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SODIUM TECHNOLOGY QUARTERLY REPORT
OCTOBER, NOVEMBER, DECEMBER 1969

February 1970

AEC RESEARCH &
DEVELOPMENT REPORT

BNWL-1200-2

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SODIUM TECHNOLOGY QUARTERLY REPORT
OCTOBER, NOVEMBER, DECEMBER 1969

by

The Staff of
Sodium Chemistry Subdepartment
R. L. Dillon, Manager

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February 1970

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SODIUM TECHNOLOGY QUARTERLY REPORT

October, November, December 1969

1.0 SUMMARYSODIUM SYSTEM CHEMISTRY

The BNW program on Chemistry of Large Sodium Systems has as its major objective the development, proof testing, and documentation of methods to characterize and control the coolant quality of FFTF in accordance with established quality standards.

FFTF Cold Trap Design Criteria

An analysis of the design basis and criteria of FFTF cold traps is underway. On the basis of a heat transfer model and a 5-minute residence time it appears that a single cold trap volume should not exceed 250 to 300 gallons in size. Analysis of probable impurity loadings showed about 500 gallons of trap capacity would be needed for a 10-year trap life on FFTF primary system and about 50 gallon capacity on each secondary system. However, consideration of system kinetics showed that to achieve a clean-up time of five days will require installation of 750 to 1000 gallons of capacity for the primary system, and 150 gallons on each secondary system. A number of assumptions were included in the analysis which should be verified by tests in the BNW Sodium Chemical Technology Facility.

Carbon Meter Evaluation

Further chemical additions of oxygen and carbon species to the BNW Sodium Purification Loop has shown that graphite alone does not increase carburization potential, but simultaneous introduction of Na_2O and graphite does increase carburization. Simultaneous introduction of NaOH and graphite produced no effect at 600 °F. Introduction of Na_2C_2 increased carburization potential extensively.

Sodium Chemical Technology Facility (SCTF)

The revised design criteria and project proposal were completed and submitted to the AEC for approval. Design of the SCTF and experimental subsystems in sodium purification, in-line instrumentation, sodium sampling, and cover gas systems are proceeding. Details of the present design description of these facilities are given in the body of this report.

SODIUM COOLANT STUDIES

The Sodium Coolant Studies Section objectives are directed at providing information needed to accommodate FFTF design and operations for the presence of fission product and corrosion product radioactivity.

Major task areas and their status at the completion of this quarter are:

Model for Fission Product Behavior

Emphasis was placed on modeling and analysis of the FFTF fuel failure detection and location systems, which are part of the cover gas system. Work status is reported under Fuel Failure Monitoring.

Radioactivity Transport

- A portion of EBR-II piping removed from service about a year ago was examined to determine the distribution of radioisotopes between the pipe surface and the sodium it contained. Radioisotopes found included ^{22}Na , ^{137}Cs , ^{54}Mn , and ^{60}Co . After alcohol cleaning to remove the sodium, the ^{22}Na and ^{137}Cs were substantially reduced, ^{60}Co was partially removed and ^{54}Mn activities remained on the pipe wall.
- An analysis was conducted on the information needed to be able to calculate FFTF out-of-core radiation level in reactor piping due to activated corrosion product transport.

A serious lack of information on corrosion under reactor conditions, solubilities of radioactive impurities in sodium, and the deposition patterns for individual impurities (Blocks A, F, I of Figure 3.3) prevents realistic assessment of FFTF problems.

- Reviews of the FFTF CSDD's were used to define more explicitly the problems relating to mass transport and radioactivity control in FFTF. Descriptions of component design specifications affected by radioactivity are transmitted to FFTF so that design refinements can accommodate the problems. Typical problems include:
 - Determine the amounts and location of radioactivity in FFTF systems.
 - Select agents and methods for decontamination and sodium removal.
 - Define requirements and standards for requalifying decontaminated components for sodium service.
 - Identify requirements and methods for servicing components contaminated with radioactivity.
 - Adjust component design specifications and geometries to accommodate radioactivity.
 - Determine the rate and effects of mass transport processes on system materials; need to define methods and standards for monitoring such effects.
 - Identify requirements for monitoring radioactivity.
- Preliminary tests were made of the stability in sodium, of various inorganic compounds that are potential trapping agents for sodium-soluble fission products in FFTF. All those tested (alumina, zirconium phosphate, zirconium oxide, titanium oxide, ammonium molybdo-phosphate, and potassium hexacyano cobalt ferrate) proved stable for short exposure at temperatures up to 650 °F.

- The Fission Product Screening and Control Test Loop, which is to be the test bed for developing an engineering device to trap sodium-soluble fission products in FFTF, was operated to check out the performance capability of the cold trap which was based on an SRE design. The cold trap design appears to be inadequate as rapid plugging occurs. Evaluation is continuing.

Decontamination

Evaluation of potential oxalic/hydrofluoric acid and steam oxidation decontamination processes for FFTF was extended. Some improvement over past performance was noted, but neither has yet proven to be adequate; decontamination factors are too low for practical use. A new approach based on heating in a vacuum was started and shows promise; 82% of the ^{137}Cs activity was removed in a preliminary test.

In a related study, the CSDD for FFTF System 24, Radioactive Waste, was reviewed. Design problems resulting from the presence of radioactive materials were identified:

- How is contaminated sodium to be removed from equipment requiring maintenance?
- There is a need to design an easier removal of devices from the waste storage tanks that may require periodic inspection or removal.
- Drain lines should slope, dead legs should be eliminated, and ventilation of receiving tanks provided.

Sodium Removal

The reference process for removing sodium from FFTF fuel subassemblies was changed from argon-moist air-water rinse to argon-moist argon-water rinse by joint RDT-BNW reviews. Development work objectives have been appropriately altered in response to this change.

Studies were begun to determine the possibility for caustic stress corrosion cracking in the FFTF reactor guard vessel in the remote event of a sodium spill between the reactor vessel and guard vessel. No cracking has been observed after the first 120 hour test.

For both sodium removal from FFTF components and decontamination, the major concern is the effect of the process on system materials. Analysis shows that sodium removal and decontamination requirements and the selection of development tasks depend strongly upon FFTF design and the schedule for design decisions.

The analysis also showed that five major elements of decontamination development work are necessary:

- Set standards and methods for quantitative measurement of system integrity.
- Perform development work needed to determine the physical state of radioactivity on the surface.
- Use decision theory to determine the scope required for the development work and the range of application of the decontamination processes.
- Perform inexpensive, quick-answer development studies when appropriate.
- Perform necessary process development work.

In addition, there are five major elements for the sodium removal development work:

- Determine requirements for sodium removal from system components.
- Set standards and methods for quantitative measurement of material integrity.
- Explore possibilities for an "inherently safe" process.

- Scope work requirements for testing the safeness of present sodium removal process concepts.
- Define work requirements for development of methods to remove sodium from fuel subassemblies and components, and decontamination.

Basic PERT charts for the decontamination and sodium removal development work indicate the organization and methodology for the work.

SODIUM ANALYSIS

Sampling and Analysis of Radioactive Sodium

The objectives of the task are the development of techniques and selection of hardware items required for remote sampling and analysis of FFTF radioactive sodium.

A mockup of an FFTF analytical hot cell is under construction to evaluate equipment and capabilities for remote analysis of impurities in sodium by standard methods. The inert atmosphere portion of the mockup has been completed and installation has started.

An operating procedure has been developed for the first model of a remotely operable, removable section bypass loop sampler. The sampler will be evaluated for adaptability to potential FFTF sampling requirements. Several sodium samples have been taken and analyzed. Modifications to the sampler are underway to improve its performance characteristics and operability.

Cover Gas System

The objectives of this task are the development of gas sampling and sodium vapor removal methods and selection of instruments for analysis of chemically reactive impurities in the FFTF argon cover gas.

Construction of the Cover Gas Evaluation Loop has been completed. Instruments for mass spectrometric, gas chromatographic and absorption spectrophotometric measurement of impurity concentrations in the loop cover gas have been installed and calibrated. The sensitivity, reliability and simplicity of operation of these instruments, as evaluated on an engineering system, will be compared with previous laboratory observations to confirm tentative FFTF gas analytical instrument selection.

Analytical studies of sodium vapor trap designs have been completed and theoretical bases upon which to predict trap performance have been established. A trap has been constructed and evaluated in a laboratory test rig. Performance was more than adequate to meet FFTF gas analytical sampling needs. A similar trap has been installed on the Cover Gas Evaluation Loop for engineering evaluation. The refluxing vapor trap design will be reviewed for application to the many (30-40) potential FFTF applications.

Development has started on an in-plenum hydrogen monitor based on the diffusion of hydrogen through a nickel membrane. Laboratory studies are promising and show the method to have adequate sensitivity, selectivity and functional simplicity for potential application as a continuous FFTF cover gas hydrogen monitor. This continuous monitor can solve the serious gas sampling problem which occurs when attempts are made to analyze for hydrogen in cover gas by gas chromatography.

Sodium Studies Facility Service Analysis

Analytical methods for measurement of calcium and halides in metallic sodium have been added to the laboratory capabilities. All of the glove boxes for the analysis of alpha contaminated sodium have arrived and installation has started.

SCTF Analytical Support

Scouting experiments on methods for particulate analyses and carbon species measurement in metallic sodium have been completed and the most promising approaches selected. Equipment for the measurement of carbon species by the sequential hydrolyses technique has been set up and calibrated. Techniques are under development for optical and scanning electron microscope examination of metallic sodium.

SODIUM SYSTEMS ENGINEERING

Prototype Applications Loop Design

Conceptual design has been completed for PAL. Detailed design is well underway and design work on the piping and electrical systems should be complete by the end of December. A design description is in preparation. Purchase requisitions have been prepared for about 80% of the components and materials on the basis of price information solicited from vendors.

A computer program has been employed to calculate thermal stress levels at about 100 points within the PAL piping system. Stress levels were all below allowable values calculated from the formulas in the USAS code for power piping, B31.1.0, 1967, paragraph 102.3.2.(c). A stress analysis for the mixing tank is in progress.

A rough draft Quality Assurance plan for the design, fabrication, and installation of PAL has been drafted and circulated for review and comment. A file for design calculations, purchase orders and other relevant documentation has been established.

Bypass Loop Sodium Sampler

The bypass sodium sampler attached to the small components test loop has been redesigned to provide more uniform cooling, a built-in system for leak checking the sample loop

has been added and union type fittings have been substituted for the original clamps to reduce the heat sink capacity at the connectors.

Low Cost Power Controllers

Further design improvements to the low cost power controllers developed at BNW for regulation of sodium loop piping temperature have reduced the control panel area requirements by a factor of 2-1/2 and improved the control performance.

OXYGEN-SENSING SOLID ELECTROLYTES

The process for fabricating a high quality, $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solution electrolyte for use in the electrochemical oxygen-sensing meter has been defined. The process yields small disc samples of both 7.5 wt% and 15 wt% Y_2O_3 with densities between 97 and 98% TD. The electrolyte is single phase with a high purity. This process is now being developed to produce full size electrolyte probes for testing in the oxygen sensing meter.

These improved electrolytes show little damage by liquid sodium containing 7 ppm oxygen at 800 °C compared to the extensive reaction previously observed with the commercially produced electrolyte tubes. In oxygen saturated liquid sodium (Na , Na_2O) at 800 °C, the improved electrolytes are moderately attacked presumably by the formation of sodium metathorate or a similar yttrium-bearing compound.

The evaluation of defective electrolyte tubes used in UNC electrochemical oxygen meters is complete. No evidence of attack by sodium was observed in any tubes. Mechanical and thermal shock are the primary causes of tube failure and appear to be enhanced by the presence of the high yttria second phase in the $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolyte.

2.0 SODIUM SYSTEM CHEMISTRY

INTRODUCTION

D. W. Shannon

The control of the sodium quality in the Fast Flux Test Facility (FFTF), is essential to long life, high operating availability, and useful testing capability. To achieve the coolant quality control needed, adequate standards must be established to define requirements, purification devices must be available to remove impurities, and analytical methods must be used to verify that control has been achieved.

The BNW program on Chemistry of Large Sodium Systems has as its major objective the development, proof testing, and documentation of methods to characterize and control the coolant quality of FFTF in accordance with established quality standards. The development and test program centers around the Sodium Chemical Technology Facility (SCTF), which is a 1500-gal sodium loop with provisions for conducting tests in all phases of sodium technology. In the initial program phases, the SCTF will be run in an isothermal, well-mixed condition (± 5 °F); however, provisions are included to convert the loop to a prototypical ΔT loop at a later date. Experimental systems will be attached to the SCTF to provide FFTF design verification tests and the development of technical basis for FFTF operation in the areas of sodium purification, in-line analysis, sodium sampling, cover gas, and chemical characterization of the overall system and its interactions. These SCTF systems will comprise two basic types: (1) equipment to define what is happening to the chemistry of the system as operating parameters are changed and (2) prototypical FFTF equipment for measurement and control of sodium quality. This combination will permit the characterization of a large tank of sodium with known impurity content, and the response of prototype reactor equipment can then be interpreted.

SODIUM CHEMICAL TECHNOLOGY FACILITY

V. P. Kelly

The SCTF is currently being proposed as a BNW-managed capital equipment project to be installed in the Sodium Studies Facility (335 Building). Herein after described are the project status, the SCTF driver loop, the SSF building arrangement, and the interconnected sodium system comprised of the SCTF driver loop, experimental subsystem equipment, and data acquisition system.

SCTF Project Status

During the past quarter SCTF Design Criteria and Project Proposals were revised based on a location of the SCTF within the 335 Building Sodium Studies Facility. Both documents have received internal BNW approvals and have been transmitted to the AEC for approval. Following the AEC approval, it is expected that detailed design will proceed on the loop and the building modifications to permit completion of the building modifications before July 1970, and of the SCTF during the first quarter of FY-1972.

Preliminary engineering planning to define the project work structure and quality assurance plan is underway. Project documents and the first draft of the SCTF conceptual systems design description are providing bases for this planning.

SCTF and Sodium Facility Building Arrangement

Plan and elevation views of the SSF (335 Building), Figure 2.1 and 2.2 show the physical facility proposed for the SCTF and the relationship of the SCTF to other loops in the building and to future experimental subsystems. As shown, SCTF will occupy the north half of the 60 ft wide, 102 ft-8 in. long building. Five smaller loops will occupy the south half of the building. An equipment pit with floor at elevation (-)8 ft and a work platform at elevation (+)10 ft (Figure 2.2)

10'-0" (REF)

15'-0" (REF)

20'-0"

32'-0"

40'-0"

44'-0"

PLAN @ EL 0'-0"

FIGURE 2.1. 335 Building Equipment Layouts

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Sheet 1 of 2

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SECTION Z-Z
SCALE 1/4" = 1'-0"

PARTIAL PLAN @ EL +10'-0"
SCALE 1/4" = 1'-0"

SCOPE

FIGURE 2.2. 335 Building Equipment Layouts

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Sheet 2 of 2

are proposed for equipment installation to provide working space for experimental subsystems and access to the SCTF sodium reservoir nozzles. The reservoir is positioned with vertical longitudinal axis so that the sodium liquid level is approximately at elevation (+)7 ft. Thus, the reservoir gas space provides the system high point for venting of subsystems located on the ground floor. Most of the SCTF driver loop and subsystem piping is located below grade in the covered and closed equipment pit. The pit provides a containment system to which appropriate fire suppressant systems can be applied. Tentative locations for experimental and prototypical in-line analysis, sampling, purification, and cover gas subsystems are also shown in Figures 2.1 and 2.2.

Building modifications for SCTF installation include the 16 x 40 ft control room located at ground floor, and miscellaneous services which must be extended or provided. A 750 kVA electrical power transformer must also be provided outside the building to meet SCTF power requirements. The transformer will connect with the existing motor control center which is contained within the new control room.

SCTF Driver Loop

The SCTF driver loop will supply sodium to experimental subsystems from a source which can be operated essentially isothermally, which can be thoroughly characterized chemically, and which has sufficient volume and mixing to form a very stable chemical "platform." The large volume source is provided by a 1500 gal capacity reservoir and recirculation supply by an external 200 gal/min piping loop, arranged as shown in Figures 2.1 and 2.2.

The reservoir is a 6-ft diameter stainless steel vessel, vessel heater and insulation canister. Vessel size is based on the required sodium volume (at 1200 °F) plus 30% gas volume.

In addition, the sodium pool has an L/D ratio between 1.0 and 1.25, based upon optimum geometry for adequate sodium mixing. Design of mixing component is based on the results of pilot-scale water-hydraulic mixing studies.^(1,2) Internally, the vessel is fitted with four thermowells (nozzle "B"), liquid level "J" probe, and components for hydraulic mixing of the sodium utilizing the recirculating piping loop return flow. Major components are the recirculating loop pump suction manifold, the mixing jet which is connected to the pump discharge, and the mixing baffle. Both the nozzle and manifold are located in the approximate center of the sodium pool and on the vessel centerline. The manifold consists of a rectangular flow channel with two 3-in. diameter inlet ports spaced 48 in. apart. The mixing jet has dual nozzles discharging vertically upward and downward. Each nozzle has a straight bore, which is 1.05 in. diameter by 5 in. length. The 6-in. diameter mixing baffle is located on the vessel centerline 3 in. to 12 in. below the sodium liquid level. Both the baffle and mixing jet are removable.

Vessel nozzles include three nozzles projecting through the vessel side, for recirculating loop pump suction, pump discharge, return, and for return of sodium from experimental subsystems. In addition, 10 experimental access nozzles are provided at the vessel top. Nozzle functions for the vessel top nozzles include mixing nozzle access port, thermowells, liquid level probe, hydrogen meter, cover gas circulation, and experimental corrosion test stringers. Nozzles may be sealed by mechanical or weld joints or by valves. High-vacuum gate valves using O-ring seals require nozzle cooling to limit operating temperatures.

A 3-zone vessel heater utilizing conventional industrial furnace design is conceptually pictured in Figure 2.3. The multizoned furnace provides the capability for sequential

FIGURE 2.3. Conceptual Design of SCTF Sodium Reservoir

H-3-29748

heating of the sodium during melting and variable power inputs during operation, and to compensate for vessel end losses. Furnace heating sections are spaced along the cylindrical length of the vessel; each will be rated for 30 to 35 kW, based on heatup time required to melt the sodium. Power to the 3-phase heating elements in each section is supplied from proportionally-controlled SCR controllers using the temperature signal from platinum RDT sensors (or equal for signal stability) located in the vessel thermowells.

The insulation canister is conceived as a vermiculite-filled carbon steel vessel with capacity to contain the entire sodium inventory in the event of vessel rupture. Incorporation of this containment function as an integral feature of the vessel heater will be reviewed during detail design of the system.

The recirculation piping loop connected to the sodium reservoir provides sodium flow for reservoir mixing as well as the connection for supply of sodium to experimental subsystems. Included in the loop are the nominal 2-in. pipe system, EM helical induction pump for forced-convective sodium flow, EM flowmeter, and valving. Manually-controlled trace heaters provide the heat source for sodium melting during startup. Piping trace heating during normal operation is not required to maintain sodium temperature due to the short length of the loop.

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SCTF EXPERIMENTAL SUBSYSTEMS

V. P. Kelly

During the past quarter the conceptual design of SCTF experimental subsystem has begun. While these subsystem designs are still subject to change, the present concept of the interconnections between the SCTF driver loop and experimental subsystems are presented in Figure 2.4. The subsystems shown in this conceptual arrangement include:

- Two sodium analytical systems
- Two sampling systems
- Sodium purification system
- Cover gas purification, analytical, and circulation systems
- FFTF prototypical samplers
- FFTF in-line instrumentation packages.

During the course of the detailed design these systems will be compared with comparable FFTF systems and the SCTF design will incorporate as many FFTF design features, hardware items, and system operating parameters as possible. As shown schematically in Figure 2.4 sodium to the subsystems is supplied through a connection located in the SCTF driver loop pump suction. Four EM pumps connected in parallel discharge sodium to the various subsystems. The discharge of Pumps No. 1 and No. 2 are interconnected to provide spare capability. Pumps No. 4, No. 5, and No. 6 supplying analytical system No. 1 and No. 2 and sampling system No. 2 are basically booster pumps required to ensure positive flow under all operating conditions. Interties between those three systems and the purification train provide several operating modes to provide maximum flexibility in system test programs.

- Independent purification system operation
- Operation of the two analytical systems in parallel or in series with each other and in series both before and after the purification system

SCOPE

FIGURE 2.4. SCTF Schematic Flow Diagram

H-3-29750

- Operation of the two analytical systems in parallel or in series with sodium sampling system No. 2.

SCTF In-Line Instrumentation Development System

W. H. Caplinger

The in-line instrumentation packages for SCTF (Figure 2.4) will include a diffusion type carbon meter, two electrochemical oxygen meters, a plugging meter, an electrochemical hydrogen meter, on-line calibration stations, and two sodium access test stations. The probable configuration of the sodium plumbing portion of each package is shown in Figure 2.5.

Two in-line instrument packages are provided so that measurements can be made of sodium purity both before and after the purification system simultaneously to provide data on purification system efficiency. Two systems are also required to check the precision and reliability of the data output from any one of the instruments.

These two systems will provide the primary design input for an FFTF instrumentation package system which will be tested as shown in Figure 2.4.

SCTF Sampling Development System

G. E. Meadows

The main objective of sodium samples for SCTF is to provide for general surveillance of impurities and assist in the overall chemical characterization of the sodium.

Two inert gloveboxes will house two sets of developmental samplers so that the main reservoir (inlet to test systems) and the output of any test system can be sampled simultaneously. This capability is required to define the efficiency of the purification system and to determine if in-line instruments are responding or affecting the sodium purity themselves.

FIGURE 2.5. SCTF In-line Instrumentation System

The following discussion briefly describes the samplers which will be located in the gloveboxes and the basis for selecting the techniques. These samplers are shown in Figure 2.6.

- Flow through tubing - The sodium sampled is obtained in a removable section of 0.5 in. tubing. BNWL analytical chemistry of methods for impurities in sodium have been developed around this sampling method. The flow-through tube method is becoming recognized as the reference method for sodium sampling.
- Vacuum distillation - This will be a modified LASL (laboratory type) distillation sampler. The sampler will be outside the glovebox enclosure and access to the distillation chamber from the box will be through an isolation valve. Residues can be removed for subsequent chemical analyses without coming in contact with air. The sample will be taken in a nickel crucible and the metallic sodium is separated from the nonvolatile residues by vacuum distillation. This technique has been demonstrated to be a reliable method for obtaining oxygen values in sodium below 5 ppm.⁽¹⁾
- Particulate filter - This is an on-line stainless steel filter unit which will be operated isothermally with capabilities of collecting insoluble particulates, and other possible metastable species. The large volume sampling capabilities provide surveillance for impurities which may be undetected when smaller grab samples are taken. Analysis of particulates has been shown to be helpful when attempting to understand corrosion phenomena.⁽²⁾

2.14

FIGURE 2.6. Sampling Development System

- Plug collector - The plug collector will be a modified plugging meter with a removable orifice place for examination of collected impurities. One mode of operation would be to operate for an extended duration at temperatures below bulk sodium temperature, but above plugging temperature for Na_2O . Impurities which exhibit a temperature dependent solubility can be concentrated in this manner.⁽³⁾

The particulate filter and plug collector sampling techniques are more developmental and perhaps at best can only become semiquantitative. However, the potential of these two techniques should be explored as they have possibilities of becoming on-line devices for reactor use.

SCTF Cover Gas Development System

G. E. Meadows

The cover gas system for SCTF (Figure 2.7) fulfills the major function of providing an inert gas blanket over the sodium in the mixing tank. In turn, this gas can serve as a medium in which impurity monitoring can provide additional information to assist in characterization of the sodium. Sampling of the cover gas will be from a recirculating gas stream and will include:

- Gas supply
- Pressure control system
- Vapor traps
- Pump or blower
- Gas chromatograph
- Mass spectrometer
- Infrared analyzer
- Water monitor and zirconia-calcia oxygen meter
- Provisions for purification devices.

FIGURE 2.7. SCTF Cover Gas System

Sampling will be at ambient temperature. A hydrogen detector with a diffusion membrane operating at elevated temperatures will be located in the gas phase of the mixing tank.

SCTF Sodium Purification Development System

D. H. Lester

The initial work on sodium purification will be confined to cold traps to define the problem areas and optimum operating modes and design verification of FFTF cold traps. Purification tests in the SCTF will involve the system as a whole and will dictate the entire loop operation while such tests are conducted. After a more thorough understanding of the operation of state-of-the-art FFTF traps is gained then it will be possible to suggest improvements and provide a more comprehensive basis for trap design.

Figure 2.8 shows a simplified block diagram of the SCTF purification system as it is now envisioned. The initial system will contain a cold trap and probably a hot trap as shown. Note that the system will be designed so that additional devices can be added and all devices may be operated either in series or parallel by opening and closing appropriate valves. The design will provide for up to 50 gal/min total flow in the subsystem and up to 1200 °F sodium inlet temperature. Presently, the proposed cold trap has a 50 gallon crystallizer tank and will be designed for a 10 gal/min flow rate with some design latitude so that other flow rates may be studied. Capability for obtaining detailed temperature profiles along the trap length and on its cross-section will be provided. The crystallizer tank cooling jacket will be designed in sections so that the temperature profile can be changed by varying coolant flow rates in different sections of the jacket, and heaters will be arranged to assist in this purpose.

FIGURE 2.8. Sodium Chemical Technology Facility Purification System (Conceptual Design)

Data Acquisition System for SCTF Experimental Subsystems

V. P. Kelly

The requirements of the SCTF experimental subsystems relating to test data storage and manipulation and relating to integration between subsystems are being studied to define needs for data acquisition within the sodium technology program. Specifically, the study is aimed at analyzing the relative technical and economic merits of conventional analog instruments versus a central digital data acquisition system.

Currently, the total list of data acquisition requirements is being developed by identifying the various experimental components within each subsystem, determining what test data must be collected for each component, and analyzing how the data must be processed to produce meaningful test results.

In addition to the data handling requirements for temperatures, flows, and pressures needed to operate the SCTF, there are data acquisition requirements for some of the SCTF experimental systems.

Some of the components and their data acquisition requirements identified to date are:

- Cold trap - radial and axial temperature profiles, flow rates, economizer temperatures, and inlet and outlet temperatures and impurity content must be measured to correlate efficiency and operating temperatures; comparison of theoretical versus experimental heat transfer profiles is required to provide firm bases for trap design; trap operation in various dynamic modes may be required in future tests.
- Carbon meter - outputs must be processed in a 2-step calculation to produce a curve of carbon flux versus carburizing potential. Real-time computational capability is required to provide the type of data needed by the system operator.

- Oxygen and hydrogen meters - meter outputs must be applied to correction curves to calculate oxygen or hydrogen activity; instantaneous readout is advantageous to the experimenter (and ultimately to a reactor operator).
- Plugging meter - automatic control of the heating and cooling cycle is required for operation in the oscillating mode.
- Vacuum distillation sampler - temperature and gas pressure data collected during the distillation sequence must be processed in real-time to optimize interpretation and analysis of results.
- Gas chromatograph - flexibility in programming to permit off-time sampling is required to optimize test results; data reduction to read areas under peaks and calculate peak areas versus concentration is also required.

The multiplicity and relative complexity of these functional requirements indicate that the overall technical needs of the sodium technology experimental program can best be met with a digital data acquisition system. Technical and economic analysis of the SCTF experimental subsystems is continuing to establish firmly the feasibility and justifications for analog versus digital data acquisition systems.

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FFTF COLD TRAP CRITERIA REVIEW

D. H. Lester

The objectives of this task are to review the conceptual design of FFTF purification systems, establish approximate source rates of impurities in the FFTF, and recommend design criteria to meet FFTF purification requirements.

Background

During the past quarter a review of FFTF conceptual purification system designs and of all available literature on cold trap operation was initiated and completed. This review was in connection with work requested through the FFTF Sodium Technology Section.

The main focus of attention has been on the reactor primary and secondary system cold traps for the purpose of establishing a basis for design of these trap systems. A computer study done by Lutz and Kaellis at Argonne⁽¹⁾ based on startup operations of the EBR-II Secondary Cold Trap resulted in the following optimizations:

- The L/D ratio should be equal to 1
- The cooling of the sodium should be spread over a long path.

Experience at FERMI and EBR-II shows that the equal flow area, counter-flow trap shown in Figure 2.9 is dependable and avoids the possibilities of plugging found in FERMI-I type traps which have a narrow outside annulus. All the reasons for the superiority of this trap are not known, but it appears to be the safest design.

A liquid coolant system for the crystallizer tank allows closer control of the temperature gradient in the trap and occupies less room in the trap galleries (the size of the galleries will be limited by economic considerations).

$$r_2 = 1.414 r_1$$

$$L/D = 1.0$$

FIGURE 2.9. Counter Flow, Equal Flow Area Cold Trap

Heat Transfer Studies

Heat transfer equations developed in a previous study⁽²⁾ were used to screen design parameters in the equal flow area, counter-flow trap. A heat balance on the sections of the crystallizer tank gives the following relationships between temperatures:

$$L \frac{dT_1}{dx} = K_1 (T_2 - T_1)$$

$$L \frac{dT_2}{dx} = K_1 (T_2 - T_1) + K_1 K_2 (T_2 - T_3)$$

$$L \frac{dT_3}{dx} = K_1 K_2 K_3 (T_2 - T_3)$$

where

$$K_1 = \frac{2\pi r_1 h_1 L}{W_m C_m}$$

$$K_2 = \frac{r_2 h_2}{r_1 h_1}$$

$$K_3 = \frac{W_m C_m}{W_c C_c}$$

and

W_c = coolant flow rate

W_m = sodium flow rate

C_c = coolant heat capacity

C_m = sodium heat capacity

h_1 = heat transfer coefficient between core and outside annulus = 120 Btu/hr-ft²-°F

h_2 = heat transfer coefficient between annulus and coolant
 = 60 Btu/hr-ft²-°F

x = vertical distance from bottom of crystallizer

T_1 , T_2 , and T_3 are shown in Figure 2.9.

The solution to these equations gives a prediction of cold trap temperature profiles. Note that these equations are based on the assumption that the flow in the crystallizer is uniform on a given cross-section.

Table 2.1 shows some pertinent results of the heat transfer calculations. The air rejection system (to cool the crystallizer coolant) is based on a NaK to air system with an air inlet temperature of 100 °F, and air heat-up equal to the NaK cool-down and a heat transfer coefficient = 8 Btu/hr-ft²-°F. All calculations are based on a 250 °F trapping temperature and a 125 °F NaK inlet temperature to the crystallizer. The economizer duty is based on a 1050 °F inlet temperature and the area is based on a heat transfer coefficient of 1000 Btu per hr-ft²-°F.

For most choices for NaK flow rate, feasible economizer and air rejection systems can be constructed for the 150 and 250 gallon cases. The systems associated with the 500 gallon trap are extremely large and the 500 gallon trap does not offer any real advantage. The results of Table 2.1 are a manifestation of the fact that as the crystallizer gets larger, the surface to volume ratio of the crystallizer tank decreases linearly with the diameter while the heat transfer requirements are increasing roughly as the cube of the diameter with a fixed residence time. A similar problem develops with the economizer. The unwieldy size of the economizer and large heat rejection system required for large cold traps suggests a maximum practical cold trap size of 250 to 300 gallons.

TABLE 2.1. Results of Cold Trap Heat Transfer Calculations

Trap Volume, gal	Sodium Flowrate, gal/min	NaK Flowrate, gal/min	Economizer Duty, Btu/hr	Econ. Area, ft ²	NaK-Air Rejection System Duty, Btu/hr	Air Flowrate, ft ³ /min	Air Rejection System Area, ft ²
150	30	150	3,053,400	53	151,200	17,500	756
150	30	60	3,070,200	56	226,800	7,020	1,134
150	30	30	3,095,400	62	210,000	3,510	1,050
150	30	15	3,137,400	76	172,000	1,755	861
150	30	10	3,171,000	91	145,000	1,170	728
250	50	250	5,180,000	106	350,000	29,300	1,750
250	50	100	5,201,000	113	322,000	11,700	1,610
250	50	50	5,229,000	122	301,000	5,850	1,505
250	50	38	5,250,000	131	285,000	4,446	1,427
250	50	25	5,285,000	147	255,000	2,925	1,278
250	50	17	5,327,000	172	216,690	1,990	1,083
500	100	500	10,598,000	286	294,000	58,500	1,470
500	100	200	10,612,000	295	504,000	23,400	2,520
500	100	100	10,654,000	323	462,000	11,700	2,310
500	100	50	10,710,000	369	406,000	5,850	2,030
500	100	33	10,766,000	448	359,000	3,861	1,798

2.25

Comparison with CSDD 81

Bruggeman⁽³⁾ showed that trap efficiency was increased significantly when the residence time was increased from 2.5 to 5 minutes but was not significantly increased from 5 to 10 minutes. For the purpose of the design it is considered that optimum residence time is 5 minutes.

The FFTF Conceptual System Design Description for System 81⁽⁴⁾ calls for use of 500 gallon traps in the reactor primary. The basis for 500 gal traps in CSDD 81 is operating experience in FERMI. Although 500-gal traps were used in this reactor system they were not operated at 5 minute residence time but rather at 8 to 10 minute residence times. Therefore, since 5 minute residence time is to be used in the FFTF, the FERMI experience is not applicable. Since low flow rates were used in 500-gal traps, the high heat transfer requirements shown in Table 2.1 were not encountered. Use of a 500-gal trap at high residence time (which appears to be unnecessary) is a waste of trap efficiency at the expense of heat transfer efficiency in that, it constitutes an unnecessary degree of over-design.

Use of traps no larger than 250 gallons would be advisable. This would mean using a number of small traps in parallel on the FFTF reactor primary.

Oxide Source Rates

Rough estimates of FFTF source rates have been made. The estimates were based on the following assumptions:

Reactor primary:	3 intermixed loops
	Volume $\approx$ 200,000 gal (26,800 ft ³)
	Surface area $\approx$ 400,000 ft ²
Reactor secondary:	3 isolated loops
	Volume (per loop) $\approx$ 30,000 gal (4000 ft ³)
	Surface area $\approx$ 53,000 ft ²

Experimental work by Eickoff et al⁽⁵⁾ showed that a typical new system will contain about 2×10^{-4} lb/ft² of adsorbed impurities (i.e., O₂). Therefore, the cold trap load for the initial cleanup of the primary would be about 320 lb of Na₂O. Addition of a 50% safety factor gives a total startup load of 480 lb. Contributions resulting from incidental leakage and oxygen in the argon purge of the reactor seals (700 cubic feet per day of argon with 2 ppm O₂) would both be negligible. Estimates from Conceptual System Drawings show that a fuel subassembly contains approximately 190 ft² of surface. If 19 subassemblies are changed every 63 days the oxide load over a 10 year period will be 176 lb of Na₂O. Based on an expected trap capacity of 20 wt% of the sodium in the mesh, the required trap volume is 463 gallons.

A similar analysis in the secondary gives:

Startup load	= 59 lb Na ₂ O
Steady-state leakage	= negligible
Subassemblies	= <u>none</u>
Total = 59 lb Na ₂ O	

The volume required to meet this capacity is 50 gallons. A 500-gal total trap capacity in the primary system would result in a time for one system turnover through the trap of about 33 hours. Since ideally at least 4 to 5 system turnovers are required to purify a system, it would be desirable to have a shorter turnover time of less than one day, which means that 750 to 1000 gal of trap capacity would be desirable for FFTF. Similarly it would be desirable to have a 150-gal trap in the secondary for a turnover time of 17 hr rather than the 51 hr associated with a 50-gal trap. The larger traps also provide additional safety factors on the capacity requirements. Thus system cleanup dynamics are a major factor in sizing the FFTF reactor primary and secondary.

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SELECTION AND TESTING IN-LINE SODIUM ANALYSIS INSTRUMENTS

W. H. Caplinger

The objectives of this task are: (a) to field test presently available instruments to establish performance, (b) to develop and test an in-line instrument system for FFTF, (c) to establish the design and test plans for an advanced in-line instrument program on SCTF, and (d) to originate and develop improvements in instruments for measurement of impurities in sodium reactor coolant. The principal experimental effort so far has been in field testing the electrochemical oxygen meter and diffusion-type carbon meter.

Carbon and Oxygen Meter

As part of a continuing program to determine species and conditions that influence sodium system chemistry and produce meter responses, more impurities were injected into the BNW Sodium Purification Loop (SPL). Table 2.2 summarizes a number of impurities injected into the 600 °F sodium. The technique of injection was to place the weighed impurity in a piece of

TABLE 2.2. Impurity Addition to BNW Sodium Purification Loop
(Loop Temperature 600 °F)

Addition	Added Carbon Equivalent, ppm	Added Oxygen Equivalent, ppm	Carbon M Resp., ngC cm ² /min	Oxygen M Response	Chemical Analysis Total Found	Remarks
Na ₂ O	---	20	---	16 ppm ^(c)		
Cold trap temp. change	---	10 ^(a)	---	7	14 ppm ⁽⁰⁾	
Graphite bar	1/4 in. bar 6 in. long	---	None	---		
NaCN	~15	---	None	---		
Na ₂ CO ₃	10	(40)	Up 0.5	Neg.		
Na ₂ C ₂	10	---	Up 22	---	1.0(C)	Varied temperature and flowrate of impurity source
Na ₂ O + C	1/4 in. bar 2 in. long	10	Up 1.1	emf down 14 mv ^(b,c)	9.11(0)	
Na ₂ O + C	1/4 in. bar 2 in. long	15	Up 2.6	emf down 6.5 mv ^(b,d)		Field overhauled cell to make insensitive to ambient tempera- ture variations
NaOH + C	1/4 in. bar 2 in. long	15	None	None	0.4-(OH) 0.1-(H)	

a. Based on averaged solubility data.
b. Cells not calibrated.

c. Cell serial No. 238
d. Cell serial No. 237

2.29

BNWL-1200 2

1/2-in. tubing, fill the tube with sodium, connect the tube to the loop and pass loop sodium through the tube. A fine screen in the tubing prevented the bulk impurity from being swept into the main loop stream.

Some insight into sodium chemistry has been gained by these additions at 600 °F, and may be compared with carbon meter responses to similar additions reported at 1400 °F.⁽¹⁾ At both 600 and 1400 °F graphite does not seem to increase the carburization potential of pure sodium. The addition of oxygen as Na₂O causes the graphite to become carburizing. Further, the greater the oxide content, the stronger the carburization level at both 600 and 1400 °F. On the other hand oxygen from NaOH produced a large increase in the carburization strength of graphite at 1400 °F but very little or none at 600 °F. This probably indicates that NaOH dissociates at 1400 but not at 600 °F. NaCN and Na₂CO₃ also apparently dissociate at a temperature between 600 and 1400 °F in sodium. So far, the largest increase in carbon activity at 600 °F has been during the addition of Na₂C₂. However, the level of carbon activity observed on the meter was not determined by the total grams of carbide added (at least in the 10 ppm equivalent carbon range), but rather by the temperature and flowrate of sodium past the carbide source. This is not surprising since the solubility of carbon at 600 °F has been estimated as about 2×10^{-3} ppm.⁽²⁾ The level of carbon activity level then becomes a balance between the solution rate, (the total solubility) and the sink rate. As it turns out in a loop of this size and temperature, the meter itself is capable of removing by its diffusion process, a significant portion of the total dissolved carbon in the loop, within a few minutes.

The carbon meter gas supply and analysis console has been modified to simultaneously feed decarburizing gas to two meter

probes and to rapidly switch from one probe to the other for analysis. A second probe is intended to operate on the Cover Gas Evaluation Loop.

Oxygen meter serial No. 238, which operated well for 14 months, was removed to allow testing of serial No. 237. Oxygen meter 237 was modified to eliminate its sensitivity to ambient temperature changes. This was accomplished by removing the electrical connection from the top of the cell and heating the cell uniformly to 110 °C in a vacuum for 24 hr. The cell was then cooled, refilled with argon and the electrical leak-through restored. Thus overhauled, the cell was unaffected by ambient temperature changes, at least from 80 to 180 °F (the range tested) but produced a voltage of about 0.7-0.8 volts. This emf is much lower than is common and the sodium temperature coefficient of the cell was much higher than is typical.

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COVER GAS EVALUATION LOOP

W. H. Caplinger, G. E. Meadows

The CGEL is a forced circulation 45 gal system intended to be operated isothermally in the range of 800 to 1200 °F. A schematic flow diagram is shown in Figure 2.10. This is a multihead loop of four pots plus a large feed tank and the intent was to provide variable cover gas composition to each of the pots to determine gas-sodium reactor rates and effects on possible containment materials. Additional experiments have been added including: (a) in-line meter evaluation and response to additions, (b) sodium chemistry changes during loop fill and heatup, and (c) FFTF cover gas vapor traps and prototype reactor chromatography performance.

FIGURE 2.10. Cover Gas Evaluation Loop

The loop was started up this quarter according to a detailed test plan to follow the sodium chemistry. A number of mechanical modifications to the loop and the glovebox atop the loop were completed. Loop operating procedures were written and approved, including job hazards, quality acceptance, routine operating, sodium sampling, and emergency actions. For the startup chemistry experiment, the gas from the loop was analyzed by a chromatograph and a mass spectrometer. Sodium samples will be taken by flow through tube samplers. The as-built loop was heated prior to sodium filling and the off-gas analysis showed rather low concentration of impurities. After bakeout at 350 °F, hydrogen was below 2 ppm, methane less than 1 ppm, nitrogen less than 50 ppm, total organics less than 2 ppm and oxygen less than 25 ppm (the limit of detection).

At this writing, sodium has been introduced into the feed tank and the startup chemistry experiments is expected to continue for six to eight weeks. While this is underway the in-line instrumentation package will be added to the loop and some limited experiments with the vapor traps may be possible. Following startup a variety of impurities in both gases and solids will be injected into the sodium and the in-line meter responses measured along with possible effects on stainless steel tabs. If possible, some of these impurity injections will be repeated at other temperatures of interest. The FFTF prototypical chromatograph is expected to become available next spring and about next summer tests on the nitriding rate of stainless steel tabs in sodium may be started.

CHEMICAL CHARACTERIZATION OF SODIUM SYSTEMS

W. H. Yunker

The object of this activity is to document the relationship between: (a) the condition (chemical contamination) of an assembled large sodium loop system, and (b) the identity

and quantities of impurities which appear in the sodium during fill and startup of the system. These results are to guide the design of large sodium systems by describing the balance between expensive precleaning and assembly procedures on one hand and intolerably high sodium contamination on the other. These data are also required to determine the fraction of the installed cold trap capacity that will be consumed during startup of a sodium reactor or loop. Little information appears in the literature on this relationship (see p. 2.26, Oxide Source Rates). The problem is logically divided into three areas: (a) the specification of cleaning procedures to be used, (b) the examination of a treated (cleaned) surface so as to specify its condition, and (c) the analysis of the sodium and gas phase as the system is filled and brought up to operating temperature. Three sodium loops which are built or planned at BNW will be used for this study. They are the Cover Gas Evaluation Loop (CGEL) of 30-gal capacity, the Prototype Application Loop (PAL) of 50-gal capacity, and the Sodium Chemistry and Technology Facility (SCTF) of 1500-gal capacity. As other BNW facilities such as the Fast Reactor Thermal Engineering Facility and other large sodium systems are filled, additional data will be obtained.

During the report period, extensive documentation has been collected on standard cleaning procedures. These include ASTM and AEC-RDT standards as well as procedures used in private industry. The initial selection of a high velocity detergent wash followed by thorough rinsing has been selected for evaluation during the construction of the PAL.

Since a new sodium loop can be started only once, only one startup experiment can be made on each loop which is built. Hence, it is important that the startup procedure and analytical procedures be worked out and tested in advance. The initial sodium fill and startup of the CGEL provides an opportunity to

develop procedures. A detailed, stepwise startup chemical characterization procedure was written, which calls for the chemical analysis of the gas phase and sodium phase of the loop before and during sodium fill, and during the temperature ascension to 1200 °F. The chemical analysis plan is shown in Table 2.3. The loop (including "cold trap") will be operated isothermally as long as possible. This test has been started. The results and experience obtained will serve as the basis for test planning for the startup of PAL and SCTF.

TABLE 2.3. CGEL Chemical Analysis Startup Test Plan^(a)

Loop Condition, °F	Cover Gas	Oxygen	Total Carbon	Nitrogen	Cyanide	Hydroxide	Metals	Iron	Chromium	Particulates	Calcium
Feed Tank Fill Line, 300	X	X	X	X	X	X	X	X	X	X	X
After Feed Tank Flow, 300	X	X	X			X				X	
After Full Loop Flow, 300	X	X	X	X	X	X	X	X	X	X	
350	X	X									
400	X	X									
450	X	X				X				X	
500	X	X									
550	X	X									
600	X	X	X			X				X	
650	X										
700	X										
750	X	X	X	X	X	X	X	X	X	X	
800	X										
850	X										
900	X	X	X			X		X	X	X	
950	X										
1000	X										
1050	X	X	X							X	
1100	X										
1150	X										
1200	X	X	X	X	X	X	X	X	X	X	X

a. Sodium and gas will be analyzed for these species at each temperature indicated.

3.0 SODIUM COOLANT STUDIES

WORK OBJECTIVES AND REQUIREMENTS

J. W. Bartlett

As described in BNWL-1200-1, the basic mission of the Sodium Coolant Studies Section is to provide information needed to properly accommodate FFTF design and operations to anticipated fission product and corrosion product radioactivity burdens.

During this quarter, a major work objective was definition and analysis of specific FFTF problems resulting from radioactivity. Conceptual System Design Descriptions (CSDD's) for FFTF were reviewed in order to identify problems accurately and to focus application of the development work on solution of the problems defined.

Work on fission product and corrosion product behavior, decontamination, and sodium removal was extended as described herein. With respect to sodium removal and decontamination, another major objective accomplished this quarter was to lay out a rationale for development work in these basically long-range areas to ensure that accomplishments and information obtained are as responsive as possible to FFTF needs and schedule.

FISSION PRODUCT RELEASE AND TRANSPORT ANALYSIS

J. W. Bartlett

Summary of Progress to Date

A model of the fission product activity burden in terms of basic physical processes has been formulated as described in BNWL-1200-1.

Progress This Quarter

As noted in BNWL-1200-1, one of the most important practical concerns for fission products in FFTF is capability to

detect and locate fuel failures that are their source. A model descriptive of fission product behavior is of no value unless it is known that the fission products are present.

Consequently, attention has been focused this quarter on modeling and analysis of the FFTF fuel failure detection and location systems, which are part of the cover gas system (described the CSDD for FFTF System 82). This work is reported herein under Fuel Failure Monitoring.

RADIOACTIVITY TRANSPORT

W. F. Brehm

Summary of Progress to Date

Previous BNW studies found that corrosion product radioisotopes (^{54}Mn , ^{60}Co , ^{58}Co , ^{51}Cr , ^{59}Fe) are transported through sodium loops at different rates. The region near the surface of the stainless steel loop is altered by the mass-transfer process i.e., the selective removal of Ni, Cr, and Mn causes weight loss and ferrite layer formation in hot legs; and weight gains and surface deposits are seen in heat exchangers, cold legs, cold traps, and surge tanks.

An evaluation of radioisotope transport for FFTF showed that only the ^{54}Mn , ^{58}Co , and ^{60}Co will contribute significantly to the out-of-core radiation field; radiation levels near 1 R/hr can be expected near some parts of the piping after one year operation at 1050 °F vessel outlet temperature. Knowledge of fission product transport is extremely sparse; it is expected that up to 10 MCi of soluble fission products could be released to the reactor coolant in case of subassembly melt-down. Once in the sodium, the fission products may undergo one or several reactions (depending on a large spectrum of "operating variables" as well as the individual properties of the fission product variables themselves) such as exchange with

cover gas, deposition on and diffusion into piping, agglomeration, oxidation, and possibly other dispositions.

Progress This Quarter

Thermal Convection Loops

Of the two loops mentioned last quarter, the first, operating at 920 °F maximum to 450 °F minimum completed 2442 hr of operation and was shut down. The specimens containing ^{54}Mn , ^{60}Co will be removed and the loop counted. The loop operating time is about three times the operating times of the other loops in the test series. At the low temperatures, longer operating times are necessary to achieve enough transported activity to obtain accurate counting. The second loop has completed 3800 hr of a scheduled 5000-hr run at 1400 to 950 °F, with deposited ^{60}Co and ^{54}Mn . The main purpose of this test is to study the migration of cobalt which was not done in the RTL program.

Examination of EBR-II Piping

J. J. McCown

A section of piping from EBR-II was received. The pipe has these characteristics:

- Type 304 SS, 2-in. Schedule 40.
- Five years service in purification circuit, between surge tank and cold trap, temperature about 700 °F.
- Out of service since about October 1968; arrived full of sodium.

The pipe was counted with the collimated diode; long-life isotopes ^{60}Co , ^{137}Cs , ^{54}Mn , and ^{22}Na were present. A summary of the counting is given in Table 3.1 and Figure 3.1.

TABLE 3.1. Results Obtained from Counting
EBR-II Pipe Section

Counts/min			
	<u>Position No. 1</u>	<u>Position No. 2</u>	<u>Position No. 3</u>
Pipe filled with sodium			
^{22}Na	171	213	144
^{137}Cs	208	265	213
^{54}Mn	141	195	202
^{60}Co	37	55	45
Pipe with Na residue on inside pipe wall; after draining			
^{137}Cs	303	307	165
^{54}Mn	260	220	109
^{60}Co	60	55	24
Pipe with clean wall (Na residue on inside pipe wall washed off)			
^{137}Cs	28	32	20
^{54}Mn	124	174	163
^{60}Co	16	22	14
	<u>Position No. 1A</u>	<u>Position No. 2A</u>	<u>Position No. 3A</u>
Pipe counted starting from opposite end (clean)			
^{137}Cs	23	23	24
^{54}Mn	207	169	96
^{60}Co	21	23	13
Sodium from inside of pipe	^{22}Na	89 counts/min	
Ethyl alcohol used to remove sodium from inside pipe	^{137}Cs	9 counts/min	

The apparent increase in count rate after removing most of the sodium is probably caused by the loss of the self shielding provided by the sodium, as shown in Figure 3.2. It appears

FIGURE 3.1. Pipe from EBR-II and Counting Positions

a. Sodium in pipe attenuates radiation from far side of pipe.

b. After removal of sodium except for adherent film, radiation from far side of pipe not attenuated, hence higher count rate.

FIGURE 3.2. Shielding Effect of Sodium in Pipe

that more ^{137}Cs than ^{54}Mn or ^{60}Co was in the adherent sodium film on the inside of the pipe. It was somewhat surprising to see the large decrease in ^{60}Co counting rate when the adherent sodium film was removed, particularly when no ^{60}Co was detected in the sodium or the alcohol cleaning fluid. In contrast, the tests in the RTL showed that more than 95% of the activity was firmly attached to the pipe wall.

Calculation of Activity in Reactor Piping

Last quarter, results of some calculations on buildup of radiation levels in reactor piping from corrosion product deposition were reported. The information and sequence of steps required to make these calculations are shown in Figure 3.3. This sequence is, of course, applicable for any isotope from Block G onward. The information in Blocks K and L of Figure 3.3 has been generated for us by C. A. Mansius of FFTF Shielding Analysis Group. A lack of really definitive data still exists for Blocks A, F, and I. For fission products the "source strength" (Block G) will have to be calculated from an extremely complex set of inputs. A measure of how complex the fission product source problem really is has been given by Bartlett on page 3.7 of the previous Quarterly.⁽¹⁾

Examination of RTL

Scanning-electron microscope (SEM) analysis was started on sections of the RTL surge tank. Figure 3.4 shows the section of the surge tank with the heaviest deposit. Section (a) of the figure shows the back-scattered-electron image; (b), (c), and (d) are the images obtained upon collecting the emitted characteristics X-rays of iron, chromium, and nickel respectively. (The lighter the color, the more material is present.) The Cr-rich layer deposit next to the base metal surface and the particles of Ni-rich area in the deposit are apparent.

FIGURE 3.3. Block Diagram - Calculation of Out-of-Core Corrosion Product Activities

700X

(a) B.S.E.

700X

(b) Fe

700X

(c) Cr

700X

(d) Ni

FIGURE 3.4. Scanning Electron Microscope Study of RTL Surge Tank

Plans include similar analysis on the other sections of the loop. These pictures may be compared with Figure 3.8 of BNWL-1200 1.

Analysis of these data will be delayed until a determination is made of what useful data can be obtained from further tests. Table 3.2 shows the approach to be used in determining what information is useful and how best to obtain it.

TABLE 3.2. Plans for Further Examination of RTL

Type of Information and How Obtained	Information Applies To:
Composition of sodium-exposed surfaces in such locations as hot and cold legs, and surge tank. Obtained by microprobe and SEM analysis, in conjunction with conventional metallography.	Determination of the actual nature of the sodium-exposed surface. If there is about a mil of altered composition induced by mass transport effects, the response of this material to cleaning and decontamination fluids will probably be different than the response of stainless steel that has experienced only exposure to isothermal sodium. Attention to this factor may alter the kind and number of solutions that can be considered for decontamination.
Mechanical property evaluations--such as strength, ductility, creep resistance. Obtained by tensile tests, burst tests, stress-rupture lifetime tests.	Definition of the effect of sodium exposure and mass transport (especially carbon transport) on the mechanical properties of the piping. This will enable us to attempt requalification standards definition, which must be based upon the condition of the material at the time it was removed from the sodium.

It is important that the following circumstance be recognized. Exposure of stainless steel and nickel-base alloy material to flowing nonisothermal sodium will result in altered surface layers induced by preferential leaching and deposition of Cr, Ni, and Mn, and carbon transport that gives carburized areas in some regions and decarburized areas in others. Exposure of material which has been heated to sensitization temperatures but exposed only to isothermal sodium probably would not give similar results as little or no mass transfer would occur. Such tests must be considered to be of limited value. The effect of nonisothermal flowing sodium on the material characteristics defined in Table 3.2 are unknown for the most part.

It is planned to examine and evaluate a stainless steel loop from the Waste Calcining Facility of the fuel processing plant at National Reactor Test Station, Idaho. This loop has experienced NaK at temperatures to 1400 °F. Extensive work has already been done with this loop.⁽²⁾ Inasmuch as the predominant oxide present in NaK is still Na₂O, the fluid properties of NaK and sodium are similar, and the solubilities of metal in NaK and sodium are probably not very different, that analysis of this loop should provide useful data.

Review of Conceptual System Design Descriptions (CSDD)
for FFTF Systems 84 and 51

The CSDD's for FFTF System 84, Cleaning and Decontamination, and System 51, Heat Transport, were reviewed to identify design problems caused by fission product and corrosion product radioactivity. The ultimate utilization of such reviews is to establish explicit end-product goals for development work aimed at providing information needed to accommodate the FFTF design for radioactivity.

Typical problem areas include:

- Need to determine the amounts and location of radioactivity in FFTF systems.
- Need to select agents and methods for decontamination and sodium removal.
- Need to define requirements and standards for requalifying decontaminated components for sodium service.
- Need to identify requirements and methods for servicing components contaminated with radioactivity.
- Need to adjust component design specifications and geometries to accommodate radioactivity.
- Need to determine the rate and effects, on system materials, of mass transport processes; need to define methods and standards for monitoring such effects.
- Need to identify requirements for monitoring radioactivity.

The design reviews identify the specific component and system design applications of information in these areas. They therefore determine, as required, the specific end-product goals for the development work. The next step is to assemble all development information requirements and devise methods for establishing priorities.

References

1. R. L. Dillon et al. Sodium Technology Quarterly Report - July, August, September 1969. BNWL-1200-1. Battelle-Northwest, Richland, Washington, November 1969.
2. T. L. Hoffman. Corrosion Experience with Type 316 Stainless Steel in Sodium Potassium Eutectic Alloy at 1400 °F IN-1185. Idaho Nuclear Corporation, Idaho Falls, Idaho, 1968.

FUEL PARTICLE TRAP

T. J. Kabele

Summary of Progress to Date

Review of available data showed that information available on the size distribution of fuel particles released by

failure of FFTF-type fuels is sparse. The few data available do indicate that most of the particles are less than $10\text{ }\mu$ in diameter, which means that they cannot be trapped by practical engineering devices that could be used in FFTF.

Progress This Quarter

Work in this area has been temporarily suspended. Data are needed from on-going FFTF fuels evaluation programs, fuel failure propagation programs, and GE's PA-10 program, with which close liaison is maintained.

DECONTAMINATION

D. L. Scott and G. R. Bloom

Summary of Progress to Date

Studies of the effectiveness of acid decontamination and oxidation decontamination methods are underway. Neither has, in preliminary work, produced the decontamination effectiveness required for FFTF.

Progress This Quarter

Acid Decontamination

A single acid decontamination experiment was conducted. A solution containing 0.8M oxalic acid, 0.2M HF and 0.015M H_2O_2 was circulated through a tube specimen at an average temperature of $94\text{ }^\circ\text{C}$. The specimen was taken from the radioisotope transport loop that had experienced sodium for 3000 hr at $1300\text{ }^\circ\text{F}$. After 14.5 hr of acid circulation, a decontamination factor (DF) of 17.5 for ^{60}Co and 11.3 for ^{54}Mn was obtained. From weight loss data a uniform penetration of 0.34 mils was calculated. In order to get a desired DF of 100, which corresponds to removal of 99% of the activity, either a more corrosive solution or longer decontamination times will be required.

Oxidation Decontamination

Tests continued with emphasis on increasing the decontamination factors per steam oxidation and oxide film removal cycle. Samples used were the tube samples from the RTL just upstream from the heat exchanger. The Type 304 SS loop specimens were exposed to flowing sodium at 1300 °F for 6000 hr prior to the decontamination tests. ^{60}Co and ^{54}Mn present in the loop sodium was deposited on the tube specimens and subsequently diffused into the material.

The samples were counted and then oxidized in a steam atmosphere at 100 psi and 550 °C for 96 hr as described previously. They were cycled through four alkaline permanganate-citrox decontamination procedures and were counted and weighed after each cycle. Decontamination factors and uniform penetrations were calculated from the data and the results are given in Table 3.3 as average values.

TABLE 3.3. Decontamination After One
Steam Oxidation Step

Number of Alkaline Permanganate- Citrox Cycles	Number of Samples	Average Decontamination Factor		Average Calculated Uniform Penetration, mils
		^{60}Co	^{54}Mn	
1	6	5.9	1.5	0.23
2	5	12	4.4	0.28
3	4	13	4.6	0.30
4	3	15	5	0.31

A surface cross section photograph taken at 250X is given in Figure 3.5. The sample was exposed to all four decontamination cycles before the metallographic examination. Maximum surface penetrations are about 1 mil. The surface grains are breaking loose up to a depth of 1 mil in the surface section photographed. This was evident at two other locations on the sample examined.

Neg 4692546A

10% Oxalic Etch

250X

 TEST CONDITIONS

- (1) Sodium, 1300 °F, 6000 hr, flowing
- (2) Steam, 1022 °F, 96 hr, stagnant
- (3) NaOH-KMnO₄, 221 °F, 2 hr, stirred
- (4) Citrox Sdn., 185 °F, 4 hr, stirred
- (5) Repeat steps 3 and 4 three times

FIGURE 3.5. Surface Cross Section of Steam
Oxidized-Alkaline Permanganate-
Citrox Sample

The decontamination factors for ^{60}Co were significantly increased over previously reported values. This increase is attributed to the complete removal of the oxide film formed during the steam oxidation step. It should be possible to obtain similar decontamination factors for another steam oxidation step on the same samples which would give decontamination factors of 100 to 200 for the ^{60}Co . The ^{54}Mn decontamination factors were lower because it was exposed to the samples longer in the sodium loop and was diffused farther into the metal. It would be expected that Type 304 SS exposed in the sodium loop longer would have lower decontamination factors. On the other hand, Type 304 SS exposed to the same concentrations of ^{60}Co and ^{54}Mn in the sodium loop at lower temperature would have higher decontamination factors.

The data obtained demonstrate that the oxidation film formation and removal procedure can be utilized to obtain DF of

15 with one oxidation cycle and four film stripping cycles of DF of 12 with one oxidation cycle and two film stripping cycles. The maximum metal damage is about 1 mil deep with an average calculated uniform penetration of 0.3 mils. The steam oxidation procedure is obviously undesirable for obtaining an oxide film both for its extreme temperature and time. An alternative oxidation procedure should be developed which is fast and has a moderate temperature requirement.

Review of the CSDD for FFTF System 24, Radioactive Waste

The CSDD for FFTF System 24, Radioactive Waste, was reviewed in order to identify possible problems resulting from radioactivity. This system provides the equipment and facilities required for the routine collection transfer, storage and disposal of radioactive liquid and solid wastes.

Under the heading "maintenance problems" a need was expressed to consider how the equipment could be designed so that sodium can be removed from it. Sodium removal prior to equipment maintenance or disposal offers the following advantages:

- Radiation levels would be reduced since most of the ^{22}Na and ^{137}Cs would be removed.*
- Sodium fire hazards would be reduced if cutting or welding is required.
- The equipment would weigh less during handling.
- The need to seal the component to prevent sodium-moisture reactions would not be critical.

A need for design to ease the removal of devices from the waste storage tanks that may require periodic inspection or removal was also noted. The effectiveness of tank decontamination, the need for shielding during maintenance, and

* See Table 3.1, Results Obtained from Counting EBR-II Pipe Section.

the need for remote maintenance equipment were also found to be problem areas requiring design attention.

An operations problem that should be considered is that of radioactive liquid backup or retention in waste source drain lines. Designs to help reduce these problems could include:

- Providing sloping drain lines of minimum practical length
- Eliminating "dead legs" or other liquid traps in the piping systems
- Providing proper ventilation of receiving tanks to prevent pressure buildup.

For system recovery requirements it was noted that underground pipe encasements should slope to the tank cells where possible waste leakage could be collected in the cell sump. The probability of waste leakage from underground piping should be reduced by requiring welded joints and fittings, proper piping supports, allowance for thermal expansion, and neutralization of corrosive acid wastes.

VACUUM DECONTAMINATION

D. L. Scott and J. A. Ayres

Possible process application problems and lack of developed technologies for liquid decontaminating agents have led to consideration of the possibility of accomplishing decontamination for FFTF by draining the sodium, drawing a vacuum on the system, and heating the piping. If practical, this approach could minimize concern for the deleterious effects of decontaminating agents on system materials, since no foreign agents would be used.

The concept is based on the premise that radioactivity is adsorbed on piping surfaces. High temperature and low pressure would shift the phase equilibrium to a new point on the adsorption isotherm which would produce desorption. The method would

be expected to work only for the more volatile fission products such as cesium, but these may in fact be the major source of radioactivity that would interfere with access to FFTF systems.

Preliminary feasibility tests were completed during this quarter. A portion of the EBR-II pipe (see p. 3.3) was held at 1000 °F and 10^{-8} mm Hg for 24 hours. Stainless steel coupons and quartz wool were placed above the pipe specimen to collect liberated isotopes.

Results obtained from counting the three isotopes present (^{54}Mn , ^{60}Co , and ^{137}Cs) indicated percent removal from the pipe of zero, 9 and 82 for ^{60}Co , ^{54}Mn , and ^{137}Cs , respectively.

These results are considered to be highly encouraging and this work is continuing. Many problems remain, including verification and extension of present data, optimization of operating conditions, definition of feasibility for FFTF, and process application requirements.

DEVELOPMENT OF SODIUM REMOVAL METHODS

G. R. Bloom

Summary of Progress to Date

The argon-moist argon sodium removal process used by EBR-II was selected as the reference concept for removing sodium from FFTF fuel subassemblies. A program to develop sodium removal methods for other FFTF reactor components was started by subjecting small valves that had seen sodium service to Dowanol cleaning and reinserting them in the FPSCTL to determine if they were still functional.

Progress This Quarter

Removal of Sodium from Fuel Subassemblies

Joint RDT and BNW review of the argon-moist air-water rinse sodium removal process selected for cleaning fuel

subassemblies resulted in a process modification. The reference sodium removal process now consists of an argon-moist argon-water rinse procedure used at EBR-II for cleaning leaker fuel elements.

The process change is to use moist argon for addition of water during the sodium reaction step instead of moist air as previously planned. The primary reasons for the change included: (a) reduction of argon purification requirements. (b) reduction of uncertainties in cladding reactions with introduction of air, and (c) reduction of hydrogen-oxygen explosion potential. The primary disadvantage with the process change from moist air to moist argon is the reduced operating experience of the moist argon as compared to the moist-air process. The development work associated with sodium removal from fuel subassemblies has been altered appropriately to support the new process.

Removal of Sodium from Complex Surfaces

A program to test the effectiveness and applicability of Dowanol and the argon-moist air processes for in-situ sodium removal from valves has been delayed this past quarter. Modifications and operating problems with the Fission Product Screening and Control Test Loop has prevented recycling the sodium valves after one sodium exposure and sodium removal cycle. The test parameters and objectives were outlined in the previous quarterly report. The primary problem at the present time is meeting the low oxygen requirement for the FPSCTL with the newly installed cold trap. The test will continue concurrently with fission product trapping experiments when the loop is operating within test limits.

FFTF Reactor Vessel

Tests are being conducted to estimate the potential for caustic stress corrosion cracking (CSCC) in the FFTF reactor

vessel. Concurrently, B. Griggs in the Corrosion Research and Engineering Section is examining inhibition of CSCC of Type 304 SS with carbon dioxide addition to an oxygen-nitrogen atmosphere.

A CSCC potential exists for the Type 304 SS reactor vessel which will operate at 900 °F in a nitrogen atmosphere containing up to 4% oxygen with trace levels of water vapor. Any sodium leak onto the reactor vessel would react with the oxygen and water present to form sodium hydroxide (caustic). The minor consequence of such an event would be slight oxidation of the stainless steel. On the other hand, the most severe case could be catastrophic failure of the reactor vessel as a result of CSCC. There are no CSCC data for these exact operating conditions and laboratory tests are required for a valid problem evaluation.

Preliminary CSCC tests were conducted using Type 304 SS fuel cladding samples since this type of sample gives a constant stress level which does not dissipate with time because of temperature relieving. Sensitized and unsensitized samples were painted with a 75 wt% NaOH solution, pressurized internally to 800 psi with argon and heated to 600, 800, 1000, and 1200 °F in air. The calculated hoop stress is 5900 psi in the sample for an internal pressure of 800 psi. Both unsensitized and sensitized samples completed a 120 hr exposure without failure. The samples will be burst tested at room temperature to test for any material strength losses resulting from corrosion testing conditions. The samples normally burst near 10,300 psi or at a hoop stress of 78,400 psi at room temperature. A facility for burst testing fuel cladding samples has been constructed by M. M. Paxton in the Cladding Evaluation Section of the FFTF Fuel Department. This facility should be checked out and be available for burst testing this next month. The test fuel pins will be stored in a vacuum until the burst testing begins.

The future tests will be made more prototypical by using a nitrogen atmosphere containing about 2% oxygen and near 0.1 to 0.3% water vapor. The samples will be wetted with sodium which will be converted to sodium hydroxide during exposure to the air. Experiments by Todd and Turner⁽¹⁾ show that Type 316L SS degreased with acetone can be wetted with 3200 °C sodium containing 4 ppm O in less than 10 minutes. Initial attempts to wet the Type 304 SS fuel pin samples were unsuccessful because of inadvertent oxygen contamination of the sodium. When such samples have been obtained they will be exposed to the same temperatures and test duration as the samples described above.

Reference

1. M. J. Todd and S. Turner. The Surface Tension of Liquid Sodium and Its Wetting Behavior on Nickel and Stainless Steels, TRGR-1459, Appendix Figure 16. National Centre of Tribology, Reactor Engineering Laboratory, Risely, England, July 1968.

INTEGRATION AND STRUCTURING OF DECONTAMINATION AND SODIUM REMOVAL WORK

J. W. Bartlett

Summary of Progress to Date

This work was started during the present quarter.

Progress This Quarter

Anticipated operating criteria for FFTF lead to the expectation that decontamination will be required to remove radioactive corrosion products and fission products from reactor and closed loop surfaces. Removal of sodium may be required prior to decontamination, and sodium removal may also be required for some maintenance situations even where decontamination is not required.

For both processes, a major concern is the effect of the process on system materials. The development work centers on

this basic problem. The methods, relevant questions, and procedural elements for the development programs are similar for both sodium removal and decontamination.

In addition, the state of technology is similarly primitive for decontamination and sodium removal. There are no proven processes for either that can readily be adapted to meet FFTF requirements. Hence, work in both areas in support of FFTF really is directed at developing new technologies.

This effort to integrate and rationalize the development programs in these two areas was undertaken because of the similarities in work and requirements, and because the FFTF design schedule requires information input and decisions in the near future. This approach may lead to the most efficient production of useful results for FFTF.

The basic approach for this effort was to identify the essential information elements (provided by FFTF design information needs and technical information needs for the development work) and to arrange them so that they produce a logical development program with appropriate work elements identified and properly sequenced. The end product of the development work would then be proven sodium removal and decontamination processes that meet FFTF needs.

The analysis showed that sodium removal and decontamination requirements will depend strongly upon circumstances dictated by FFTF design, and the schedule for design decisions. Typical questions that illustrate this are:

- (a) What circumstances require sodium removal from components other than fuel subassemblies? There appear to be two basic situations: a need for maintenance, and a need for decontamination.
- (b) What circumstances require that the component actually be removed from the system? Does this mean that sodium removal can or must be done on a removed component?

- (c) Is there a need for decontamination and, presumably, prior sodium removal, in the absence of a need for maintenance? Can radiation fields from nearby components complicate contact maintenance required on another component?
- (d) Does a need for decontamination (resulting from a need for maintenance) demand in situ sodium removal?
- (e) Is in situ sodium removal (without destroying component integrity) possible? Is remote handling capability required when radiation fields are high?
- (f) How thorough must the sodium removal process be? What determines the thoroughness required? How is it measured, for both in situ and removed components?
- (g) What are the sodium removal process application requirements? Are both in situ and removed-component facilities required? Under what circumstances would either be required?
- (h) Under what circumstances is it important that the sodium removal process preserves component integrity? How is it known that the material condition just prior to sodium removal is adequate for continued service?

The logic chain associated with these questions can be summarized as follows:

- (a) The only reason for sodium removal from a component is that it needs maintenance or replacement.
- (b) The only occasion for caring if the sodium process damages the component is if it is to be placed back in service.
- (c) If there are no complications resulting from radiation, the component to be re-used would normally be removed from the system for servicing.

- (d) If high radiation fields prevent contact access to remove the component, in situ sodium removal and decontamination or remote handling capability must be provided.
- (e) Unless special provisions are available with the in-place system (changes within the radiation field are not permitted), in situ sodium removal and decontamination must involve the entire system. All of the system would have to be qualified for continued service.
- (f) If remote handling is provided, the component can be removed from the system prior to sodium removal and decontamination. The rest of the system is not affected.

As a result of these circumstances, two major consequences emerge and require evaluation:

- (a) For any component subjected to sodium removal, there will be an economic breakpoint where the costs and problems involved in qualifying the component for continued service exceed the value of the component.
- (b) If radiation fields prevent personnel access, we must have in situ sodium removal and decontamination or remote handling capability probably on an ad hoc basis. The economic breakpoint for providing a safe in situ cleanup process versus providing remote handling must be determined.

Note that decisions can depend on knowledge of the probability and frequency of access-limiting radiation fields.

Clearly, these circumstances, when all are properly defined for FFTF and organized, will dictate the direction for development work on sodium removal from components and decontamination. A thorough analysis and delineation of FFTF circumstances must precede the actual development work. One can foresee the possibility that safe sodium removal procedures and decontamination should be developed only for certain components.

The analysis also showed that five major elements of decontamination development work are necessary:

- (a) Set standards and methods for quantitative measurement of system integrity.
- (b) Perform development work needed to determine the physical state of radioactivity on the surface.
- (c) Use decision theory to determine the scope required for the development work and the range of application of the decontamination processes.
- (d) Perform inexpensive, quick-answer development studies when appropriate.
- (e) Perform necessary process development work.

In addition, there are five major elements for the sodium removal development work:

- (a) Determine requirements for sodium removal from system components.
- (b) Set standards and methods for quantitative measurement of material integrity.
- (c) Explore possibilities for an "inherently safe" process.
- (d) Scope work requirements for testing the safeness of present sodium removal process concepts.
- (e) Define work requirements for development of methods to remove sodium from fuel subassemblies and components, and decontamination.

The organization and methodology for this work is shown in Figures 3.6 and 3.7, which are basic PERT charts for the decontamination and sodium removal development work, respectively. Note, in Figure 3.7, that synthesis of results from both programs is required to make proper selection of a decontamination process for FFTF.

FIGURE 3.6. Basic PERT Diagram for Decontamination Development Work

FIGURE 3.7. Basic PERT Diagram for Sodium Removal Development Work

The first step in implementing this approach is to obtain detailed information on FFTF design requirements and to flesh out the basic diagrams by identifying all key elements and doing work structure breakdowns and CPM studies.

SOLUBLE FISSION PRODUCT TRANSPORT AND CONTROL

R. V. Bowersock

Summary of Progress to Date

Work in this area was begun recently and has been devoted largely to planning and preparing equipment. Preliminary stability tests have been made of inorganic compounds that are candidates for trapping media of sodium-soluble fission products in FFTF. The Fission Product Screening and Control Test Loop (FPSCTL) has been put in place to serve as a test bed for candidate agents.

Progress This Quarter

Solubles Trapping Agent Development

Development of a trapping agent capable of removing radioactive fission products dissolved in the sodium coolant is being pursued as part of the overall development programs with control of radioactivity within the FFTF primary and closed loops systems. Design of engineered devices and proof testing in the Fission Product Control Screening Test Loop are major objectives of this study.

Various inorganic materials have been proposed as sorption, ion exchange, or reaction gettering agents. Screening tests to check compatibility of these materials with sodium are in progress. Preliminary tests of the compatibility of alumina, zirconium phosphate, zirconium oxide, titanium oxide, ammonium molybdo-phosphate, and potassium hexacyanocobalt ferrite with sodium have been made. All appear to be compatible up to 650 °F as determined by observation of open beaker tests. The next step will be to seal the chemicals in stainless steel capsules containing sodium and to heat

the capsules to a range between 900 and 1200 °F for long exposure times. The chemicals that prove to be stable will then be tested for their capacity to pick up soluble fission products in sodium.

FPSCTL Operations

A small cold trap (volume of the packed portion is about one gallon) was installed on the FPSCTL to aid in bringing oxygen in loop sodium to low levels. Test operations with the loop were suspended during installation and checkout of the cold trap. These activities occupied essentially all of the report period.

Extensive operations with a variety of temperature and flow conditions revealed that the trap would not operate properly. Plugging and reduction of flow occurred for essentially all conditions. The testing led to the conclusion that the principal cause for poor performance was the relatively deep open region beneath the packing. This section apparently allows substantial cooling (as much as 50 °F) of the sodium after it leaves the packing.

Testing to provide useful information on cold trap performance will continue as appropriate. Design modifications for this trap are being considered.

FUEL FAILURE MONITORING

R. J. Cash and T. J. Kabele

Summary of Progress to Date

The reference concept for fuel failure monitoring in FFTF has been to sample sodium downstream from each driver fuel sub-assembly for the presence of gaseous fission products. Our portion of the development work for this concept, which was directed at testing the performance of the sampling lines, has identified major information needs required for a valid test program using a full scale water mockup.

Progress This Quarter

The FY 1970 work plan for the failed-fuel sample line as detailed in the reference concept of CSDD 94 was approved and forwarded to RDT in October.

Westinghouse has partially fulfilled a request for design information on the sample line by furnishing sketches depicting the configuration of a typical sample line. The remaining information would have been forwarded, but all development on the present reference concept was suspended on October 13, 1969.

The design and development work suspension was a direct result of a series of evaluation meetings held in early October. A review board of 10 members evaluated the present concept and made the following recommendations:

- (a) Design and development effort in the present FFM concept should be suspended, but alternative methods should be pursued and evaluated.
- (b) A reliable FFM system should enhance plant availability, and efforts should continue to arrive at a workable system for the FFTF.
- (c) Gas tagging should be considered as an integral part of the location subsystem.
- (d) Additional locating capability should be pursued through design and development of other in-vessel instrumentation but no concept should be considered which requires multiple piping penetrations for sample withdrawal from the reactor vessel.

Another evaluation meeting held October 31 considered a schedule and approximate cost breakdown for the six alternatives proposed for fuel failure monitoring. The two systems which appeared most promising for a 1973 startup were gas tagging and in-vessel gas separation. Phases of both concepts could be developed under former Task FS-B.

As an outgrowth of the recommendation that gas tagging should be the basic method for location of failed fuel, a design analysis is being made to determine the basic requirements for an FFTF cover gas system that would operate with a radiation monitor for fuel failure detection, a mass spectrometer for failed fuel subassembly location using stable xenon isotope tagging, and a purification system to maintain a low background activity in the cover gas. The objectives of this analysis are: (a) to define a set of design parameters that will allow compatible and efficient operation of all parts of the cover gas system, (b) to define limits for FFTF operation with failed fuel which will permit rapid detection and location of subsequent fuel failures, and (c) to suggest potentially effective gas purification methods.

A basic block diagram of the proposed FFTF cover gas system is shown in Figure 3.8. Work on the design analysis this quarter concentrated on the detection and location subsystem design requirements with several purification rates. The work will continue into the next report period.

Fuel Failure Detection Subsystem

A necessary requirement of the cover gas system shown in Figure 3.8 is that the purification flow rate be high enough to maintain a low activity background for fuel failure detection. This requires at least a 10% increase in signal response over the background activity. After a fuel failure has occurred, the purification flow rate should be sufficient to lower rapidly the radioactivity burden in the cover gas to a level at which a subsequent failure can be detected. On the other hand, the location subsystem must have adequate time to collect and analyze a cover gas sample for the particular ratio of xenon tags released by the fuel pin failure. Based on analyses at EBR-II, a 10 ft³ uniformly mixed sample of cover gas is

sufficient to determine the xenon tag ratio provided at least 10% of the original tag gas inventory is released to the cover gas.⁽¹⁾

A compromise between the location and detection subsystems must therefore be achieved whereby the purification flow rate is low enough to allow collection of a tagged gas sample and yet rapid enough to clean up the cover gas for detection and location of a subsequent failure. Rapid cleanup is also necessary to remove traces of the xenon tag gas in order to prevent improper location of a subsequent failure whose unique xenon tag has a different isotopic ratio. (If such a flow rate is not possible, then a 2-mode operational procedure would have to be followed.) For this case a normal low purification rate would be employed until a failure was detected and a sufficient quantity of gas was collected for location analysis (approximately two hours). The purification mode could then be switched to a rapid cleanup rate thereby quickly reducing the background to tolerable levels. The larger the purification rate, the greater the cost for such a system. Thus, the overall cover gas system problem resolves itself to one of trade off analyses among the three subsystems.

FIGURE 3.8. Block Diagram of Cover Gas Model Using Xenon Tagging

Cover Gas Activity Calculations. An equation was derived for the contribution to the cover gas activity by the i^{th} radioactive noble gas species released as a result of periodic fuel pin failures. The following assumptions were made in analyzing the activity.

- (1) Fuel pins fail by "burst" release of a fixed percentage of fission gas in the pin; thereafter they continue to leak a uniformly fixed percentage of gas in the pin.
- (2) There are delay times associated with (a) the transport of the fission gas from the point of formation to the failure site for leaking pins, T_p ; (b) the release of fission gas from the pin upon "bursting," T_B ; and (c) the transport of fission gas from the failure site through the sodium to the cover gas T_s .
- (3) The cover gas is well mixed.
- (4) Leakage from the cover gas volume is zero.
- (5) The location and detector subsystem loop volumes are a small fraction of the total cover gas volume.
- (6) Purification is assumed to be 100% effective; i.e., equivalent to a makeup rate equal to the purification rate with all purge gas being discharged.
- (7) The argon, neon, sodium, or potassium radioactivity is negligible compared to the fission gas burden (less than 3 curies).⁽²⁾
- (8) The cover gas volume is 1200 ft^3 at 1050°F and 14.7 psia .
- (9) The fuel pins fail at even intervals in such a manner that 1.0% of the pins have failed after 320 days--the average target lifetime for FFTF fuel. The pins remain in the reactor and continue to leak fission gases.
- (10) The release fraction of fission gas is 50% of the fuel pin's inventory at time t .

- (11) The average holdup time of fission gas in a pin for a leaker, T_p , is 2×10^5 seconds (2.3 days).
- (12) The average holdup time of fission gas in the sodium, T_s , is 100 seconds.
- (13) Average holdup times of 10 sec, 10^3 sec, and 2×10^5 sec were used to calculate the cover gas activity produced by "burst" releases.
- (14) Purification flow rates of 0.6 scfm, 0.8 scfm, and 10 scfm were used to calculate the cover gas activity. The 0.6 scfm is the argon purge or makeup rate necessary to maintain the integrity of the double seal system which prevents leakage to areas occupied by personnel. Purge rates of 0.8 and 10.0 scfm were chosen to show the effects of small and large changes in the purge rate on system performance.

Integration of the linear differential equation for the rate of change of the number of atoms of the i^{th} species in the cover gas with time yields

$$\begin{aligned}
 A_i(t) = & \frac{C_i}{\lambda} \left[t - \frac{1}{\lambda} + \frac{e^{-\lambda t}}{\lambda} \right] - \frac{C_i e^{-\lambda_i t}}{\lambda_p} \left[t - \frac{1}{\lambda_p} + \frac{e^{-\lambda_p t}}{\lambda_p} \right] \\
 & + \frac{D_i}{\lambda} [1 - e^{-\lambda t}] - \frac{D_i e^{-\lambda_i t}}{\lambda_p} [1 - e^{-\lambda_p t}] + A_{i0} e^{-\lambda_i t}.
 \end{aligned}
 \tag{3-1}$$

For $t \geq 10$ days and the most abundant xenon and krypton isotopes of consideration ($^{83\text{m}}\text{Kr}$, $^{85\text{m}}\text{Kr}$, ^{85}Kr , ^{87}Kr , ^{88}Kr , ^{89}Kr , $^{131\text{m}}\text{Xe}$, $^{133\text{m}}\text{Xe}$, ^{133}Xe , $^{135\text{m}}\text{Xe}$, ^{135}Xe , ^{137}Xe , and ^{138}Xe),

Equation (3-1) is reduced to

$$A_i(t) = [1 - e^{-\lambda_i t}] \left[\frac{C_i}{\lambda} \left(t - \frac{1}{\lambda} \right) + \frac{D_i}{\lambda} \right]
 \tag{3-2}$$

where $C_i = \frac{0.005P_i}{320} e^{-\lambda_i(T_p + T_s)}$

$$D_i = \frac{0.005P_i}{320\lambda_i} e^{-\lambda_i(T_B + T_s)}$$

A_i = no. of atoms of i^{th} species in cover gas at time t

P_i = average production rate (atoms/sec) at 400 MW for i^{th} species

λ_i = decay constant (time^{-1}) for i^{th} species

λ_p = decay constant (time^{-1}) for cover gas atoms because of the purification flow rate; λ_p = purge rate divided by cover gas volume.

$$\lambda = \lambda_p + \lambda_i \text{ (time}^{-1}\text{)}$$

T_p = holdup time (sec) for fission gas release from fuel pin

T_s = holdup time (sec) of fission gas in the sodium

T_B = holdup time (sec) for fission gas release from a "burst"

and

A_{i0} = no. of atoms of i^{th} species present at $t = 0$.

The "burst" activity per pin is calculated from the following equation:

$$B_i(t) = \frac{0.5P_i}{16,500\lambda_i} e^{-\lambda_i(T_B + T_s)} [1 - e^{-\lambda_i t}] \quad (3-3)$$

where B_i = no. of atoms of the i^{th} species in the cover gas volume at time t

Equations (3-2) and (3-3) were programmed on the Wang LOCI-2 computer for each of the 13 isotopes listed above for $t = 20, 40,$ and 80 days with $T_B = 10, 10^3,$ and $2(10^5)$ seconds at purification flow rates of $0.6, 0.8,$ and 10 scfm (14.7 psia and 70 °F). After converting the inventory of each species to curies a signal to background ratio was calculated for each of the 9 cases using Equation (3-4):

$$S/B \text{ Ratio} = \frac{\sum_i A_i(t) + \sum_i B_i(t)}{\sum_i A_i(t)}. \quad (3-4)$$

The S/B ratio is the ratio of the summation of all radioactivity associated with specific fuel failure to the summation of the background activity of all species.

Results and Discussion. One of the biggest uncertainties in the cover gas system analysis is the delay time required for the fission gas to reach the cover gas from a failed fuel pin. This delay includes: (a) the time for the gas to reach the defect point, (b) the time to escape to the sodium, and (c) the holdup time in the sodium. For a leak in the gas plenum region of a fuel pin, this delay time is probably short--on the order of $T_p + T_s = 110$ seconds. But, if a small defect occurs near the bottom of the fuel pin, the delay time could be significant. At Rapsodie,⁽³⁾ significant delays between the formation and detection of ^{133}Xe and ^{135}Xe were encountered in several failures. The delay time was calculated to be about 36 hours (1.3×10^5 sec); hence, the use of $T_B = 2 \times 10^5$ sec in the present study. It is felt that these holdup times adequately bracket this uncertainty.

The resulting signal-to-background (S/B) ratios calculated from Equation (3-4) ranged from 1.32 (for the 0.6 scfm purge rate after 80 days continuous operation with $T_B = 2 \times 10^5$ sec) to 59.4 (for the 10 scfm purge rate after 20 days with

$T_B = 10$ sec). Note that operating times of 20, 40, and 80 days were used for calculation purposes.

The results of these calculations are shown in Figures 3.9, 3.10, and 3.11, where the signal-to-background ratio is plotted versus time, purge rate, and T_B , respectively. The effect of the purification rate and the long holdup time are clearly evident. The greater the purge rate, the larger the S/B ratio. The longer holdup times, on the other hand, tend to reduce the S/B ratios particularly in the case of 10 scfm in Figures 3.9, and 3.11.

The worst case, however, which is a S/B ratio of 1.32, can be detected, and this presents the best case for the location subsystem as far as maintaining the greatest concentration of tag gas per unit volume and being able to identify the tag gas ratio. In terms of a subsequent failure, however, this purification rate provides an effective half life of 8.1 hours for the stable xenon isotopes. Considering a span of 5 half lives to lower the background, a dead time of approximately 40 hours would be necessary between failures to prevent improper tag ratio identification. Although failure detection would be possible any time during the period, the location capability would be lost.

Consider now a different set of parameters such as the same 0.6 scfm purification rate with a 2-hr sampling time for the location subsystem, after which the purification mode is switched to 10 scfm. At this rate the effective half life drops to 0.5-hr for an overall deadtime of only 4.5 hr between failures. Meanwhile the detection system would have increased sensitivity and would have indicated any intermediate failures. Even at a continuous purification rate of 10 scfm, the location subsystem is capable of identifying a tag ratio if the defect size is large enough. This is discussed in more detail in the next section.

FIGURE 3.9. Signal to Background Ratio Versus Time

FIGURE 3.10. Signal to Background Ratio Versus Purge Rate

FIGURE 3.11. Signal to Background Ratio Versus T_B , 80 Days Operation

The activity equation used in this analysis assumed that failures occur at even intervals in such a manner that 1.0% of the pins have failed after 320 days. In actuality most failures will occur early in the life of a pin or near goal exposure and most probably under transient conditions. Such cases do not present any burdensome problems to the detection subsystem because the S/B ratio is greatest early in the pin life time, and more failures near goal exposure result in a lower background since a smaller number of leakers are present than was assumed in Equation (3-2). Only simultaneous or nearly simultaneous failures present any problem and then essentially only for the location subsystem.

The major uncertainties involved in the analysis of the cover gas system are: (a) the delay time for the fission gas to reach the cover gas space whether it be in the fuel pin or entrainment in the sodium, (b) the mechanism of fuel failure occurrences (whether they occur by "bursts" or by slow depressurization), and (c) the subsequent mechanism of leakage from a failed pin, i.e., whether it is a uniform release or a burp--pause--burp type occurrence. These uncertainties affect greatly the S/B ratio, particularly the background from the "leakers." Burp-type releases from the "leakers" result in a highly statistical background which complicates accurate determination of activities from a fuel pin failure.

Fuel Failure Location

It has been proposed to accomplish location of fuel failures in the FFTF driver core by mass spectrometric identification of stable xenon isotopes released by the failed pin. To achieve reliable failure location, sufficient tagging gas must be accumulated at the mass spectrometer. Also, tagging gas from two sequential failures must not mix, otherwise an erroneous result for the failure locations would be obtained. Thus, in evaluating the technical feasibility of a fuel failure

location system based on gas tagging, the most important considerations are the amount of tagging gas released to the cover gas, the rate that the tagging is released to the cover gas, the rate of and the time required for accumulation of tagging gas at the mass spectrometer, and the probable time interval between successive failures. In summation, the length of time required to get the necessary sample of tagging gas and to cleanse the cover gas of the remaining gas from one failure must be shorter than the expected time interval between successive failures.

Summary of Results. Given the current FFTF cover gas design concept, it appears that the collection of a useful sample of the tagging gas will take less than 4 hr and that the cleansing of the cover gas will be accomplished in less than about 36 hr, provided that the tagging gas is not delayed by entrainment in the sodium or adsorption on system surfaces, and that sufficient tagging gas (at least 0.1 cm^3) is released from the failed pin over a short time period (less than one hour). Within the above limitations, it should be possible to locate fuel failures as small as 2×10^{-4} in. in diameter and occurring more than one day apart in high burnup pins.

The above limitations are highly significant. If the gas is delayed or released too slowly, it may not be possible to get a sufficient amount accumulated at the mass spectrometer in order to obtain accurate location. Delay also increases the time interval over which two successive failures can be located.

General Considerations. If a nonvented fuel pin suddenly develops a leak, accumulated fission gas and tagging gas isotopes initially present in the pin will escape to the coolant and then to the cover gas space. The amount of gas that escapes from the pin and the rate at which it escapes are complex functions of the type and location of the failure and the

conditions that exist inside the pin at failure (pressure, temperature, and state of fuel). Furthermore, the amount released and the rate of release of gas from the pin to the cover gas are also functions of the delay time of the gas in the sodium and any adsorption of the gas on system surfaces.

For the location system to work, not only does the tagging gas in the pin have to reach the cover gas, but an amount of tagging gas sufficient for accurate mass spectrographic analysis must be collected from the cover gas. In the next section, an estimate is made of the sample requirements for a successful analysis.

Sample Size. The estimate of the amount of gas necessary for the successful location of a failure was based upon experience from EBR-II. At EBR-II, it was determined⁽⁴⁾ that 0.1 cm³ of xenon gas in a cover gas volume of about 625 ft³ was sufficient for identification purposes when a 10 ft³ sample of the cover gas was taken. The gas sample was collected on a charcoal bed over a period of from two to four hours. With the best of current technology, this sampling and identification process should be capable of improvement by about a factor of ten.⁽⁵⁾ The limiting factors for the location system therefore lie more in the mechanics of the release of gas from the failed pin to the cover gas than with the collection or mass spectrometer systems.

Single Pin Failure. In order to estimate the concentration of tagging gas in the cover gas following a fuel pin failure, a model of the gas release from an FFTF fuel pin developed by General Electric⁽⁶⁾ was used to relate the concentration of tagging gas in the cover gas to the size of the failure and the cover gas purge rate, all as a function of time. A fuel burnup of 45,000 MWd/T (320 days exposure) was assumed.

According to Reference (6), the rate of change of molecules of the i^{th} species in the cover gas is given by

$$\frac{dN_i}{dt} = (X_i K \beta) \exp(-\beta t/M_0) - \lambda_i N_i \quad (3-5)$$

where X_i = the fraction of atoms of the i^{th} species in the fuel rod plenum

K = the factor to convert mass to atoms

λ_i = the decay constant of the i^{th} species

N_i = the number of atoms of i present at time, t

M_0 = initial mass of gas in the plenum

β = a "constant" containing pressure, density, and hole size information. β is directly proportional to the area of the failure.

This is integrated to:

$$N_i = \frac{X_i K \beta M_0}{\lambda_i M_0 - \beta} [\exp(-\beta t/M_0) - \exp(-\lambda_i t)] \quad (3-6)$$

Since the " i^{th} species" with which we are concerned is a mixture of stable xenon isotopes, λ_i , the decay constant, refers to the removal of the tagging gas from the cover gas by purging or purification and is given by:

$$\lambda = F/V \quad (3-7)$$

where F = the purge or purification flow rate

V = the volume of the cover gas space.

For these calculations, it was assumed that the FFTF location system would function successfully if the concentration of tagging gas in the cover gas was at least one-half of the concentration of tagging gas which was successfully analyzed in EBR-II. This means that during the sampling of the cover

gas following a failure, the amount of tagging gas present in the cover gas must be at least 10% of the amount of xenon gases initially charged into the fuel pin. With this requirement, Equation (3-6) can be rewritten for the stable xenon isotopes:

$$\frac{N}{XKM_0} = \frac{1}{10} = \frac{\beta}{\lambda M_0 - \beta} [\exp(-\beta t/M_0) - \exp(-\lambda t)]. \quad (3-8)$$

Equation (3-8) represents all of the conditions which satisfy the concentration requirements of the analytical system. For a fixed purge rate and failure size, the time interval during which the concentration of tagging gas is high enough to successfully sample can be calculated by use of this equation. The minimum time interval required for location of successive failures can also be estimated.

Minimum Fuel Failure Size. Tagging gas required to supply the failure location system will not accumulate in the cover gas if the rate of removal of tagging gas by purification or purging of the cover gas equals or exceeds the rate at which tagging gas escapes from a failed fuel pin. This condition will occur if the purge or purification rate is too high or the leak rate of gas from the pin is very low.

By assuming various purge rates and gas release factors as previously described, the size of failure required to produce amounts of tagging gas needed to ensure reliable failure location may be calculated as a function of purge rates. Calculations were made using Equation (3-6); results are shown in Table 3.4. Fuel failures with effective radii less than those given in Table 3.4 could not be located at the indicated purge rates. Unfortunately, no information is available currently on the size of defects likely to occur in FFTF fuels.

Sampling and Cleanup Time. For a given purge rate and hole size, the time necessary for the tagging gas concentration to build up to the level required in the cover gas for accurate

location and the time elapsed before the purging or purification again reduces that concentration below the required amount can be calculated using Equation (3-8). Table 3-5 summarizes the results for several combinations of purge rates and hole sizes, for an assumed holdup time of zero.

TABLE 3.4. Minimum Fuel Failure Size that Can Be Located

<u>Purge Rate, scfm</u>	<u>Corresponding Effective Decay Constant, hr⁻¹</u>	<u>Fuel Failure Radius, Inches</u>
0.60	0.085	1.25×10^{-5}
2.46	0.35	8.0×10^{-5}
10.0	1.43	1.6×10^{-4}

TABLE 3.5. Time Intervals for Operation of the Location System

<u>Hole Radius, in.</u>	<u>Purge Rate, scfm</u>	<u>Elapsed Time, hr</u>	
		<u>Buildup</u>	<u>Removal</u>
0.0001	0.60	0.2	29
0.001	0.60	Rapid	27
0.0001	2.46	0.2	9
0.001	2.46	Rapid	6.5
0.0001	10.0	0.25	3
0.001	10.0	Rapid	1.6

It is apparent from Table 3.5 that for failures larger in radius than 0.0001 inch, the tagging gas released to the cover gas will be sufficient for successful collection and analysis about 15 minutes after the failure occurred. At low purge rates (<2.5 scfm), the concentrations necessary for successful sampling are present for many hours. Indeed, with a sampling time of less than four hours, a purge rate of up to 4 scfm could be tolerated, as it would enable the collection of a useful sample. Purge rates higher than the 0.60 scfm rate

necessary to maintain the seals in the vessel cover (e.g., 2-4 scfm) would have the advantage of more rapid cover gas cleanup time, thus enabling the location of a second failure sooner than would be possible with the low purge rate. With a purge rate of 4.0 scfm, a second failure could be located about four hours after the first one; for a purge rate of 0.60 scfm, a second failure could be located if it occurred more than 27 hours after the previous failure. Thus there may be advantages in using the higher purge rates, even though greater gas volumes would have to be processed. High purge rates also favorably effect the operation of the detection system (see Fuel Failure Detection Subsystem, page 3.30).

Calculations were also made for a new fuel pin, such as would be present upon startup after fueling. The internal pressure of such a pin at reactor temperatures would be about 50 psia, which is too low pressure for much gas to escape against the external sodium pressure. Consequently, detection of failure in new pins will be extremely difficult because of low tagging-gas release rates. However, pressure buildup within a fuel pin is nearly linear with time. It is estimated that gas release from new pins will become sufficient for accurate failure location after approximately 25 days of service.

The above estimates are the best that can be obtained at this time. The greatest uncertainties in these results are:

- The amount of gas entrained in the liquid sodium.
- The length of time that gas is entrained in the sodium before release to the cover gas.
- The amount of gas adsorbed on system surfaces.
- The probable modes of fuel failures (meltdowns, cracks, pin holes, splits, etc.).
- The release rate of gas from failed pins.

Several follow-on programs are suggested from this study.

- (a) Determination of the extent of noble gas entrainment in the sodium coolant.
- (b) Determination of the extent of noble gas adsorption on system surfaces.
- (c) Correlation of sweep rate and purification requirements for the removal of chemically reactive species in the cover gas with those needed to provide adequate fuel failure detection and location capabilities.
- (d) Development of a purification system concept and, as required, an argon recycle capability, appropriate for fission product gas removal and holdup and for removal of chemically reactive impurities.

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4.0 SODIUM ANALYSES

SAMPLING AND ANALYSES OF RADIOACTIVE SODIUM

F. A. Scott

High Radiation Level Analytical Facility Design

J. F. Jarosch, L. F. Lust, and S. E. Nichols

The objectives of this activity are to provide proven equipment and techniques to analyze radioactive sodium from the FFTF and to develop design criteria and requirements for the FFTF chemical analysis laboratory.

Analytical procedures are well established for the determination of impurity levels in nonradioactive sodium. In order to adapt these procedures to the analysis of highly radioactive sodium coolant, a mockup facility is being constructed. This facility will consist of two adjacent portions, one containing an air atmosphere and the other a pure argon atmosphere. Since its purpose is to test each analytical operation and each piece of apparatus under conditions simulating actual hot cell operations, it will be equipped with master-slave manipulators, viewing windows, air locks and a purification system for the argon atmosphere.

The air-atmosphere portion of the mockup facility has been constructed and equipped with manipulators. Fabrication of the inert-atmosphere enclosure has been completed. All seams and joints have been welded and the interior welds have been polished. The viewing window has been installed and the evacuable antechamber has been attached. Installation of the sliding door over the manipulator load-out port is awaiting receipt of the retainer for the inflatable seal.

A survey of available sites for the mockup resulted in selection of the EDL-146 mezzanine in 324 Building. Selection of this site forced a decision to delay testing of manipulator

handling procedures because of the lack of adequate head room for the cask in EDL-146. The delay is also prompted by several developments which may make it unnecessary to devise manipulator slave transfer techniques. Favorable results with the new Model L manipulators, the shielded glove box approach or the new large-volume full flow gas purification system will reduce markedly the need for transfer cask development. Preparation of the site has begun. Installation of the entire mockup facility should be completed during the next report period.

Design, assembly and mechanical testing of equipment for the remote determination of total carbon has begun. Complete assembly and laboratory testing of this equipment will be performed before installation in the mockup facility.

A detailed discussion of the need for shielded sampling and analysis facilities for the FFTF has been prepared and issued.⁽¹⁾

Remote Sampler Development

K. C. Knoll and E. L. Osborne

The objective of this activity is to develop and proof test remotely operable samplers for highly radioactive sodium from FFTF. Little or no technology exists for the sampling and immediate handling of sodium under these conditions. As reported in the Sodium Technology Quarterly Report for July-September,⁽²⁾ a removable section bypass loop sampler has been designed and constructed at BNW specifically for remote operation. It was installed on the Small Components Test Loop (SCTL). It is a dual loop sampler designed to be operated with master-slave manipulators and will be used to define problems associated with remote operations and to develop practical solutions to these problems.

As a preliminary step in the evaluation of the as-built sampler a study was made of the cooling of the sample tube with

an air quench. Twelve thermocouples were spaced along an empty nickel sample tube and cooling profiles were taken. These revealed nonuniform cooling near the inlet and outlet ends of the sample tube. This was probably caused by the large mass of metal used to clamp the Conoseal connectors of the sample tube to the sampler. Considerable hysteresis was also introduced into the heating and cooling of the tube by this heat sink. The design called for in-place crimping of the sample hairpin with a Manco guillotine crimper. During remote testing it was found to be very difficult to get the crimper head in position because of the quench tube and clamp. To make remote operation practical it became necessary to shorten the quench tube, further accentuating the undesirable temperature differentials during sample cooling. The large clamps were therefore abandoned in favor of Conoseal nuts.

Sodium has been admitted to the sampler and a satisfactory operating procedure developed. Three samples have been taken at 600 °F and one at 800 °F using this procedure. A sample was also taken with the SCTL sampler concurrent with the last bypass sampling. The inlet, outlet and center sections of three bypass samples and the center section of the SCTL sample have been analyzed for oxygen with the following results:

<u>Sample</u>	<u>Sodium Temp., °F</u>	<u>Collection Time, hr</u>	<u>ppm Oxygen</u>		
			<u>Inlet End</u>	<u>Center</u>	<u>Outlet End</u>
1	600	4	32	14	13
2	600	4	14	13	19
3	800	5	48	31	34
SCTL	800	5		24	

With one exception, the results from samples taken at 600 °F are within the expected variation of the analysis, indicating that segregation levels are acceptable in spite of the relatively poor cooling profiles.

The SCTL was shut down to permit transfer to Building 335. During the shut down, modifications are being made to the sampler to eliminate some of the problems found in cooling and crimping. Only the upper sampler is being modified. It will use an "L" shaped tube connected at each end with Conoseal nut connectors. The quench tube will be in a position which permits quenching along the full length of the sample tube and still permits crimping with the guillotine. Also a permanent connection will be installed for testing the upper sample tube for leaks without requiring a side arm on the sample tube.

Modifications to the sampler will be completed early in the next report period and the development of a procedure for completely remote operation begun.

COVER GAS SYSTEM

G. B. Barton and H. P. Maffei

Cover Gas Impurity Reactions Over Sodium

The objectives of this activity are to establish cover gas purity specifications for each gas application in a sodium reactor, determine that the required gas purity can be produced, and define the design criteria for special purity requirements.

The reaction rates of methane and carbon monoxide with molten sodium have been measured and reported.⁽³⁾ The predominant sodium vapor impurity reaction in a typical cover gas system was found to occur in the gas phase. Preliminary specifications for these two impurities in FFTF cover gas have been calculated.

During the report period preparations have been made for the verification of laboratory measured values of impurity reaction rates over sodium using a small engineering system. Construction of the Cover Gas Evaluation Loop has been completed

and instrumentation for mass spectrometric and gas chromatographic measurement of impurity concentrations installed. Tabs have been prepared and installed for nitriding studies and the loop filled with sodium. Measurements during the temperature ascension run early in the next report period should provide valuable information concerning system contamination and impurity reaction rates.

Development and Testing of Cover Gas Instruments and Sampling Systems

The objective of this activity is to provide proven sampling and analysis equipment and technology for the cyclic on-line monitoring of impurities, including fission gases, in the FFTF sodium cover gas.

Analytical and laboratory evaluation of means to monitor impurities in the FFTF cover gas have resulted in the selection of gas chromatography as the most promising approach.⁽⁴⁾ This decision has shifted the emphasis in the development effort to the solution of the sodium vapor removal problem. A trap to accomplish this removal should: (a) be self draining, (b) be highly efficient, (c) have a low dead volume, and (d) cause a minimum perturbation of the composition of the residual gas.

Sodium Vapor Trap Design Study

Scouting experiments were performed on several currently used trap designs and their results suggest that the relatively poor performance of these traps results from the generation of and the failure to remove a sodium mist.

During the report period two analytical studies have been completed in an effort to obtain theoretical bases for an effective trap design and for the prediction of trap performance. The preparation of a brief topical report discussing these studies is planned during the next quarter.

It is readily concluded that either the formation of the troublesome mist must be prevented or it must be efficiently removed once formed. The failure of existing vapor traps demonstrates amply the difficulties entailed in mist removal. Therefore, mist prevention has been chosen as the basis for trap design.

Consideration of nucleation thermodynamics and the relationships of vapor pressure and the sodium mist particle size led to the formulation of an equation predicting the maximum temperature gradient over which the gas should be cooled to prevent the formation of particles larger than the critical radius for particle growth. An experimental program has been undertaken to verify that the equation will predict trap performance adequately. As an initial step in this program a trap has been designed to reduce the vapor content of a 1500 cm³/min gas stream saturated at 1400 °F to approximately 0.05 ppm. Calculations indicated that a 2.1-in. ID trap with a 19-in. long packing of 1/4 × 1/4-in. stainless steel Raschig rings would be required. Sketches of the trap and its placement in the test system are shown in Figure 4.1. The temperature profile which is required has been calculated and is shown in Figure 4.2. Temperatures along the trap were measured by thermocouples welded to the outside of the trap shell at approximately 4-in. intervals.

The trapping efficiencies obtained under three operating conditions along with the measured temperature profiles are summarized in Table 4.1. The results shown in the first group were obtained under conditions favorable to mist formation because of sample cooling prior to entry into the trap. Trapping efficiencies are low. A dramatic improvement in performance is obtained in the second group of results when this cooling is prevented. The results in the third group show that the

FIGURE 4.1. Sodium Vapor Trap, and Arrangement of System

FIGURE 4.2. Calculated Temperature Profiles for Sodium Vapor Traps

trap approaches, but does not reach, the performance predicted by the design equations. There is a suggestion of improvement in performance with time in the data. It may be possible to explain both the deviation from predicted performance and this gradual improvement by assuming a gradual rather than instantaneous wetting of the packing material.

The results demonstrate that we have a usable trap for analytical samples. Engineering evaluation of this trap will be made on the Cover Gas Evaluation Loop. Upon completion of the evaluation on the CGEL a trap will be incorporated into the FFTF gas sampling and analysis mockup and prototype tested

TABLE 4.1. Performance of Sodium Vapor Trap Under Various Conditions

Initial Flow Rate, liters/min	Packing Depth, in.	Sodium Pot	Top of Pot	Temperature, °C							Total Volume, liters	Sodium Conc., ppm	Sodium Removal, %
				Inlet	TC 1	TC 2	TC 3	TC 4	TC 5	TC 6			
1.10	13	760			470	540	480	330	240	175	213	1,380	99.52
1.50	13	760			400	420	360	260	197	153	36.6	86,100	60.0
1.50	13	649			310	325	271	190	155	125	23.9	32,500	52.27
1.50	19	649			365	395	350	250	185	165	94	12,000	82.40
0.65	19	649				396	345	245	185	136	70	1,840	97.30
1.00	19	649				450	398	284	205	150	45.3	7,366	89.20
0.65	19	649				400	350	274	220	190	110	20	99.97
0.44	19	649				395	348	269	215	190	66	3.8	99.9944
1.08	19	649		380		357	305	227	175	158	188	59	99.9135
1.80	19	649		410		350	295	206	150	127	234	173	99.746
0.685	19	649	380	375	355	350	300	200	140	120	110	0.1	
2.06	19	649	405	404	393	395	342	240	175	150	274	6.4	99.9906
1.34	19	760	450	438	405	390		234	170	153	280	3.8	99.9987
0.77	19	760	448	437	407	393		232	170	156	128	0.28	99.9999
0.142	19	760	445	433	409	397		238	177	165	52	0.02	
2.58	19	760	462	457	438	418		254	190	173	309	3.2	99.9989
3.07	19	539	333	345	358	363		247	187	164	368	2.3	99.9798
3.22	19	760	431	427	412	387		276	230	217	148	30.3	99.9894
2.19	19	760	436	430	415	390		238	178	160	307	2.0	99.9993

Group 1 results were with the trap on top of the pot outside the furnace as shown on Arrangement A of Figure 4.1. Group 2 results were with Arrangement B of Figure 4.1 and Group 3 results were with the same arrangement of trap and pot but with the insulation rearranged to raise the inlet temperature.

4.9

on the SCTF. Efforts to improve the design will continue. Two areas will be investigated initially, the minimization of dead volume required and the addition of a preheat section to permit the trap to handle gas samples from a variety of sources.

In-Plenum Hydrogen Meter Development

The hydrogen concentrations in the cover gases of many sodium cooled reactors have been constantly monitored and reported. These cover gases have been monitored either by grab samples or by pumping a gas sample from the cover gas plenum through small sample lines to an analytical instrument. These methods have never resulted in a quantitative hydrogen analysis. This is because of the scavenging effect that sodium has on hydrogen. The hydrogen present in the cover gas, is in equilibrium with the sodium hydride in the sodium of the sodium pool and cover gas plenum. During sampling of the cover gas the cooling of the gas sample changes the equilibrium conditions and results in erroneous hydrogen values.

A detector which could measure the hydrogen within the gas plenum would eliminate the sodium scavenging problem and give a quantitative hydrogen measurement. Such a detector is presently being developed and tested at BNW based upon work reported by Drummond.⁽⁵⁾ The detector employs the principle of hydrogen diffusion through a nickel membrane. The diffused hydrogen is purged with argon gas through a thermal conductivity detector and its concentration measured. A photograph of the disassembled detector is shown in Figure 4.3. The half-inch diameter nickel tube contains a 3-in. section with a wall thickness of 5 to 6 mils which acts as the diffusion membrane. The nickel tube is inserted into the gas plenum chamber of sodium-containing capsule and sealed by the lower Swagelok connector. The heater is positioned inside of the nickel tube

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FIGURE 4.3. Disassembled In-Plenum Hydrogen Detector

opposite the membrane portion and the tube is sealed to the detector head by the upper Swagelok connector. During operation, the argon purge gas is introduced through the center of the heater and passes up along the inside surface of nickel tube. The detector head serves as the connector for the purge gas inlet and outlet, power for the resistance heater, and the controlling thermocouple.

Initial testing revealed that the detector was quite sensitive to hydrogen in the sodium cover gas. With 100 ppm hydrogen in the cover gas above 800 °F sodium, a concentration of 20 to 45 ppm of hydrogen was found in the argon purge gas depending upon the purge rate. During these tests, the nickel membrane was maintained at 1400 °F. The effect of changing the flow rate on the purge gas is shown in Figure 4.4. The average change in sensitivity (ppm H₂ detected) is 2 ppm for every 10 ml/min change in purge gas flow rate. Control of the purge gas flow rate should not present a problem as long as an accurate gas flow regulator is used.

The effect of probe temperatures on the detectors sensitivity was also investigated and is shown in Figure 4.5. It can be seen that increases in probe temperatures did not cause large fluctuations in apparent hydrogen concentration. In fact at 1400 °F with a temperature control of ±10 °F the hydrogen readings fluctuated by only 0.5 ppm.

To date only one test has been performed to determine the detectors' sensitivity to hydrogen concentration changes in the sodium cover gas. The system was allowed to equilibrate with a 100 ppm H₂ in the sodium cover gas and an argon purge flow of 50 ml/min. The amount of hydrogen present in the purge gas was 36 ppm. The hydrogen concentration in the cover gas was then increased to 1000 ppm with a resulting increase of hydrogen in the purge gas to 400 ppm in six minutes.

FIGURE 4.4. Effect of Purge Gas Flow Rate on Hydrogen Diffusion

FIGURE 4.5. Effect of Probe Temperature on Hydrogen Diffusion

This detector will be tested further during the next quarter and means for its calibration developed.

SODIUM STUDIES FACILITY SERVICE ANALYSIS

R. F. Keough and M. B. Hall

The objective of this activity is to provide analytical support for existing BNW sodium technology programs.

Procedures and equipment for the determination of oxygen, total carbon, hydrogen species, total hydrogen, cyanide, Kjeldahl nitrogen, and trace metals in sodium have been in place for some time and have been used for service analysis during the reporting period. In addition, a laboratory manual describing the established procedures has been compiled and issued. To improve their performance the more difficult procedures are continually under review and modification. During the reporting period a number of changes have been made to the carbon apparatus, two new analytical methods have been developed, and plans are being made for evaluation of vacuum distillation as a technique for separation of trace metals from sodium. Facilities for the analysis of plutonium contaminated sodium are under construction.

Halide (Chloride) Determination

A method has been developed for the determination of chloride plus bromide and iodide in sodium. Chloride is presumed to be the predominant halide because of its introduction during the production of metallic sodium. The halides must be separated from the bulk of the sodium before any analytical method can be applied. This is done conveniently by using the amalgamation technique commonly associated with oxide determinations in sodium. The sodium, in a separatory funnel, is dissolved in mercury and the mercury insoluble solids (oxide, halides, carbonate, etc.) are dissolved in an 80% methanol

water mixture after draining nearly all of the amalgam from the funnel. The resulting solution is made slightly acidic with perchloric acid and, after boiling briefly to remove cyanide and sulfide, the halide is titrated with mercury (II) perchlorate. The detection limit is about 0.5 ppm of halide as chloride. Typically, BNW loop sodium had been found to contain 2 ppm halide expressed as chloride by this method.

Calcium Determination

A method for calcium determination in sodium has been developed based on coprecipitation of calcium from sodium salt solutions with strontium oxalate and subsequent atomic absorption analysis. The procedure is simple, specific, and provides a detection limit of 0.1 ppm of calcium. BNW loop sodium typically contains 3 ppm of calcium. Preliminary results indicate that calcium may segregate radially on cooling in 1/2-in. diameter bypass loop samples with the sodium adjacent to the walls having a slightly higher calcium concentration than that in the middle of the tube.

Carbon Determination

The apparatus for total carbon determination by combustion has been upgraded by several changes. The old glove box has been replaced by a new Vacuum/Atmospheres box. The atmosphere purification train remains the same except that an automatic pressure controller has been added. A helium diffusion furnace (Electron Technology Inc.) has been installed in the system so that grade A commercial helium can be used in place of ultra pure helium. The head of a Manco crimper was attached to the inside wall of the new glove box (Figure 4.6). By using broad flat jaws in this device, it makes an effective sample extruder, squeezing approximately 98% of the sodium from 1/2-in. stainless tubing (Figure 4.7).

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FIGURE 4.6. Installed Crimp Extruder

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FIGURE 4.7. Sample Tubing After Extrusion

Vacuum Distillation

One of the most promising techniques for trace metal analyses in sodium involves vacuum distillation of the bulk of the sodium followed by analysis of the residue. During the next report period the construction of a still will be completed and the assessment of this technique for use at BNW will begin. The design of the still will be based on the one in use at ANL, Idaho Falls, and will handle up to a 50 g charge of sodium. A Perkin-Elmer combination atomic absorption and flame emission spectrophotometer has been ordered to do the actual analyses.

Plutonium Laboratory

The laboratory for analysis of plutonium contaminated sodium is still under construction. The glove boxes and associated equipment are on site but room modification is not complete. During the next report period the installation and check out will be completed and experimental work will begin.

SCTF ANALYTICAL SUPPORT

W. O. Greenhalgh

The objective of this activity is to establish the extended analytical capability required to support the sodium technology program.

A complete chemical characterization of sodium (as far as current technology will permit) will be required in the sodium chemical technology program. In addition to those already in place, several published procedures will be required. Two such procedures will be those for particulate identification and carbon species measurement.

The Analysis of Sodium Particulates

Methods being considered for particulate analysis include scanning electron microscopy and electron microprobe analysis,

optical microscopy and metallography, amalgamation, direct filtration, and aqueous or alcoholic dissolution and filtration.* All of the methods except direct filtration have been or are presently being examined and their usefulness evaluated. Electron microscopy combined with scanning electron microprobe analysis shows considerable promise. Measurement of the total number of particles, characterization of all particles, and identification of all major constituents in the particles whose atomic numbers are greater than aluminum are potentially possible. Optical microscopy will provide a measure of the total number of particles and some identification and characterization data. Amalgamation and filtration methods can separate many of the particulates of interest, but subsequent handling and analysis techniques present problems.

Techniques for microscopic examinations are presently inadequate for particulate analysis. Preparation of the sodium surface is the outstanding problem. A technique for chemically polishing sodium developed at BNL⁽⁶⁾ has been examined. Optical examination of a sodium sample at 250X magnification was performed in room atmosphere with little problem. The topography of the sample was clearly distinguishable and the surface, protected by a layer of mineral oil, was relatively oxide-free during examination. One problem with the preparation technique is that acetone forms an insoluble product that gets into the crevices and is difficult to remove. A combination acetone-alcoholic polishing technique would probably work better and plans are being made to evaluate it.

* *Sodium distillation is another method that can be used for certain particulates and undoubtedly will be used at this laboratory. The responsibility and operation of the method will be under a different program.*

A sample handling procedure for scanning electron microscopy has been worked out except for surface preparation discussed above. Cross section slices of sodium from the bypass loop sampler are cut, mounted, and enclosed in the microscope sample cell while inside an inert-gas sodium facility. Oxidation of the sample during handling and transfer to the electron microscope is minimal and no problem in scanning sodium has been encountered. Future work in microscopy will be directed toward solving surface preparation problems, and toward development analyses of actual samples particularly those available from the CGEL loop.

Other work with filtered and amalgamation solids is straightforward and is continuing. At present some problems are being encountered with low recoveries, low sensitivity and high blanks. Most of these can be overcome.

The Analysis of Carbon Species

An analytical method for carbon species in sodium is being set up for evaluation; it consists of aqueous or alcoholic dissolution followed by subsequent collection and measurement of carbonaceous gases and solids. A gas chromatograph with a tritium ionization detector is in place and a sample gas handling system has been assembled for the analysis. The chromatograph has been calibrated for CO_2 , CH_4 , and C_2H_2 gases representing carbonate, methyl sodium, and carbide species in the original sodium; detection limits for the system are presently about 0.3 ppm for CO_2 , and 0.5 ppm for CH_4 and C_2H_2 . Solids are filtered off, combusted, and analyzed in the total carbon apparatus. Future work will involve actual development analyses using sodium analyzed for total carbon as a reference.

The Chemical Analyses of Sodium Systems

The final report on the Chemical Analyses of Sodium Systems Program still has not been issued. It is currently in the editing process and should be issued late in the next reporting period.

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5.0 ENGINEERING SUPPORT FUNCTIONS

INTRODUCTION

V. F. FitzPatrick

The mission of the Sodium Systems Engineering group is to provide engineering support to the Sodium Chemistry Subdepartment. The specific functions, presently, include responsibility for the design, fabrication, installation and checkout of sodium facilities required for experimental programs in the Sodium Chemistry Subdepartment, and the development and improvement of engineering devices to advance the state-of-the-art in sodium systems. Attendant with these major functions are the establishment of appropriate Quality Assurance procedures to ensure that the fabricated sodium facilities are safe, operable, and that they meet the needs of the experimental program.

The activities during the reporting period were centered on: (a) design of the Prototype Applications Loop (PAL), (b) design changes for the Remote Sampler, and (c) development of improved power controllers.

PROTOTYPE APPLICATIONS LOOP (PAL)

V. F. FitzPatrick and T. J. Owen

The design of the Prototype Applications Loop (PAL) was begun late in the last reporting period and is continuing at a satisfactory pace. The design should be completed and the fabrication begun as per the schedule issued last reporting period.⁽¹⁾

The PAL is an isothermal, forced convection, controlled chemistry sodium loop. The PAL is a versatile, experimental sodium system capable of operation to 1200 °F and 40 psig, and is designed for experimental flexibility without modifying the basic components. The center of PAL is the 50-gal mixing tank; 360 degree access to the tank is provided by the work platform-confinement arrangement shown in Figure 5.1. A view port has

FIGURE 5.1. Prototype Applications Loop

been provided to study the surface of sodium at elevated temperatures and to verify that mixing is adequate. The main piping is located below the work platform, but the decking of the work platform can be removed readily for access to make minor repairs or replace trace heaters or other equipment. The mezzanine provides access to the top of the mixing tank for the addition or removal of experimental devices through the nozzles. The size of the mezzanine has been enlarged from 10 ft × 14 ft to 10 ft × 22 ft to provide a larger area for experimental access to the mixing tank.

Modes of Operation

The PAL is designed so that several compatible experiments can be conducted simultaneously. Figure 5.2 is a combination flow schematic and plan view of PAL. The main recirculation or driver loop is from the tank through EM Pump No. 1, valve No. 1, flowmeter No. 1, makeup heater No. 1, and back to the tank. The flow rate in the driver loop will be between 4 and 9 gal/min, and the maximum flow will be 10 gal/min at 40 psig. The tank is mixed with the pumping power of the loop using a double jet nozzle and deflector plate arrangement described by D. H. Lester.⁽²⁾ The temperature in the driver loop and tank may be controlled at any value from ambient to 1200 °F ± 5 °F.

There are two auxiliary loops--the purification loop and the experimental loop. The flow enters the purification loop between EM Pump No. 1 and valve No. 1, and flows through flowmeter No. 3, the service cold trap, valve No. 6 and can return to the driver loop via valve No. 8 or return to the tank, independent of the driver loop, via valve 15 and makeup heater No. 2. Four lines and six valves (valves 2 through 7 inclusive) have been placed in the purification loop so that experimental devices can be added in series (either up- or downstream) or in parallel with the service cold trap. The temperature in

FIGURE 5.2. Combination Plan View Layout/Flow Schematic View of PAL

the purification loop will be the same as the driver loop except in the economizer and cold trap.

The service cold trap has a 5-gal volume. The economizer is designed to handle flow rates of 1 to 5 gal/min with a residence time in the economizer of 0.8 minute at 1 gal/min. The residence time in the service cold trap can be varied between 1 and 5 minutes.

The flow in the experimental loop is from the mixing tank, through EM pump No. 2, flowmeter No. 2, valves 9, 10, and 11, through experimental analytical and sampling devices, valves 12, 13, and 14, makeup heater No. 2 and back to the mixing tank--but not through the double jet mixing nozzles. The maximum flow in the experimental loop is 10 gal/min at 40 psig and the temperature is the same as in the driver loop, except when it is necessary to change the temperature for experimental devices.

Mixing Tank

The mixing tank is a pressure vessel 42 in. high and 24 in. in diameter with an ellipsoidal head on each end. The vessel walls will be 3/8-in. thick. The vessel will be designed and fabricated in accordance with the rules in the ASME Boiler and Unfired Pressure Vessel Code, Section VIII, Division 1, 1968.

A cutaway view of the tank is shown in Figure 5.3. The side of the tank has four penetrations: (a) the view port, (b) the line to feed both EM pumps, and (c and d) two return lines. The view port is a 4-in. schedule 10 pipe, which is reduced to 2-1/2-in. at the valve and view port. The other three lines are 1-in. schedule 40 pipe and each is equipped with a siphon break. The siphon break serves two purposes: (a) if there is a major break in the piping only 3 to 5 gallons of sodium can be siphoned from the tank, and (b) the siphon

FIGURE 5.3. PAL Mixing Tank (Cutaway View)

breaks are located in the highest part of the lines and they act as vent holes or points for gas disengagement.

The pumping power of the driver loop provides the mixing in the tank via the double jet-deflector plate arrangement shown in Figure 5.3. The double jet assembly is located midway between the bottom of the tank and the deflector plate. The deflector plate can be adjusted either up or down as necessary to ensure adequate mixing. The outlet line to feed the EM pumps has two suction ports on the same plane as the mid-point of the jet nozzle and on either side of the jets.

One the top of the tank, shown in Figure 5.4, there are four large (~2-in.) access nozzles for:

- Inserting the double jet-deflector plate and liquid level probes
- A materials surveillance stringer
- Materials addition and light port for illumination during viewing
- A spare nozzle for experiments that require top entry.

The nozzle for material addition and illumination is equipped with an isolation valve at the top of the nozzle. The two nozzles (materials addition and viewing) are equipped with a butterfly type valve near the top of the tank to reduce the rate of sodium deposition in the top of the nozzle. The other two nozzles are equipped with diffusion baffle plates that fit almost flush with the top of the tank, to reduce sodium vapor transport into the nozzle and also to provide supports for the liquid level probes and deflector plate support. Entry through the four 2-in. nozzles on the top of the tank will be through a portable glovebox or portable chamber.

In addition to the access nozzles on the top of the tank there are also two vapor traps for gas inlet and outlet and five thermowells for temperature measuring devices. The

FIGURE 5.4. PAL Mixing Tank (Top View)

temperature of the sodium in the vessel can be measured at four locations: the center, near the wall, near the bottom of the vessel, and near the liquid-gas interface. The fifth thermowell is for measuring the temperature of the gas phase. There are four thermocouples attached to the vessel to measure the skin temperature at selected locations.

The liquid-gas interface in the mixing tank is the highest point of sodium in PAL. Therefore the mixing tank also acts as a surge tank. The gas space above the sodium is about 30% of the tank volume.

The mixing tank is inside a furnace, which provides both heating and confinement. The top of the furnace, but not the heating element, is above the liquid level in the tank. The furnace is a single zone unit, and is equipped with an automatic control unit with rate and reset, and should maintain temperature control within ± 3 °F. The furnace is rated at 10 kW, about 2-1/2 times the power required to melt solid sodium in the tank in 10 hours. The extra power will be used to maintain the temperature in the mixing tank when there are high flow rates (5 gal/min) through the cold trap.

Status

The conceptual and preliminary designs have been completed. A design description has been prepared and approved by the Sodium System Chemistry Section, the group that will conduct the experiments in PAL, and a copy forwarded to the AEC RDT site representative for information. The detailed design is well under way and the detailed work on the piping and electrical should be completed in about three weeks. Approximately 90% of the materials and components have been let for bids. However, no purchase orders will be placed until the AEC has reviewed the design description.

A computer program for stress analysis of piping systems has been set up, based on the program originally described by J. H. Griffin.⁽³⁾ The program was debugged and successfully run to calculate the thermal stress levels at about 100 points in the PAL piping system. The stress levels were all below the allowable value for expansion stresses, calculated from the formula in the USAS code for Power Piping, B31.1.0, 1967, paragraph 102.3.2(c). The successful use of the program established a significant in-house capability that will be used for future systems. An approximate estimate indicates that a thermal stress analysis for a piping system about the size of PAL will cost \$40 to \$50 for machine time.

A stress analysis for the mixing tank is in progress and should be finished in about three weeks.

Quality Assurance

A rough draft Quality Assurance Plan for the design, fabrication and installation of PAL has been drafted and issued for review and comment. A file of all of the design calculations, purchase orders and other relevant documentation has been established. A document describing the procedures for cleaning, handling, and fabrication of the PAL is in progress and will be issued prior to fabrication. The design criteria for a clean area to be used for the fabrication of PAL and future sodium systems are also being prepared.

Remote Sampler

J. L. Gibson

The Sodium Analysis Section requested Sodium Systems Engineering to provide design changes to the remote sampler to improve some of the operating characteristics and the versatility. The modifications were:

* Reference 1, pp. 4.5-4.9.

- Rapid uniform cooling
- A built-in system for leak checking the sample loop
- Redesign of the clamp for connecting the sample tube to remove the large heat sink.

The design changes that were requested and were made are shown in Figure 5.5 between valves V-1 and V-2.

The sample tube was changed from a "U" to an "L" configuration, and sloped about 2 degrees so the inlet of the sample tube is below the outlet. The quench tube is located directly behind and parallel to the sample tube, to provide uniform cooling and adequate room to crimp the sample tube. The manifold arrangement and additional holes in the quench tube will permit higher gas flow rates and more rapid cooling.

A permanent evacuation line and tank were located immediately upstream of the sample tube to drain and evacuate the sample tube and the lines between V-1 and V-2. This eliminates the side arm on the existing sample tubes, reducing the cost of fabricating sample tubes and eliminating a possible safety hazard. The evacuation tank is equipped with a vacuum gage and a liquid level probe. The vacuum gage may be used to determine if the sample tube connections are properly made up and if the tube is properly evacuated. The liquid level gage is provided to determine when the tank should be drained.

The clamp for closing the connectors, which was a large heat sink, was eliminated. The new connectors are a union type fitting and much smaller.

A recommended operating procedure was forwarded along with the new design to help ensure safe operation of the remote sampler when the modifications are completed.

FIGURE 5.5. Remote Sampler

Low Cost Power Controllers

T. J. Owen

In the previous report,* a manual, low-cost power controller, developed at BNW was described. The 3.6 kVA controller cost about \$75, requires about 15 in.² of panel area, and has an ammeter to indicate the power level. During the reporting period the controller was improved and miniaturized.

The cost is about the same, and the required panel area has been reduced to 6.25 in.² (2-1/2 × 2-1/2 in.) as shown in Figure 5.6. The single-turn carbon pot used to regulate the power has been replaced with a 10-turn wire wound potentiometer. The new potentiometer provides more uniform control throughout the range. A dc millivoltmeter with a range of 0 to 50 mV has been incorporated to indicate the temperature, measured by a chromel-constantan thermocouple. Some modifications to the dc voltmeter were required to ensure the accuracy of the temperature indication.

Preliminary evaluation indicates the improved power controller is accurate within 20 °F, and can be used with a wide variety trace heaters.

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* Reference 1, pp. 5.6-5.9.

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FIGURE 5.6. Trace Heater Power Controller

6.0 SODIUM TECHNOLOGY SECTION, FFTF

(No contribution this quarter)

7.0 OXYGEN-SENSING SOLID ELECTROLYTES

FABRICATION AND CHARACTERIZATION

P. E. Hart

The task goal is the fabrication of high-density, Y_2O_3 - ThO_2 (ss) electrolytes with improved stability and reproducibility and inert to attack by liquid sodium at high temperatures.

This report details the fabrication process resulting in high-density ThO_2 - Y_2O_3 (ss) with greatly improved resistance to sodium attack. The effect of process variables on the sintering behavior of both 15 wt% Y_2O_3 -85 wt% ThO_2 and 7.5 wt% Y_2O_3 -92.5 wt% ThO_2 system is also discussed.

The processing regime that yields highest sintered densities is:

- The ThO_2 and Y_2O_3 powders are wet milled in water for 2 hr using a 3:1 ratio of ZrO_2 balls to powder in high purity Al_2O_3 pint-size mills.
- The mixed powders are prepressed at 40,000 psi, granulated through a 30-mesh screen with a final press in a double-acting die at either 20,000 psi with precompaction or at 30,000 psi with no precompaction. No binder or lubricant is required. The average green density is 5 g/cm^3 .
- The pellets are placed in a tungsten crucible packed with ThO_2 setting sand and are sintered in a graphite furnace in argon at a flow rate of $0.3 \text{ ft}^3/\text{hr}$. The heating and cooling rate are $300 \text{ }^\circ\text{C/hr}$ with 2 hr at temperatures of $1700 \text{ }^\circ\text{C}$ or above. The temperature required for maximum density is dependent upon the Y_2O_3 content and source of ThO_2 powder.

- Lot C ThO₂ powder* yields highest sintered densities obtained to date.

Sintered density of the electrolyte is strongly influenced not only by the milling per se, but by batch size as well. The effect of milling and mill charge on the density of 15 wt% Y₂O₃-85 wt% ThO₂ pellets sintered at 1800 and 2100 °C is summarized in Table 7.1. At increased sintering temperature, the sintered density of unmilled powders is increased slightly.

Milling does not appear to introduce impurities into fabricated specimens. Impurity levels of 15 wt% Y₂O₃ pellets fabricated by the optimum procedure (92-6), as well as one of those prepared from powders by mixing only (98-3), are listed in Table 7.2. Both specimens were fired at 1900 °C. Impurity levels are below those of the starting powders, suggesting that enhanced sintering does not result from impurity introduction.

Milling, however, causes a change in powder morphology as shown in Figures 7.1 through 7.4. The block-like ThO₂ platelets (Figure 7.1) lose surface detail during milling (Figure 7.2), and additional detail is lost when the Y₂O₃ and ThO₂ are milled together (Figure 7.3). Mixing alone causes no change in detail. Micrograph of as-received Y₂O₃ powder is shown in Figure 7.4.

In Figures 7.5 and 7.6, the effects of sintering temperature and time on final density of the 15 and 7.5 wt% Y₂O₃ compacts are shown. Sintering data for a Lot D ThO₂ powder** is

* Supplied by Electronic Space Products, Inc. (ESPI), Los Angeles, California, with cation impurities less than 0.1%. All specimens were fabricated from this lot unless noted. ESPI is also a source of Y₂O₃ powder containing less than 100 ppm impurities.

** Supplied by ESPI, with cation impurities less than 0.01%.

TABLE 7.1. Effect of Milling on Sintering Density

<u>Specimen</u>	<u>Density, (g/cm³)</u>	<u>Charge (g)</u>
<u>1800 °C Sintering</u>		
98-4	7.05	None
98-1	7.02	200
92-10	8.45	100
<u>2100 °C Sintering</u>		
98-6	7.39	None
98-7	8.07	200
92-2	8.39	100

TABLE 7.2. Impurity Concentration of Pellets
Sintering at 1900 °C

	<u>Specimen, 98-3</u>	<u>Specimen, 92-6</u>
Al*	<2	<2
Ca	50	20
Fe	50	20
Zn	<50	<50
Mg	5-	2

* In ppm, precision ± 2

10,000X

FIGURE 7.1. Scanning Electron Micrograph of Lot C ThO₂ Powder, As-Received

10,000X

FIGURE 7.2. Scanning Electron Micrograph of Lot C ThO₂ Powder, Ball Milled for 2 hr

10,000X

FIGURE 7.3. Scanning Electron Micrograph of Lot C ThO₂ Powder Ball Milled with 15 wt% Y₂O₃

3,000X

FIGURE 7.4. Scanning Electron Micrograph of Y₂O₃ Powder, As-Received

FIGURE 7.5. Effect of Sintering Temperature on Density of 15 wt% Y_2O_3 -85 wt% ThO_2 Electrolyte

FIGURE 7.6. Effect of Sintering Temperature on Density of 7.5 wt% Y₂O₃-92.5 wt% ThO₂ Electrolyte

included. The 7.5 wt% Y_2O_3 specimens require lower sintering temperatures of about 50 °C to reach highest obtainable densities than 15 wt% Y_2O_3 specimens. Sintering times of more than 2 hr result in increased densities. On the basis of initial Y_2O_3 analyses,⁽¹⁾ the decrease in densities with increasing temperature above 1800 °C for three of the pellet series appears to be related to the Y_2O_3 loss during sintering. The C powder - 7.5 wt% Y_2O_3 pellets lost no Y_2O_3 during sintering; whereas, the 15 wt% Y_2O_3 pellets fired lost 4.6 wt% Y_2O_3 at 1700 °C and lost 9.2 wt% Y_2O_3 at 2100 °C. The grain size also increased with increasing sintering temperatures (Figures 7.7 and 7.8).

The atmosphere in the furnace used for sintering has a low oxygen partial pressure resulting from the large mass of high temperature graphite in the radiation shields. The surfaces of pellets fired at 2000 °C and 2100 °C are dark grey in color. Since chemical and X-ray analysis indicate neither carbon nor tungsten pickup during firing, the dark coloration apparently resulted from the reduction of the solid solution. Firings are now being made in ThO_2 and tungsten crucibles under neutral and oxidizing conditions to determine the influence of atmosphere on densification.

Isostatic pressing is now being investigated as an alternative means for probe fabrication. Bags and mandrels have been fabricated for this work.

SODIUM COMPATIBILITY

L. R. Bunnell

The objective of this task is to examine the high temperature (to 800 °C) sodium compatibility of yttria-doped thoria and to establish the failure mode and temperature limitations for both commercially available and high purity electrolytes. This is being done by exposure of electrolyte materials to sodium of various oxygen contents in sealed capsules and by examination of failed electrolyte tubes.

500X

FIGURE 7.7. Micrograph of 7.5 wt% Y_2O_3 -92.5 wt% ThO_2
Specimen Fired at 1800 °C. (Sample 80-5)
Cathodic Etch.

500X

FIGURE 7.8. Micrograph of 7.5 wt% Y_2O_3 -92.5 wt% ThO_2
Specimen Fired at 2100 °C. (Sample 88-15)
Cathodic Etch.

Several features of the Na-Na₂O system make it attractive for use as a reference electrode for the electrochemical oxygen meter. Besides having an oxygen activity close to that being measured, the system is liquid at operating temperature and would thus avoid electrical contact problems.

Past work⁽²⁾ has shown that oxygen-containing sodium vigorously attacks the commercially available electrolyte, presumably because of a reaction with a second phase composed of yttria and silica. To determine whether high purity samples produced at BNW are more resistant to attack by oxygen-rich sodium, Pellet 74-12, previously tested with no effect in oxygen-free sodium,⁽³⁾ was placed in a capsule with sodium containing more than 10,000 ppm oxygen (saturated sodium, with excess Na₂O₂ in capsule) and heated to 800 °C for 100 hours. The pellet changed in color from gray to blue which was probably the result of capsule metals dissolved in the oxygen-rich sodium and transported to the pellet (microprobe analysis indicated iron). The edges of the pellet were loose; metallographic examination revealed a grain boundary attack at sample surfaces as shown in Figure 7.9. Microprobe analysis of the gray second phase areas (identified as) revealed sodium, thorium, and yttrium. Other work⁽⁴⁾ has indicated that sodium metathorate, Na₂ThO₃, can be formed by heating thoria and sodium oxide to 750 °C. The gray phase observed here may be Na₂ThO₃ or a similar yttrium-containing compound. Attempts to produce enough of this material for X-ray diffraction have so far been unsuccessful, but a capsule containing crushed pellet fragments should yield a sample satisfactory for X-ray examination.

To explore the effects of various pellet variables on sodium compatibility, a series of nine pellets was exposed to sodium containing about 7 ppm oxygen. Table 7.3 lists the fabrication data for the pellets, and indicates comparisons intended by the experiment. Post-exposure examination of the

FIGURE 7.9. 160X Photomicrograph Showing Extensive Attack in Pellet 74-12, Exposed to Oxygen-rich Sodium

- A = New phase containing Na, Th, Y.
- B = Potting compound.
- C = Area of grain boundary attack.
- D = Unaffected matrix.

pellets revealed little damage by sodium in all cases except one; the exception was the pellet (92-4) heated in an oxidizing atmosphere before exposure. Lack of attack in its unoxidized counterpart (Pellet 88-6) suggests that the small amount of oxygen introduced by the treatment is responsible for the attack, perhaps by the formation of Na_2ThO_3 at grain boundaries.

EVALUATION OF DEFECT TUBES

J. L. Bates and P. E. Hart

Two defective electrolyte tubes, UNC Models TPE-1-293 and TPE-1-294, have been received from MSA Research Corporation. These probes failed mechanically during either insertion or removal from the test loop. On the basis of operational

TABLE 7.3. PNL Pellet Variables and Post-Exposure Observations

Variable	Pellet Number	Type ThO ₂ *	Wt% Y ₂ O ₃	Firing Temp., (°C)	Observations
Firing Temp.	88-2	C	7.5	1700	No cracks at edge, some second phase at edges, shown by microprobe to be Ni, P Th, apparent reaction product with capsule parts. Another second phase was shown to be the Si-Y-Al second phase found in commercial probes (Figure 7.10)
	80-5	C	7.5	1800	Same metallic second phase as 88-2 at edges. Very little cracking by sodium exposure.
	88-6	C	7.5	1900	Same metallic phase as shown above at edges. No cracking.
Oxidation of Alloy	80-9	C	7.5	2000	Very small cracks near edge, small amount of metallic phase.
	88-15	C	7.5	2100	Very small amount of cracking.
	88-7	D	7.5	1900	One small crack, radial, probably pressing defect.
ThO ₂ Purity	88-8	C	15	1900	No damage from sodium, some pressing defects in pellet.
	88-9	D	15	1900	Few very small cracks.
	92-4	C	7.5	1900	Oxidized at 1000 °C in air preparatory to insertion in capsule. A large amount of grain boundary cracking was noted, to a depth of about 150 μ (Figure 7.11).

* Types C (99.9% ThO₂) and D (99.99% ThO₂) were purchased from ESPI and are being evaluated for possible differences in sintering or compatibility.

FIGURE 7.10. 160X Photomicrograph Showing $\text{SiO}_2\text{-Y}_2\text{O}_3$
Second Phase in Pellet 88-2 (gray phase)

FIGURE 7.11. 160X Photomicrograph Showing Cracking
in Pellet 92-4

history communicated by MSA on electrolyte TPE-1-293, failure resulted from thermal shocking when the tube was removed from the test loop after 15 weeks service. Typical microstructures of the electrolyte are shown in Figure 7.12. Crack and second phase distribution is similar to that of other defective probes. Second phase, grey areas, are not distributed evenly throughout the probe. Large pockets of second phase are concentrated at the probe outer surface, while the interior 0.1 to 0.2 mm of the probe have low second phase concentration.

UNC Probe No. TPE-1-294 failed while it was being inserted into the cell housing. Phase distribution and cracking are similar to that of TPE-1-293. The uneven distribution of the second phase is a result of the slip casting process. The second phase, high in Al and Si, is introduced during calcining of the ThO_2 and Y_2O_3 powders prior to slip casting.

As discussed previously,⁽³⁾ probe mechanical and thermal shock behavior is believed to be related to the second phase distribution. On the basis of reported experimental results, removal of the second phase will reduce sodium attack.

Since examined defect probes all had similar phase and crack distribution, further examination of defect probes is not planned.

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Neg 4C536C

160X

Inner Surface

Neg 4C536B

160X

Outer Surface

FIGURE 7.12. Typical Microstructure of 15 wt% Y_2O_3 -85 wt% ThO_2 (TPE-1-293) Electrolyte Showing Circumferential Cracking and Second Phase Distribution (160X as-polished)

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