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SODIUM TECHNOLOGY QUARTERLY REPORT

October-December 1971

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

SODIUM TECHNOLOGY QUARTERLY REPORT
October-December 1971

L. Burris	Manager, Sodium Technology Program
J. E. Draley	Asst. Manager
P. A. Nelson	Section Head, Engineering Development
F. A. Cafasso	Section Head, Chemical Development
T. F. Kassner	Group Leader, Metallurgical Development
J. M. McKee	Problem Leader, Engineering Development
C. C. McPheeters	Problem Leader, Engineering Development
R. J. Meyer	Group Leader, Analytical Development
M. H. Barsky	Asst. Group Leader, Analytical Development

Compiled and Edited by
G. M. Kesser

May 1972

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FOREWORD

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

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ABSTRACT

The research, development, and management efforts of Argonne National Laboratory's Sodium Technology Program for the period October-December 1971 comprised activities in the following areas: (1) In the national meter program, performance-characterization of an improved electrochemical oxygen meter has emphasized meter calibration using the vanadium-wire equilibration method for determining oxygen activity; other work has included testing of on-line monitors for hydrogen and leak detectors for steam generators, development of a method for relating the outputs of carbon meters to the carbon activity of sodium, and testing of meter modules for FFTF. (2) In the analytical standards program, efforts continued on the preparation of RDT standards relating to specifications for measuring and controlling the purity of sodium and cover gas; laboratory work included further studies of the effect of line length on the validity of sodium samples, evaluation of the uranium-getter method for determining oxygen in sodium, characterization of particulates filtered from various sodium systems, and development of methods for determining oxygen and hydrogen activities in sodium by the equilibration of niobium wires. (3) Development work was continued on a gas-chromatographic method for separating ^{23}Ne from noble-gas fission products in cover gas, a sparging technique for monitoring the ^{135}I content of reactor primary sodium, and an on-line diffusion meter for monitoring tritium in sodium. (4) Studies of the chemistry of liquid sodium have been directed toward investigations of oxygen-hydrogen interactions in sodium using deuterium as a stand-in for hydrogen, and evaluation of vacuum distillation as a means of determining oxygen, hydrogen, and nitrogen in sodium. (5) A program is under way to determine the integrated effects of fast-neutron and sodium environments on the properties of stainless steel, to develop postexposure testing methods for the stainless steel specimens, and to correlate the results from experimental and reactor sodium systems; work has continued on the study of carbon transport in sodium-steel systems.

SUMMARY

On-Line Impurity Monitors

A national program is in progress for developing, testing, and establishing commercial availability of meters for the Fast Flux Test Facility (FFTF) and LMFBR sodium systems. Argonne National Laboratory (ANL) is coordinating this program as well as participating in it. At present, five types of units are being developed: oxygen meters, hydrogen meters, carbon meters, modules for installing these meters in reactor sodium systems, and steam-generator leak detectors.

Oxygen Meter Development. The immediate objective of this program is to characterize the performance of an improved electrochemical oxygen meter, intended for use in the FFTF. The meter utilizes an improved solid electrolyte tube (thoria-7.5 wt % yttria) and a gas reference electrode. ANL is participating in the performance characterization and field-testing of these meters, and is also responsible for coordinating the efforts of the contractors in the program, principally Hanford Engineering Development Laboratory (HEDL), Westinghouse, and the Zirconium Company of America (Zircoa).

Zircoa has produced 200 electrolyte tubes to HEDL process specifications. Westinghouse has incorporated more than 30 of these tubes in oxygen meters with gas reference electrodes. Performance testing of 20 of these meters began during the quarter in a joint ANL-Westinghouse meter characterization program. Ten meters are being tested at each site and have been operated ~1800 hr at 700°F after a two-day conditioning treatment at 930°F. The meters have been calibrated by the vanadium-wire equilibration method at eight oxygen levels in the range from 0.5 to 16 ppm oxygen in sodium. The calibration curves for the 10 meters at ANL are described by the equation:

$$\text{Meter emf (volts)} = K_1 - (0.049 \pm 0.0026) \log \text{ ppm O}$$

where K_1 ranges from 1.711 to 1.7334 V. The 2 σ deviation in K_1 for all calibration points per meter averaged 16 mV. This uncertainty in K_1 resulted mainly from downward drift of meter voltage during the calibration period. The stability of the meters appears to be improving, and it is expected that subsequent determinations of K_1 will show considerably smaller deviations. It is also expected that changes in operating conditions, particularly higher temperature, may improve the stability of K_1 , so that a single-point calibration check not oftener than once a month will provide adequate accuracy for reactor operators.

The oxygen concentrations measured at ANL and Westinghouse by vanadium-wire equilibration at 1382°F have been compared. When plotted versus cold-trap temperature, the results from the two sites differed slightly from each other and from the oxygen solubility curve based on cold-trap temperatures. Possible sources of this difference are being investigated.

The first vanadium-wire specimens equilibrated in EBR-II primary sodium gave an oxygen content of 0.85 ± 0.06 ppm. Additional runs will be made to determine the calibration stability of the oxygen meters and to characterize the oxygen level in this reactor coolant system.

Hydrogen Meter Development. The goal of this program is the development of an on-line hydrogen meter for measuring the hydrogen activity in the primary and secondary sodium of LMFBR systems.

During this period, the solubility of hydrogen in sodium was re-measured at various cold-trap temperatures on the Oxygen Meter Rig (OMR). The results of these solubility studies are in very good agreement with similar data reported earlier. Ion-pump currents obtained from the meter operation in the dynamic mode correlated well with the concentration of hydrogen in sodium. The correlation, however, was not linear.

The hydrogen meter on the module in Cell B, operated in the dynamic mode at 700°F, has indicated a hydrogen content of 10 to 100 ppb for EBR-II primary sodium. Attempts to operate this meter in the equilibrium mode at 700°F have not been successful because of outgassing problems.

Carbon Meter Development. The effort to devise a calibration technique to relate carbon meter outputs to the carbon activity in sodium have continued. An experimental survey of potentially useful tabs revealed that Fe-12 wt % Mn behaves similarly to the Fe-8 wt % Ni alloy tested earlier. The Fe-12 wt % Mn has the advantage that the equilibrium carbon concentration of the tab in contact with sodium is 3 to 4 times higher than that of Fe-8 wt % Ni. Other tab materials tested were titanium, tantalum, cobalt, zirconium, vanadium, and molybdenum.

Calibrations of both a United Nuclear Corporation (UNC) carbon meter and a Brookhaven National Laboratory (BNL) carbon meter were performed using carbon activity data obtained with Fe-8 wt % Ni. A linear plot of meter reading vs. carbon activity was obtained with the UNC meter. With the BNL meter, the cell potential appears to approach a limit in the region of greatest interest, i.e., low carbon activities.

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

Two oxygen-hydrogen meter (O-H) modules were in use during the quarter, one in EBR-II primary sodium and one on the Test and Evaluation Apparatus (TEA) at ANL-Illinois. A third module is being built. The O-H module in Cell B of the RSCL at EBR-II has operated a total of 956 hr with the meters at 700°F. One of the two oxygen-meter electrodes failed at 413 hr and was replaced. The failed electrolyte assembly has been returned to Westinghouse for examination.

Carbon meter-equilibration (C-E) modules were used for measuring oxygen in sodium by vanadium-wire equilibration at EBR-II, ANL-Illinois, and Westinghouse during the quarter. Two additional C-E modules are being built at ANL. One will be used for measurements of carbon activity and tritium at EBR-II, the other will be installed on the Apparatus for Monitoring and Purifying Sodium. Feasibility approval for the test at EBR-II has been received and the request for Approval-in-Principle (AIP) has been submitted to RDT.

Working drawings and a design description of a low-cost equilibration device were made available to potential users of the specimen-equilibration method.

Detection of Leaks in Steam Generators. EBR-II personnel are preparing a procurement package for a system of 10 leak detectors for the EBR-II steam generators, based on detailed drawings and stress analysis completed at ANL. ANL is also preparing to supply a leak detector for use on the Sodium Components Test Installation at the Liquid Metal Engineering Center. Necessary design revisions in the EBR-II type of leak detector were completed, long-lead items were ordered, and fabrication has been started.

A bellows configuration, formed from 270 nickel sheet, is being evaluated for use as the membrane in the leak detector and hydrogen meter. Examination of a cross section revealed no defects and a uniform 10-mil wall thickness. Pressure testing of four bellows to collapse showed that this configuration has adequate strength for LMFBR steam-generator service. Preliminary tests in sodium indicate good performance as a hydrogen-permeable membrane.

Apparatus for Monitoring and Purifying Sodium, AMPS. Substantial progress on the construction of AMPS was achieved during the quarter. The main vessels and one-third of the piping-spool pieces are in place. Fabrication of the cold traps and meter modules is nearing completion.

Analytical Standards Program

Effects of Line Length on Sample Validity. The second series of experiments to determine the effect of line length on sample validity has been completed. Experiments conducted at 450 and 565°C and at flow rates of 2.5 and 5 gpm indicated that the concentrations of hydrogen and of oxygen remain essentially unchanged while passing through a 100-ft section of stainless steel tubing.

Uranium-Getter Method for Oxygen in Sodium. Experiments are continuing to investigate the feasibility of determining oxygen in flowing sodium systems using the uranium-getter method. Recent results indicate that the amount of oxygen picked up by the uranium tab is flow-rate dependent. This finding makes measurements based on the rate of oxygen pickup unattractive. Preparations are now being made to investigate a method based on oxygen material balance using uranium tabs.

Analysis for Particulates in Sodium. Examination of particulates on a filter placed in EBR-II primary sodium has been completed. The examination revealed that (1) most of the radioactive species found on the filter were also found on an EBR-II primary pump when it was examined; (2) the radioactive species are firmly fixed to the filter, either by deposition, isotope exchange, or alloy formation; (3) the quantity of particulates in EBR-II primary sodium is extremely small ($\sim 3 \times 10^{-3}$ ppm); and (4) the particulates are predominantly metallic.

Analysis of Nonmetallic Impurities in Sodium by the Equilibration Method. Work on distribution of oxygen between vanadium and sodium, which forms the basis for the vanadium-wire equilibration method for determining oxygen activity in sodium, has been completed. The temperature dependence of the distribution coefficient determined from the combined data at 650, 700, and 750°C is given by

$$\ln K_A = \ln \frac{N_{O_V}}{N_{O_{Na}}} = -7.73 - \frac{20,960}{T} + \frac{40,330}{T} (1 - N_{O_V})^2$$

where N_{O_V} and $N_{O_{Na}}$ are the atom fractions of oxygen in vanadium and sodium, respectively, and the temperature is in °K. A purchase specification has been prepared for obtaining vanadium wire for use in the measurement of oxygen activity by the equilibration method.

The required technology is being developed for the use of niobium as a detector for measuring oxygen activities in sodium at a lower equilibration temperature (e.g., 650°C) than is commonly employed with vanadium. The measured distribution coefficient for oxygen (in units of atom fraction oxygen) between niobium and sodium is much smaller than for vanadium and sodium, being of the order of ~ 100 in the Nb-O-Na system compared with $\sim 10,000$ for the V-O-Na system. As a result, oxygen concentrations in sodium of interest in LMFBR applications yield oxygen concentrations in niobium in the range 30 to 100 ppm upon equilibration at 650°C. A comparison of the automatic and manual inert-gas fusion methods for determining oxygen in niobium with internal friction methods indicates that the latter is the most sensitive in the concentration range of interest. Procedures for improving the sensitivity of the inert-gas fusion methods are being investigated.

An investigation is in progress to determine the feasibility of the equilibration method for measuring the hydrogen activity in liquid sodium. The equilibration procedure being used is similar to that for oxygen analysis by the vanadium-wire equilibration method. The inert-gas fusion technique is being used to measure the hydrogen concentration in the vanadium and niobium detector metals after exposure to sodium. The results for the hydrogen concentrations in the detector metals, obtained as a function of both the cold trap temperature (105 to 175°C) and the equilibration temperature (450 to 750°C), were converted to hydrogen-pressure data by means of experimental Sieverts' law constants for the materials. These values were compared with hydrogen-pressure data from the two meters present on the system. The hydrogen pressures determined from the niobium-wire equilibrations were higher than those obtained from the hydrogen meters although both showed the same dependence on the cold trap temperature. It was also found that there is no significant effect of meter operating temperature in the range 450 to 750°C on the hydrogen pressure readings.

Fission Product and Cover Gas Technology

FEDAL Methods Development for FFTF. Further investigation has been made of the separation of neon from xenon by gas-chromatographic techniques for the purpose of eliminating ^{23}Ne interference in the radioactive assay of gaseous fission products. A column 8 ft long by 1/8 in. ID, vacuum packed with 60-80 mesh Porapak Q, gave satisfactory separation at flow rates greater than 100 ml/min and with sample sizes up to 100 ml. Further investigations into the decontamination factor (DF) achievable with this system indicate that the DF between xenon and neon may be as high as 10^8 .

Work is continuing on the development of a method for detecting fuel-element failures by monitoring reactor sodium for dissolved gases and ^{135}I . In the proposed method an isolated sample of primary sodium is sparged with inert gas to strip out dissolved fission gases, which are assayed with a Ge(Li) detector system. After a predetermined time (~ 2 min), the sample is sparged again, and the effluent gases are assayed for the $^{135\text{m}}\text{Xe}$ daughter of ^{135}I . The ^{135}I content of the sodium is determined from the amount of $^{135\text{m}}\text{Xe}$ in the second sparge. Recent tests have shown that at sparge rates of 1000 cm^3/min , the time to remove essentially all of the xenon from 350°C sodium is reduced from about 1.5 to 1 min by using argon rather than helium as the sparge gas.

Prototypes of the cover-gas analysis system and the sparger and sparge-gas analysis system will be tested on EBR-II. Detailed design of the cover-gas analysis system has been started. Design drawings of the sparger vessel are nearly complete and preliminary piping-layout drawings for the sparger module have been made. A request for Approval-in-Principle (AIP) for the cover-gas analysis system and the sparger and sparge-gas analysis system have been submitted to RDT. A definite schedule for installation of the systems in EBR-II will be developed when the AIP is received from RDT.

On-Line Tritium Monitor. A diffusion-type meter is being evaluated for use as a tritium monitor. In operation of the monitor, tritium and hydrogen would diffuse through the iron membrane of the meter and would be swept by a carrier gas to a proportional counter for the measurement of tritium activity. A computational study is in progress to determine the optimum conditions for monitoring tritium by this method. Preliminary calculations indicate that with hydrogen concentrations in the sweep gas of 1% or greater, the tritium level in the sweep gas leaving the monitor will be independent of the hydrogen concentration in the sodium. These computations are continuing.

Sodium Chemistry

Oxygen-Hydrogen Interactions in Sodium. The program to determine whether or not hydroxide forms in liquid sodium under conditions of interest to reactor technologists is continuing. The method of investigation involves an isotope-exchange technique in which sodium deuterioxide (NaOD) is used as a stand-in for NaOH. Current work has concentrated on preparing solutions of NaOD in sodium that are suitable for this study.

Vacuum Distillation as an Analytical Method for Impurities in Sodium. In experiments to study the effect of impurities on the determination of oxygen in sodium, measured quantities of sodium carbonate and disodium acetylide were added separately to sodium in a distillation crucible. After 7 hr at $\sim 380^{\circ}\text{C}$ (the time and temperature of a distillation), essentially all of the carbonate and $\sim 50\%$ of the acetylide were found in residues. These findings suggest that the presence of either species in distillation samples will result in errors in analyses for oxygen unless the carbonate and/or acetylide contents of residues are determined and appropriate corrections are made. The possibility is being explored that modification of the distillation procedure may result in total decomposition of acetylide and, thereby, in the elimination of the need for a separate acetylide determination.

Materials-Coolant Interactions and Mechanical-Property Evaluations

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

(5) develop a sufficient understanding of nonmetallic-element transfer to predict compositional changes in reactor sodium systems and ultimately relate these changes to the mechanical properties. In order to accomplish these goals, work has proceeded in a number of areas.

Integrated Effects of Fast Neutron and Sodium Environments on the Properties of Austenitic Stainless Steel. A conceptual design of a modified Mark Q 19-pin subassembly that contains a sizeable number of mechanical property and corrosion specimens, which will be used to determine the relative and integrated effects of high-temperature sodium and fast-neutron irradiation on the properties of austenitic stainless steel, was submitted to the EBR-II Project for a feasibility review. This subassembly, which also contained short, mixed-oxide fuel elements with bottom plenums in the lower half of the core region, was thought to be technically feasible. A request to RDT for Approval-in-Principle (AIP) for the experiment is now in preparation.

Reactor and Experimental Sodium Systems Correlation. To correlate corrosion and mechanical-property data from materials exposed to sodium in various systems including EBR-II, which is considered "prototypic" of the Fast Test Reactor (FTR) and future LMFBRs, capability must be developed to expose a large number of specimens to EBR-II primary system sodium at high temperatures and velocities in an out-of-core facility. A conceptual design of a high-temperature Materials Test Station (MTS) for installation in Cell A of the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II has been made. The technical feasibility of incorporating this specimen-exposure device on the RSCL has been reviewed by the EBR-II Project. Potential problem areas identified by the EBR-II Project will be resolved during the design stage of the Materials Test Station. A request for Approval-in-Principle (AIP) for this experiment is also in preparation.

Development of Specimen-Exposure Facilities and Post-exposure Mechanical-Property Testing Capability. Capability is also being obtained for exposing standard uniaxial and biaxial test specimens to sodium of controlled nonmetallic-element concentrations in an ex-reactor loop. A small system (vll gal), comprising four specimen-exposure vessels that operate at temperatures of 750, 700, 650, and 600°C, has been designed. The loop has provision for determining the activity of nonmetallic elements in sodium by exposure of wire and foil specimens in the four test vessels. In addition to the cold trap and a carbon-control device, electrochemical oxygen meters and diffusion-type carbon and hydrogen meters will be included on the system.

To perform the required number of mechanical property tests on specimens from this program, effort has continued on the relocation and modification of a number of uniaxial creep-rupture machines. Specimen grips for all of the machines have been designed, the quality assurance package has been developed, and the purchase specifications have been released for competitive bids. Various types of biaxial testing facilities are being evaluated for use in flowing sodium and in vacuum or inert gas. The specimen materials that will be used in this program are presently defined in consultation with HEDL representatives.

Studies of Carbon Transfer in Sodium-Steel Systems. In the course of obtaining information on the equilibrium distribution of carbon between

sodium and a number of iron-base alloys, experience on the monitoring and control of carbon in sodium systems has also been obtained. A UNC diffusion-type carbon meter was incorporated into the specimen-exposure section of the existing nickel loop that is being used for the carbon distribution experiments to (1) continuously monitor the carbon concentration in the sodium, (2) demonstrate control of the carbon activity in the sodium, and (3) relate the response of the meter to carbon concentrations in foil specimens of Type 304 stainless steel and other alloys equilibrated in sodium. The response of the meter to changes in the carbon concentration in sodium and its stability during the equilibration runs demonstrate that it is a valuable instrument in an experimental program of this type.

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

Argonne National Laboratory (ANL) is coordinating, as well as participating in, a national program for developing, testing, and establishing commercial availability of meters for use in the Fast Flux Test Facility (FFTF) and in other LMFBR sodium systems. The meters that are being developed and characterized in this program are monitors for oxygen, carbon, and hydrogen impurities in sodium and leak detectors for steam generators. Meter modules that provide flow and temperature control are being developed for FFTF. Prototype modules are being tested in radioactive sodium at EBR-II.

A. Oxygen-Meter Characterization

1. Electrolyte Development (J. M. McKee)

The first objective of the oxygen-meter program has been the development of an improved solid-electrolyte tube (isostatically pressed thoria-7.5 wt % yttria) for use in electrochemical oxygen meters. This objective has been substantially realized. The electrolyte production process was developed at Hanford Engineering Development Laboratory (HEDL); 200 tubes have been produced by the Zirconium Company of America (Zircoa); platinum/gas reference electrodes are being installed at the Westinghouse Research Laboratories (WRL) as needed; and selected electrode assemblies are being tested in sodium by the Westinghouse Advanced Reactors Division (WARD) and at ANL. ANL is coordinating these efforts.

During the quarter, HEDL completed characterization testing of the initial three shipments totaling 200 tubes. Zircoa subsequently produced and delivered replacements for all tubes rejected by HEDL. HEDL has begun characterization of these replacement tubes.

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

Performance testing of 20 gas-reference oxygen meters manufactured by Westinghouse began during the quarter. Ten meters are being tested at ANL and 10 at WARD.

At ANL, the 10 meters are connected in series with a cold trap and a laboratory prototype carbon meter-equilibration (C-E) module in a system called the Oxygen Meter Rig (OMR). An eleventh meter, which utilizes the same type of electrolyte and reference electrode adapted to fit a United Nuclear Corporation (UNC) meter housing, is also being operated in series with the ten "standard" meters. Circulation of sodium through the oxygen meters began on October 15 at ANL and shortly thereafter at WARD. Shake-down tests of the OMR were completed early in November with the oxygen meters at 700°F. The sodium temperature at the meters was then raised to 930°F for 44 hr to "condition" the electrolyte tubes, as recommended by Westinghouse.

During the five-week period ending December 16, the eleven meters on OMR were operated at 700°F and calibrated at eight preselected cold-trap temperatures in the range from 230 to 410°F following a staggered order

specified in the joint ANL-WARD test plan. (These cold-trap temperatures correspond to oxygen concentrations of ~ 0.5 to 16 ppm.) The highest and lowest cold-trap temperatures were repeated at the end of the series, giving a total of 10 calibration points for each meter. Two or more days were allowed for the system to reach steady state at each cold-trap temperature. Twelve vanadium wires were equilibrated with the sodium at 1382°F (750°C) during the last 20-24 hr at each level. Six or more wires were then analyzed for oxygen by inert-gas fusion, and from these results the oxygen activity of the sodium was determined. During the last 4 hr of each equilibration the system temperatures were held constant within narrow limits as specified in the test plan, and the meter voltages varied less than 1 mV with few exceptions. Immediately following each wire-equilibration period, a sodium bypass sample was isolated and removed for determination of oxygen by the amalgamation method. Since December 16, the meters have been run at 700°F and the cold trap at 250°F except for one day at 350°F. Two additional oxygen determinations were made by vanadium-wire equilibration during this period, giving a total of 12 calibration points. (The results of vanadium-wire equilibrations are discussed later in this section.)

While these data were being plotted during the calibration period, it became clear that the meter voltages (except for the eleventh meter, OM-11, which is discussed separately below) were drifting downward, the effect being most pronounced for those at the low end of the voltage range. However, the response of the meters to changes in oxygen level was quite consistent from meter to meter when measured over short times (1 to 2 days) throughout the six-week period. Thus, the drift in meter voltage consisted primarily of gradual changes in K_1 in the standard equation for the calibration curve:

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

The slope of the curve, K_2 , calculated between points 5 and 6 and points 11 and 12, was 0.0492 ± 0.0026 (2σ) for all eleven meters. This means that a decrease in meter voltage of 49 mV is equivalent to a factor of 10 increase in oxygen activity. This value of K_2 was used to calculate K_1 for the calibration points (see Table I-1). The changes in K_1 with time for any meter provide a measure of its drift. In general, K_1 for the ten standard meters decreased by 15 to 25 mV until December 8, at which time a brief evacuation¹ of the reference electrodes produced a large increase in voltage on all meters. Smaller decreases have occurred since then.

The average values of K_1 for the ten standard meters were used to determine the 2σ envelope for the calibration curves, as shown in Fig. I-1.

¹The cover gas pressure in the expansion tank was reduced to near 0 psia without interrupting the sodium flow to sweep out any gas bubbles which might have accumulated in the stagnant sodium region of the oxygen-meter housings. During this operation (~ 3 hr) the air pressure inside the oxygen meter electrodes was also held near 0 psia to avoid stressing the thorium-yttria tubes. The semi-permanent increase in meter emfs observed on returning to normal pressure was later shown to be due to evacuation of the reference gas rather than to removal of bubbles from the sodium.

TABLE I-1. K_1 Values Calculated from the Equation: $\text{Emf (volts)} = K_1 - 0.0492 \log (\text{ppm O})$

Calibration Point No. ^a	$K_1, \text{ V}$										
	OM-1	OM-2	OM-3	OM-4	OM-5	OM-6	OM-7	OM-8	OM-9	OM-10	OM-11
1	1.7166	1.7277	1.7228	1.7314	1.7220	1.7360	1.7169	1.7518	1.7180	1.7477	1.7756
2	1.7202	1.7323	1.7260	1.7356	1.7224	1.7366	1.7195	1.7543	1.7208	1.7480	1.7588
4	1.7047	1.7153	1.7108	1.7258	1.7079	1.7241	1.7034	1.7424	1.7038	1.7367	1.7583
5	1.7009	1.7153	1.7048	1.7209	1.7009	1.7195	1.6964	1.7394	1.6962	1.7321	1.7606
6	1.7001	1.7140	1.7057	1.7214	1.7021	1.7204	1.6962	1.7394	1.6967	1.7321	1.7600
8 ^b	1.7293	1.7300	1.7241	1.7386	1.7224	1.7315	1.7223	1.7380	1.7253	1.7432	1.7723
10	1.7170	1.7203	1.7108	1.7219	1.7130	1.7229	1.7179	1.7306	1.7188	1.7343	1.7608
11	1.7130	1.7189	1.7102	1.7208	1.7117	1.7215	1.7129	1.7300	1.7154	1.7329	1.7609
12	1.7122	1.7192	1.7111	1.7234	1.7131	1.7234	1.7135	1.7298	1.7154	1.7334	1.7561
Avg	1.7126	1.7214	1.7140	1.7266	1.7128	1.7262	1.7110	1.7395	1.7122	1.7378	1.7626
2 σ ^c	0.019	0.014	0.016	0.014	0.017	0.013	0.020	0.018	0.022	0.013	0.011

^aPoints 3, 7, and 9 were obtained at oxygen concentrations >16 ppm, the maximum level at which the vanadium-wire equilibration is valid. Therefore, these points were not used in the calibrations.

^bFirst calibration point after a brief (~3 hr) evacuation of the reference electrode.

^cStandard deviation.

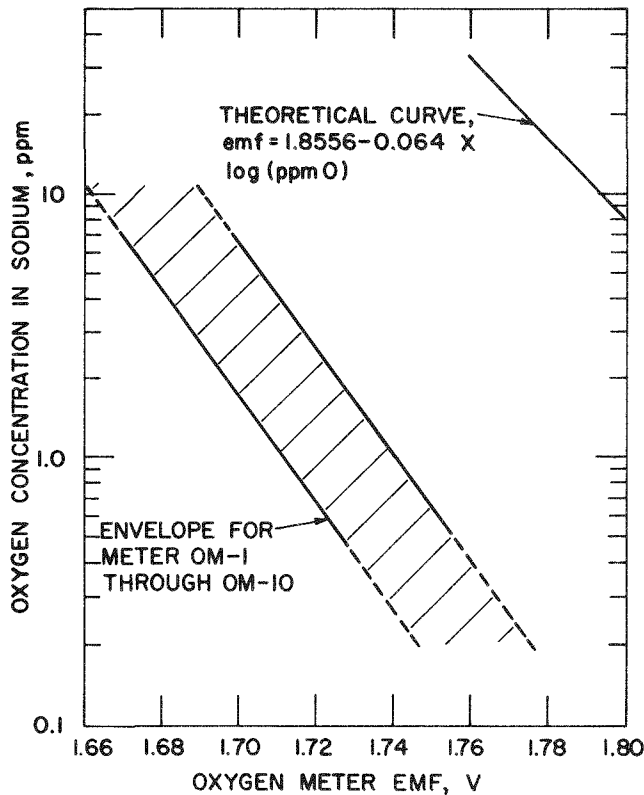


Fig. I-1

Calibration Curves for Oxygen Meters on OMR (temperature of meters, 700°F)

The theoretical curve calculated for an electrochemical cell of this type, also shown in Fig. I-1, is seen to be considerably higher in voltage and also steeper in slope (i.e., higher in sensitivity) than the experimental curves. The 2σ deviation in K_1 (see Table I-1) is a measure of the uncertainty attached to the oxygen activity determined from any single reading during the calibration period; the 2σ values for the ten standard meters cluster around 16 mV. The envelope within which 95% of all readings would fall for an average oxygen meter calibrated at a single oxygen level (1 ppm) is shown graphically in Fig. I-2. The meters are apparently becoming more stable with time; hence, this envelope is expected to be narrower for the period following the initial calibration.

It can be seen in Table I-1 that the emf of Meter OM-11 is substantially higher than that of the 10 standard oxygen meters for all calibration points and is also more stable. The improved performance is believed to be due to the fact that the tip of the electrolyte tube projects $\sim 1/2$ in. farther down into the sodium stream than the electrolyte tubes of the ten standard meters.

In discussions with Westinghouse representatives, it was noted that the ten meters being tested at WARD have also exhibited a downward drift in voltage of similar magnitude to those at ANL during calibration; however, it is believed that the meters had largely stabilized near the end of the calibration period. E. Berkey, of WRL, has examined Zircoa electrolyte tubes with a scanning electron microscope and identified grain-boundary impurities, e.g., aluminum, at the inner surface. These impurities may have reacted with the platinum film during firing and impaired its performance.

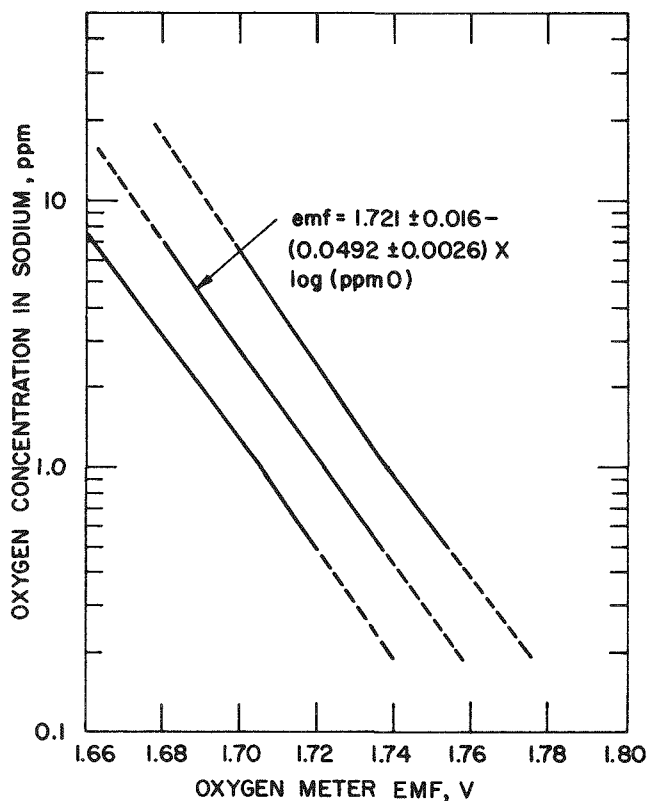


Fig. I-2

2 σ Envelope for the Average Oxygen Meter Calibrated at 1.0 ppm Oxygen in Sodium (meter temperature, 700°F)

As the program continues, efforts will be made to determine the causes of drift in oxygen meter voltage and how to minimize it. Evacuation tests on OMR suggest that the meter voltage is more sensitive to changes on the inner (air) side of the tube than to gas bubbles trapped on the sodium side.² The effect on meter stability of operating variables such as sodium temperature, fin temperature, oxygen potential in the reference gas, and depth of electrode tip in the housing will be investigated as rapidly as opportunities permit. The goal is to reduce drift enough so that a single-point calibration once a month will provide adequate accuracy for the needs of reactor operators.

ANL is also preparing to add a twelfth oxygen meter to OMR incorporating a tin/tin oxide reference electrode in a Zircoa isostatically pressed electrolyte tube.

The results of vanadium wire equilibrations performed at both ANL and WARD are plotted versus reciprocal cold-trap temperature in Fig. I-3, together with a curve of the solubility of oxygen in sodium.³ The ANL results are seen to be slightly higher and the WARD results slightly lower than would have been predicted from cold-trap temperatures. The cause of this difference is being investigated. ANL and WARD have exchanged vanadium wires from each set and are analyzing these to see how well the results

²The problem of gas bubbles was discussed previously in ANL-7846, p. 12.

³D. L. Smith and R. H. Lee, *Characterization of the Vanadium-Wire Equilibration Method for Measurement of Oxygen Activity in Liquid Sodium*, ANL-7891 (in press).

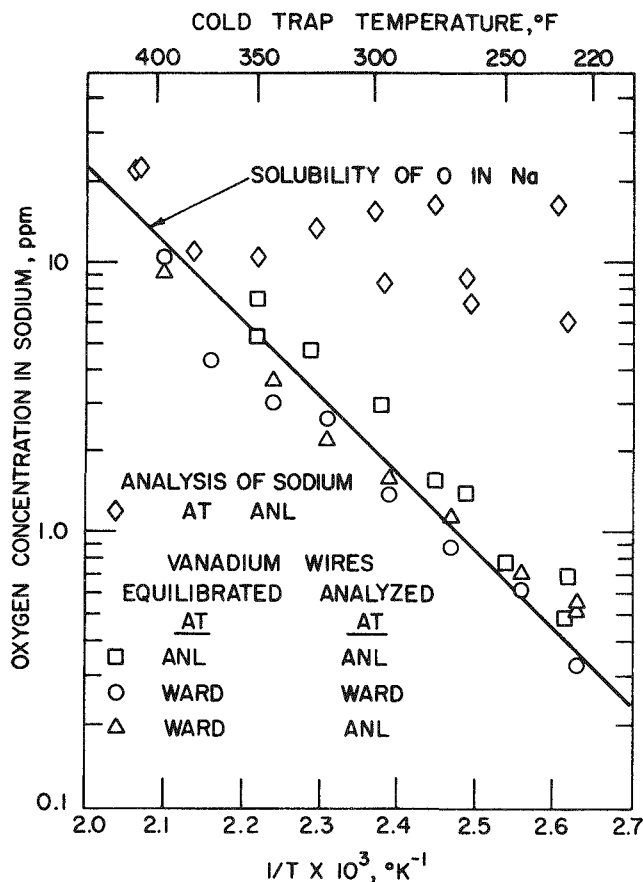


Fig. I-3

Determination of Oxygen in Sodium by Equilibration of Vanadium Wires

check. The accuracy of the cold-trap temperature measurements at both sites is also being checked. If these checks do not reveal any systematic differences, it may simply mean that different ratios of oxygen-bearing species are present in the two sodium systems.

Because the oxygen activities measured at ANL were higher than predicted, the vanadium wires equilibrated at the two highest cold-trap temperatures, 385 and 410°F, had oxygen contents exceeding the solubility of oxygen in vanadium at 1382°F. The formation of solid vanadium oxide imposes an upper limit (~16 ppm) on the concentration of oxygen in sodium that can be determined at 1382°F; hence, these points are not plotted in Fig. I-3 and were not used in calibrating the oxygen meters.

Also plotted in Fig. I-3 are the oxygen concentrations in sodium obtained by chemical analysis of sodium bypass samples taken at the end of each wire-equilibration period on OMR. The results, obtained by the amalgamation method, are higher than and do not correlate with the oxygen contents determined by vanadium-wire equilibration and predicted from cold trap temperatures. As expected, the amalgamation method does not appear to be valid for determining oxygen activity in sodium.

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

During this quarter, the two oxygen meters in the oxygen-hydrogen meter (O-H) module in Cell B of the Radioactive Sodium Chemistry Loop (RSCL)

at EBR-II were operated for a total of 522 hr at about 700°F. The meters underwent one complete freeze-thaw cycle, numerous changes in reactor power level, and exposure to high levels of radioactivity during reactor operation and to low levels during reactor shutdown.

Meter 1 was operated for an additional 434 hr in the previous quarter (see ANL-7868, p. 16); however, the electrolyte tube of Meter 2 failed after 413 hr. The failed electrode assembly (Westinghouse II-E-3 with HEDL electrolyte tube 49-1-1) was shipped to the Westinghouse Research Laboratory for examination, and was replaced with an electrode assembly designated Westinghouse II-E-5 with HEDL electrolyte tube 49-1-3.

Both meters have exhibited downward drifts in voltage during the 522 hr, but they appeared to be stabilizing toward the end of the period. The voltage of Meter 1 decreased by about 4 mV and that of Meter 2 by about 14 mV. The voltage changes could not be obviously correlated with reactor power level, fuel-handling operations, or bypass of sodium flow around the primary cold trap for a period of one week. Also, the difference in behavior of the two meters indicated that at least part of the drift was due to meter instability rather than actual change in the oxygen level in the sodium. However, the current operation of the meters confirms that there is no measurable short-range effect of ^{24}Na radiation (up to 1400 $\mu\text{Ci/g}$ of sodium) on the performance of the oxygen meters.

The first vanadium-wire equilibration in the C-E module in Cell C of the RSCL was made on December 6 and 7, 1971, at an equilibration temperature of $1386 \pm 5^\circ\text{F}$. Analysis of 10 wire specimens, which were divided into six analytical samples, gave an equivalent oxygen content of the sodium of 0.85 ± 0.06 (2σ) ppm. During the 4-hr equilibration period the oxygen meters, operating at 710°F , were giving stable voltages: 1.7434 ± 0.0001 for Meter 1 and 1.7711 ± 0.0001 for Meter 2. From these data, single-point calibration curves were drawn (see Fig. I-4) using an average slope of 0.055, which was previously measured for the two oxygen meters operating on the Test and Evaluation Apparatus (TEA). (The meters on EBR-II and TEA, which have electrolyte tubes produced by HEDL, are expected to behave similarly.) The theoretical slope of 0.064 is also shown, for comparison. It may be seen that the difference in slopes would have little effect on the indicated oxygen concentration near the calibration point.

4. Oxygen-Meter Performance on TEA (V. M. Kolba, P. Mack)

Both oxygen meters in the O-H module on TEA at ANL-Illinois continued in operation during the quarter, and as of December 31, 1971, had accumulated total operating times as shown below:

Module Meter No.	Westinghouse Meter No.	HEDL Tube No.	Time, hr, at Temp			Total Time, hr
			700°F	800°F	900°F	
0-1	II-E-2	73-1-2	2448	2818	336	5602
0-2	II-E-1	72-2-1	2256	2482	336	5074

The calibration points obtained to date by equilibrating vanadium wires in TEA are displayed in Fig. I-5. During the quarter, the emf of

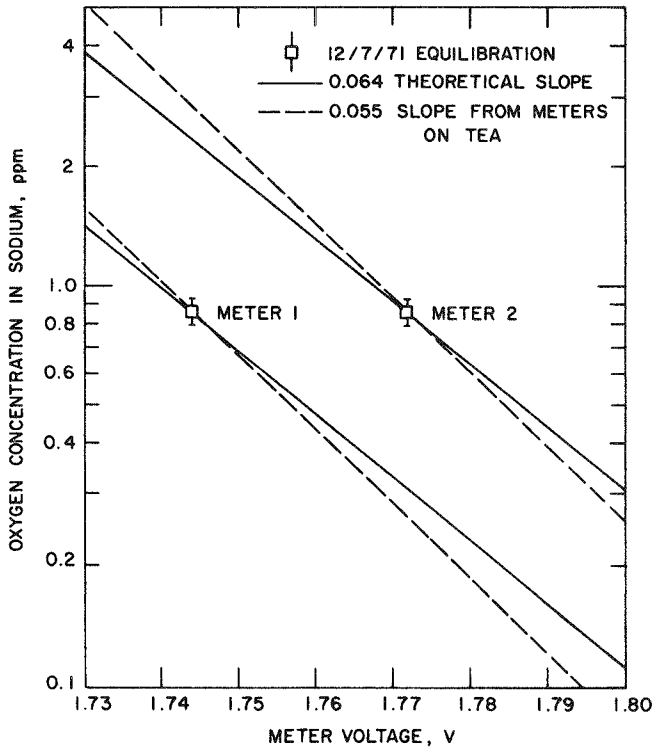
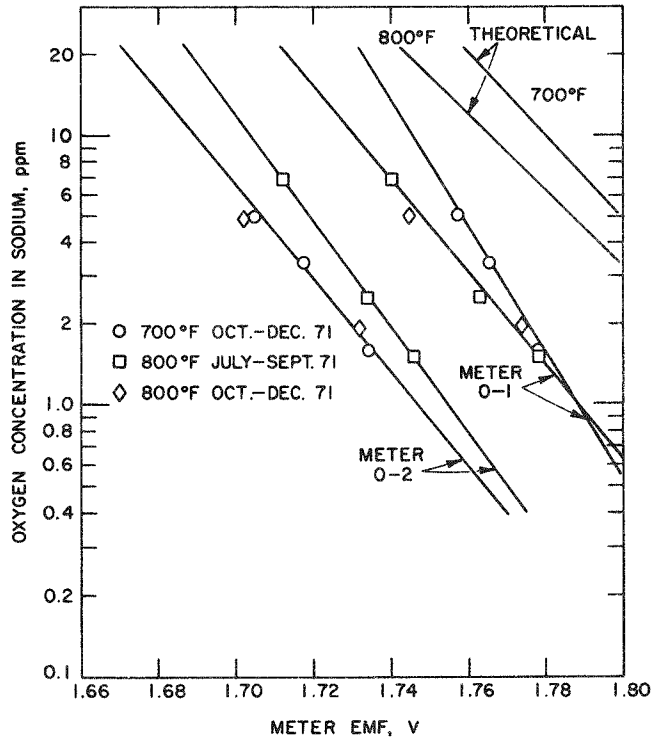


Fig. I-4
 Oxygen-Meter Calibration:
 O-H Module on RSCL of
 EBR-II (temperature of
 meters, 710°F)

Fig. I-5
 Calibration Data for
 Oxygen Meters on TEA



Meter O-2 continued to drift downward, although at a lower rate than that previously reported for electrolyte tube 72-2-1. This shift may be seen by comparing the new and old calibration points at 800°F for Meter O-2. Calibration data were also obtained at 700°F during the quarter to provide a more direct comparison with the oxygen meters in EBR-II sodium. The uncertainty associated with the slopes of the curves drawn in Fig. I-5 is large because of the considerable time interval between points. In future calibrations, the slopes will be determined more accurately by decreasing the time interval and increasing the difference in oxygen concentration between calibration points.

5. Oxygen-Meter Performance on Oxygen Meter Calibration Apparatus (OMCA) (D. L. Smith)

The sodium apparatus used for the development and characterization of the vanadium-wire equilibration method (Section II.B.4) is equipped with electrochemical oxygen meters as an alternative method of monitoring the oxygen concentration in sodium. The meters are used primarily to demonstrate that (1) contamination is not introduced into the sodium during insertion or removal of equilibration specimens, (2) oxygen in the cold trap is not depleted, and (3) constant oxygen concentrations are maintained during a wire exposure. Experience gained with the meters during these investigations may be of interest to the national meter program.

A Westinghouse oxygen meter, No. II-E-6 (HEDL electrolyte 49-1-4) that was previously operated for ~1350 hr (see ANL-7817, p. 10-12), is now being used after a shutdown of several months for loop modification. The calibration curve obtained by the vanadium-wire equilibration method is given in Fig. I-6 for an operating temperature of 750°F (400°C). The oxygen concentration determined by the equilibration method agreed within 3% of the value obtained from the oxygen solubility data at the cold-trap temperature. The previously reported calibration curve for the same meter and the calculated curve are also shown in Fig. I-6. The observed decrease of ~20 mV from the previous calibration curve further points up the need for meter calibration.

B. Hydrogen-Meter Development (D. R. Vissers)

The goal of this program is the development of an on-line hydrogen meter for measuring the hydrogen activity in the primary and secondary sodium of LMFBR systems. The meter is also expected to be a useful tool for hydrogen activity measurements in laboratory studies. The hydrogen meter developed at ANL, which is based on the diffusion of hydrogen through a nickel membrane, can be operated in two modes. The first is a static mode, in which the equilibrium hydrogen pressure above the sodium is measured directly and related to the hydrogen concentration in the sodium by Sieverts' law. The second is a dynamic mode, in which the hydrogen flux across the diffusion membrane is monitored by the ion-pump current and related to the hydrogen concentration of the sodium.

At present, four such meters are in operation at ANL facilities. They differ in construction as follows:

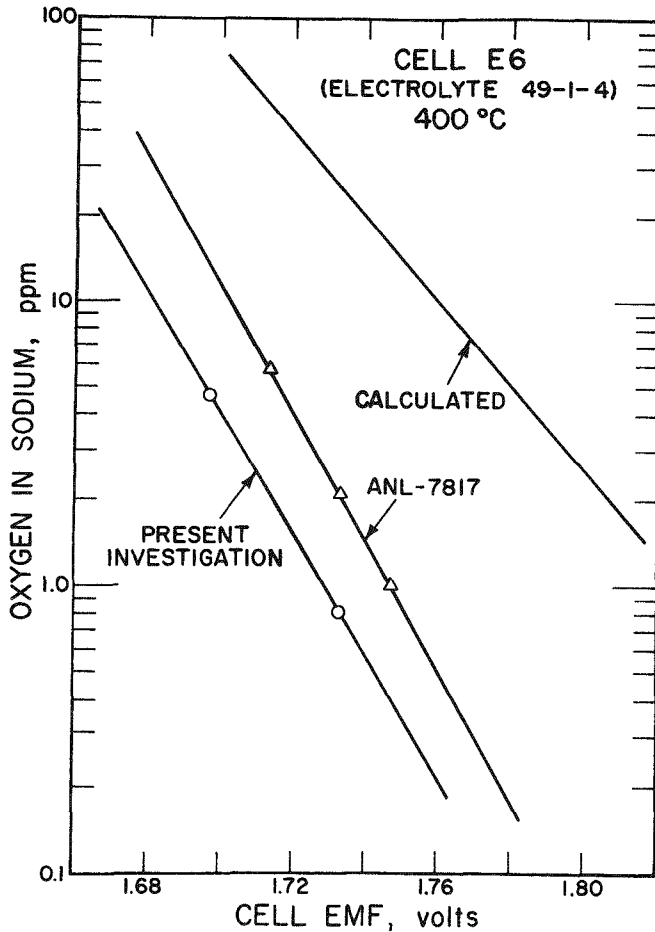


Fig. I-6

Calibration Curve for Oxygen Meter Operated at 750°F on OMCA. Neg. No. MSD-56671.

Location	Ultek Ion Pump			Normal Operating Temp, °F
	Type	Capacity, liters/sec	Vacuum Valve	
O-H module on TEA	D-I	11	polyimide	700-900
O-H module at EBR-II	D-I	11	all metal	700
OMR	Hydrogen	20	all metal	900
SAL	D-I	11	all metal	900

Because of the different type of ion pump (a pump specially designed for pumping hydrogen) used on the OMR meter, dynamic-mode data from this meter cannot be directly compared with data from the other meters.

1. Hydrogen-Meter Studies on OMR (D. R. Vissers, L. G. Bartholme, L. J. Marek)

During the calibration studies of the oxygen meters on OMR, the solubility of hydrogen in sodium was remeasured at various cold-trap temperatures using a hydrogen meter operated in the equilibrium mode. The results of these studies are presented in Table I-2 along with values predicted from

TABLE I-2. Solubility of Hydrogen in Sodium

Cold-Trap Temp of OMR, °F	Hydrogen Solubility in Sodium, ppm	
	Determined on OMR	Predicted
245	0.050	0.050
243	0.052	0.048
228	0.039	0.033
298	0.159	0.162
385	0.85	0.80
326	0.275	0.280
242	0.046	0.047
262	0.073	0.075
350	0.46	0.44
410	1.40	1.20
274	0.094	0.097
408	1.38	1.16

earlier studies⁴ on the Sodium Analytical Loop (SAL). The agreement between predicted and measured values is excellent except at the higher levels of hydrogen, where the measured levels are slightly higher than the predicted values.

The hydrogen meter on the OMR is equipped with a 3/4-in. all-metal Varian valve, which is greatly superior to the polyimide-gasketed valves used earlier in our hydrogen-activity meters. The ion-pump currents developed for various hydrogen concentrations during operation in the dynamic mode at 900°F are shown in Fig. I-7. The correlation between the ion-pump current and the hydrogen concentration of the sodium is excellent; however, it is not linear, as predicted theoretically.⁵ This nonlinear correlation indicates slight changes in ion-pump pumping speed with changes in the hydrogen flux entering the pump. Although the ion-pump used in this hydrogen meter has a rated pumping speed of 20 liters/sec, calculations³ based on theoretical hydrogen fluxes for the respective hydrogen concentrations indicate that the actual pumping speed within the pump during these studies was about 60 liters/sec. This high pumping speed is caused by hydrogen activation,⁶ i.e., hydrogen molecules are pumped directly by sorption on the activated titanium cathodes. This mode of pumping occurs in addition to the normal mode, in which the hydrogen is first ionized to H⁺ before it is transferred to the titanium cathode. Hydrogen activation⁶ of an ion pump is typically caused by operation of the pump at high hydrogen levels for prolonged periods. Such a condition existed during the initial

⁴D. R. Vissers, J. T. Holmes, and P. A. Nelson, *Hydrogen Activity Meter for LMFBRs*, Trans. Amer. Nucl. Soc. 14(2), 610 (1971).

⁵D. R. Vissers, J. T. Holmes, P. A. Nelson, and L. G. Bartholme, Nucl. Technol. 12, 220 (1971).

⁶J. H. Singleton, *Hydrogen Pumping Speed of Sputter-Ion Pumps*, J. Vac. Sci. Technol. 6, 316 (1969).

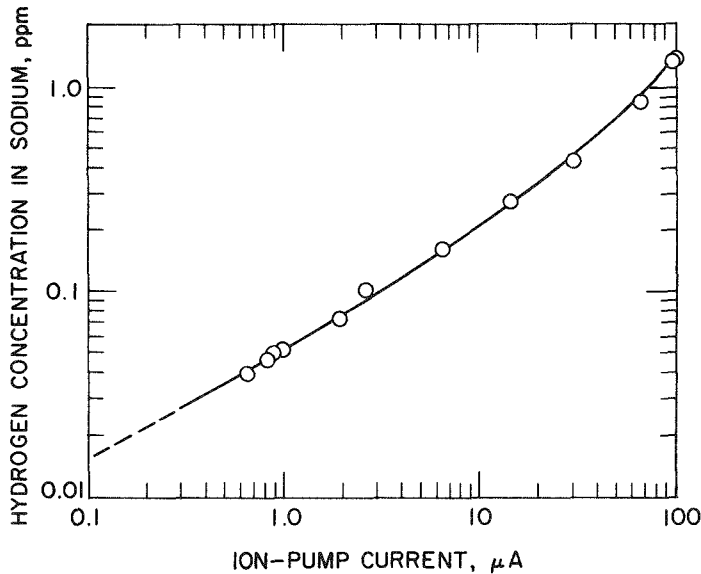


Fig. I-7

Dynamic-Mode Hydrogen-Meter Measurements on OMR (meter temperature, 900°F)

startup of the OMR when the hydrogen levels in sodium were in the range from 3 to 4 ppm.

Earlier studies with ion pumps that had not been activated indicated a more linear relationship between the ion-pump current and the hydrogen concentration of the sodium. It is clear from the recent studies that for operation in the dynamic mode the correlation between the ion-pump current of a hydrogen meter and the hydrogen concentration of a sodium system should, when possible, be determined experimentally by operation of the meter in the equilibrium mode.

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

The hydrogen meter in the O-H module in Cell B of the RSCL at EBR-II has been operated mainly in the dynamic mode. The operating temperature of this meter is currently limited to 700°F , which is the operating temperature of the oxygen meters in series with it. The dynamic mode operation gave a steady ion-pump current of $1.0 \pm 1 \mu\text{A}$ at a membrane temperature of 705°F . This low ion-pump current (the sensitivity limit of the present meter) indicates a hydrogen concentration in the sodium of 10 to 100 ppb, based on a diffusion-theory calculation. One equilibrium-mode measurement was attempted after two vacuum valves having polyimide seats and seals had been replaced by an all-metal vacuum valve and the system had been baked out for 70 hr at 260°F . The ion gauge (direct reading) gave a constant pressure increase of 1×10^{-6} Torr/min after the vacuum valve was closed. There was no indication of an equilibrium plateau even after 40 min of pressure rise. The constant rate of pressure increase is thought to have resulted from outgassing of the metal surfaces. The rate of diffusion of hydrogen is low when (1) the driving force on the sodium side is 10^{-6} Torr (10 ppb) to 10^{-4} Torr (100 ppb) and (2) the temperature of the membrane is only 700°F . Also, it should be noted that a constant outgassing rate of 1×10^{-6} Torr/min would produce large errors in the equilibrium pressure measurements in the range 10^{-6} to 10^{-4} Torr. For operation in the dynamic mode, this outgassing rate would contribute only about 5% of the total ion-pump current at $1.0 \mu\text{A}$.

Experience at ANL-Illinois indicates that before the nickel membrane will function properly in the equilibrium mode, it may have to be conditioned at a high temperature ($\sim 900^\circ\text{F}$) and a high hydrogen level after sealing off the vacuum system. This hydrogen conditioning is not required for operation of the meter in the dynamic mode.

3. Hydrogen-Meter Operation on TEA (V. M. Kolba, P. J. Mack)

In the studies on TEA, efforts were continued to achieve satisfactory performance of the hydrogen meter in the equilibrium mode at low hydrogen concentrations (<0.05 ppm) and low meter temperatures (700°F). Several equilibrium runs were made at low cold-trap temperatures (~ 255 to 275°F), which approach the cold-trap temperature of EBR-II, and meter temperatures of 700 , 800 , and 900°F . Approach to equilibrium was slow, particularly for the run at 700°F . After periods of ~ 5 hr, the pressures attained at 700 and 800°F were equal to each other, but were lower than the pressure attained at 900°F . It appears that this particular meter, when operated at 700 - 800°F in the equilibrium mode, cannot be used to measure hydrogen concentrations in sodium below ~ 0.15 ppm. Its performance is much better at 900°F .

The hydrogen meter on TEA was also operated in the dynamic mode. A log-log plot of ion-pump current versus hydrogen concentration, based on equilibrium values, is shown in Fig. I-8 for meter temperatures of 700 , 800 , and 900°F . The ion-pump current shown in the figure was corrected by subtraction of the residual ion-pump current obtained after the pump was isolated from the membrane by closing the vacuum valves.

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

The objective of this work is to devise a calibration technique to relate the carbon-flux output of the United Nuclear Corporation (UNC) diffusion-type carbon meter or the voltage output of the Brookhaven National Laboratory (BNL) electrochemical carbon meter to the chemical activity of carbon in the sodium. The method chosen to measure the carbon activity in sodium, which is similar to that being used to measure the oxygen activity in sodium,⁷ is based on the equilibrium distribution of carbon between a metal specimen and sodium. At equilibrium, the carbon activities (with graphite as the standard state) in the metal and in the sodium are equal. The carbon activity of the metal, and consequently that of the sodium, can be derived from carbon analysis of the metal specimen and from the established relationship between carbon concentration and carbon activity in the specimen material. A direct activity-measuring method will provide intermittent on-line calibration capabilities for the continuously operating carbon meter. With a standard calibration method, results obtained at various sites will be directly comparable. Also, a direct activity-measuring method can supplement and possibly replace the traditional methods of analysis.

Initial calibration experiments conducted in Type 304 stainless steel and Croloy vessels using a UNC meter have been reported previously (ANL-7868, p. 12). In these experiments, a correlation was obtained between the meter

⁷D. L. Smith, *An Equilibration Method for Measuring Low-Oxygen Activities in Liquid Sodium*, Nucl. Technol. 11, 115 (May 1971).

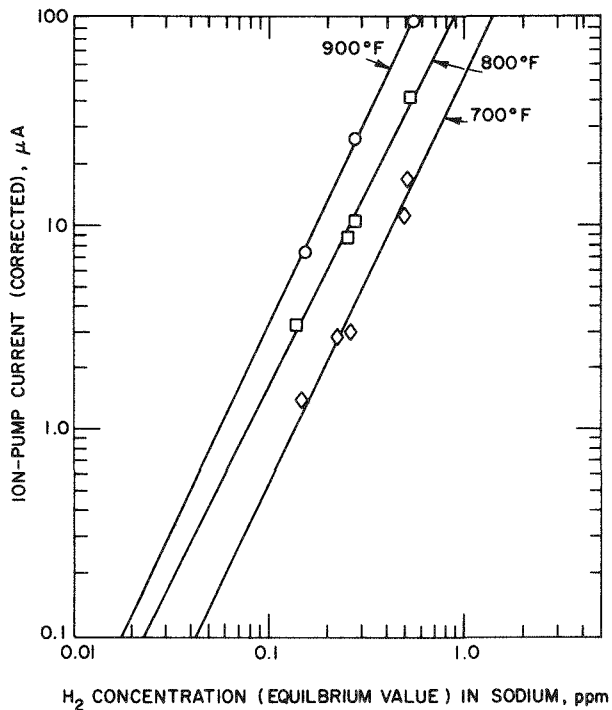


Fig. I-8

Calibration Curves for Hydrogen Meter on TEA Operated in the Dynamic Mode

readings and the activity of carbon in the sodium determined by equilibration of both nickel and Fe-8 wt % Ni (Fe-8Ni) tabs. However, because the carbon concentration at equilibrium in both tab materials was extremely low in the stainless steel system, accurate measurement of the activity was difficult. This finding prompted a survey study to identify other tab materials which would have a higher equilibrium carbon concentration at low carbon activities in sodium and which would exhibit a large change in carbon concentration with a change in carbon activity in sodium. This survey study is being conducted simultaneously with the meter calibration study.

The experiments are performed in an inert-atmosphere box equipped with two furnace wells. Each well holds a pot containing about 2 liters of stirred sodium at 700°C. One of the pots, made of 200 nickel, has a high carbon activity; the other pot, made of Type 304 stainless steel, has a low carbon activity. These pots control the carbon activity in the sodium and thus control the carbon concentrations in the equilibrated tabs. The pots are equipped with either a UNC or a BNL carbon meter. Between runs, the meters are periodically interchanged between pots. Tabs are inserted into the pots on a holder capable of holding 11 tabs. While immersed in the sodium, the tabs are held at temperature for the time required to achieve equilibrium, withdrawn at temperature, cooled to room temperature in the glovebox, cleaned with alcohol and then water, and analyzed for carbon. During an experiment the output of the carbon meters is continuously recorded.

The time required to achieve equilibrium is an important factor in these pot-type experiments. Calculated equilibration times for the tabs were generally less than 8 hr,^{8,9} but the meters indicated that the system required

⁸P. L. Gouzin *et al.*, Russ. Met. 5, 96 (1969).

⁹J. Askill, ORNL-3795, Pt. II (1965).

about two days to reach a constant value. Because many of the tabs removed a relatively large amount of carbon from the sodium, the system behavior was probably dominated by reestablishment of a steady state with the thick pot walls. Accordingly, the samples were equilibrated for 4 to 7 days rather than for the calculated equilibration times.

1. Tab Survey Experiments

The new tab materials investigated to date are Fe-12Mn, titanium, tantalum, cobalt, zirconium, vanadium, and molybdenum. Additional exposures of nickel tabs were also made to substantiate our previous data on nickel. Each of the experiments also included at least one Fe-8Ni tab. For each experiment reported below, the equilibrium carbon content of the Fe-8Ni tabs was used to calculate the carbon activity (a_c) in the tabs, and hence in the sodium, according to the equation of Bodsworth *et al.*¹⁰ This equation, which results from a fit of theoretical treatment to experimental data, is as follows:

$$\log a_c = \log \frac{N_c}{1 - 5 N_c} + \frac{2080}{T} - 0.640 + 1.67 N_{Ni}, \quad (1)$$

where N_c is the mole fraction of carbon in the alloy, N_{Ni} is the initial mole fraction of nickel in the alloy, and T is the temperature in °K.

Figure I-9 presents the data accumulated to date with Fe-12Mn tabs at 700°C. The line labelled "Fe-8Ni" is the relationship between carbon activity and $N_c/(1 - 5 N_c)$ for Fe-8Ni given in Eq. 1. The carbon activity in Fe-12Mn was taken to be equal to that in the simultaneously equilibrated Fe-8Ni, whereas the value of $N_c/(1 - 5 N_c)$ for Fe-12Mn was calculated from the equilibrium carbon concentration in the tabs. Even though the data in Fig. I-9 are limited, we have drawn a linear correlation between carbon activity and $N_c/(1 - 5 N_c)$. Bodsworth *et al.*¹⁰ have found that a linear correlation applied very well to a wide range of austenitic alloys including Fe-C-Ni and Fe-C-Mn. It should be noted that the scatter in the data at low carbon activities reflects analytical uncertainty in determining carbon in both Fe-8Ni and Fe-12Mn.

The data for titanium are plotted in Fig. I-10 in the same manner as the Fe-12Mn data. Although there is considerable scatter, the large slope of the line indicates that titanium acts as a carbon getter. Hence, titanium is not attractive as a tab material for measuring carbon activity, and no further work will be done with this material.

Work will also be discontinued with nickel and cobalt (these tabs exhibit lower equilibrium carbon concentrations than either Fe-8Ni or Fe-12Mn) and with tantalum and zirconium (these tabs show no correlation with carbon activity). The results for these four tab materials are given in Table I-3.

Experiments are in progress to obtain more data for Fe-8Ni and Fe-12Mn. Data on molybdenum and vanadium are not yet available.

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

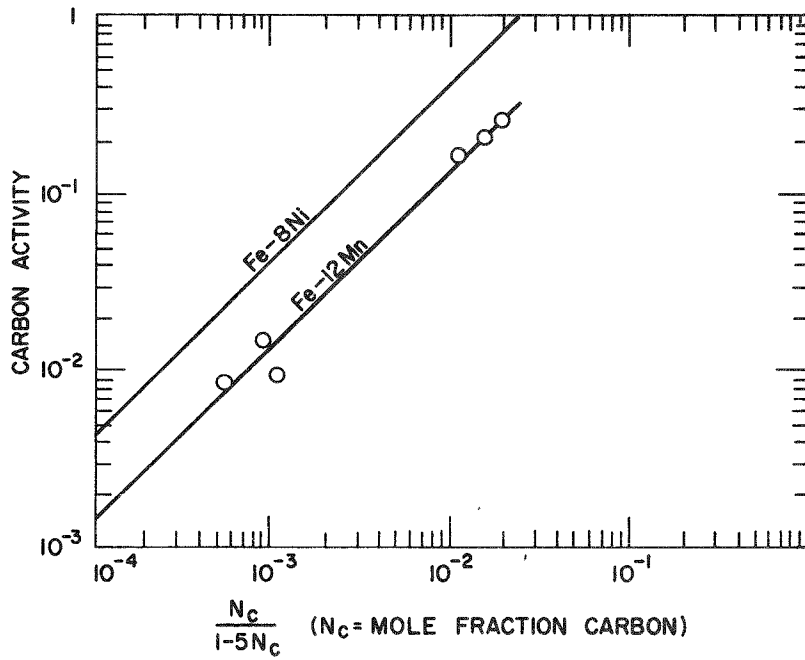


Fig. I-9. Carbon Activity in Fe-8Ni and Fe-12Mn Equilibrated in Sodium at 700°C

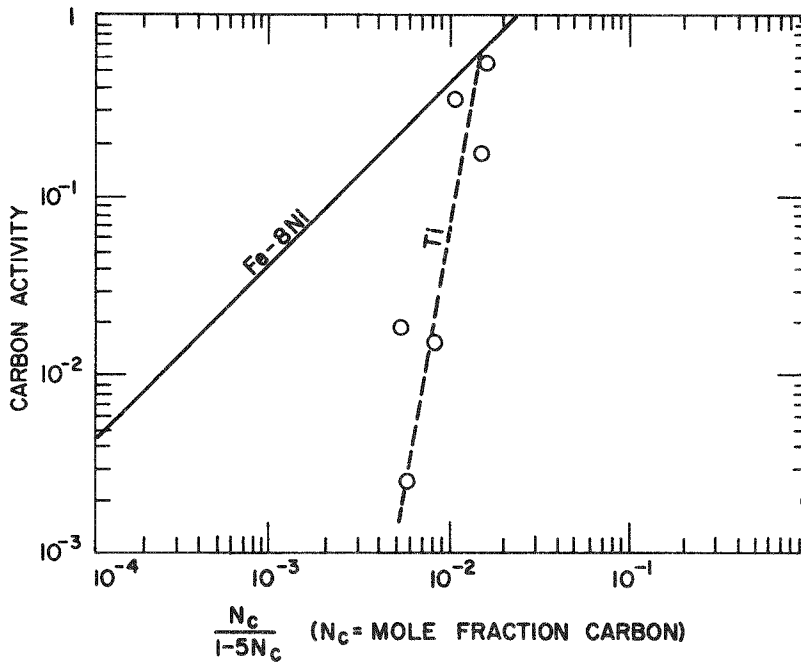


Fig. I-10. Carbon Concentration in Titanium after 7 days in Sodium at 700°C

TABLE I-3. Summary of Results Obtained with Nickel, Cobalt, Tantalum, and Zirconium Tabs

Carbon Activity in Sodium ^a	Carbon Concentration in Tab, ppm			
	Ni	Co	Ta	Zr
0.523	256	-	220	
0.443	284	159	834	
0.347	197	116		
0.205	-	-		400
0.172	-	-	174	266
0.048	90	39	244	
0.018	18	36		
0.015	3	-	221	223
0.008	-	-		152
0.003	-	-	72	

^aCarbon activity determined using the equilibrium carbon content of Fe-8Ni tabs and Eq. 1.

2. Experiments with UNC Carbon Meter

Calibration of the UNC meter with standard CO sources permits conversion of the flame ionization detector (FID) readings to carbon flux.¹¹ With decarburizing gas flow rates of 13.5 cm³/min, a reading of 10,000 FID units was found to correspond to a flux of 0.211 μg/(cm²)(min). Through the application of simple diffusion theory, one can calculate the carbon activity just inside the surface of the iron probe that is in contact with sodium. (Such a calculation does not take into account changes in activity through the stagnant layer of sodium adjacent to the probe, and thus may be expected to yield a somewhat low result.) For 10,000 FID units, the calculated carbon activity at the iron-sodium interface is 0.145. Figure I-11 is a plot of FID readings versus carbon activity determined with Fe-8Ni tabs. The straight line drawn through the data gives a carbon activity in the sodium of 0.172 for a FID reading of 10,000. As expected, this is somewhat higher than the results of the simple calculation made above; nevertheless the agreement between theory and experiment is considered good.

The region of primary interest for loop and reactor systems is not at the higher activity levels in Fig. I-11, but at very low activities and very low meter readings. Our measurements in the stainless steel pot quite clearly indicate the difficulty of calibrating the meters at low levels:

¹¹The operation of the UNC meter is based on diffusion of carbon through the membrane and reaction of the carbon with a flowing, moist, hydrogen-argon gas mixture to form CO. The CO is then catalytically converted to CH₄, which is measured with a flame ionization detector.

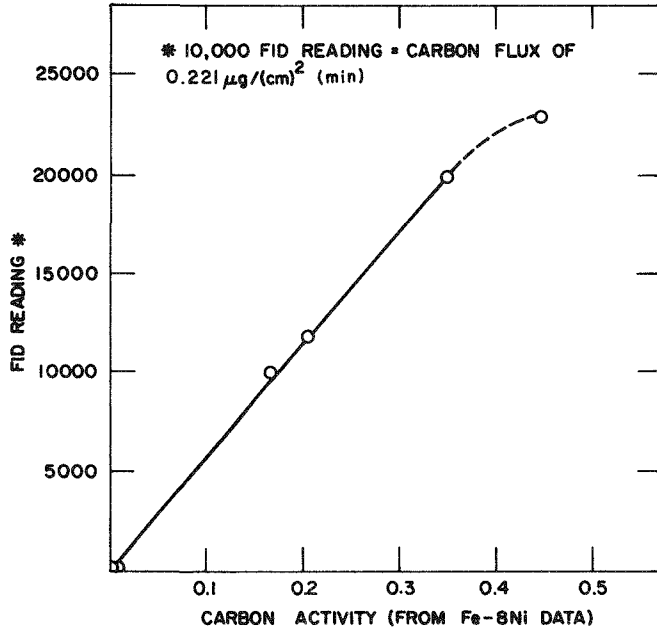


Fig. I-11
Calibration of UNC Carbon
Meter in 700°C Sodium

Meter Reading, FID Units	Carbon Activity	
	Calculated from Fig. I-10	Measured with Fe-8Ni
95	0.0016	~0.0025
77	0.0013	0.0086

It is obvious that at these very low levels, the carbon activities measured with Fe-8Ni agree only roughly with those indicated from the meter calibration. An approach to calibrating the meter might be based on measurements at carbon activities in the range of 0.1 to 0.3, where the agreement between meter output and activity measurements with tabs is quite good. However, such a calibration cannot be done easily in a large system such as a reactor, where the carbon activities are low.

Several alternative methods of increasing the response of the UNC meter are being considered. Among these are (1) increasing the surface area of the iron membrane, (2) operating the meter at low flow rates to allow CO to build up and then increasing the flow when a reading is desired (this results in a sharp peak in the FID output), and (3) decreasing the background by purifying the decarburizing and/or fuel gases.

Construction of a meter having a membrane with a larger surface area is planned. Preliminary investigations into the second and third alternatives have been performed. The conclusions are that (1) the pulsed flow (second alternative) increases sensitivity but would be a somewhat complex mode of operation and (2) purification of the decarburizing gas decreased the background by a factor of three, but before this approach becomes practical a more efficient purification scheme would have to be employed. No attempt has been made to purify the fuel gases as yet.

3. Experiments with BNL Carbon Meter

The BNL electrochemical meter, developed by F. J. Salzano, L. Newman, and M. R. Hobdell,¹² consists of a graphite electrode immersed in a $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ melt which is contained in an iron cup with a 5-mil wall. The iron wall is expected to equilibrate with the sodium, and the potential (E) developed by the cell is, in principle, related to the carbon activity (a_c) in the wall by the equation

$$E = \frac{RT}{4F} \ln a_c \text{ (wall)} \quad (2)$$

As a rule, the development of full potentials in carbonate-melt cells requires isolation of the anode and cathode compartments from each other because of the involvement of gases such as CO and CO_2 in the various equilibria.¹³ Moreover, the materials of construction are usually limited to MgO, gold, and Au-Pd alloys because of corrosion problems with other materials.¹³ Salzano *et al.* have noted that their cells tend to short out after some hundreds of hours of use due to the growth of iron whiskers on the graphite center electrode,¹² and the whisker growth seems to be accelerated at higher cell potentials.¹⁴ We have observed the iron whiskers in our cell, which shorted out to zero mV during the fourth run. Cell operation was restored by the recommended procedure of breaking off the whiskers.

Our carbon activity data based on Fe-8Ni are plotted in Fig. I-12 against BNL meter output; the deviation of the cell potential from the theoretical curve may be due to a combination of the factors outlined above. The cell potential appears to approach a limit in the region of lower carbon activities--the region of greatest interest. An attempt will be made to determine the effect produced on the cell output by isolation of the anode and cathode compartments of the BNL meter.

D. Meter Modules for FFTF (V. M. Kolba, E. C. Filewicz,¹⁵ M. A. Slawcki¹⁵)

The objective of this work is to design, proof-test, and establish commercial availability for on-line meter modules to be installed at FFTF. These modules include the meters for monitoring impurities and the flow and temperature controls for proper meter operation. Two types of modules have been designed and fabricated, an oxygen-hydrogen meter (O-H) module and a carbon-meter equilibration (C-E) module. The proof-testing is being carried out in laboratory sodium systems and in the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II.

¹²F. J. Salzano, L. Newman, and M. R. Hobdell, Nucl. Technol. 10, 335 (1971).

¹³A. Borucka, Electrochim. Acta 13, 295 (1968).

¹⁴F. J. Salzano, Brookhaven National Laboratory, private communication.

¹⁵E. C. Filewicz, EBR-II Project, prepared the mechanical and structural designs and M. A. Slawcki, Chemical Engineering, prepared the electrical design for the O-H modules, the C-E modules, and the RSCL (Cell B and Cell C) installations.

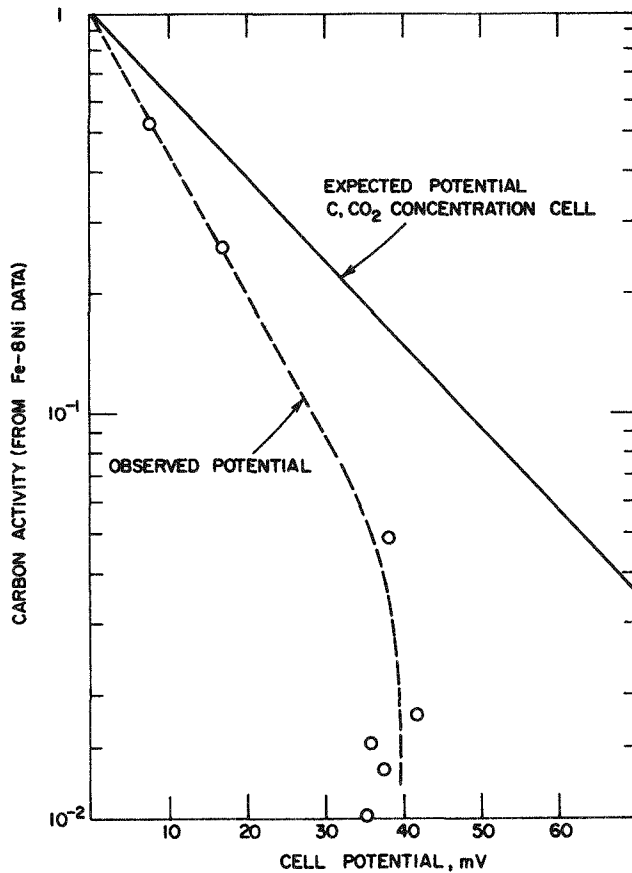


Fig. I-12
Calibration of BNL Carbon
Meter in 700°C Sodium

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

The O-H module contains two oxygen meters and one hydrogen meter in series with a regenerative heat exchanger, flow control valve, and flow indicator. Two of these modules have been built. One is being tested at ANL-Illinois on the Test and Evaluation Apparatus (TEA). The other is being tested in radioactive sodium at EBR-II. A third module is being built for use on the Apparatus for Monitoring and Purifying Sodium (AMPS). The performances of the oxygen and hydrogen meters in the O-H modules on TEA and on EBR-II were discussed above in Sections I.A and I.B.

a. O-H Module on EBR-II (J. T. Holmes)

The O-H module installed in Cell B of the RSCL at EBR-II has been operated in sodium of varying levels of radioactivity for a total of 956 hr, mostly at 700°F. Both oxygen meters were in stable operation when the module was shut down automatically on December 27, 1971, by the failure of a thermocouple connector in one of the high-temperature alarm circuits.

The oxygen-meter electrode assembly that had failed previously (see ANL-7868, p. 18) was replaced with a new assembly in a manual operation which required about 2 hr. The replacement operation involved the use of a temporary heater to melt the freeze seal and an argon-purged glove bag to prevent combustion of the sodium film on the electrode. The setup for the replacement operation is shown in Fig. I-13.

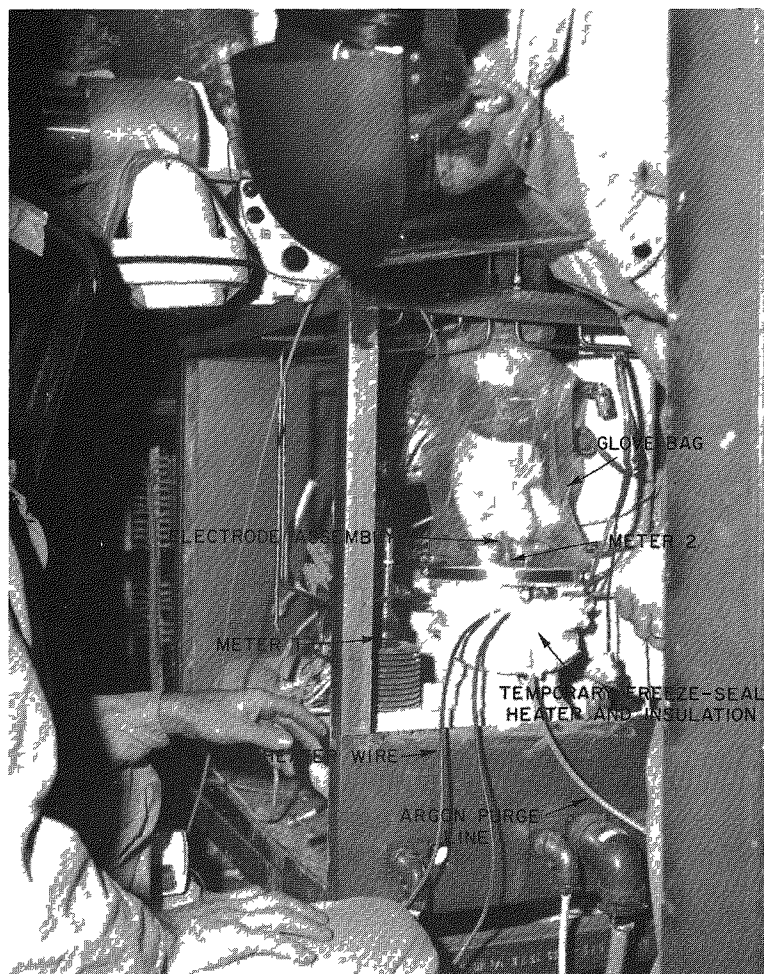


Fig. I-13. Replacement of Oxygen-Meter Electrode Assembly at EBR-II. ANL Neg. No. ID-103-Q5246A.

b. O-H Module on TEA (V. M. Kolba, P. J. Mack)

The O-H module on TEA has been tested at sensor temperatures of 700, 800, and 900°F and an inlet-sodium temperature of 700°F.

During this quarter, considerable difficulty was experienced with the silicon control rectifier (SCR) temperature controllers, especially the chopper circuit. These controllers have now been repaired. The replacement of a burned-out swaged heater and repair of a lead to another heater caused a 2-day shutdown of the module. Operation of the module on TEA has generally followed the requirements of uranium-tab-exposure experiments (see Section II.A.2).

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

The C-E module contains a preheater and an isothermal zone (for the carbon-meter probe or for equilibration of metal specimens) in series with a regenerative heat exchanger, flow control valve, and flow indicator. Two of these modules have been built at ANL: one is in use at ANL on the

Oxygen Meter Rig (OMR); the other began operation during the quarter at EBR-II in Cell C of the RSCL. Both are being used initially for calibrating oxygen meters by the equilibration of vanadium metal specimens. A module was also built at WARD and is being used for calibrating oxygen meters there. Two additional C-E modules are being built at ANL: one will be used for monitoring carbon activity and tritium¹⁶ in Cell C of the RSCL; the other will be installed on the Apparatus for Monitoring and Purifying Sodium.

a. C-E Module 1 at EBR-II (J. T. Holmes)

The C-E module now installed in Cell C of the RSCL at EBR-II is now being used for equilibrating vanadium specimens to obtain calibration data for the oxygen meters and will be used later for equilibrating metal specimens for calibration of the carbon meter and possibly the hydrogen meter. In the initial run with this module, made on December 6 and 7, 1971, vanadium-wire specimens were equilibrated during reactor shutdown when the level of radioactivity in the sodium was low. The results of this equilibration are discussed in Section I.A.3.

A second equilibration of vanadium specimens was made on December 15 and 16, 1971. The specimens have not yet been removed from the module because of difficulties encountered with draining the sodium from the specimen holder. A special procedure, which will permit the use of an alternative draining method, has been written and is being reviewed for safety considerations. The specimens from the second equilibration will be removed from the module early in January.

The goal of the runs to be made in the next quarter will be to accumulate data on the calibration stability of the oxygen meters and to characterize the impurity levels of oxygen and possibly carbon in EBR-II sodium by specimen-equilibration methods. A determination will also be made of how quickly access can be gained to equilibrated specimens when runs are made in highly radioactive sodium (1400 $\mu\text{Ci } ^{24}\text{Na/g}$ of sodium).

b. C-E Module 2 at EBR-II (V. M. Kolba, J. T. Holmes)

A second C-E module is being prepared for installation in Cell C of the RSCL at EBR-II. A carbon meter probe with an iron diffusion membrane will be installed in this module with sweep gas systems for monitoring both carbon and tritium in EBR-II primary sodium. Drawings for the mechanical portion of the module have been issued. Long-lead items have been ordered. Electrical drawings and gas-line and manifold drawings are being prepared. The gas supply and analysis console for the carbon meter, obtained from United Nuclear Corporation, is being modified to incorporate equipment required for the monitoring of tritium. The sodium piping for this module is already installed in Cell C (see ANL-7848, p. 18). Feasibility approval has been obtained from EBR-II, and the request for Approval-in-Principle has been submitted to RDT.

¹⁶Development of a tritium monitor is discussed in Section III.B.

c. C-E Module on OMR (J. M. McKee, D. R. Vissers, L. J. Marek, L. G. Bartholme)

The C-E module on OMR and its counterpart at WARD were both in active use during the quarter, as described in Section A.1, and a dozen or more sets of vanadium wires were equilibrated at each site over a wide range of oxygen activities. Operating experience with the two modules has been generally satisfactory. WARD reports that replacing vanadium wires usually takes less time than replacing a bypass sample tube, the operation required in obtaining a sodium sample for oxygen analysis by the amalgamation method.

Evidence is accumulating at ANL that sufficient iron, nickel, and chromium dissolves in the sodium at the hot end of the C-E module (1382°F) to cause fouling, by formation of metallic deposits, of any fine flow passages in cooler regions downstream from the module. This is particularly true for sodium of high oxygen content because of the increased corrosion rate. It appears that flow restrictions such as throttling valves should be avoided in the outlet stream leaving the module.

d. Low-Cost Equilibration Device (V. M. Kolba)

Design was completed of a simplified specimen-equilibration device which could be adapted by laboratories and other installations to fit existing equipment and provide for wire equilibration with a minimum of expense. A schematic flow diagram of this device is shown in Fig. I-14. Detailed mechanical and electrical drawings and instructions for installation and operation were prepared, approved, and released to RDT for use by all interested parties.

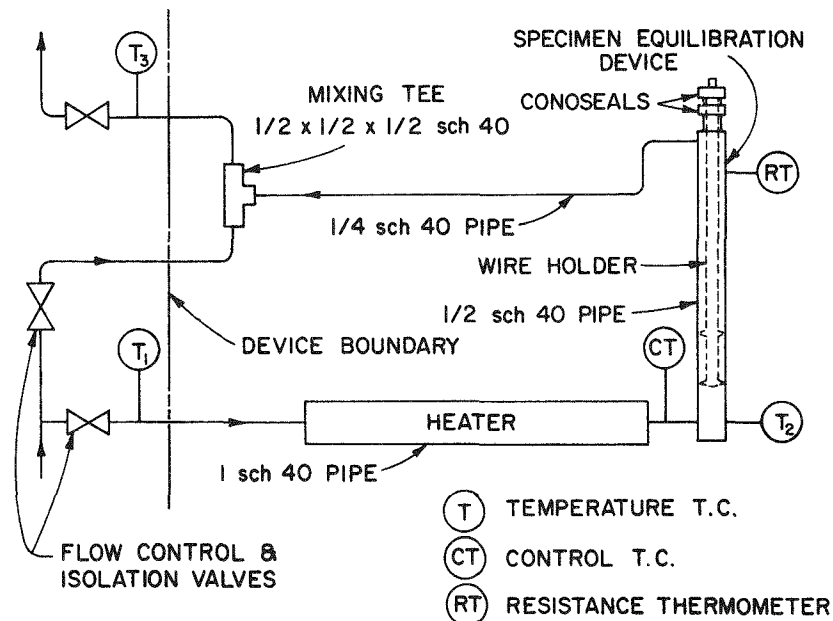


Fig. I-14. Flow Diagram of Low-Cost Equilibration Device

E. Detectors for Leaks in Steam Generators

1. Leak Detector for Liquid Metal Engineering Center (LMEC) (V. M. Kolba, P. J. Mack)

A compact, self-contained leak detector, based on the design of the steam generator leak detector developed for use on EBR-II, is being built for LMEC. Drawings of the EBR-II leak detector have been modified to permit attachment of the unit to the piping of the Sodium Components Test Installation (SCTI) at LMEC. Electrical drawings of the console and diagrams for interconnection of instrumentation have been made.

Long-lead items for both electrical and mechanical components are on order. Materials that were not on hand at ANL have been received from LMEC and fabrication has begun. Modifications to the linear inductor for the pump are being made to permit use of the 3/8-in. pipe and sufficient insulation for proper operation.

2. Leak Detectors for EBR-II Steam Generator (J. T. Holmes, V. M. Kolba)

The detailed design (drawings and stress analysis) of the hydrogen-meter leak detector described in the last quarterly has been completed and supplied to EBR-II. A procurement document is being prepared¹⁷ for a system of 10 modules and instruments for the EBR-II secondary-system steam generators. The procurement package will be based on the detailed design drawings supplied by ANL, and on RDT Standard C 8-6T Hydrogen Meter for Service in Liquid Sodium, which has recently received approval by RDT as a tentative standard.

3. Nickel-Bellows Membranes for Steam-Generator Leak Detector and for Hydrogen-Activity Meter (D. R. Vissers, J. T. Holmes)

Nickel bellows, deep-drawn from 270 nickel sheet, have been received and are currently being evaluated as hydrogen-diffusion membranes. These bellows are approximately 2 in. long and 1/2 in. in outside diameter with a hemispherical end.

Metallographic studies of a cross section of one of the bellows indicate that the walls are apparently free of defects. The average wall thickness of the bellows was found to be 10.3 ± 2 (2σ) mils except for the hemispherical end, where the wall thickness was 18 ± 1.3 (2σ) mils.

Four of these bellows were assembled into mockups for pressure testing. The completely annealed membranes were welded to the mating base by the electron-beam process in ANL Central Shops. Each mockup was then encased in a short pipe section so that the exterior of the bellows-shaped membrane could be pressurized. The hydraulic testing was done with a small hand-operated pump. Prior to the application of any pressure, the interior of the membrane was filled with water so that collapse could be observed. Pressures up to about 500 psig produced gradual displacement of

¹⁷By C. Livengood and L. Christenson of EBR-II Project.

some water, but this appeared to be due to axial flexure of the membrane. Between 900 and 2100 psig, a series of abrupt displacements occurred; these were accompanied by metallic sounds. These displacements are believed to have resulted from stepwise collapse of the membrane against its internal support structure. At 3000 psig, the maximum pressure obtainable with the test apparatus, there was no indication of penetration through the membrane in any of the four mockups. The four mockups were then subjected to an argon leak test. No leakage was detected with a Uson leak detector while the mockups were pressurized to 50 psig. Figure I-15 shows the four mockup assemblies after pressure testing; also shown in the figure is a new membrane and a pipe-section pressure enclosure.

The results of these tests indicate that the supported bellows-shaped membrane is satisfactory as primary containment for sodium in the EBR-II secondary system. The nickel membrane can withstand considerably higher pressure than the ion (vacuum) pump that was shown to be satisfactory for secondary containment in the event of a sodium leak through the membrane (see ANL-7868, p. 19).

On the basis of these tests, the bellows configuration should satisfactorily withstand a pressure pulse that might be generated by a major steam-to-sodium leak. A maximum pressure pulse of about 1300 psig has been calculated¹⁸ for a steam leak rate of 7 lb/sec. This leak rate

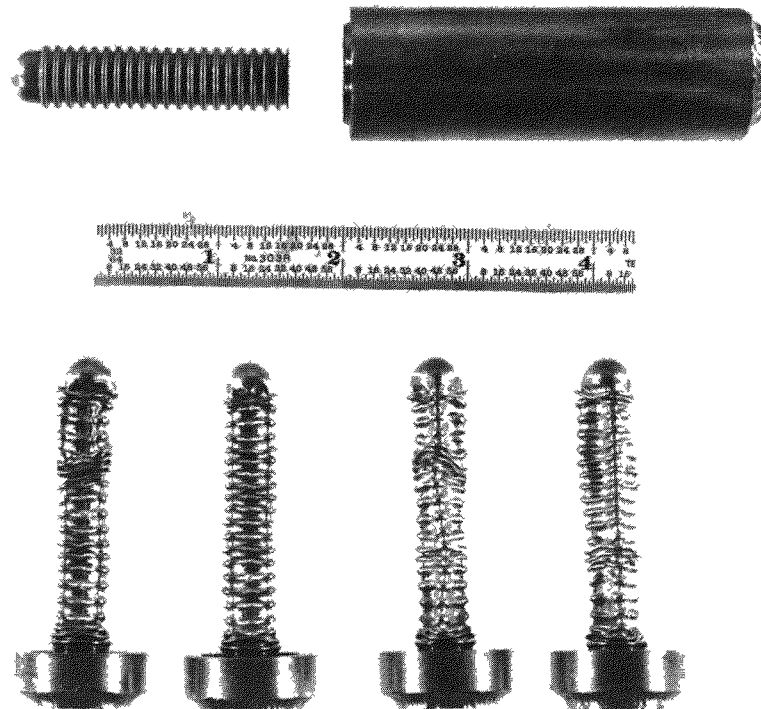


Fig. I-15. Leak-Detector Membranes before and after Hydraulic Pressure Test.
ANL Neg. No. ID-103-Q5008.

¹⁸T. A. Zaker and M. A. Salmon, Illinois Institute of Technology, private communication, Sept 30, 1968.

was based on a complete rupture of a single heat-transport tube. Collapse of the membrane in the leak detector does not represent a safety-related failure, but it is undesirable from the standpoint of meter operation because of impaired conductance within the vacuum system.

Preliminary tests in sodium have indicated that the nickel bellows will function very well as the hydrogen-permeable membrane in the steam-generator leak detector.

F. Apparatus for Monitoring and Purifying Sodium (AMPS) (J. M. McKee, C. C. McPheeters, D. J. Raue)

Substantial progress was made on the construction of AMPS during the quarter. The main vessels and seven of the 28 piping-spool pieces, as well as two pumps, one flowmeter, and six valves, are now in place. Twenty-seven of the 71 field-assembly welds have been made and radiography has been completed on 20 of these. Fabrication of the two cold traps, the getter trap, the O-H module, and the C-E module is nearing completion. Design of the hanger system, the in-line sampler, the gas-vacuum system, and the enclosure ventilation system is well advanced. A control panel 16 ft long by 6 1/2 ft high has been assembled. Most of the power-control components are in place and wiring of these has begun. Wiring is also in progress on a system for automatically diverting the exhaust air through a high-performance scrubber if sodium smoke is detected. Delivery of the scrubber is due in January 1972.

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

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

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

The status of each of the standards presently being prepared on sodium and cover-gas purity is given in Table II-1.

B. Laboratory Activities

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

One of the ANL lead assignments related to FFTF needs is the determination of the effect of sampling-line length on sample validity. Of

TABLE II-1. Status of RDT Standards

Standard Designation	Title	Status	Next Action
RDT A 1-5	Purity Specifications for Operating Sodium Systems	Initial draft nearing completion	Review and comment at next NASWG ^a meeting (Feb 1972)
RDT F 3-40	Interim Methods for the Analysis of Sodium and Cover Gas	Revision nearly complete	Review and comment at next NASWG ^a meeting (Feb 1972)
RDT M 13-1T	Reactor Grade Sodium--Purchase Specifications	2nd amendment transmitted	None
RDT M 13-1 ^b Rev. 1	Reactor Grade Sodium--Purchase Specifications	Review and comment nearly complete	Revise and issue for approval (April 1972)
RDT M 14-1	Sodium Cover Gas--Purchase Specifications	Approval draft in preparation	Issue for approval (Feb 1972)

^aNational Analytical Standards Working Group.

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

¹EBR-II Project.

principal interest is the effect on the determination of (1) nonmetallic impurities, mainly oxygen, hydrogen, and carbon, (2) metals and halides, and (3) radioactive species.

In the first set of experiments (see ANL-7817, pp. 35-39) the effect of line length (100 ft of Type 304 stainless steel tubing) on the oxygen content of sodium was investigated at 350°C and flow rates of 2.5 and 5 gpm. It was concluded that, under these conditions, no significant line-length effect occurred.

The second phase of this investigation, a study of line-length effects on hydrogen concentration, has now been completed. The experiments were conducted at the same flow rates as in the initial experiments (2.5 and 5 gpm) but at higher temperatures. The recent studies also included a simultaneous check for line-length effects on oxygen at the higher temperatures.

Modifications made to the loop for the second set of experiments consisted of (1) replacing the United Nuclear Corporation oxygen meters with Westinghouse meters, (2) installing hydrogen meters of the type described in ANL-7868, pp. 22-23, and (3) adding a cold trap to the section of the loop containing the 100-ft length of tubing. The modified apparatus is schematically depicted in Fig. II-1.

The test procedure used in these experiments was identical to that used in the previous oxygen experiments. Briefly, it consisted of (1) establishing a relationship between the inlet and outlet impurity monitors under equilibrium conditions at various impurity levels (a typical intercomparison is shown in Fig. II-2), (2) isolating the main and auxiliary

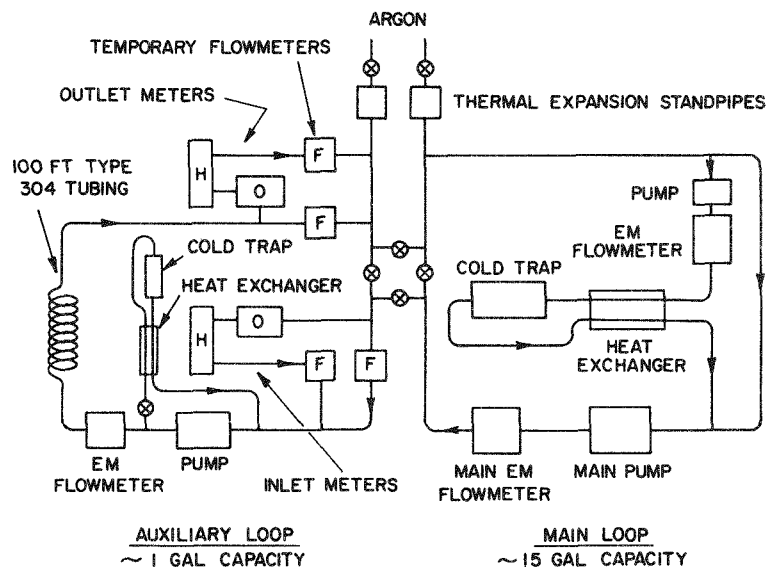


Fig. II-1. Schematic Diagram of Equipment for Testing Line-Length Effects on Sodium Impurities

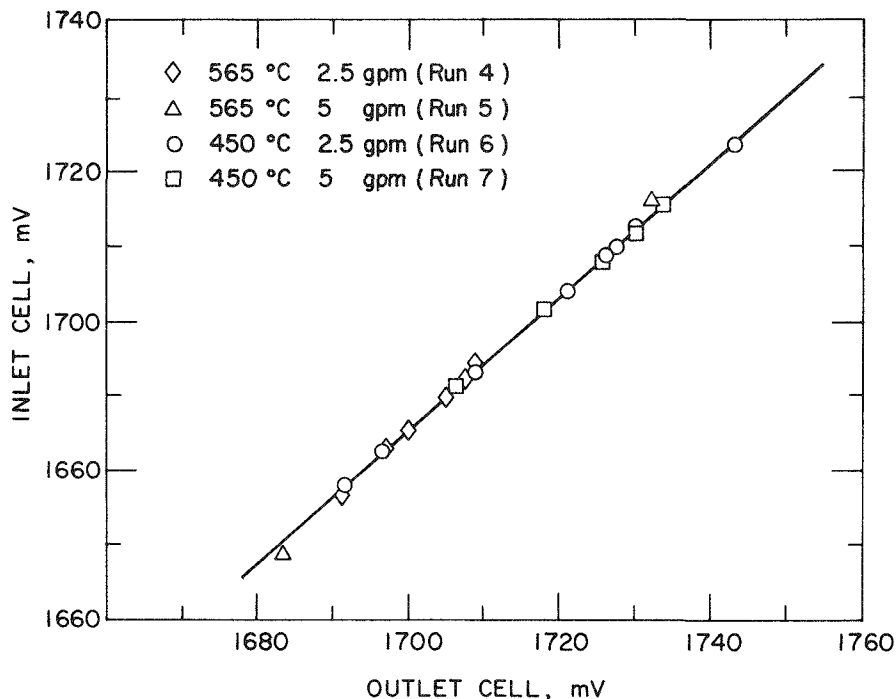


Fig. II-2. Intercomparison of Equilibrium Cell Voltages for Westinghouse Oxygen Meters

loops and adjusting the impurity concentrations to different levels in each loop, and (3) interconnecting the loops so that the monitors were subjected to a rapid change in impurity concentration.

The results obtained at 450 and 565°C for oxygen are given in Table II-2 and those for hydrogen in Table II-3. The agreement obtained between the expected and actual time delay for response of the outlet meters is considered to be within experimental error. The maximum deviations between the expected and observed output voltages of the meters were $\pm 4\%$ for oxygen and $\pm 6\%$ for hydrogen. Hence, it was concluded that, under the conditions of the experiments, no significant line-length effects occurred for either oxygen or hydrogen.

2. Uranium-Getter Method for Oxygen in Sodium (H. S. Edwards, R. J. Meyer, F. A. Cafasso, M. H. Barsky, P. J. Mack)

The uranium-getter method for determining oxygen in sodium² is being investigated as a backup method for the vanadium-wire equilibration procedure for the calibration of oxygen meters. In the uranium-getter method, weighed tabs of uranium are immersed in the sodium for a measured time (~ 1 hr) at a known temperature ($> 500^\circ\text{C}$); then they are removed, cleaned, and reweighed. In pot-type experiments, Isaacs² found a correlation between an oxygen-meter reading and the rate of weight gain per unit area of tab. Our experiments with the uranium-getter method, which are being conducted

²H. S. Isaacs, J. Nucl. Mater. 36, 322-330 (1970).

TABLE II-2. Response of Westinghouse Oxygen Meters Separated by
100 ft of Type 304 Stainless Steel Tubing

Run	Temp, °C	Flow Rate, gpm	Time Delay for Response of Outlet Meter, sec		Approximate Oxygen Conc., ppm		Inlet Meter Voltage after Transient, mV	Outlet-Meter Voltage after Transient, mV	
			Expected	Actual	Before Transient	After Transient		Expected	Actual
1	450	2.5	36	33	~2	>10	1659	1654	1654
2	450	2.5	36	32	~2	>10	1665	1664	1664
3	450	5	18	17	~3	>10	1662	1658	1657
4	565	2.5	36	32	~3	~10	1667	1682	1682
5	565	5	18	17	~3	~10	1667	1682	1683
6	450	2.5	36	32	>10	<1	1731	1752	1754
7	450	5	18	16	>10	<1	1727	1746	1744
8	565	2.5	36	34	>10	<1	1733	1751	1749
9	565	5	18	18	>10	<1	1731	1747	1749

TABLE II-3. Response of ANL Hydrogen Detectors Separated by
100 ft of Type 304 Stainless Steel Tubing

Run	Temp, °C	Flow Rate, gpm	Time Delay for Response of Outlet Cell, sec		Approximate Hydrogen Conc., ppm		Inlet-Meter Voltage, ^a mV		Outlet-Meter Voltage, mV		
			Expected	Actual	Before Transient	After Transient	Before Transient	After Transient ^b	Before Transient	After Transient	Expected Value after Transient
1	450	2.5	34	26	0.1	3	8.6	36	1.6	26	24
2	450	5	17	14	0.4	3	10.8	34	1.8	26	24
3	565	2.5	34	26	0.1	0.4	15	58	22	75	76
4	450	2.5	34	26	9	1	215	6	256	24	11
5	450	5	17	15	4	1	68	6	83	15	11
6	565	2.5	34	26	1	0.1	243	11	297	39	30

^aThe ion-pump current of the hydrogen meter was converted to voltage by passage through a 1000-ohm resistor.

^bValues taken at 150 sec for tests run at 5 gpm and 300 sec for tests run at 2.5 gpm.

in the Test and Evaluation Apparatus (TEA), have the immediate objective of intercomparing this method with other existing methods of determining oxygen in flowing sodium systems.

In the first set of exposures, tabs of uranium, 4 in. long by 0.50 in. wide by 0.027 in. thick, were electropolished, rinsed with distilled water and acetone, dried, weighed, and inserted in tandem into the tab holder. Insertion of the tab holder was made through an inert-gas isolation lock. After exposure for the desired time at 500 to 530°C, the tabs were withdrawn into the inert-gas lock and cooled. The sodium was removed with ethanol, and the tabs were washed with distilled water and ethanol, dried, and reweighed.

It is an operational necessity in TEA to shut off the sodium flow in the exposure device while the tab holder is being inserted. Since the tab holder could carry an appreciable quantity of oxygen into a small volume of sodium and hence expose the tabs to sodium of an abnormally high oxygen level, it is important to restore flow quickly. For the first two runs, the insertion time was excessive--10 to 15 min. The third run was terminated because of difficulty in locking the tab holder in place. After modification of the holder to eliminate this problem, insertion times of about 1 min and removal times of about 0.5 min were achieved in Runs 4, 5, and 6. Consequently, the latter three runs are considered to be more reliable indicators of tab behavior in flowing sodium.

The data presented in Table II-4 indicate that the "rate constant," which is a measure of the correlation between the oxygen content of the sodium and the rate of weight gain per unit area of the tab, is markedly dependent on sodium flow rate. Thus, oxygen measurements based on the rate of oxygen pickup would require careful monitoring of flow rates. Furthermore, it should be noted that in each run the downstream tab picked up less oxygen than the upstream tab. This suggests that nonuniform oxygen pickup is also occurring along the face of the tab and indicates that careful control of such parameters as tab length and tab placement would be extremely important. These disadvantages make oxygen measurements based on rate of oxygen pickup unattractive.

Examination of the data presented in Table II-4 indicates, however, that a rough correlation exists between the amount of oxygen lost from the system (on the basis of meter readings) and the amount picked up by the tabs. This observation suggests that a method based on oxygen material balance, proposed by Minushkin and Goldmann,³ might be applicable to small flowing sodium systems or to small isolatable side loops on large sodium systems. Experiments are now in progress to obtain data which will test this possibility.

3. Particulate Analysis (M. D. Adams, M. F. Roche, W. H. Olson)

a. Particulate Analysis of EBR-II Primary Sodium

A filter assembly was designed, fabricated, and tested on the EBR-II primary sodium system (see ANL-7868, p. 31). The purposes of this

³B. Minushkin and K. Goldmann, "A Technique for Calibration of Electrochemical Oxygen Meters in Potassium," *The Alkali Metals*, Special Publication, No. 22, The Chemical Society (July 1966).

TABLE II-4. Summary of Data for Exposure of Uranium Tabs to Flowing Sodium

Run No.	Flow Rate, gpm	Avg Flow Velocity, cm/sec	Exposure Time, hr	Weight Gain, mg		Rate Constant, ^a $\mu\text{g}/(\text{cm}^2)(\text{hr})(\text{ppm})$		Oxygen Conc. in Sodium, ^b ppm	
				Upstream Tab	Downstream Tab	Upstream Tab	Downstream Tab	Beginning of Exposure	End of Exposure
1	0.047	2.4	2.0	5.3	5.0	45.5	43.0	2.55	1.95
2	0.168	8.5	2.0	12.1	10.9	78.5	70.6	3.5	2.6
4	0.047	2.4	2.0	3.5	2.6	43.8	32.6	1.83	1.48
5	0.168	8.5	0.74	2.7	2.0	91.2	67.8	1.73	1.30
6	0.104	5.2	2.0	5.8	4.1	69.5	49.2	1.90	1.40

^aFor comparison, Isaacs² obtained a rate constant of 16.3 $\mu\text{g}/(\text{cm}^2)(\text{hr})(\text{ppm})$ in stagnant sodium.

^bDetermined from oxygen meter readings.

test were to (1) check the adequacy of the design under the operational restraints imposed by the EBR-II sampling station and (2) to provide a sample containing radioactive species to further test procedures being developed for characterizing particulates.

Approximately 1085 gal of EBR-II primary sodium at 600°F was passed through the filter in a period of 49.5 hr. Minor problems with flow stoppage were encountered because of a gas bubble that had been inadvertently introduced into the assembly. However, the overall performance of the filter assembly was considered satisfactory.

After disassembly, the filter was examined for radioactive species and for total particulates. The results of these analyses are given in the paragraphs below.

Radioisotope Analysis. A gamma spectrum of the filter, after 1.4 g of residual sodium had been removed by distillation, was obtained by exposing the filter to a 20-cm³ Ge(Li) detector for 20 min. The spectrum is shown in Fig. II-3, where the principal gamma peaks and their energies (in keV) are identified. It will be noted that the dominant activity is ⁵⁴Mn, with lesser amounts of ⁶⁰Co, ¹³⁷Cs-^{137m}Ba, ¹¹³Sn-^{113m}In, ¹⁴⁰Ba-¹⁴⁰La, and ¹⁸²Ta.

The levels of activity found on the filter, corrected back to the time of removal of the filter from EBR-II primary sodium, are given in Table II-5. For comparison, the normal levels of activity for these isotopes in EBR-II sodium are also given. If concentration of the radioisotopes on the filter had not occurred, one would expect the activity levels on the filter to be comparable to the levels normally found in one gram of sodium (the amount left on the filter). It is obvious that a deposition of these isotopes (particularly ⁵⁴Mn) on the filter has occurred.

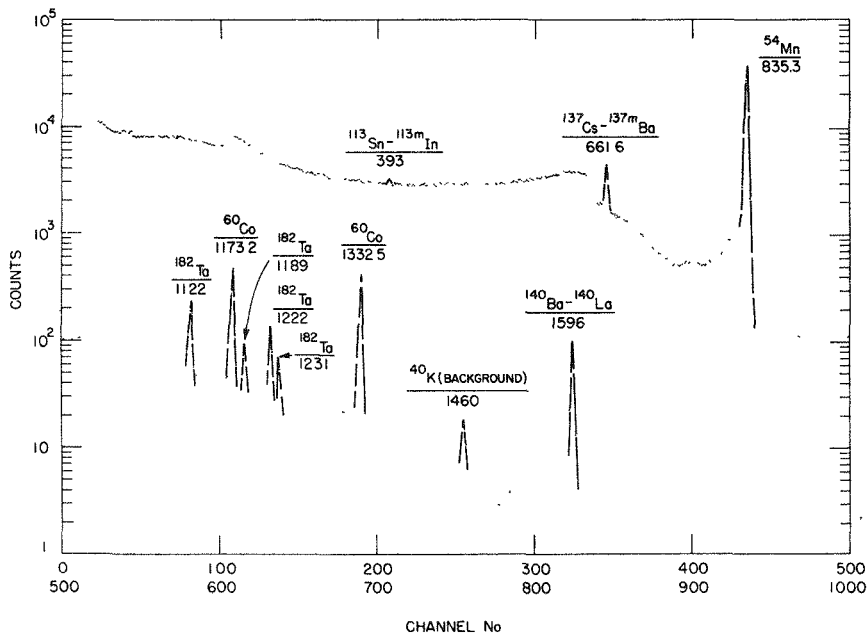


Fig. II-3. Gamma Spectrum of Filter from EBR-II Primary Sodium System. ANL Neg. No. 308-2782.

TABLE II-5. Radioisotopes Found on EBR-II Filter

Isotope	Activity on Filter, μCi	Normal Level of Activity in EBR-II Sodium, $\mu\text{Ci/g}$
^{54}Mn	7.0	$(2-8) \times 10^{-6}$
^{60}Co	0.1	a
$^{137}\text{Cs}-^{137\text{m}}\text{Ba}$	0.5^{b}	2×10^{-2}
$^{113}\text{Sn}-^{113\text{m}}\text{In}$	0.04	$(4-5) \times 10^{-3}$
$^{140}\text{Ba}-^{140}\text{La}$	0.6	a
^{182}Ta	0.16	a

^aThe levels of ^{60}Co , $^{140}\text{Ba}-^{140}\text{La}$, and ^{182}Ta found in EBR-II are so low they are normally not reported.

^bThis number includes the ^{137}Cs which was present in the 1.4 g of residual sodium distilled from the filter.

Similar depositions of radioisotopes were found⁴ upon examination of the No. 1 primary pump of EBR-II; the predominant activities found were ^{54}Mn , ^{60}Co , ^{137}Cs , and ^{182}Ta .

Autoradiographs of the filter showed that the activity deposits were concentrated in isolated spots. Such a deposition pattern has been observed previously⁵ on stainless steel tabs simply immersed in sodium containing ^{137}Cs and ^{131}I tracers; hence, the spotty deposition pattern does not necessarily imply the presence of activity-containing particulates in the sodium. Furthermore, the fact that repeated attempts to ultrasonically clean the activity from the filter were unsuccessful suggests that deposition and not filtration had taken place.

Total Particulate Analysis. The filter was cleaned ultrasonically with various prefiltered solvents: xylene, water, and Freon-11. The solvent was passed through a 1.2- μm Millipore filter; the Millipore filter was then mounted and examined by microscopically transmitted light. Each time the filter has been ultrasonically cleaned (once with xylene, twice with water, and once with Freon), large numbers of $\leq 1\text{-}\mu\text{m}$ particles were shaken loose. Only a few particles were larger than 5 μm . The total mass of the four residues was estimated to be ~ 10 mg. This amount corresponds to a particulate concentration in the filtered sodium of $\sim 3 \times 10^{-3}$ ppm.

After a water wash of the residue, which would remove any Na_2O formed upon distillation of residual sodium from the filter, the particles remaining were predominantly metallic in nature. No evidence of particles of the Na-Cr-O type or of silicates was found. This finding is in direct contrast to the results obtained on most small loops, where the predominant species have been in the oxidized form.

⁴C. R. F. Smith *et al.*, *Reactor Development Program Progress Report*, March 1971, ANL-7798, p. 12 (1971).

⁵R. P. Colburn, *Nature of Cs and I Deposits in Sodium Systems*, Trans. Amer. Nucl. Soc. 14, 626 (1971).

Several of the larger particles were selected for further examination by electron microprobe. A soft metal particle that had the appearance of having been molten was principally aluminum, with minor amounts of iron and magnesium. A flat metallic particle was principally aluminum with minor amounts of iron, magnesium, and calcium. A wire-like particle was found to be stainless steel.

Conclusions. The conclusions drawn from the examination of the EBR-II filter are as follows: (1) most of the radioactive species found on the filter were also found previously on an EBR-II primary pump; (2) the radioactive species are firmly fixed to the filter, either by deposition, isotopic exchange, or alloy formation; (3) the quantity of particulate in EBR-II primary sodium is extremely small ($\sim 3 \times 10^{-3}$ ppm); and (4) the particulate in EBR-II is predominantly metallic in nature.

b. Filter for the Core Component Test Loop (CCTL)

Because of the high temperature (1050°F) and pressure (60 psi) of CCTL sodium, an all-welded filter cartridge will be used to collect particulates for analysis. The filter has been tested on the Test and Evaluation Apparatus (TEA) and was found to operate satisfactorily. A filter of this design will be installed on CCTL in the first quarter of 1972.

The analysis of particulates collected on the filter in TEA is in progress.

4. Analysis of Nonmetallic Impurities in Sodium by the Equilibration Method (D. L. Smith)

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

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

A standardization and characterization program has been conducted to further qualify the vanadium wire equilibration method as a standard method for analysis of oxygen in sodium for the LMFBR sodium technology program. Results of this investigation have been reported in detail in a topical report, ANL-7891, entitled "Characterization of the Vanadium-Wire Equilibration Method for Measurement of Oxygen Activity in Liquid Sodium."

The temperature dependence of the distribution coefficient determined from the combined data obtained at 650, 700, and 750°C is given by

$$\ln K_A = \ln \frac{N_{Ov}}{N_{ONa}} = -7.73 - \frac{20,960}{T} + \frac{40,330}{T} (1 - N_{Ov})^2$$

where N_{Ov} and N_{ONa} are the atom fractions of oxygen in vanadium and sodium, respectively, and the temperature is in °K.

For some applications of the equilibration method, the use of larger (>0.25 -mm-dia wire) vanadium detector specimens is desirable. Various specimen sizes and geometries (both slab and cylinder) may be used as long as oxygen equilibrium is attained and all surface contamination is removed from the specimens before analysis. The cylindrical geometry minimizes the surface-to-volume ratio of the detector and is, therefore, advantageous in both respects. Simultaneous exposures to sodium of 0.25- and 0.50-mm-dia (10- and 20-mil) wire specimens have been conducted to demonstrate that satisfactory results are obtained. A minimum of 16 hr at 750°C is required for equilibration of the larger diameter wire. The agreement between duplicate analyses obtained with the larger wire is better than with the smaller wire. The more consistent results for the larger wire are believed to be due primarily to the fact that larger samples of the 0.50-mm-dia wire were used in the analysis, i.e., ~ 40 mg compared with ~ 15 - 20 mg for the 0.25-mm-dia wire, which has generally been used with the automatic analyzer. More consistent results were also obtained on larger samples (50 mg) analyzed by the manual fusion technique during the initial investigations of the method. The oxygen concentrations determined with the automatic analyzer for the larger wires average $\sim 4\%$ less than corresponding values obtained for 0.25-mm-dia wires. These lower values from the 0.50-mm-dia wires are in good agreement with the previous oxygen analyses⁶ on which the V-O-Na distribution-coefficient data were based. Those results,⁶ which were obtained on ~ 50 -mg samples by the manual inert gas fusion technique,⁷ average $\sim 3\%$ less than corresponding values determined with the automatic analyzer on smaller samples. Additional samples from these tests are being analyzed by the manual fusion technique for comparison.

A purchase specification⁸ has been written for procuring vanadium wire to be used for the measurement of oxygen activity in sodium by the vanadium-wire equilibration method.

b. Niobium Equilibration Method for Analysis of Oxygen in Sodium

The base technology required for the use of niobium as a detector for measurement of oxygen activity in sodium is also being developed. The primary advantage of niobium as a detector, compared with vanadium, is the capability of measuring oxygen concentrations in the range of interest, i.e., ≤ 20 ppm, at lower equilibration temperatures. An equilibration temperature of 650°C is satisfactory for oxygen concentrations encountered in LMFBR applications. Since the diffusivity of oxygen in niobium is considerably higher than that in vanadium, the equilibration times are only 1 hr at 750°C and 4 hr at 650°C for a 0.25-mm-dia (10 mil) wire, and 4 hr and 16 hr for a 0.50-mm-dia (20 mil) wire at the respective temperatures.

The measured distribution coefficient for oxygen (in units of atom fraction oxygen) between niobium and sodium is much smaller than that between vanadium and sodium, being of the order of 100 for the Nb-O-Na system compared with $\sim 10,000$ for the V-O-Na system. Oxygen levels in sodium of

⁶D. L. Smith and R. H. Lee, *Characterization of the Vanadium-Wire Equilibration Method for Measurement of Oxygen Activity in Liquid Sodium*, ANL-7891.

⁷B. D. Holt and H. T. Goodspeed, *Anal. Chem.* 35, 1510 (1963).

⁸Written by D. L. Smith and N. J. Carson.

primary interest for LMFBR applications give oxygen concentrations in niobium in the range from 30 to 100 ppm after a 650°C equilibration.

Three methods have been used to measure the oxygen concentrations in niobium: (1) automatic inert-gas fusion using a LECO RO-16 analyzer, (2) manual inert-gas fusion, and (3) internal friction. The internal friction measurements are the most sensitive at these levels and are being used in the determination of the distribution coefficient. Procedures for improving the automatic inert-gas fusion analyses of niobium samples containing low oxygen contents are being investigated. Improvements in the inert-gas fusion techniques may provide adequate sensitivity for determining oxygen concentrations in LMFBR sodium by the niobium equilibration method at 650°C.

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

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

Both niobium and vanadium are being considered for use as detectors for measuring the hydrogen activity in sodium. Data are available in the literature for relating equilibrium hydrogen partial pressures to hydrogen concentrations in both niobium and vanadium.⁹⁻¹³

The equilibration procedure for measurement of hydrogen activity is similar to that used for oxygen analysis by the vanadium equilibration method.¹⁴ Larger diameter (0.50 to 1.00 mm) wire samples are used because of the high diffusivity of hydrogen in the detector metals and because of the lower distribution coefficients, which require larger (~200 mg) samples for sensitive analysis. The inert-gas fusion technique is used to measure the hydrogen concentration in the detector metal after exposure to sodium. Equilibration temperatures in the range from 450 to 750°C are being used in the development program.

The testing is being done in a sodium apparatus equipped with a cold trap for control of the hydrogen concentration. In the initial tests, sufficient oxygen was available that the oxygen concentration in sodium was also controlled by the cold trap. For equilibration, the detector wires are attached to a holder which is inserted into a high-temperature vessel containing approximately 2 liters of sodium. After exposure at the desired temperature, the wires are quenched by withdrawing the holder into a room-temperature helium gas chamber immediately above the sodium vessel. The

⁹P. Kofstad and W. Wallace, *J. Amer. Chem. Soc.* *81*, 5019 (1959).

¹⁰E. Veleckis and R. K. Edwards, *J. Phys. Chem.* *73*, 683 (1969).

¹¹S. Komjathy, *J. Less-Common Metals* *2*, 466 (1966).

¹²W. Albrecht, M. Mallett, and W. Goode, *J. Electrochem. Soc.* *105*, 219 (1958).

¹³O. Katz and E. Gulbransen, *Columbium Metallurgy*, pp. 523-557, D. Douglas and F. Kunz, Eds., Interscience Publishers, New York, N. Y. (1961).

¹⁴D. L. Smith, *Nucl. Technol.* *11*, 115-119 (1971).

gas chamber is isolated from the sodium cover gas during the quench. Any sodium adhering to the wires is dissolved in alcohol at room temperature, after which the wires are rinsed in distilled water and dried. Surface contamination is removed from the niobium detector wires by a slow chemical polish conducted without significant heating of the wire. The electro-polishing procedure used to clean vanadium wires for hydrogen analysis is that used for the vanadium wires analyzed for oxygen. The hydrogen concentration in the detector wires, as measured by inert gas fusion, is related to hydrogen pressure from the data of Veleckis and Edwards.¹⁰

The square roots of the hydrogen pressures from a series of niobium exposures at 750°C are plotted in Fig. II-4 as a function of the reciprocal cold-trap temperature. The error bands on the data points represent the scatter of duplicate hydrogen analyses. The hydrogen pressures determined from the niobium wires show a good correlation with the cold-trap temperatures; however, the values are somewhat higher than pressures obtained by extrapolation to lower temperatures of the combined data for the H₂-Na-NaH equilibrium of Herold,¹⁵ Addison *et al.*,¹⁶ and McClure and Halsey¹⁷ (see Fig. II-4). Similar curves extrapolated from the H₂-Na-NaH equilibrium data of Meacham *et al.*¹⁸ and Vissers *et al.*¹⁹ are also included in the figure for comparison. Although the hydrogen pressures determined by the niobium wires are considerably higher than the other data in Fig. II-4, the slopes of all the curves are in reasonable agreement. Possible reasons for the large difference in pressure are being investigated. Niobium exposures at lower temperatures have also been conducted and the results are being analyzed.

During this investigation, two diffusion-type hydrogen meters have been operated on the sodium apparatus. One meter is operated on-line at 450°C for comparison with the results of Vissers *et al.*¹⁹ and the other is located in the wire-equilibration vessel that operates at temperatures between 450 and 750°C. Performance of these meters in the equilibrium mode is very similar to that of other meters operated on ANL sodium systems.²⁰ For either low meter temperatures (<550°C) or low hydrogen concentrations in sodium (cold-trap temperatures below 175°C), considerable drift in the pressure reading occurs with time. The hydrogen pressures determined under these conditions are, therefore, dependent on the time at which the reading is taken after isolation of the meter from the vacuum pump. Fairly consistent results were obtained in the present investigation by standardizing the time at which the pressure was recorded after isolation of the meter (e.g., 30 min at 750°F, 40 min at 650°C, 50 min at 550°C, and 60 min at 450°C). Results of the square root of hydrogen pressure determined from the two meters as a function of the reciprocal cold-trap temperature are plotted in Fig. II-4 for comparison with other data. The pressures measured with the ionization gauges were multiplied by 3.0 to obtain the hydrogen pressure (the gauges are initially calibrated with nitrogen). Values obtained in this manner indicate no significant effect of meter temperature

¹⁵M. A. Herold, *Compt Rend.* 228, 686 (1949).

¹⁶C. C. Addison, R. J. Pulham, and R. J. Roy, *J. Chem. Soc.* 116-121, 1965.

¹⁷D. W. McClure and G. D. Halsey, Jr., *J. Phys. Chem.* 69, 3542 (1965).

¹⁸S. A. Meacham, E. F. Hill, and A. A. Gordus, USAEC report APDA-241 (1970).

¹⁹D. R. Vissers, J. T. Holmes, and P. A. Nelson, *Trans. Amer. Nucl. Soc.* 14(2), 610 (1971).

²⁰V. M. Kolba, personal communication (December 1971).

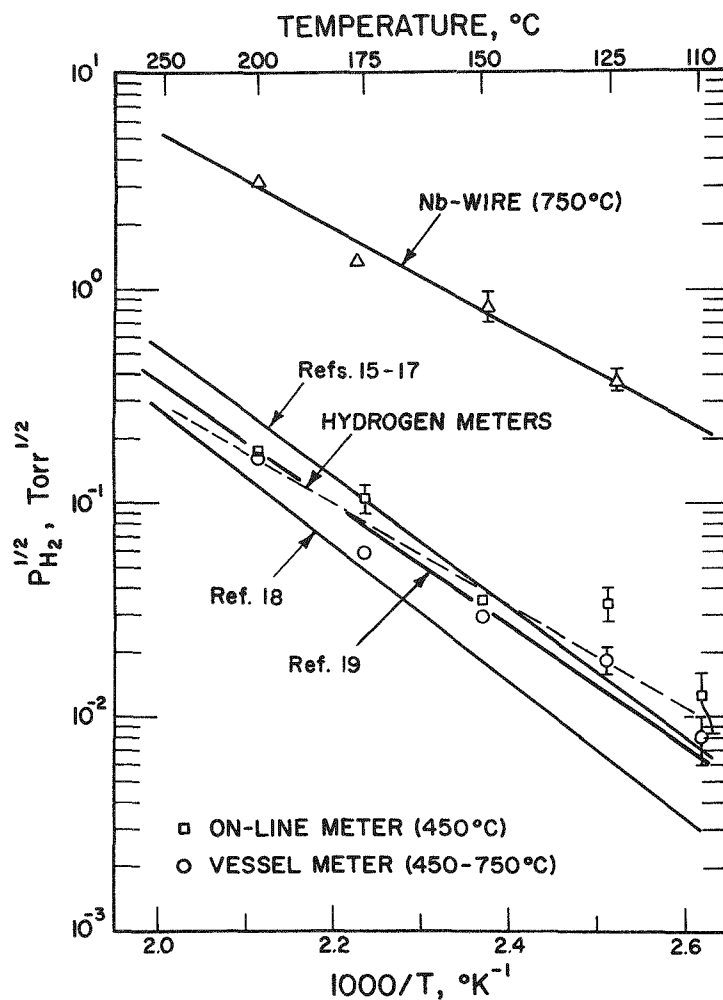


Fig. II-4. Comparison of Temperature Dependence of Hydrogen Pressures Determined by Niobium-Wire Equilibrations at 750°C with Hydrogen Meter Data and Literature Data.¹⁵⁻¹⁹ Neg. No. MSD-56670.

on the hydrogen pressure and little difference between the meters was detected. The results from these meters are in fairly good agreement with hydrogen-meter data obtained by *Viissers et al.*¹⁹

The results to date indicate that the hydrogen concentration in niobium is dependent on hydrogen concentration in sodium, i.e., cold-trap temperature. Thorley and Tyzak²¹ have stated after an extensive investigation of the Nb-H-NaK system: "It has been clearly established that, in a pumped circuit circulating hydrogen-contaminated NaK at 350°C, the degree of hydrogen uptake by niobium specimens at this temperature is controlled by the temperature of cold trap operation." Their tests involved niobium exposures in the range 350 to 600°C. The hydrogen concentration in vanadium wires exposed to sodium in the present investigation have also indicated a dependence on the cold trap temperature, that is, the hydrogen concentration in sodium.

²¹A. Thorley and C. Tyzak, *Proc. Symp. Thermodynamics of Nuclear Materials*, pp. 365-397, IAEA, Vienna (May 1962).

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

A. Development of FEDAL Methods for FFTF

Detection and characterization of fuel element failures in liquid-metal-cooled fast reactors such as the FFTF are required to prevent gross contamination of the primary coolant, loss of fuel from the failed fuel element, and possible progressive damage to adjacent fuel pins. Two types of systems for detection and characterization of fuel-element failure are under development for FFTF application: a cover-gas analysis system and a sparger and sparge-gas analysis system. These systems may be incorporated in the Reference Fuel Failure Monitoring System for FFTF.

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

1. Analysis of Cover Gas (M. H. Barsky, A. F. Panek, R. J. Meyer)

During reactor startup at EBR-II, minor discrepancies have been encountered in the assay of the cover gas for rare-gas fission products; these were attributed to ^{23}Ne interference.¹ The cover gas of FFTF may have a background level of ^{23}Ne that is as much as 10^6 times the background of the radioactive krypton and xenon fission products from tramp uranium; thus, counting problems more severe than those experienced at EBR-II are anticipated in assaying the activity of fission-product gases at FFTF.

A gas-chromatographic technique is being developed for the separation of the neon prior to the radioactive assay of fission gases. In this technique, the gases are eluted from the chromatographic column in the order neon, krypton, xenon. The procedure is as follows: (1) introduce a sample of reactor cover gas (or gas from the sodium sparger) onto a chromatographic column, (2) flow argon carrier gas through the column for a preestablished period of time so that the ^{23}Ne activity remaining on the column is no more than 10^{-6} times the amount originally introduced, (3) stop the carrier-gas flow and obtain a gamma spectrum of the radioactive species on the column, (4) immediately introduce another sample (the krypton and xenon from the previous cycle will be eluted as the chromatographic process continues), and (5) repeat the cycle.

Our initial studies were made using inactive neon, krypton, and xenon and a thermal-conductivity detector. The decontamination factor (DF)

¹G. S. Brunson and P. B. Henault, *Reactor Development Program Progress Report, October 1971*, ANL-7872, p. 1.20 (1971).

between ^{23}Ne and the xenon isotopes is of major interest; however, in studies with the Ge(Li) detection system, work was directed toward determining the DF between ^{85}Kr and ^{133}Xe . (The 38-sec half-life of ^{23}Ne made its use impractical in laboratory experiments.) From the data obtained in the experiments with ^{85}Kr and ^{133}Xe , and an assumed DF of ~ 10 for the neon-krypton separation, an overall DF of $\sim 10^6$ was calculated for the separation of ^{23}Ne and $^{133,135}\text{Xe}$ (see ANL-7868, p. 37).

Recent efforts have been in three areas: (a) continued work with inactive noble gases to determine the best chromatographic conditions for the reduction of tailing effects, (b) additional support work with radioactive krypton and xenon aimed toward developing the most advantageous counting geometry, and (c) further investigations to define the neon-krypton separation more exactly.

A considerable number of column materials, packing procedures, and chromatographic techniques have been tested with the inactive gases and a thermal-conductivity detector. Results indicated that (a) the use of column packing material of a uniform particle size decreases the tailing effects; (b) vacuum packing yields uniformly packed columns with minimum particle breaking; (c) columns as small as 3 ft long by 1/8 in. OD (0.065 in. ID) can handle samples up to 100 ml without significant loss in krypton-xenon resolution; (d) because of pressure drop, 3/16 in. OD (1/8 in. ID) is the required minimum diameter for flow rates greater than 100 ml/min.

In tests with radioactive isotopes, the column having the most advantageous counting geometry was 8 ft long by 1/8 in. ID (3/16 in OD), vacuum packed with 60-80 mesh Porapak Q, with only the last 3 ft exposed to the detector. Such a column can accommodate much greater flow rates than was possible with previous columns with essentially no loss in resolution or sensitivity and no increase in tailing. To simulate an actual sampling situation, a 100-ml "bypass" sampling loop was constructed. Mixtures of the radioactive isotopes with inactive argon were prepared in the loop. Several identical mixtures were swept onto the column at various flow rates. The sample was then eluted from the column with pure argon carrier gas. This procedure simulated flowing actual samples onto the column for periods of 0.5 to 1.5 min. Comparison of these results with the results from instantaneously injected small samples showed no difference between the two sample injection methods.

The same column was attached to a thermal-conductivity detector and experiments were performed with inactive neon and krypton to obtain a better estimate of the neon-krypton DF. The experiments yielded a DF of ~ 350 instead of the conservative value of 10 that had been assumed previously. Chromatograms obtained with inactive krypton and xenon verified the results obtained previously with the active krypton and xenon isotopes.

When the decay of ^{23}Ne during the 3-min analysis time and the width of the krypton peak are included in the overall calculations, a DF of $\sim 10^8$ between neon and xenon is indicated for the cover-gas analysis system.

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

The analysis method currently under development for monitoring reactor sodium is based on analysis of the sodium for dissolved fission gases and ^{135}I . Fuel failures in which the fuel is contacted by the sodium coolant would be detected by this method. The method consists of isolating a small volume of primary sodium, sparging the sodium with inert gas to strip out dissolved fission gases, and assaying the sparge-gas effluent for fission gases (xenon and krypton) by Ge(Li) spectrometer. Any fission-gas isotopes subsequently found in the sparge gas are those produced from decay of halogen isotopes in the sodium. After a predetermined time (~ 2 min), the ^{135}I in the sample is determined on the effluent from a second sparge by gamma assay of its daughter $^{135\text{m}}\text{Xe}$. The monitor system includes a sampling/sparging device with automatic timer controlled valves, a chromatographic column for fission-gas separation, a Ge(Li) detector for counting fission gas, and a computer for data analysis.

a. Xenon-Removal Studies

The time required to sparge dissolved xenon from sodium is important in assessing the feasibility of operating a monitor based on the above principle. Experimental data obtained on ^{133}Xe removal from 350 and 450°C sodium sparged with helium have been reported previously (ANL-7868, p. 40). Data have recently been obtained on the removal of ^{133}Xe from sodium sparged with argon.

The equipment used and the general procedure followed in four argon-sparge tests were similar to those previously used in the helium-sparge tests. The time constants for removal (defined as the time to decrease the ^{133}Xe concentration in the sodium by a factor of e^{-1}) were obtained from plots of cumulative activity released to a cooled ($\sim -117^\circ\text{C}$) activated charcoal trap. The counting was done with a Ge(Li) spectrometer/computer programmed for a 3-sec count period during each 3.06 sec.

Experimentally determined times for xenon removal from 350°C sodium by sparging with argon are compared with previously reported results from helium sparge tests in Table III-1. In each case, sparge-gas flow through the 500-cm³ sodium sample was 1000 cm³/min. Under the experimental conditions, the time required for 99% removal of the dissolved xenon was reduced from approximately 1.5 to 1 min by using argon rather than helium as the sparge gas. The sparger being designed for use in FFTF will utilize argon sparge gas to prevent contamination of the primary system with helium. The presence of helium in the argon cover gas could interfere with the chromatographic analysis for hydrogen.

b. Sparger Equipment Development

The design of the sparger employed in the xenon-removal studies, which was described previously (ANL-7817, p. 49), is being modified for reactor use. In the modified version, the sampling and sparging are done in a vessel constructed of 2-in. pipe. In operation, sodium is circulated through the device with the gas space isolated to prevent the sodium level from rising to flood the sparger. After a sufficient circulation

TABLE III-1. Time Required for Removal of Dissolved Xenon from Sodium by Sparging (sodium temperature, 350°C; sparge rate, 1000 cm³/min)

Experiment	Sparge Gas	Time Constant for Removal, ^a sec	Time for 99% Removal, sec
11	Argon	13	60
12	Argon	9	41
13	Argon	13	60
14	Argon	12	55
4 ^b	Helium	21	97
5 ^b	Helium	24	110
8 ^b	Helium	16	74

^aTime to decrease xenon concentration in sodium by a factor of e^{-1} .

^bPreviously reported data (ANL-7868, p. 40).

time, the sodium outlet valve is closed and the gas phase is vented to permit sodium to rise in the vessel until a signal from an inductive liquid-level sensor closes the sodium inlet valve. Sparge gas bubbled through the sample is directed through an aerosol trap system consisting of a wire-packed vapor condenser and a high-efficiency filter. The gas then enters the gas analysis system in which activities are monitored by gamma counting.

Tests were performed with water in a glass mockup of the sparger to obtain preliminary data on (a) the reproducibility of sampling with the use of the inductive liquid-level sensor (a conductivity-type level sensor was previously used in the mockup) and (b) the time required for complete sample change in the vessel as a function of liquid flow rate. The sensor and valves were connected to a timer which permitted repeated cycling through the operations of liquid circulation, sample volume adjustment, and sparging. Data on the time required for sample change were obtained by adding an electrolyte to the water to be circulated through the sparger and measuring the conductance change of the water in the sparger as a function of time after circulation was initiated. The tests indicated that the reproducibility of sample volumes during 88 total cycles was $\pm 0.5\%$. The time for complete sample change in the vessel was < 2 min at a flow rate through the sparger of 0.5 gpm and < 1.5 min at a flow rate of 1.5 gpm.

A prototype sparger and gas analysis system will be built for testing of sparger operation of ANL-Illinois. The system will be fabricated, where feasible, from off-the-shelf components. Fabrication of an apparatus to feed sodium containing dissolved gaseous activities to the sparger module has been started. An existing glovebox is being modified to serve as a ventilated enclosure for this system. The prototype sparger module will be built when the piping-layout drawings are completed for the installation of a sparger on EBR-II (described below).

3. Installation of Prototype Detection System on EBR-II
(C. C. McPheeters)

Prototypes of the cover-gas analysis system and the sparger and sparge-gas analysis system will be tested on EBR-II. The cover-gas analysis system will be installed in a small building outside the primary containment building. The sparger and sparge-gas analysis system will be installed on the Radioactive Sodium Chemistry Loop (RSCL). The sparger module will be located in Cell B of the RSCL and the sparge-gas analysis system outside Cell B.

Detailed design of the cover-gas analysis system has been started. The required design of the chromatographic column for this system has been established. The cover-gas analysis system is capable of taking cover-gas samples of 1- and 100-ml volumes. A sample is transferred to the column with a flow of argon. The argon flow continues until ^{23}Ne is eluted from the column, and the xenon and krypton isotopes of interest are then counted with a Ge(Li) detector. A 100-ml cover-gas sample will be used for determining the normal levels (from tramp uranium) of the isotopes of interest. In the event of a fuel failure that causes a count rate high enough to saturate the Ge(Li) detector, the sample size will be reduced to ~ 1 ml by operation of a different sample valve. The sample operation sequence, sample size selection, and data analysis will be controlled with a spectrometer-computer.

The cover-gas analysis system will sample the cover gas on a cycle of ~ 4 min. To obtain a new 100-ml sample in this time period, the argon that replaced the previous sample must be flushed out and replaced with fresh cover gas. If we assume that eight volumes must be flushed through the sample tube before a representative sample is obtained, the required minimum cover-gas flow rate is ~ 200 ml/min. Efficient chromatographic separation of the fission gases requires an argon carrier-gas flow rate of ~ 100 ml/min. Various methods are being considered for disposing of the effluent from the chromatographic column (300 ml/min total flow).

Design drawings of the sparger vessel are nearly complete and preliminary piping layout drawings for the sparger module have been made. Specifications for purchasing long-lead time items such as valves and the liquid-level sensor are being written. The fabrication schedule will be largely dependent on the availability and delivery of these long-lead items.

A request for Approval-in-Principle (AIP) for the cover-gas analysis system and the sparger and sparge-gas analysis system have been submitted to RDT. A definite schedule for installation of the systems in EBR-II will be developed when the AIP is received from RDT.

A single spectrometer/computer system controls both the cover-gas analysis system and the sparger and sparge-gas analysis system. An RDT standard, RDT C 14-3, is being written to define the requirements of the spectrometer/computer system to be purchased for use on FFTF.

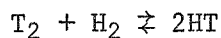
B. On-Line Tritium Monitor (C. Luner, M. S. Foster*)

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

Operation of the tritium monitor currently being evaluated is based on diffusion of tritium (and hydrogen) through an iron membrane and determination of the tritium activity. The iron membrane is in the form of a 10-cm-long tube with one end closed. A smaller tube is positioned inside the iron tube, or probe, to direct a sweep gas to the closed end. The sweep gas ($\text{Ar} + \text{H}_2$) flows along the inside of the iron tube from the closed end to the exit. The gas is then directed to an internal gas proportional counter where the tritium activity is determined.

A calculational study is in progress to obtain an estimate of the tritium level in the effluent sweep gas as a function of (1) the composition and flow rate of the incoming sweep gas and (2) the hydrogen and tritium levels in sodium. The following model was used for this study: The iron membrane was considered as a series of independent cylindrical sections. Two cases were considered, in which the 10-cm membrane length was divided into 100 and 1000 sections, respectively. The hydrogen and tritium concentrations in the sodium at the exterior surfaces of each membrane section were considered to be constant.

As the sweep gas flows through the probe, tritium and hydrogen diffuse from the sodium through the iron membrane into the sweep gas. The volumes of hydrogen and tritium diffusing into each section were calculated. The concentrations of hydrogen and tritium in the gas leaving the section and entering the next section were then calculated from the equilibrium constant for the reaction



The total volume of HT leaving the probe was obtained by summing the incremental volumes of HT formed in each section.

Preliminary results indicate that the tritium in the sweep gas leaving the membrane area is a function of the tritium level in the sodium, the hydrogen level in the sodium, the hydrogen concentration in the incoming sweep gas, the membrane temperature, and the sweep-gas flow rate. For constant temperature and sweep-gas flow rate and for a hydrogen concentration in the sweep gas of ~1% or greater, the tritium concentration in the sweep gas leaving the monitor is a function only of the tritium concentration in the sodium. For hydrogen concentrations in the sweep gas increasing from

*Computer Applications Group, Chemical Engineering Division.

0 to 1%, the tritium concentration in the sweep gas leaving the monitor increases because the tritium on the membrane wall reacts more readily with the available hydrogen to form HT molecules.

Calculations are continuing so that optimum operating conditions of the monitor can be defined more precisely.

IV. SODIUM CHEMISTRY (V. A. Cafasso)

A. Oxygen-Hydrogen Interactions in Sodium (A. K. Fischer)

This program is concerned with determining whether or not hydroxide forms in liquid sodium under conditions (temperature and concentrations of oxygen and hydrogen) of interest to reactor technologists. An isotope-exchange technique, in which sodium deuterioxide (NaOD) is used as a stand-in for NaOH, is being used. The method and the principles behind this approach to the problem were described in the preceding quarterly report (ANL-7868, pp. 46-48). Briefly, the method involves (a) preparing a solution of NaOD in liquid sodium, (b) establishing that NaOD is not present as a condensed phase, (c) quenching the liquid solution, and (d) establishing the existence, or nonexistence, of deuterioxide (and thus hydroxide) by mass-spectrometric examination of the exchange products resulting from the alcoholysis of the quenched sodium solution.

Previous work has been concerned with the preparation of solutions of sodium deuterioxide in sodium and with the demonstration that no solid deuterioxide existed in contact with these solutions. It was reported (ANL-7868) on the basis of preliminary experiments that rather extensive decomposition of deuterioxide appeared to have occurred over the time the samples were at temperature (500°C), but there was some reservation about ascribing the decomposition to the effect of sodium alone. Carbon that had been found in the sodium, and which originated in the nickel capsule, could conceivably have participated in the reduction of deuterioxide. Since then, the carbon has been removed from the nickel capsules before use in the experiments; the decarburization was accomplished by heating the capsules in hydrogen at 800°C for several days. The decarburized nickel capsules were then dehydrogenated at temperature (500°C) to a low background pressure ($\sim 6 \times 10^{-9}$ Torr).

To avoid ambiguity in the interpretation of results, experiments have also been conducted to assure the absence of a condensed phase of Na₂O, as well as the absence of a condensed phase of NaOD (NaOH). A separate phase of Na₂O could dissolve NaOD, and the source of any deuterium detected after the alcoholysis could not be firmly established; i.e., it could be ascribed either to NaOD in solution in Na₂O or to NaOD in solution in sodium. This ambiguity would invalidate the experiment, since the question under study is the existence of hydroxide in solution in liquid sodium.

To aid in the preparation of Na-NaOD samples that would not eventually contain precipitated Na₂O, the various available equations for the solubility of oxygen in sodium were examined. All the equations predict that a system containing less than the equivalent of 0.17 mol % Na₂O at 500°C would satisfy the solubility condition. Experiments embodying these conditions have been performed, and final analytical data are being generated.

It has become apparent that the sensitivity of mass-spectrometric detection of OD⁻ (as HD following the alcoholysis exchange) will not be adequate for experimentation at the lower concentrations of hydroxide (1-10 ppm) that will be of interest. To overcome this problem, preparations

are being made to perform experiments with tritium-labelled NaOH. With liquid scintillation counting as the tritium-detecting technique, adequate sensitivity for studies at low levels of hydroxide in sodium is expected.

B. Vacuum Distillation as an Analytical Method for Impurities in Sodium (R. A. Blomquist)

The objectives of this study are to (a) characterize the impurity interactions that may occur during the evaporation-concentration step of a sodium distillation analysis and (b) determine whether or not such interactions lead to significant errors in analyses for nonmetals in sodium. Initial efforts are being concentrated on the influence of impurities on the determination of oxygen in sodium.

Conventionally, oxygen is determined from acid titration of the residue from the distillation of a sodium sample; the assumption is made that the residue consists only of sodium oxide. The presence of other titratable impurities would obviously result in error. As a consequence, principal interest is in the distillation behavior of impurities other than oxygen that are likely to be found in sodium samples and are also likely to form residues containing titratable species. Two impurities that fall into this category are sodium carbonate and disodium acetylide. Hence, the stability of these compounds under our distillation conditions was studied. (In our apparatus, ~800 g of sodium is distilled at ~380°C; at this temperature, the distillation requires about 7 hr.)

The decomposition of sodium carbonate in sodium is a function of time as well as temperature. Although the decomposition of carbonate has been reported¹ to be negligible during distillation below 400°C, this evidence was based on considerably shorter distillation times (~3 hr) than are required in our equipment.

Our experiments to examine the distillation behavior of carbonate involved adding 1.31 mg of Na₂CO₃ to ~800 g of sodium, distilling at 380°C, and then collecting and analyzing the residue. The quantity of carbonate found in the residue corresponded, within analytical uncertainty, to that added. This finding confirms the reported stability of carbonate in sodium during distillation below 400°C and supports the concept that carbonate in distillation samples will lead to errors in analyses for oxygen unless a suitable correction is made for the carbonate in the residue. The magnitude of the correction can be determined by performing a carbonate analysis along with the oxide analysis.

The experiments with sodium acetylide (Na₂C₂) involved a procedure similar to that for carbonate. A known amount of Na₂C₂ (0.46 mg) was added, the sodium was distilled, and the residue was collected and analyzed. Approximately 50% of the added acetylide was found in the residue; hence, even after 7 hr at ~380°C decomposition was incomplete. Thus, the presence of acetylide in samples will also result in errors in oxygen analyses unless a correction is made for the acetylide content of the residue or other steps

¹V. M. Sinclair, J. L. Drumond, and A. W. Smith, TRG-Report-1185D (1966).

are taken to assure total decomposition of the acetylide (to carbon) in the residue. In the latter connection, we are exploring the possibility of decomposing the acetylide by continued heating of the residue after completion of the distillation.

Further experiments are planned in which Na_2CO_3 and Na_2C_2 and other contaminants will be added singly, and in combination, in the presence of varying quantities of Na_2O in sodium to assess the effects of their interactions on the determination of oxygen in sodium by this method.

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

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

A. Integrated Effects of Fast-Neutron and Sodium Environments on Properties of Austenitic Stainless Steel (J. Y. N. Wang, W. E. Ruther, J. D. B. Lambert)

Present uncertainties regarding the mechanical and swelling behavior of austenitic stainless steels in an LMFBR environment require more reliable design data and a better understanding of the combined effect of high-temperature sodium and fast-neutron irradiation. Criteria for a suitable test vehicle for the in-core exposure of mechanical-property and corrosion specimens and an evaluation of the capabilities of present EBR-II subassemblies for this purpose were discussed in the preceding quarterly report (ANL-7868, pp. 50-52). It has been decided that a Mark Q 19-pin subassembly, modified to contain short, mixed-oxide fuel elements with bottom plenums in the lower half of the core region, and a sizeable number of mechanical property and corrosion specimens in the upper half of the core, would best meet our experimental requirements. A conceptual design of the subassembly was submitted to the EBR-II project for review and was considered to be technically feasible provided that (1) the total number of such subassemblies in the reactor would not exceed about four or five, (2) the gas plenum-to-fuel volume ratio in the pins would be greater than unity, and (3) grid positions would not be adjacent to control or safety rods.

A request to RDT for Approval-in-Principle (AIP) giving the details of the experimental schedule is in preparation.

B. Reactor and Experimental Sodium Systems Correlation (T. F. Kassner W. E. Ruther)

The objective of this work is to obtain the technical basis for correlating experimental corrosion and mechanical-property data from materials exposed in various sodium systems. The establishment of activities of the nonmetallic elements in EBR-II sodium, in which FFTF fuel and components are being proof-tested and in-core and ex-core materials property data are being generated, represents a near-term program requirement. The ability to reproduce EBR-II sodium conditions in ex-reactor loop systems is also a necessity. This will allow mechanical-property data from specimens exposed in these systems to be correlated and will provide the basis for

understanding previous, conflicting mechanical-property results from various sodium loops operated under ostensibly the same conditions.

The implication of this work is that a large segment of the mechanical testing may be conducted with confidence in ex-reactor systems provided the sodium conditions are adequately defined and can be varied in a manner representative of advanced reactor systems. Thus, the potential for correlating corrosion and property data and eliminating anomalous results rests primarily on the improved capability to characterize sodium quality in EBR-II, the Fast Test Reactor (FTR), and experimental loop systems. At present, effects of temperature and sodium velocity can be adequately taken into account; the critical area of concern is the determination of the non-metallic element concentrations in the sodium. These parameters will be accurately established in EBR-II and several ex-reactor loop systems where comparisons of mass-transfer rates and the effects of carburization-decarburization phenomena on the mechanical properties will be investigated.

At present there is no provision to expose a large number of corrosion and mechanical property test specimens to EBR-II sodium at high temperatures and high sodium velocities. A conceptual design has been made of a high-temperature specimen-exposure device, the Materials Test Station (MTS), for installation in Cell A of the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II. The technical feasibility of incorporating this specimen-exposure device on the RSCL has been reviewed by the EBR-II Project. Specific potential problem areas concerning the reliability of the sodium pumps, safety of equipment operating at $\sim 1200^{\circ}\text{F}$ with primary system sodium, and space limitations in Cell A were identified by EBR-II Project personnel. These problems will be resolved during the design stage of the MTS. A request for Approval-in-Principle (AIP) giving the details of the experiment and schedule is in preparation.

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

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

The relocation and modification of the creep machines for this program, described in the preceding quarterly report (ANL-7868, p. 53), has continued. Specimen grips for all of the machines have been designed, the quality assurance package has been developed, and the purchase specifications have been released for competitive bids. Various types of biaxial testing facilities are being evaluated for use in flowing sodium and in vacuum or inert gas.

A small sodium loop has been designed for the exposure of standard mechanical-property test specimens to flowing sodium to produce a range

of carbon and nitrogen concentrations in the alloys prior to mechanical-property testing in vacuum or inert gas. The system will be constructed of nickel 200 so that the concentration of carbon and nitrogen in the sodium can be conveniently varied over a wide range without seriously affecting the mechanical properties of the loop piping. Other materials, with the exception of stainless steels, were considered; however, in many instances oxidation from the air side would have required double-walled vessels or operation in a vacuum system. The loop will contain \sim 11 gal of sodium, most of which is contained in four specimen-exposure vessels that will operate initially at temperatures of 750, 700, 650, and 600°C. Depending upon the requirements of the experimental program, the temperatures of the four specimen-exposure vessels can be varied over a wide range. The minimum pipe size in the main flow system is 1/2 in. to avoid possible plugging problems in a small loop when diffusion-type carbon meters are used on the system. (Hydrogen in the Ar-10% H₂ sweep gas, used to convert carbon to methane, diffuses across the thin iron membrane into the sodium and results in sodium hydride precipitation in the cooler regions of the loop, e.g., the cold trap.) The number of valves in the system was also minimized for this reason. The sodium flow rate will be \sim 1/4 gpm, which is adequate for studies of nonmetallic-element transfer.

The loop has provision for determining the activities of nonmetallic elements in sodium by the exposure of wire and foil specimens in the four test vessels. Two carbon meters can also be installed in each vessel; both electrochemical and diffusion-type meters are being considered and could be used in various combinations depending upon the temperatures. A hydrogen-meter probe could also replace one of the carbon meters in the lowest temperature test vessel. Oxygen meters will be also included on the system. Sodium samples for determining the concentrations of metallic and non-metallic elements can be obtained through vacuum distillation sampler ports on the reservoirs and by line samplers located before and after the cold trap. These samples will be used to supplement the information obtained from the wire and foil activity monitors and the various meters.

The oxygen and hydrogen concentrations in the sodium will be controlled and varied by adjusting the cold-trap temperature. Carbon and nitrogen control will be accomplished by adjusting the temperature of a vessel containing a material having a low carbon and a low nitrogen activity (e.g., austenitic or ferritic stainless steel) and a large surface area. This material can be removed and replaced periodically as required by the system operating conditions. The carbon concentration in the sodium will be controlled at specified levels by establishing steady-state conditions between the input of carbon to the sodium from the nickel loop material (or a carbon source) and the removal rate in the carbon-control device. The choice of material, surface area, and temperature of the trap will permit the desired range of carbon levels to be achieved by this method.

The specimen materials that will be used in this program are presently being defined. A limited number of uniaxial test specimens are being made from Type 316 stainless steel (with 20% cold work) from FFTF heat V87210. Some of the Type 316 stainless steel biaxial test specimens will be made from N-lot fuel-clad tubing (heat V87210) that was obtained from HEDL. Material to be supplied by HEDL from FFTF heat K81425 will be also used in this program.

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

The objectives of this work are an understanding of the thermodynamics and kinetics of carburization-decarburization processes involving austenitic and ferritic steels and the eventual correlation of the results of these studies with microstructural changes and mechanical properties of the alloys. Thus, predictions regarding the structural integrity of these steels in a reactor system will be made possible.

Data for the distribution of carbon between sodium and several iron-base alloys, obtained by simultaneous exposure of foil specimens to flowing sodium at 750°C, were reported in the preceding quarterly report ANL-7868, p. 64. In the course of this work, information has also been obtained on the monitoring and control of carbon concentrations in liquid sodium that is essential for future experiments involving the exposure of mechanical-property test specimens to flowing sodium of controlled carbon activity. A United Nuclear Corporation (UNC) diffusion-type carbon meter was incorporated into the specimen-exposure section of the existing nickel loop that is being used for most of the carbon distribution experiments. The UNC meter is being used to (1) continuously monitor the carbon concentration in the sodium, (2) demonstrate control of the carbon activity in sodium, and (3) relate the response of the carbon meter to carbon concentrations in foil specimens of Type 304 stainless steel and other alloys equilibrated in sodium.

Figure V-1 shows the response of the carbon meter, in flame ionization detection (FID) units, as a function of time in three different runs at 750°C. Even though the FID readings are high at the time of sample insertion into sodium, it is evident that the meter response is almost constant after about 40-50 hr, thus indicating that the carbon concentration and, in turn, the carbon activity at 750°C in sodium can be maintained constant throughout a given run. Most of the runs in the equilibration experiments were terminated after about 200 hr, since this period is sufficient for equilibration of 1-mil-thick stainless steel foils in sodium at 750°C.

Figure V-2 shows the relation between carbon concentrations in the range from 0.3 to 0.8 wt % in foil samples of Type 304 stainless steel and carbon meter readings in FID units (minus the background due to small hydrocarbon contents in the Ar-10% H₂ decarburizing sweep gas) at 750°C. Carbon equilibration experiments are being continued in the range from 0 to 300 FID units of the carbon meter, i.e., <0.2 wt % carbon in Type 304 stainless steel.

The period of time that was required to produce the incremental decreases in the carbon concentrations in the loop sodium for the series of runs in Fig. V-2 (corresponding to carbon concentrations in the range 0.8 to 0.3 wt % in the Type 304 stainless steel) had led us to examine the kinetic aspects of carbon movement in this sodium loop. A mathematical analysis of the "effective" driving force for carbon transfer from the kinetic and thermodynamic contributions, similar to the one reported in ANL-7868, pp. 65-68 for a stainless steel system, was made by incorporating data for the diffusion of carbon in nickel, carbon activity and solubility data for both nickel and sodium, and relative surface areas of nickel that are at high and low temperatures, as well as other loop parameters.

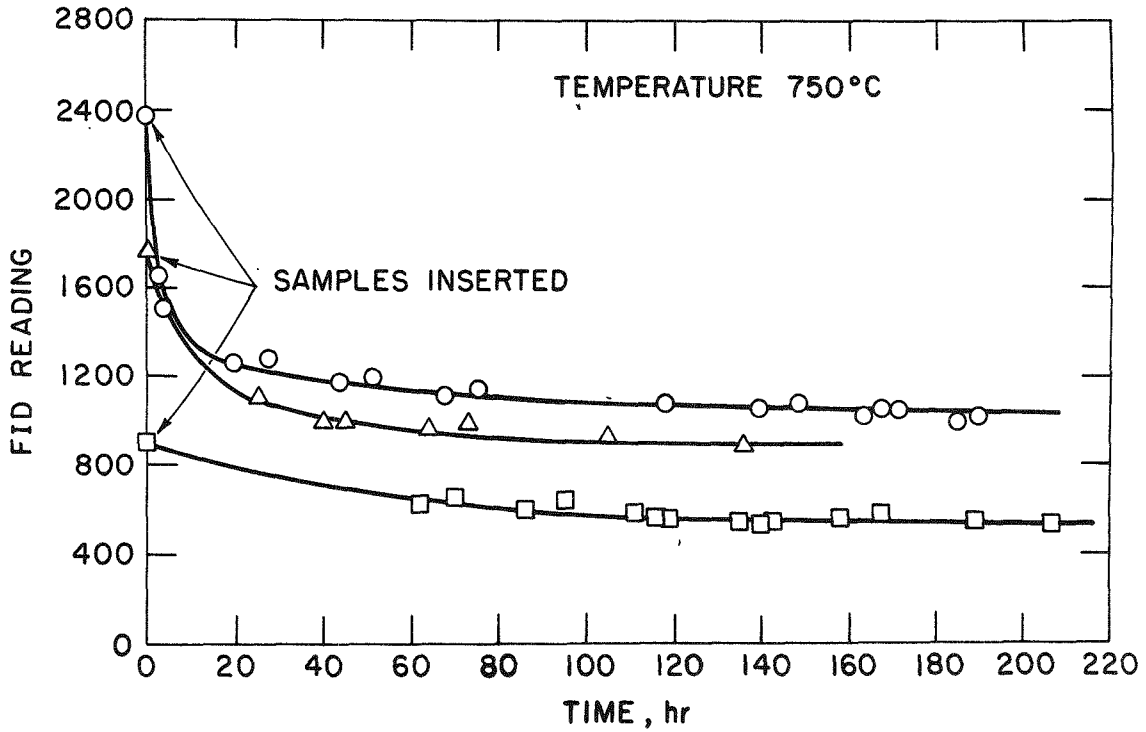


Fig. V-1. Response of UNC Carbon Meter vs. Time for Three Carbon Equilibration Runs in Flowing Sodium at 750°C. Neg. No. MSD-56667.

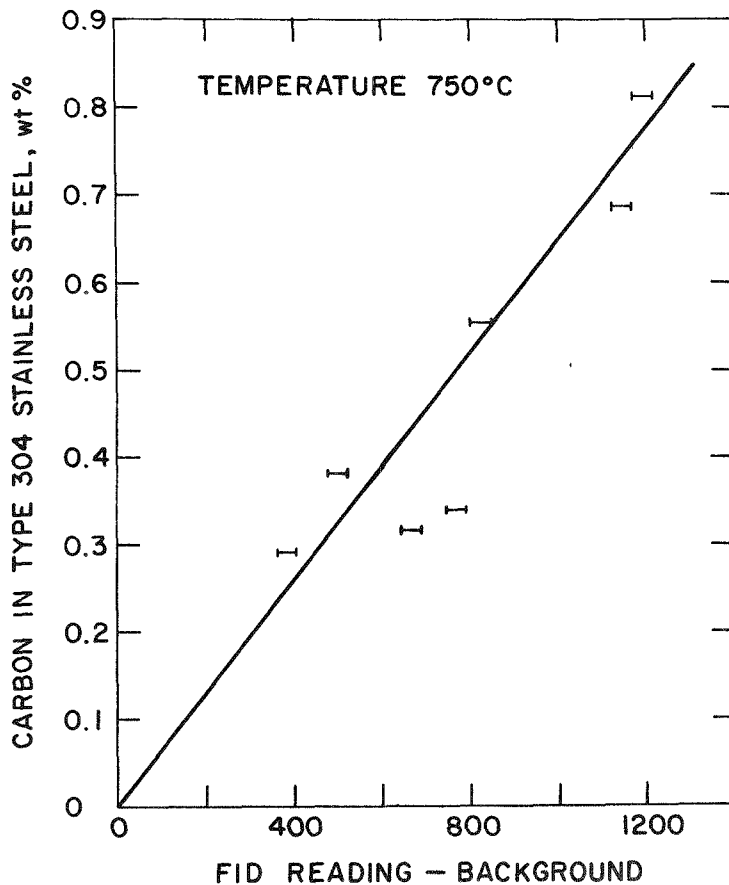


Fig. V-2
Relationship between Equilibrium Carbon Concentration in Type 304 Stainless Steel and Net Response from a UNC Carbon Meter for Experiments in Flowing Sodium at 750°C. Neg. No. MSD-56668.

This approach clearly established that there was no carbon sink in the loop (other than the specimens) for any carbon concentration in sodium below ~ 5 ppm and that nickel with a nominal carbon content of ~ 0.06 wt % would tend to decarburize or remain at the initial carbon concentration at high and low temperatures, respectively. Thus, carbon transfer in this loop primarily involves decarburization of the nickel and relatively high carbon concentrations in the sodium in the absence of an effective carbon sink. In order to easily achieve and maintain carbon levels below ~ 0.1 ppm in the sodium, a carbon trap is required in the system. Such a trap has been designed on the basis of an analysis of (1) the mass flux of carbon out of the nickel as a function of time and temperature, and (2) the rate of diffusion and precipitation of carbon in several stainless steel sink materials. Following installation of the trap on the system, the effectiveness of various materials and operating temperatures for achieving accurate carbon control will be evaluated.