments were obtained for carbon and nitrogen analyses. The capsule (CN-7) that had the highest cyanide concentration in sodium (1282 ppm) and the one in which no cyanide was added to the sodium (CN-8) were examined. Material along two 0.5-in. lengths was removed to a depth of 2 mils in a lathe. Material from another cut 3 mils deep was used to assess the carbon and nitrogen penetration depths. Samples of the molybdenum from which the capsules were fabricated were also analyzed. The results of the analyses are given in Table 6-3.

A substantial increase in carbon concentration was observed in the region 2 mils from the inner surface of the capsule that contained cyanide. Provided this carbon concentration is representative of the entire inner area of the capsule, the percentage of carbon accounted for increased from 14% to 70% for capsule CN-7. The improvement in the mass balance, coupled with experiments which demonstrated satisfactory cyanide recovery from sodium in the capsules, indicates that the cyanide analyses at the conclusion of the tests represent near-equilibrium conditions in the system. Carbon concentrations in the Fe-18 wt % Cr-8 wt % Ni alloys are plotted as a function of the cyanide concentration in sodium in Fig. 6-4.

Results for the distribution of nitrogen between the alloys and sodium containing cyanide in these experiments are shown in Fig. 6-5. More than 70% of the nitrogen was accounted for from a mass balance after equilibration.

The curves in Figs. 6-4 and 6-5 indicate that the nitridation potential of cyanide in sodium is greater than that for carburization at 800°C.

6.2 Candidacy of Vanadium-Base Alloys for Cladding LMFBR Fuels (T. F. Kassner, D. L. Smith)

Rotating-Disk Corrosion Studies. The corrosion of vanadium in liquid sodium has been investigated under the well-defined

Table 6-3

Carbon and Nitrogen Analyses of the Molybdenum
Capsule Material

<u>Capsule No.^a</u>	<u>Nitrogen Concentration (ppm)</u>	<u>Carbon Concentration (ppm)</u>
CN-7A	53	940
CN-7B	8	108
CN-8A	10	169
CN-8B	4	92
Mo, as received	4	109

^aA and B denote material from the 2- and 3-mil cuts, respectively.

Fig. 6-4. Equilibrium Distribution of Carbon Between Fe-18 wt % Cr-8 wt % Ni Alloy and Sodium Containing Cyanide at 800°C.

Fig. 6-5. Equilibrium Distribution of Nitrogen Between Fe-18 wt % Cr-8 wt % Ni Alloy and Sodium Containing Cyanide at 800°C.

hydrodynamic conditions produced by the rotating-disk sample geometry (ANL/ST-2, p. 4-7; ANL/ST-3, p. 6-4). Kinetic data were obtained by removing the disk sample from the sodium at several time intervals and determining the weight and dimensional changes. The linear time law for the amount of metal lost was followed at 450, 500, 600, and 700°C under both laminar and turbulent flow conditions. The effect of velocity and oxygen concentration in sodium on the corrosion rate was determined. The results indicate that the corrosion rate becomes independent of the oxygen concentration in sodium above ~4 ppm at 450°C, ~10 ppm at 500°C, and ~20 ppm at 600°C; however, the half-power velocity dependence is still observed under conditions where the rates are independent of the oxygen concentration. This type of behavior indicates that the rate limiting step in the corrosion process undergoes a transition from the diffusion of oxygen to the sample to the diffusion of corrosion product away from the sample as the oxygen concentration in sodium increases above a critical level.

Information on the temperature dependence of the $V_{(O, sat)}^{-V_{50-0-Na}}$ phase equilibrium⁹ and corrosion-rate data under conditions where the rate is a function of both velocity and oxygen concentration in sodium can be used in the convective-diffusion model for mass transport to a disk to obtain values for the diffusion coefficient for oxygen in liquid sodium.

The convective-diffusion flux of oxygen, J_o , to the disk sample under laminar flow conditions can be written as:¹⁰

$$J_o = 0.554 I_{(D/\nu)}^{-1} D_o^{2/3} \nu^{-1/6} \omega^{1/2} (C_{O-Na}^B - C_{O-Na}^S) \quad (2)$$

where

$I_{(D/\nu)}$ = values of an integral in the solution of the convective-diffusion equation. This term is a function of the reciprocal Schmidt number (D/ν)

D_o = diffusion coefficient of oxygen in liquid sodium, cm^2/sec

ν = kinematic viscosity of sodium,¹¹ cm^2/sec

⁹ D. L. Smith and T. F. Kassner, Corrosion by Liquid Metals, Plenum Press, 1970, pp. 137-149.

¹⁰ T. F. Kassner, J. Electrochem. Soc. **114**, 689-694 (1967).

¹¹ G. H. Golden, J. V. Tokar, "Thermophysical Properties of Sodium," ANL-7323 (1967).

ω = angular velocity of the disk, radians/sec

C_{O-Na}^B = oxygen concentration in the bulk sodium at the disk temperature, g O/cm³

C_{O-Na}^S = oxygen concentration at the surface of the disk sample given by the $V_{(O \text{ sat})} - V_{5O-0-Na}$ equilibrium. (Based upon unpublished data for the free energy of formation of V_5O and VO ,¹² the oxygen activity in sodium for the $V_{(O \text{ sat})} - V_{5O-0-Na}$ equilibrium is only slightly lower than that for the $V_5O-VO-0-Na$ equilibrium.)

Vanadium corrosion rates (g V/cm²-sec) are related to the diffusional flux of oxygen to the disk by the stoichiometric relation $V + \frac{O}{Na} = VO$ for the vanadium monoxide corrosion product. Experimental data from 21 runs were used with Eq. 2 to obtain a plot of the diffusion coefficient of oxygen in liquid sodium versus reciprocal temperature, shown in Fig. 6-6. At each temperature the average value of D and the spread in the data are indicated by the point and vertical line, respectively.

Although these data are encompassed by the lower limit of the range of diffusion coefficients commonly observed in liquid-metal systems, an extrapolation to lower temperatures results in unreasonably low values. In comparison with another measurement, the data at 500°C are approximately two orders of magnitude lower than those obtained by Siegel and Epstein¹³ with a diffusion cell. The reason for this difference is being investigated as part of the task of reporting the results of this investigation. No further experiments are planned.

¹²W. L. Worrell, University of Pennsylvania, private communication (1969).

¹³S. Siegel, L. F. Epstein, GEAP-3357 (1959).

Fig. 6-6. Temperature Dependence of Diffusion Coefficient of Oxygen in Liquid Sodium.

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