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ATLANTIC RICHFIELD HANFORD COMPANY
QUARTERLY REPORT
WASTE MANAGEMENT AND TRANSPORTATION
TECHNOLOGY DEVELOPMENT
JANUARY 1975 THROUGH MARCH 1975

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ABSTRACT

This document is the third in a series of quarterly progress reports on work in support of management of Hanford high-level wastes. The work reported here was performed during the period January through March 1975. The specific topics discussed are grouped into the subject areas of: salt cake retrieval, tank integrity; storage system improvements; waste immobilization; and preparation of failed, contaminated equipment for disposition.

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INTRODUCTION

The high-level radioactive wastes resulting from Hanford Operations must be stored or disposed of in a manner that at all times positively assures the protection of the public and the environment. A "Technology Program for Storage of Hanford High-Level Radioactive Waste" projects four alternative modes for long-term storage of these wastes. The first is simply to leave the solid wastes in the underground tanks where they will be when the present Hanford Waste Management Program is completed; the entries in this report under Storage System Integrity are directed toward evaluating this option. The second alternative provides for adding system improvements to the existing high-level wastes storage system. Engineered Responses supports this second option. Salt Cake Retrieval and Waste Immobilization subscribe to the third option, removal of the waste from the tanks followed by further immobilization and onsite storage. The fourth alternative is similar to the third except for transportation to an offsite storage repository. Equipment Decommissioning addresses the ultimate disposition of failed and radioactively contaminated processing equipment.

SUMMARY

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Experiments to determine combustion limits in sodium nitrate and carbon mixtures have substantiated predicted behavior.	7
For tank degradation work, steel corrosion studies are in progress at Battelle-Columbus and concrete degradation studies are still in the preparatory phase. A planning document for this work is nearing completion.	10
Comments were received for final revision of the draft Fault Tree Analysis Preliminary Report. Its issuance in revised form has been delayed by awaited approvals. Both the Fault Tree Analysis computer program package and the Fault Tree Graphics program by Computer Sciences Corporation received final revisions. Reports are being prepared covering the use of these two programs.	15
Plans were made to investigate the effects of Cold Creek valley irrigation on the Hanford hydrologic flow system. Plans to evaluate the effect of the aquaculture project just northwest of the Reservation are also being made. Corrections were made to regional field gravity data, leading to improved maps of local gravity distributions and a better knowledge of the formations underlying the Hanford Reservation. Good progress was achieved this report period in the areas of supporting data, mathematical models, and the simulation computer program for vapor phase transport in soil.	18
The validity of calculated predictions from groundwater simulation computer models are being checked by comparing with observed field values. This work is leading to a more comprehensive and accurate picture of Hanford groundwater behavior.	22
Salt Cake retrieval work proceeded in the areas of mechanical mining development, hydraulic retrieval, pneumatic retrieval, retrieval hazard evaluations, and characterization and materials handling studies. Mechanical mining development was delayed until additional procurement requirements can be	24

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satisfied. Additional bid information was submitted to all three original competing vendors to design and supply the mechanical mining equipment. Conceptual design and cost studies started at Norman Engineering Company, Los Angeles. Other design and costing work is being performed by Vitro.

Hydraulic booms and impact hammers are concepts being investigated for fracture of hard salt cake. 26

A barrel elevator is a concept which is being evaluated for salt cake and sludge removal from tanks. 29

Plans were made to obtain two agitator-pumps for bench-scale tests with simulated salt cake and sludges. They will be driven hydraulically. 32

Pneumatic retrieval cold tests, some with high-pressure water jet breakup of the salt cake, gave an improved definition of the method's capabilities. 35

A hazards evaluation of the predicted waste retrieval operations, especially considering suspension of radioactive materials, is being performed by Battelle-Northwest. An informational survey document with recommendations for additional work will be completed and submitted soon. 39

Materials characterization work for the wastes to be retrieved is directed toward learning how to handle them, both as they are being retrieved and during later transport. Solids flow properties are being studied offsite by Jenike and Johanson, Inc. Viscosity of wet salt cake and sludges are being studied by ARHCO scientists. 40

A preferred plan was made for characterizing candidate tanks for retrieval. Probes can yield data on gamma and neutron radiation levels, hardness of the wastes as a function of depth, and temperature. 48

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An offsite architectural-engineering subcontractor began scope design and costing studies which have been identified as promising for the high-level waste radionuclide removal and immobilization processes. These include the glass and aqueous silicate immobilization processes, and the precipitation and ion exchange operations which are included in the conceptual radionuclide removal process. Design assumptions and conceptual flowsheets are presented for these processes.

52

A final evaluation was made of the United Technology Center inert carrier process for aqueous silicate production. Separation of the organic carrier implies extra processing steps and equipment if the process is used. No further work is planned.

62

Three alternative Aqueous Silicate process routes were demonstrated for immobilization of Tank 110-BX terminal liquor.

68

A possible route for the Clay Calcination process was examined in which a loose mixture of synthetic salt cake and clay (kaolin or bentonite) was fired at 900° to 1000° C to yield a crystalline nepheline mineral. Leach rates of approximately 10^{-5} g/cm²-day were observed for products that contained a zinc silicate binder.

72

Aqueous silicate products prepared from Purex sludge, clay, and 50% NaOH solutions leach in deionized water at rates of 4.6×10^{-6} to 7.5×10^{-6} g/cm²-day when based on ⁹⁰Sr and from 1.5×10^{-5} to 2.9×10^{-5} g/cm²-day when based on ¹³⁷Cs.

83

Using a stoichiometric amount of bentonite and simulated terminal liquor, the course of cesium uptake in the solid phase in aqueous silicate products was studied as a function of time. At 100° C, cesium entrapment rapidly reached a maximum at 15 minutes, while the solid phase was essentially all bentonite. As cancrinite crystallized, however, the cesium level in the solids diminished fractionally and leveled out at three hours.

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The volatility of ^{137}Cs from Hanford salt cake upon conversion to soda-lime and borosilicate glasses was determined. The total percentage of ^{137}Cs volatilized from the salt cake for all of the formulations tested ranged from 1.25 to 7.6 when the mixture was heated from ambient temperature to 1200°C in a time span of 3.5 hours. 90

Glass waste forms prepared by melting mixtures of synthetic salt cake and basalt do not devitrify when stored at 500°C for two months; they devitrify readily, however, when stored at 700°C for two months. When sea sand (99.7% SiO_2) is substituted for basalt in the formulation, the glass products are resistant to devitrification when stored at either 500° or 700°C for two months. 95

Addition of 5 wt% lime (CaO) to sand-salt cake mixtures is beneficial to reduce the leach rates of the silicate melt products. Product leach rates increase considerably, however, when greater than 10 wt% lime is added to the formulations. 99

Microstructural and compositional characteristics of representative products from the Silicate Melt process were studied using conventional microscopy and microprobe methods. Both the basalt-type and soda-lime-type glasses were found to have a highly uniform microstructure and composition. 102

The design specifications for the power supply system of the one-ton per day pilot glass melter were completed. The off-gas system has been designed and the equipment is on order. 111

The concentration of ^{90}Sr in salt cake solution was reduced from 31 to $0.29\text{ }\mu\text{Ci/liter}$ by adding H_3PO_4 and inert $\text{Sr}(\text{NO}_3)_2$ to precipitate $\text{Sr}_3(\text{PO}_4)_2$. The resulting liquor containing $5.2 \times 10^3\text{ }\mu\text{Ci/liter}$ ^{137}Cs was passed through three fresh beds of Duolite ARC 359R ion exchange resin and the effluent from the final resin bed contained $0.45\text{ }\mu\text{Ci/liter}$ ^{137}Cs and $0.19\text{ }\mu\text{Ci/liter}$ ^{90}Sr . These values are well below the MPC (maximum permissible concentration) of $1\text{ }\mu\text{Ci/liter}$ for insoluble ^{137}Cs and ^{90}Sr in water in a controlled zone. 118

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The Equipment Decommissioning team received a conceptual design for a sweeping electrode arc melter. The initial attempt to perform a demonstration thermite-type melt in a ground surface basalt cavity was unsuccessful. Arrangements were completed to have other contractors perform off-gas analyses, product evaluations, and conceptual design and cost evaluations. A solar furnace for melting failed equipment is conceptually attractive and technically feasible, but the successful use of the concept poses practical difficulties.

STORAGE SYSTEM INTEGRITY

Salt Cake StabilityObjective

The objective of this task is to identify if explosive or combustion reactions between carbonaceous matter and salt cake nitrates are possible.

Prior Work

Initial concerns about nitrate-organic explosions have been supplemented with several shock sensitivity tests conducted by Stanford Research Institute on NaNO_3 -organic resin (ion exchange) mixtures. Tests conducted in July 1974 have shown no evidence of shock-initiated detonation. During the past four months a literature survey has been conducted and the program objective has been formalized.

Laboratory experiments to determine combustion limits for NaNO_3 -carbon mixtures have been designed and laboratory space has been located.

Progress During Report Period

All of the apparatus required to initiate the combustion tests has been assembled. Some preliminary tests have been conducted and the results are discussed below. Testing will receive increased emphasis as soon as a technician, now being hired, becomes available.

Five mixtures consisting of sodium nitrate and activated charcoal (about 85% combustible carbon) were made. The granular components were mixed and ground with mortar and pestle. The mixture was pressed into a tubular aluminum foil container 7.5 mm in diameter and 25 mm long. Density,

particle size, and moisture content were not measured. The unconfined mixtures were ignited with a 28 gauge nichrome wire heated to approximately 1000° C.

The results are shown plotted on the theoretical flame temperature curve which is described in ARH-ST-110 B.^[1] As predicted, the mixture (18.1% C) with the highest theoretical flame temperature burned the most violently. The mixture (4.2% C) with a theoretical flame temperature of 800° C (assuming zero moisture content) could not be ignited. The mixture of 90% NaNO₃, 8.5% C and 1.5% unknown (noncarbon components of charcoal) which has a maximum theoretical flame temperature of 1500° C would ignite, but when the nichrome coil was removed it would self-extinguish. The combustion process could be maintained only by supplying heat from the ignition coil.

Bids are being requested on a total carbon analyzer. The instrument will be used in the salt cake characterization to provide organic and total carbon analysis of the salt cake. These instruments are an essential part of the salt cake stability programs.

Problem Areas

None.

Summary

Preliminary experimental results are in very good agreement with previous predictions. The probability of hazardous in-tank reactions is small.

Future Work Planned

- Ignition experiments will be continued.
- A final report of the work will be issued.

FIGURE 1

PEAK THEORETICAL FLAME TEMPERATURES FOR DRY NaNO₃ MIXTURES
Experimental Mixture's Behavior Indicated - □

Storage Structure Degradation (D. C. Lini)

Objective

The primary objective is to evaluate the effects of corrosion and deterioration on the Hanford waste storage tanks. This information will be a factor in evaluating the feasibility of using the existing storage tanks as an interim storage mode.

Prior Work

The first milestone set for this project was achieved with the issuance of a draft report titled "Compilation and Review of Hanford Corrosion Studies" (ARH-ST-111). This document is a "state-of-knowledge" report correlating corrosion modes and in-house experience.

The other aspects of this activity involve experimental corrosion and deterioration studies on the waste storage tanks. The first draft of the planning document has been completed. The proposed project will include: an experimental program utilizing electrochemical techniques to investigate corrosion of the mild steel liner and reinforcing bar; an experimental program involving long-term immersion tests to investigate the deterioration of the concrete waste storage tanks; and a literature search to investigate the effects of radiation on the degradation of the waste storage tanks. The planning document also includes a discussion of the corrosive environment which will contribute to tank failure.

Progress During Report Period

The initial phase of the subtask is being conducted by Battelle Institute-Columbus Laboratories. They are making electrochemical measurements on mild steel

specimens exposed to simulated wastes. Based on information supplied by us and contained in an earlier report they conducted their experiments at 50° and 90° C in the following test solutions:

<u>Solution</u>	<u>Concentration in moles/liter</u>			
	<u>NaOH</u>	<u>NaNO₂</u>	<u>NaNO₃</u>	<u>NaAlO₂</u>
1	10	1.6	0.625	1.3
2	10	1.6	2.40	1.3
3	1.5	4.2	0.65	1.3
4	1.5	4.2	2.40	1.3
5	5.75	2.9	1.50	1.3
6	5.75	2.9	1.50	0

They conducted potentiodynamic polarization, slow strain, and linear polarization experiments on A-283 mild steel.

The results of the potentiodynamic polarization measurements indicate that sodium aluminate, sodium nitrite, and sodium nitrate act as inhibitors to the corrosion of mild steel in caustic solutions. A comparison of the measurements of the test solutions with that of the measurement of 40% NaOH indicates that the open circuit corrosion currents are greatly decreased and the corrosion potentials are shifted to more anodic potentials.

The slow strain experiments were conducted in the various test solutions heated to 90° C. The mild steel specimens were polarized to the average cracking potential as indicated by the potentiodynamic polarization measurements. In no case was there any evidence for caustic cracking.

After 200 hours of testing at 50° C in the various test solutions, linear polarization measurements on mild steel provide no indication of pitting corrosion. Further, the relative rate of corrosion is decreasing with time.

The remainder of the contract period will be devoted to determining the effects of additions of minor constituents, especially Cl^- , on the tendency of mild steel to pitting and cracking corrosion; to quantify the inhibitory nature of sodium aluminate and sodium nitrite/sodium nitrate; and to perform the slow strain experiments at the highest possible temperature (about 110°C) in the most corrosive environment.

It was suggested that an additional proposal might be necessary to extend the contract in order to complete the agreed-on work.

The radioactive phase of the metallurgical corrosion experiments will be conducted both in the waste storage tanks and in the laboratory. The electrochemical equipment needed to conduct the in-tank experiments is being ordered. This equipment could be used also in the laboratory but additional equipment has been requested for the laboratory-controlled experiments. The radioactive phase of the work cannot be implemented until the equipment for the in-tank experiments is delivered.

Proposals have been received from both the Portland Cement Association and Battelle Institute-Columbus Laboratories for conducting the nonradioactive phase of the concrete deterioration program and providing concrete specimens for the radioactive onsite tests. Neither proposal was acceptable as submitted. Revised proposals were solicited and these will be reviewed as soon as they are received. This program will be started as soon as contracts can be awarded.

Evaluation

The task is on schedule. Nonradioactive corrosion

studies are being conducted by Battelle-Columbus. Their initial results are encouraging. Bids have been placed on equipment for the radioactive phase of the corrosion studies. Some delay has been experienced in getting the concrete deterioration program started, but a contract for the work should be ready for approval in the near future.

Problem Areas

For the short-term there are no pressing problems. There has been some unavoidable delay in getting the concrete deterioration program started. Negotiations on the various proposals should rectify this situation.

Summary

The planning document for this task will be issued in the near future. However work has started on several of the experimental phases. The nonradioactive corrosion experiments are being conducted by Battelle-Columbus. They have conducted potentiodynamic polarization, linear polarization, and slow strain experiments. For the conditions studied they have found that sodium aluminate, sodium nitrate, and sodium nitrite serve as inhibitors for mild steel in the presence of concentrated caustic solutions. Further, the slow strain experiments did not indicate any tendency toward caustic cracking. Lastly, the linear polarization measurements indicate the absence of any pitting corrosion. These data are only the initial results and represent idealized conditions.

The radioactive phase of the corrosion work and the concrete deterioration program have not entered the experimental phase. Equipment was ordered for the former and contracts are being solicited to conduct the latter.

Future Work

A contract will be awarded in the near future to conduct the nonradioactive phase of the concrete deterioration program. At the same time specimens will be made that can be placed in the waste storage tanks.

As soon as the equipment for the radioactive corrosion work is obtained this phase of the task can be initiated.

Fault Tree Analysis (W. J. Van Slyke)

Objective

The primary objective of this work is to identify those High-Level Waste Storage System characteristics which should receive the highest priorities of attention with respect to engineered improvement or revised administrative procedures. The original (now secondary) objective of the work is to provide information useful to determining the relative urgency for wastes retrieval, reprocessing, and storage in new or improved repositories. These studies have as their continuing objective to provide system reliability evaluations which can be combined with the complementary cost and technical feasibility results for evaluation of waste management alternatives.

Prior Work

Work on this task began in June 1973--the first such study undertaken on Hanford high-level wastes. Early work was focused on obtaining a valid fault tree diagram for the high-level wastes storage system, developing computer fault tree analysis techniques demanded by the unique nature of the high-level waste system analysis problem, and

developing a computer-graphics method for producing fault tree diagrams (by Computer Sciences Corporation) for reports.

The completed preliminary analysis identified a very large number of cutsets, most of which had probabilities or consequences too slight to be of concern. The preliminary analysis ranked the causal (bottom) events by their cumulative probability of contribution to the system failure. Less than half of the postulated events were found to be of significance.

More recently risk index calculations were completed to identify the most serious 15 system failure scenarios. Work continued to incorporate major improvements to the fault tree analysis computer program and to the fault tree graphics program (by CSC).

Progress During the Report Period

The fault tree analysis preliminary draft report was completed in January and issued for comment. Constructive comments were received both from ARHCO and Energy Research and Development Administration personnel for incorporation into the final version of the preliminary report. It will be revised and issued following receipt of approvals which are pending.

Revision of the Fault Tree Analysis program was completed during the report period following the receipt of helpful advice from ARHCO, Battelle Pacific Northwest Laboratories, and consultant personnel. The code incorporates probability calculational routines according to the improved methodology presented in the Rasmussen Report, WASH-1400. It now has the capability for rapidly finding all the cutsets (representing system failure scenarios) within any range of cutset sizes between 1 and 10 events ordered by cutset size

or by probability. Importance calculations for the bottom events of all cutsets found may be printed out, and the data for all the cutsets found may be transferred out to a data file for subsequent processing by other reliability analysis computer programs. All the gate paths leading from the top event to any given fault tree gate may be listed as part of the output data and all the cutsets which incorporate any given bottom event may be identified. A report is being prepared which will publish the program, together with instructions for its use.

The revisions to the fault tree graphics program were completed during this report period by Computer Sciences Corporation. This graphics code now permits the rapid, interactive generation of fault tree subtree plots which are compatible with report page proportions. It was used to make the subtree diagrams which will be incorporated into the preliminary fault tree analysis report.

Evaluation

Final revisions of the preliminary fault tree analysis report are awaiting receipt of approvals. The fault tree analysis computer programs revisions are completed and are being documented in report-form to make the code available to potential users. The fault tree graphics computer program has been revised into a very useful supporting tool to fault tree analysis reporting.

Problem Areas

The preliminary fault tree analysis report draft approvals were delayed over two months while awaiting review.

Change in Plans

Issuance of the preliminary fault tree analysis report has necessarily been postponed until the next report period.

Future Work

Future work planned is summarized by the following major items:

- Complete revisions of the preliminary fault tree analysis for issuance during the next report period.
- Revise the fault tree diagram to incorporate ARHCO internal responses to the preliminary report.
- Provide input to the ARHCO efforts in engineered responses.
- Obtain improved estimation of the characteristics for each contributing event identified as important in the initial analyses.
- Modify the fault tree efforts as required by Atlantic Richfield Hanford Company and the Energy Research and Development Administration continuing requirements.
- Prepare periodic reports and a final report of the work accomplished.

Radionuclide Migration in Soils (R. A. Deju)

Objectives

The objectives of this subtask are:

- Define the Hanford groundwater flow system and its hydrological properties so as to be capable of predicting the long-term movement of radionuclides and potential hydrologic impact of irrigation-type activities on the Hanford high-level waste practices.
- Identify all radionuclide transport mechanisms and evaluate relative rates of radionuclide movement in the Hanford environment by each mechanism identified.
- Develop an efficient and accurate computer model for assessing the rate and direction of radionuclide movement from high-level waste areas to points of potential uptake by man.
- Assess the potential impact of radionuclide movement through the Hanford environment on man.

Prior Work

Field Activities. The required pumping test equipment and supporting materials were identified and ordered. All equipment purchases are expected onsite by the end of the next quarter.

Geophysical gravity field data have been collected from 600 locations distributed throughout the Hanford Reservation. All data corrections such as the Bouguer, terrain, and latitude were completed.

Mathematical Studies. The research and development effort on this project has moved successfully through major milestones in reaching the present stage of progress. In particular, formation of equations, the selection and development of the several required numerical algorithms were completed, and the computer programming step was started prior to the beginning of this reporting period. In the process of reaching that point, a major effort was completed to study and evaluate a broad cross-section of literature cutting across numerous technical fields since the descriptive equations for the combined air, water, vapor, heat, and temperature-induced flow are not well established or generally accepted. Through carefully choosing, critically selecting, and, where necessary, further extending the concept involved, the best description we believe possible has been brought together for subsequent experimental scrutiny.

Progress During Report Period

Field Activities. A research plan was scoped and outlined for conducting a detailed geohydrologic study of the Cold Creek Valley. Irrigation activities in this valley may impact on the hydrologic flow system underlying the Hanford high-waste storage areas. During the quarter the drilling of the first research well was completed and waste samples were taken for chemical analysis.

A hydrologic impact study of the aquaculture project located just northwest of the Reservation was initiated. All ponds and water drainage ditches were mapped. In addition, sediment samples were collected for laboratory determination of their water-transmitting properties. This study will determine the potential hydrologic impact of the

aquaculture project on Hanford high-level waste areas.

All data corrections were made and incorporated into the field gravity values for the regional geophysical survey. Two residual maps were generated by subtracting two different regional gravity distributions. Preliminary results reveal a rather complex tectonic structure and paleochannel network underlying Hanford. This work will assist in identifying the most likely radionuclide travel paths.

Mathematical Studies. The major programming effort to provide predictive results has progressed well during the report period and the batch program will be completed as the final debugging and testing now under way are finished. Three weeks now appear necessary to complete the debugging.

A corrected problem during the report period of considerable importance involved a change of Gear's Solution Algorithm to allow solving a mixed set containing both algebraic and differential equations. This turned out to be more involved than originally expected to meet the requirements although greater flexibility resulted since now either sets of nonlinear algebraic equations, differential equations, or a combination of the two are readily solved.

The assembling of representative material input characteristics also progressed during the report period. The soil conductivity and heat capacity data are more readily available than originally expected. In fact, the ARHCO-measured heat conductivity values reported in February by G. K. Allen will be very useful to this work. Those measurements in the SX Tank Farm are only on dry soils and the conductivity variations over the moisture content range

are required for our work. However, by initially using the ARHCO values as matching point in the DeVries' theory for heat conductivity-saturation changes, better hydraulic characteristics are available.

The remaining parameter requiring attention is the "Vapor Flow Enhancement Factor." Continuing effort with enhancement involves better definition of the particular factor that should be used; *i.e.*, determining which terms required enhancement factors and then determining their magnitudes insofar as possible from the experimental literature.

Evaluation

All objectives of this subtask are being accomplished on schedule.

Future Work

Field Activities. Documentation will be completed next quarter on the geophysical delineation of Hanford paleochannels. A hydrologic study of the aquaculture project will be released during the next three months.

Following the drilling of two additional research wells near the Yakima Barricade, a high discharge pumping test will be conducted at the site. Geohydrologic cross-sections across the Cold Creek Valley are also planned.

Mathematical Studies. Emphasis of the continuing programming work is upon debugging and testing of the batch computer program. Once the batch program is running, an interactive front-end processor will be provided to enable input from a terminal at 200 West Area.

Long-range work and additional planning will be

required beyond the present project to experimentally verify the theoretical results obtained and to better measure the particular nonisothermal soil conditions at Hanford.

Groundwater Management (R. A. Deju, R. E. Gephart, and R. K. Ledgerwood)

Objectives

The objectives of this subtask are to (1) define the hydrologic properties comprising the Hanford groundwater flow system to predict the long-term radionuclide transport, (2) develop methods for controlling the rate and direction of radionuclide movement in the high-level waste disposal areas for improving radionuclide immobilization and containment capability, and (3) determine the extent of groundwater management needed for the high-level waste facilities.

Prior Work

Drilling data and sediment descriptions from over 300 Hanford groundwater wells were assembled, analyzed, and plotted. By assigning hydrologic values to various sediment types, two geohydrologic maps were drafted showing the distribution of hydraulic conductivity and transmissivity values over the Reservation. A map showing the distribution of these two hydrologic values was also constructed by using only raw pumping test values.

Progress During Report Period

Two computer plots showing the distribution of hydraulic conductivity and transmissivity were run using the Transmissivity Iterative Routine (TIR) and Variable Thickness Transport (VTT) models. The results of this analysis

are being compared with previously determined field value distributions of hydraulic conductivity and transmissivity. The results of this study will comprise the latest and most comprehensive evaluation of the distribution of these properties across the Reservation with emphasis on the 200 Areas. Since these maps will be based upon all acceptable past field tests and analyses, map changes and/or improvements will be possible only by conducting new hydrologic tests.

Evaluation

The objectives of this subtask are being accomplished on schedule.

Future Work

Documentation will be completed during the next reporting period on defining the distribution of hydraulic conductivity and transmissivity across the high-level waste disposal areas.

SALT CAKE RETRIEVAL

The Salt Cake Retrieval project has been divided into three phases, each having a number of tasks. These tasks have been assigned to selected individuals and organizations. Specific efforts are reported by the individual(s) assigned that task.

PROJECT MANAGEMENT (D. O. Schuler, D. A. Turner, and
N. C. Rodewald)

Prior Work

1. A task was set up to investigate hydraulic mining schemes.
2. Programmed and Remote Systems Corporation (PaR) was selected to provide preliminary design of a mechanical miner.
3. A contract was issued to Jenike and Johanson, Inc. (J&J, Inc.) to study the solid flow properties of simulated solid waste.
4. Started a review of the project to seek optional plans that would lead to more full-scale hardware for cold testing.

Progress During Report Period

1. Received a report from J&J, Inc., summarizing their analysis of our synthetic samples.
2. Issued Purchase Orders for two models of a high-solids pump. Bench-scale testing of these two pumps scheduled for June will show under what conditions this hydraulic system can retrieve salt cake or sludge.
3. Identified several short-term programs that would lead to alternative equipment for evaluation; namely:
 - The hydraulic retrieval system as listed in Item 2.
 - A large-scale feasibility demonstration of pneumatic retrieval using an in-tank

manipulator, our truck-mounted vacuum system, and the 277-T Building test stand.

- An in-house effort to procure a mechanical miner. Most components would be purchased from highly qualified manufacturers. Vitro Engineering Division of Automation Industries, inc., was asked to help with this task.
- 4. A presentation was made to Energy Research and Development Administration officials as part of the Mid-Year Review. We were asked to consider sludge retrieval techniques. Vitro was selected to assist with testing, selection, and design of sludge retrieval techniques and were issued a \$25,000 Work Order.
- 5. Computer Sciences Corporation PERT experts were retained to assist with preparing new schedules and budgets. They were given the necessary input data.
- 6. A contract was issued to Norman Engineering, as described later.

Problem Areas

Additional requirements for written design criteria and submission of vendor proposal evaluation to the three firms who originally bid on the mechanical miner has resulted in a four-month's delay in awarding a contract for the mechanical mining equipment.

Future Work Planned

Prepare PERT input on the agitator-pump evaluation task.

Issue a contract to PaR when approval is granted by the ERDA Richland Operations Office contract personnel.

MECHANICAL MINING AND COLD TEST STAND (D. O. Schuler)

Objective

The objective of this task is to design, build, and evaluate a prototype mechanical miner.

Prior Work

Two members of the Solid Waste Design Subsection visited four hydrocrane manufacturers and later received proposals from three of these vendors. Program and Remote Systems Corporation (PaR) was selected because of the company's experience in fabricating remote handling equipment. Atlantic Richfield Hanford Company legal counsel prepared a contract which was sent to ERDA-RL for approval.

Progress During Report Period

Outside Contracts. Following the recommendations of ERDA Procurement, a letter listing the general criteria for a waste retrieval system and the basis on which a vendor's proposal would be judged was drawn up and sent to the vendors who had responded to our initial request for proposals. The three companies involved [Programmed and Remote Systems (PaR), Hydrasearch, and Food Machinery Corporation (FMC)] have resubmitted their proposals for evaluation. It is planned that a vendor will be selected and a contract placed in early April. This contract will be for

conceptual design of a waste retrieval system with an option to provide prototype hardware if the design shows promise.

As part of a conceptual design and cost evaluation study, Norman Engineering Company of Los Angeles, California, is preparing scope designs and cost estimates for three possible options for a waste retrieval system and a fourth conceptual system is being designed to accomplish final in-tank cleanup. This study will include an evaluation of the technology, a preliminary safety and environmental analysis, and preliminary cost estimates for each option. Contract initiation meetings were held at Norman Engineering's office March 10 through March 12, 1975.

Mechanical Mining. The hydraulic power unit for the clamshell bucket is operational. Preliminary tests indicate the clamshell is incapable of retrieving even moderately hard material when operated off a cable suspension. Plans are under way to adapt the clamshell to a backhoe arm to evaluate the effect of increased force loading on digging ability.

A \$5,000 Work Order was issued to Vitro for the "conceptual design and cost estimate - cold test stands options." Four site options are being considered: 277-T, 190-D, 202-S (Redox), and a complete new facility, Figure 2.

Vitro is proceeding with designs and cost estimates for the cold test stand. Delays have resulted in a revised target date of April 4, 1975, for completion of the study.

FIGURE 2
PROTOTYPE MINING EQUIPMENT COLD TEST STAND

Future Work Planned

- Select a vendor and place a contract for design and fabrication.
- Continue testing the clamshell bucket to determine its capabilities for fracturing and retrieving hard salt cake.

IN-HOUSE MECHANICAL MINER, SLUDGE REMOVAL, AND MECHANICAL BREAKUP DEVICES (J. Baldridge - Automation Industries, Inc., Vitro Engineering Division)

Objective

The objective of this task is to identify, test, and evaluate alternative mechanical breakup devices and sludge removal techniques.

Progress During Report Period

Work has continued on the search for removal methods and suitable contractors for equipment shown in Figure 3. Several elevator-dumb waiter manufacturing companies have shown interest in bidding on a barrel elevator to remove waste from storage tanks in 55-gallon drums. Companies included Otis Elevator - New York, New York; Spokane Elevator - Spokane, Washington; H&S Builders - Spokane, Washington; and F. T. Crowe - Seattle, Washington. These companies were sent identical specification sheets, description, and requests for bids as prepared last quarter. In January we received a bid proposal to supply a hopper elevator. The bidder quoted one year for delivery. We have asked them for another bid based on a more conventional elevator speed of 0.3 m/sec.

Since the alternative retrieval concepts require

FIGURE 3
MECHANICAL MINING SYSTEM
SINGLE DRUM LOADOUT AND PACKAGING

moving a retrieval device to the materials at all locations within each waste tank, a high priority has been assigned to obtaining or developing suitable arm-like mechanical devices to carry one or more of the retrieval devices. Hydraulic arms or booms, similar to those used in hydraulic cranes and backhoes, are commercially available and would appear to meet the requirements of the task after suitable design modifications. Idaho Falls Aerojet was visited to examine a hydraulic boom installed in their high bay test area. This boom can be made available to us. Initial examination indicates that we may be able to operate it in a waste tank which has 1.1-m openings. A current design-layout effort is directed toward achieving a good, workable design for mounting and operating the boom in a tank.

Discussions with the manufacturer of the hydraulic boom resulted in our receiving rough estimates of 6 to 8 weeks after receipt of order for a standard boom; and 12 to 18 months for design, fabrication, and delivery of a version of this boom specially modified to retract to an overall length of about 4 meters. The method of attachment of the several retrieval devices remains to be defined.

Several pneumatically and hydraulically driven impact hammers were examined. J. A. Jones personnel were requested to prepare a cost estimate to assist us in the test and evaluation of these types of breakup devices on concrete pads of varying thickness and fracture strength. Sales literature reports that breakup rates of "up to about 12 m³/hr of concrete" are possible.

Summary

Hard sludge layers can be removed using a hydraulic boom to break up the layers. If necessary a

hydraulically driven impact hammer can be mounted on the boom to break large pieces into small "conveyable" ones.

Future Work

Using drawings of the Idaho Falls boom, a support structure and mechanism will be designed to fit into and over tank openings. Conduct test sample evaluations.

Hydraulic Mining (D. Robbins and N. C. Rodewald)

Objective

The objective of this task is to evaluate feasibility of hydraulic mining.

Prior Work

We were contacted by a representative of a Yakima, Washington, firm about the possibility of using a special patented agitator-grinder-pump-recirculation device for retrieving salt cake. We received and started a review of a bid.

Progress During Report Period

Work continued, with the cooperation of a Yakima, Washington, agitator-pump manufacturer, to define a workable agitator-pump and hydraulic drive motor combination for breakup and retrieval of the salt cake and interstitial liquor materials being formed in the Hanford waste tanks. Simulation of actual in-tank service conditions is expected to be a challenging task.

After three months of considering many alternatives, a decision was made to order two models of an agitator-pump offered by the Yakima firm. Both pumps will

be driven by hydraulic power systems. This appears to be an excellent way of varying pump speed and measuring pump performance, and has the additional advantage that the hydraulic motor and agitator-pump combination is small enough to easily fit through 1.11 m-or 30.5-cm risers.

A purchase order was placed for the medium-sized agitator pump. This unit is sized to chop and emulsify 8-cm solids. The unit length is 3.5 m and the mixer/recirculation nozzle is located 1.2 m from the pump inlet. Shipment is scheduled for six to eight weeks after order issue (first week in April). The unit is powered by an 1800 revolutions per minute (r/min) maximum, 100 hp hydraulic motor. This arrangement allows us to vary the speeds downward from 1800 r/min.

A decision was also made to order a smaller model that could fit through an 0.3-m riser. This unit has two potential applications--as a fixed point retrieval system or as a boom-mounted pump. This pump has a higher speed rating and is capable of pumping to much greater heads than the larger unit. Since the larger unit might require a booster pump, this smaller unit was ordered and will be tested.

A hydraulic mining system is shown in Figure 4, illustrating how the agitator-pump might be used. The inventor and manufacturer suggested that we use a heavy outlet pipe to support the pump. This simplification, coupled with a small throttleable hydraulic motor short-coupled to the pump, conceptually results in an attractive ready-to-go retrieval system.

Problem Areas

None.

FIGURE 4
HYDRAULIC MINING SYSTEM
LOADOUT TO A TRANSFER TANK

Summary

Agitator-pumps are considered to be feasible devices for breakup and retrieval of moist sludges from storage tanks. A variable speed motor pump demonstration is needed to establish speeds and capability.

Future Work

Work planned for the near future includes preparing a work plan, continuing site preparation, making simulated salt cakes, and testing the agitator-pumps.

Pneumatic Retrieval (N. C. Rodewald and D. O. Schuler)

Objective

Evaluate feasibility of pneumatic retrieval.

Prior Work

The vacuum truck test was scheduled for January 6, 7, and 8.

Progress During Report Period

Twelve retrieval tests were conducted with a vacuum truck. The truck unit tested has a nominal 76,500 liters/min triple-stage suction fan. A 20-cm suction hose extends forward from the driver's cab and is remotely positioned by a hydraulically driven boom. A receiver tank is an integral part of the unit.

Three tests were conducted in the future SY Tank Farm where the vertical elevation is approximately 18.25 m. With two men manually manipulating the suction nozzle, the truck retrieved approximately 100 liters (one-half barrel) of wet, sticky synthetic salt cake at the slow rate of

approximately 1000 liters/hour. Next the retrieval rate of a barrel of caustic liquor was checked, but after 1.5 minutes when one-half of the barrel was recovered, the lines plugged with a liquid leg. This anomaly was blamed on "excessive air leak around the quick-release clamps." When this problem was corrected, two barrels of water were recovered at the rate of 12,500 liters/hr. The suction rate increased to approximately 50,000 liters/hr when the vertical elevation was reduced to approximately 4.7 m and the nozzle was manipulated remotely. Synthetic salt cake retrieval under similar conditions was slow but dependent on the breakup rate of the synthetic salt cake by the air stream, indicating that a breakup device/method is required.

Seven retrieval tests were conducted to study the ability of high-pressure water jets to cut up various waste forms. Water systems tested had pressure ratings of 84, 140, and 703 kg/cm² at flow rates of 15 to 19 liters/min. The 84 and 140 kg/cm² sprays were directed onto the material to be retrieved through five nozzles attached to a concentric ring surrounding the suction nozzle. The spray was directed straight ahead or impinged approximately 15 cm below the suction nozzle. Tests showed that the 140 kg/cm² water spray was incapable of breaking up either frozen salt cake or reacted clay-caustic products. The manually directed, 140 kg/cm² single nozzle easily broke up the clay product at approximately 1250 liters/hr. Inspection of the retrieved clay showed a highly emulsified product which was best described as orange "slop." Approximately 1000 liters/hr of high-pressure water were required to retrieve approximately 1250 liters/hr of clay.

Additional tests were conducted with the 84 kg/cm² water system to study the retrieval of jelly-type salt cake.

It was concluded that the retrieval rate was still slow (less than 2100 liters/hr). It was also apparent that the test should be conducted in a tank somewhat larger than a barrel.

These feasibility tests clearly point out the need to develop hydraulic and mechanical breakup devices. As a follow-up to this conclusion a bid was requested to develop a high-pressure, water-cutting system attachable to a 20-cm suction nozzle. The firm proposed a joint effort with a local industrial cleaning company who would furnish pumping equipment. This proposal is being reviewed.

As a result of this testing, however, pneumatic retrieval does not appear to be a primary retrieval system. It does show a great deal of promise as a retrieval technique to recover liquids and soft sludges from tank bottoms. A conceptual application is shown in Figure 5.

Problem Areas

A cold spell occurring over the weekend froze the salt cake in our 1.8-m diameter tank, thus preventing comprehensive retrieval tests on jelly-type salt cake. A shortage of manpower for this project has limited progress.

Future Work

These feasibility tests clearly point out the need to develop hydraulic and mechanical devices. This work will be carried forward as resources of time, manpower, and funding permit.

Consideration will be given for purchasing pneumatic equipment for cold testing.

FIGURE 5
PNEUMATIC MINING SYSTEM
LOADOUT TO A TRANSFER TANK

Hazards During Salt Cake Retrieval and Handling

(S. L. Sutter, L. C. Schwendiman, and J. Mishima - Battelle Pacific Northwest Laboratories)

Prior Work

This study has been a compilation and assessment of information relevant to developing the capability of predicting the possibility of airborne resuspension and release of radioactive salt wastes from the Tank Farms. This information was formulated into a draft document on potential airborne release of salt wastes during retrieval operations.

The American Society for Testing and Materials (ASTM) Standard Test 241-51, "Abrasion Resistance of Stone Subjected to Foot Traffic," was evaluated and the results submitted as a letter report.

Progress During Report Period

A document, "Potential Salt Cake Airborne Release: Background Information and Proposed Research Related to Retrieval Operations," is nearing completion. Some delay in completing the research plan and schedule outlined in this document has resulted from a recasting of scope and the experimental approach to be taken in the follow-on study.

Tasks have been identified, with the goal of determining the potential of airborne release from routine operations or unanticipated events during retrieval operations. The information to be generated is considered necessary for preparing the environmental report and safety analysis reports needed before full-scale retrieval operations. Because of the developing nature of retrieval options, it will be necessary to work closely with the ARHCO

personnel who are responsible for developing the concepts and characterizing the materials to be removed from the tanks. The variability in composition poses particular problems in designing an experimental study. Information from core drilling and other characterization studies will be used in the airborne release assessment.

Summary

The salt cake release document is nearing completion, with the experimental program section being revised.

Future Work

The salt cake release document will be sent to ARHCO and will be published. The experimental program will be initiated. This program will respond to salt cake technology development and be redirected as the technology indicates.

Close liaison with ARHCO waste retrieval personnel will be maintained through follow-on contacts on a regular frequency and attending pertinent meetings and discussions concerning retrieval concept development.

Materials Flow Properties (C. H. Delegard and N. C. Rodewald)

Objective

Characterization of the flow properties of salt cake, sludge, and other waste forms.

Previous Work

Characterized mother liquor content of salt cake as a function of crystal size, formulated a test plan for

J&J, Inc., to characterize solid flow properties, and prepared and shipped test samples to J&J, Inc.

Progress During Report Period

Viscosity measurements have been made on a variety of agitated simulated salt cake and simulated sludges (Tables I, II, III, and IV) in studies supporting the engineering tests of the agitator-pump.

Tables I and II show the results of these measurements on salt cake. As expected, viscosity for a given composition decreased with increasing temperature. Also as expected, viscosity increased with decreasing terminal liquor content in the salt cake (saturation was set at 30 wt% liquor in the salt cake--75% saturated then means 25% less terminal liquor for a given sodium nitrate solids content). Salt cake samples of the same composition, on cooling, showed increased viscosity as the mixing temperature increased. This thermal hysteresis was especially evident at the 80° C measurements. Fifty percent saturated salt cake models were tested in the same way as the saturated and 75% saturated were, but none had measurably low viscosities. At room temperature the composition of the highest measurable viscosity was found at 67.5% saturation. At 60° C this limit dropped to 57.5% (Table II).

Viscosity measurements were also made on sludge and hydrated ferric hydroxide gels. The five simulated sludges were compounded (Table III) by varying the water content of the sludge while fixing the amounts of salt components. Several important observations were made. Hydrated ferric hydroxide gels appeared to be the primary thickening agents in sludge. Agitation significantly lowered the viscosity of sludge and ferric hydroxide

(Table IV). Both the sludge and ferric hydroxide are highly thixotropic. As expected, lowered water content in the sludge increased viscosity. Curiously, neither simulated sludge nor ferric hydroxide showed a viscosity temperature dependence.

As part of the sludge characterization task, a compilation was made of surface sample observations (Table V).

TABLE I
VISCOSITY VERSUS TEMPERATURE FOR VARIOUS
MODEL SALT CAKE COMPOSITIONS

<u>Salt Cake</u>	<u>Viscosity, g/cm-sec</u>			
	<u>21° C</u>	<u>40° C</u>	<u>60° C</u>	<u>80° C</u>
Saturated	30.	11.	6.5	3.9
Saturated, cooled		13.	16.	21.0
75% saturated	47.	20.	9.8	6.7
75% saturated, cooled		26.	24.	65.
70% saturated	174.			
67.5% saturated	291.			

TABLE II
SLURRYING SIMULATED SALT CAKE AT 60° C

<u>Salt cake, %</u>	<u>Viscosity, g/cm-sec</u>
67.	18.4
60.	36.0
57.5	48.0
55.	Not measurable

TABLE III
COMPOSITION OF SIMULATED WASTE SLUDGE

Salt Components Present in all Sludge Products	Weight, g	H ₂ O Added	Sludge Product
		Weight, g	
NaOH	40.8		
45% NaAlO ₂	55.4		
Fe ₂ (SO ₄) ₃	40.0		
Fe(NO ₃) ₃ ·9H ₂ O	23.8		
SrCO ₃	18.2		
Na ₂ CO ₃	22.0		
NaNO ₂	25.5		
		40.8	A*
		30.0	B
		20.0	C
		10.0	D
		0	E

*Chemical Technology Laboratory composition.

TABLE IV
SLUDGE VISCOSITIES

Sludge Product	Spindle Speed, r/min	Viscosity, g/cm-sec		
		Fresh, 20° C	60° C	Aged*, 20° C
A	60	13.4	13.5	15.8
	30	23.2	21.1	
B	60	16.	21.1	20.5
	30	24.8	36.	
C	60	39.	20.1	22.
	30	55.	34.	
D	60	68.	49.	83.
	30	106.		
E	12	450.	430.	
	6	860.		690.
Fe(OH) ₃ ·nH ₂ O	60	17.7	19.6	19.
	30	33.	32.	36.
	12	67.	72.	80.
	6	117.	93.0	13.8

*Three days.

TABLE V
SUMMARY OF ACTUAL SLUDGE^a OBSERVED MATERIALS PROPERTIES

Tank	Sample Date	Layer, Vol%		Color and Consistency
		Top ^b	Bottom	
102-SX	06/14/74	25	75	Top: Large yellow crystals, H ₂ O-soluble. Bottom: Grayish with very hard chunks.
105-SX	06/19/74	15	85	Top: Dark-gray, soft. Bottom: Dark-brown, hard with large chunks.
107-S	07/01/74			Grayish-brown, large granular crystals.
110-S	08/09/74	10	90	Top: Dark-brown, soft. Bottom: Gray with hard, large white chunks.
111-S	08/02/74	100		Gray--suspect nonrepresentative sample.
110-U	07/03/74	100		Dark-brown, mud-like sludge with large, grayish-brown chunks.
106-C	10/10/74	100		Dark-brown, very soft.
103-AX	09/19/74	100		Dark-brown, very soft.
104-AX	05/10/74			Dark-brown soft solid with hard, small chunks.
102-AX	08/10/75			Reddish-brown, very soft material.
104-A	07/23/74			Quite fluid--similar to heavy cream.

^aSample length ~30.5 cm, sample diameter 3.8 cm.

^bTop layer may be comprised of crystals from post-precipitation and slow growth.

Laboratory experiments show that damp salt cake is likely to release huge quantities of previously nondrainable interstitial liquid during mining. This liquid will separate and have the same curie content as terminal liquor even though salt cake activity is only 5000 times MPC.

Jenike and Johanson, Inc., completed their test on our simulated samples of sludge, salt cake, wet and dried reacted clays, reacted diatomaceous earth and caustic liquid, and trisodium phosphate. These tests have pin-pointed potential solid flow problems with sludge and reacted diatomaceous earth and caustic liquid which both require large hopper openings and steep sides to insure gravity flow. Details of the results will be presented soon in another report.

Problem Areas

We are still seeking a good correlation for interstitial liquid content.

Future Work

Analysis and compilation of surface sample data will continue to be made as the samples become available.

Laboratory work on the effect of porosity on mother liquid content of drained salt cakes will continue.

All sludge data will be compiled according to location by tank and quantity.

The purchase of J&J, Inc., test equipment will be considered since ERDA-RL has approved a consulting contact with this firm.

In Situ Measurements (R. C. Lawrence and R. Landsiedel -
Battelle Pacific Northwest Laboratories)

Objective

Develop probes and make measurements of radiation, hardness, and temperature in several waste tanks.

Prior Work

Prior work consisted of hardness calibrations in various waste forms, test and evaluation of new penetration techniques.

Progress During Report Period

A list of candidate tanks for probing was prepared (Table VI).

Several meetings were held with the director of Tank Farm operations, to discuss Research and Engineering's need for in-tank data and salt cake samples for the Waste Management and Transportation programs.

Problem Areas

Tank Farm operations have high-priority operational problems, making it difficult to schedule a firm date for probe installation or salt cake sampling.

Future Work

Prepare a report summarizing results and continue scheduling negotiations.

TABLE VI
CANDIDATE TANKS FOR PROBING

No. of Probes	Tank	Solid Level	Surface Sample	Waste Type	Remarks
1 to 3	116-TX	19' 9"	Yes	Salt cake, T-evaporator with diatomaceous earth	Salt cake--well pumped.
1	105-S	17' 0"	Yes	Salt cake, S-evaporator	Salt cake--well pumped.
1 from this group	107-SX	3' 9"	No	Air-cooled Redox sludge	Leaker, stabilized.
	108-SX	3' 1"	No	Air-cooled Redox sludge	Leaker, stabilized.
	119-SX	8' 3"	No	Air-cooled Redox sludge	Leaker, stabilized.
	111-SX ^a	4' 3"	No	Air-cooled Redox sludge	Leaker, stabilized.
	112-SX ^a	3' 8"	No	Air-cooled Redox sludge	Leaker, stabilized.
	114-SX ^a	6' 6"	No	Air-cooled Redox sludge	
1 optional	105-BY	19' 7"	No	ITS-1 and ITS-2	Salt--well pumped.
1 optional	106-C ^b	2' 10"	Yes	Sludge	Hot--contains 8×10^6 curies Sr.

^a_q >50,000 Btu/hr after 30 years (ARH-2400).

^b12' 4" liquid level.

WASTE IMMOBILIZATION

ECONOMIC ANALYSIS

Objective

The goal of this study is to define and compare the cost impact of each of the alternative waste solidification strategies. The immediate thrust of activity focuses on definition of capital costs associated with each alternative.

Prior Work

Previous preliminary analyses showed that storage volumes have high cost impact and that further definition of capital cost for anticipated production-scale facilities is necessary to make an economic evaluation.

Progress During Report Period

The Norman Engineering Company of Los Angeles, California, started work to provide scope designs and define plant capital costs for alternative waste immobilization strategies. The alternatives under consideration in this contract are defined schematically in Figure 6. Process flowsheets are based on the estimated waste compositions which are described in Table VII. Each alternative assumes a 15-year processing campaign.

Silicate Melt

Prior laboratory investigations defined potential glass compositions and associated product qualities. From these studies, production of a glass with the following weight ratio has been specified for the economic analysis:

$$\text{Waste/sand/CaO/B}_2\text{O}_3 = 50:40:5:5$$

FIGURE 6
WASTE IMMOBILIZATION PROCESS ALTERNATIVES

TABLE VII
WASTE IMMOBILIZATION FEED COMPOSITIONS

	<u>Salt Cake</u>	<u>Terminal Liquor</u>	<u>Sludge</u>
H ₂ O	11.5 wt%	50.5 wt%	31 wt%
NaOH	2.0 wt%	15.7 wt%	
NaNO ₃	77.0 wt%	16.4 wt%	6 wt%
NaNO ₂	1.0 wt%	9.9 wt%	8 wt%
NaAlO ₂	1.5 wt%	8.2 wt%	10 wt%
Na ₂ CO ₃	6.0 wt%		14 wt%
Na ₂ SO ₄	1.0 wt%		17 wt%
Fe(OH) ₃			11 wt%
Sr(OH) ₂			3 wt%
¹³⁷ Cs (Ci/gal)	0.5	2.0	0.6
⁹⁰ Sr (Ci/gal)	0.03	-	5.3
Density (lb/gal)	11.7	11.7	12.5
Quantity (gal)	38 x 10 ⁶	10 x 10 ⁶	8.6 x 10 ⁶

Norman Engineering was requested to engage a knowledgeable consultant from the glass industry to assist in the specification of flowsheet and equipment for silicate melt plant design. Evaluation of preliminary contacts resulted in the selection of Rhett International of Tukwila, Washington, as the consultant for the glass conversion facilities.

Aqueous Silicate (R. A. Watrous)

Conceptual aqueous silicate flowsheets and equipment sizing and layout definitions were developed as input to the (Norman Engineering) facility design task.

The following objectives were assumed for this flowsheet option:

- Immobilize over a 15-year campaign period all salt cake and terminal liquor by conversion to an aqueous silicate solid contained in steel

canisters.

- Integrate salt cake, terminal liquor processing with concurrent silicate melt processing of sludge.

Figures 7 and 8 present a simplified schematic of this production-scale operation, showing stream flow and equipment sizing information in key areas of the process. Equipment sizing and layout studies have indicated that relative to the Hanford Purex plant the scale of in-cell operations could be comparable or larger:

- Processing tanks of 5,000- to 20,000-gallon capacity will be required.
- An estimated 12 curing or drying ovens (moving belt-type) could be required, each having horizontal belt areas of 4' x 30'.
- Depending on canister size, the frequency of performing the operations of filling, lid-welding, surface decontamination, and transport to vault would be as follows:

<u>Canister</u>	<u>No. per Day</u>
2' diam x 15'	173
8' diam x 10'	16

The practicality for remote operation of the large drying ovens still remains the major uncertainty associated with this "dry" product concept.

FIGURE 7
AQUEOUS SILICATE PROCESS - FEED PREPARATION AND MIXING
 (Production-Scale - Salt Cake + Terminal Liquor)

FIGURE 8

AQUEOUS SILICATE PROCESS - PRODUCT CURING AND PACKAGING
(Production-Scale - Salt Cake + Terminal Liquor)

Radionuclide Removal (J. R. Irish)

Flowsheet conditions for the radionuclide removal plant have been determined. Foundation assumptions for the flowsheet include:

- A 15-year processing campaign.
- A plant on-line efficiency of 70%.
- An average feed rate of all waste forms to the plant independent of instantaneous waste retrieval rates.

Figures 9 and 10 present a simplified schematic of this operation, showing stream flow and equipment size information in key process areas.

Major process operations include removal of ^{90}Sr by scavenging precipitation, removal of ^{137}Cs by absorption on Duolite ion exchange resin followed by subsequent concentration on zeolite resin, and removal of ^{99}Tc by absorption on Dowex exchange resin. Decontaminated chemical waste effluents will undergo moisture removal and solidification by evaporation techniques.

Preliminary plant design estimates indicate facility size will be equal to or larger than Purex-scale operations. Total waste feed rate to the plant is approximately 600 gallons/hour. Process storage tank sizes extend to 13,000 gallons. Thermal concentration, nitric acid recovery, and ammonium solution recycle units are additional process features.

Flowsheet and preliminary equipment requirement information is being sent to Norman Engineering.

FIGURE 9
RADIONUCLIDE REMOVAL PROCESS: SHEET 1

FIGURE 10
RADIONUCLIDE REMOVAL PROCESS: SHEET 2

Evaluation

Definition of capital costs associated with three alternative waste immobilization strategies has been initiated by the Norman Engineering Company of Los Angeles. They have retained Rhett International as a consultant for assistance in flowsheet and equipment specification for the Silicate Melt process. Atlantic Richfield Hanford Company personnel have supplied flowsheet and equipment information to Norman personnel for evaluation of the Aqueous Silicate and Radionuclide Removal processes.

Future Work

Design guidance and support will be given to Norman Engineering personnel as required. Capital cost will be defined and then detailed economic evaluation of waste immobilization strategies will be performed.

INERT CARRIER PROCESS EVALUATION

Objective

Current plans call for cold (nonradioactive) pilot-plant-scale testing of the Aqueous Silicate process as one alternative for immobilizing high-level wastes such as terminal liquor, salt cake, or sludges. For mixing clay with waste solutions, this pilot-plant will test the use of (1) a conventional solids-liquid mechanical mixer; and, possibly (2) the Inert Carrier Mixing process developed by United Technology Center (UTC). The objective of work during the past fiscal year has been to evaluate the UTC mixing process in regard to its being included in the ARHCO cold pilot-plant.

Prior Work

In July 1974 the United Technology Center of Sunnyvale, California, was engaged by ARHCO under Special Agreement SA-179 to conduct mixing tests (clay plus simulated Hanford wastes) using their existing Inert Carrier Process (ICP) pilot equipment. In the first series of tests Normal Paraffin Hydrocarbon (NPH) was used as the inert carrier, and two synthetic waste formulations were tested in combination with two types of clay (calcined kaolin and uncalcined kaolin). By observation the mixing results were mostly favorable, however some NPH carrier was entrained and/or expelled along with the aqueous silicate product. Product samples from the UTC tests were analyzed in ARHCO laboratories; percent NPH diluent entrained in the samples ranged from 1.3 to 3.4.

During October 1974 a second series of pilot-plant tests was defined and performed using the UTC pilot-plant and personnel. Two of the major objectives designed into this second series of mixing tests were:

- Test the use of normal heptane as the carrier in lieu of NPH.
- Test several deentrainment techniques suggested by UTC for lowering the carrier content of clay/waste mixtures.

United Technology Center found no difference in mixing characteristics or carrier transfer with the product between heptane and NPH.

Running the product over a moving belt screen removed most of the free, but none of the entrapped, carrier. It was concluded by UTC that improved removal of carrier would depend upon developing a means of applying heat to take advantage of the relatively high volatility of heptane as

compared with NPH.

Following the October demonstration tests, UTC made a further effort to improve the product-carrier separation. A belt conveyor was fabricated to provide automatic belt drive, vibration, heat, and forced air draft. A preliminary run was made with a clay-caustic solution ratio of 1.0 which obtained very good separation. All free carrier and some entrained carrier were removed. Three clays were then tested and liter-samples of the mixed products shipped to ARHCO's Chemical Technology Laboratory to be examined and analyzed.

At CTL the densities and cesium retention abilities of representative UTC products and their mechanically mixed counterparts were determined as reported in ARH-ST-110 B. The evaluation of carrier-entrainment, however, required a longer time schedule for development of an analytical method and, thus, was not completed until this report period.

A proposal was received from UTC outlining a two-phase program aimed at providing ARHCO with an inert carrier process prototype having a 40-pound clay per minute capacity. Phase I of this proposed program would involve (1) pilot-plant testing aimed at equipment optimization, and (2) preliminary process design. Phase II work would include detailed design, equipment fabrication, and startup (in the ARHCO cold pilot-plant, 202-S Building) support services.

Progress During Report Period

Laboratory evaluation of the UTC product samples was completed. Using these data, a conceptual production-scale process flowsheet was developed for study. As a result of these evaluations it was decided not to pursue further development of the UTC mixing process at this time. The

following Sections give details of these activities.

Evaluation of UTC Carrier Removal Test Samples

(C. H. Delegard)

To provide the samples for carrier entrainment evaluation, UTC conducted a series of test runs with three clays--calcined kaolin, uncalcined kaolin, and uncalcined bentonite. Samples were taken directly from the separator column (which retained the free carrier) and from the end of the carrier removal belt. One series (six samples each) was sealed immediately and was not cured. The second group was cured at 75° C. Each sample in the third group was weighed, given a 20-minute vacuum treatment, weighed, cured at 75° C, and weighed again. The weight losses were reported in ARH-ST-110 B.^[1]

The carrier contents of these samples were analyzed by a gas chromatography method designed by CTL personnel. First, approximately 0.5 g of sample was weighed analytically into a small vial. Then 1,000 μ liters of 6.25×10^{-4} v/v *n*-decane ($C_{10}H_{22}$) in *n*-tridecane ($C_{13}H_{28}$) was pipetted into the vial. Following not less than 20 minutes of violent agitation on a Vortex stirrer, the clay/organic mixes were allowed an additional 24 hours of contact before the organic (now containing the extracted UTC heptane carrier) was decanted. Meanwhile, standards also containing 6.25×10^{-4} v/v *n*-decane in *n*-tridecane with varying concentrations of UTC heptane were made up. The *n*-decane in both the standards and samples served as internal reference for the UTC heptane. Comparison of peak height ratios (UTC heptane/*n*-decane) of the samples versus the standards yielded, on calculation, the carrier content of the UTC products.

Table VIII details the weight percent of carrier left in the various UTC products described above. Both the uncured belt and separator bentonite samples had decantable carrier as received. They were therefore not analyzed as representative portions could not be taken for analysis.

Engineering Analysis (R. A. Watrous)

Data from the CTL analytical work (Table VIII), coupled with the UTC observations¹ of heptane deentrainment equipment led to the conclusions that a volatilization technique is needed to remove entrained heptane in the mixed product to less than 1 wt%. Studies aimed at defining production-scale feasibility of the UTC mixing process were, therefore, modified to include a processing step in which the soft clay/waste mixture would be transported on a heated, vibrating belt while being contacted by a flow of hot gas to vaporize the released heptane bubbles.

Figure 11 shows a production-scale flowsheet (193 tons of product per day) which incorporates the suggested deentrainment equipment as a subsequent processing step to the inert carrier mixing system. One objective of the process is recovery of volatilized heptane such that the total heptane emission rate (to the atmosphere) is less than about 4 lb/min. Thus it appears that a refrigerated condenser (operating at 26° C) or alternately an adsorption system will be required to separate heptane from the carrier gas to the degree necessary.

Another feature of the deentrainment scheme is the use of inert gas (nitrogen) to avoid the hazard of flammable

¹UTC 2515FR, November 1974, "Demonstration of ICP Mixing for Radioactive Waste Fixation," United Technology Center, Sunnyvale, California.

TABLE VIII
TEST RUNS AND PRODUCT TREATMENT FOR UTC HEPTANE DEENTRAIMENT

Clay ^a	Clay/Waste Ratio g/ml	Sample Location	wt% Heptane Carrier Treatment ^b		
			No Cure	75° C Cure	20 min Vacuum and 75° C Cure
Calcined kaolin	0.77	Separator column	4.54	2.31	0.786
		Belt	0.858	0.641	0.478
Kaolin	0.89	Separator column	2.39	1.58	2.00
		Belt	0.608	1.39	0.867
Bentonite	1.0	Separator column	-	1.36	1.14
		Belt	-	0.936	0.899

^aCalcined kaolin = Engelhard's Satintone 1[®].

Kaolin = J. R. Simplot's PAB[®].

Bentonite = Federal Bentonite's Wyo-Bond[®].

^bwt% heptane carrier = $\frac{\text{wt UTC heptane}}{\text{wt sample}} \times 100\%$.

FIGURE 11
UTC INERT CARRIER MIXING PLUS HEPTANE DEENTRAINMENT

heptane-air mixtures. Finally, a major point of uncertainty in this flowsheet is the throughput capability of this vibrating belt technique for heptane deentrainment.

The above items--vibrating belt, inert gas, refrigerated condenser--are all seen as disadvantages associated with the UTC inert carrier mixing process. Unless future testing (not currently planned) proves otherwise, the minor advantages of inert carrier mixing (as compared with mechanical mixing) will probably be outweighed by these disadvantages of system complexity plus higher cost.

Future Work

No further work is planned in the area of evaluating applicability of the UTC inert carrier mixing technique to the Aqueous Silicate process.

AQUEOUS SILICATE PROCESS: LABORATORY STUDIES

Objective

The objective of this task is to develop a low-temperature aqueous process for reacting high-level fission product waste with clay minerals to yield a solid, insoluble product suitable for long-term storage or disposal.

Prior Work

The low temperature reaction of waste solutions with powdered aluminosilicate clays such as bentonite or kaolin produces the mineral cancrinite. Salts, including radioactive ones, are trapped in the cancrinite crystal lattice. The stoichiometry of the reaction requires two moles of NaOH for each mole of cancrinite formed.

The reaction occurs at temperatures as low as 30° C.

However there is a large temperature effect on the rate. The half-times for the reaction of uncalcined kaolin with a standard waste solution at 100°, 75°, and 50° C are, respectively, 1, 10, and 150 hours. The corresponding half-times for the uncalcined bentonite reactions are 1, 9, and 60 hours. Half-times for calcined kaolin and calcined bentonite are about 5 to 30 times less for the uncalcined clays.

The heat of reaction for calcined kaolin is -190.7 ± 3.5 calories per gram compared with -49.5 ± 3.6 calories per gram for uncalcined kaolin. Values for commercial clays vary significantly from the above values depending on the source.

The melting range for cancrinite products is about 900° to 1200° C. Zeolitic water is removed over the range of 100° to 300° C and trapped NaNO_2 and NaNO_3 begin to decompose at about 700° C. A change in crystal structure to nepheline occurs at 530° to 595° C. The thermal conductivity ranges from 0.11 to 0.67 Btu/(hr)(ft²)(°F/ft).

The mechanical strength of cancrinite products can be improved by the addition of binders. Portland cement, lime, sodium silicate-curing agent, and several organic polymers are effective binders.

The quantification of several alternate processing modes has been achieved. The volume and composition of each process stream has been determined.

Bulk leach rates for massive samples range from about 10^{-2} to 10^{-5} g/cm²-day based on geometric surface areas of the samples. Leach rates of products strongly depend on the processing mode used.

The maximum permissible leach rates (MPLR) for solidified radioactive waste forms were calculated based on the

assumption that water, after contacting the solid waste, may safely contain radionuclide concentrations less than or equal to the maximum permissible concentration in an uncontrolled zone.

The effects of water leaching on the surface of massive cancrinite products were studied using the scanning electron microscope (SEM). Results showed leach rates to be dependent on surface porosity.

Application of the Aqueous Silicate process to immobilization of the water-soluble portion of an actual salt cake/sludge mixture was demonstrated; the leach rate of the cancrinite product in deionized water was 1×10^{-4} g/cm²-day (based on ⁹⁰Sr) after 528 hours of leaching.

Ruthenium in terminal liquors is not effectively immobilized by the Aqueous Silicate process. This is not considered a serious problem with respect to long-term immobilization product-forms because of the short half-life (approximately one year) of ¹⁰⁶Ru.

Progress During Report Period

Immobilization of Terminal Liquor (C. H. Delegard)

Results of earlier Aqueous Silicate process tests with synthetic waste have led to definition of the conceptual flowsheet shown in Figure 12. Waste forms with widely varying properties such as leach rate, hardness, volume, and cost can be produced by using the alternatives shown in Figure 12 with various clays as starting materials. The simplest, least expensive route called the Rich Clay process yields a product with relatively high leach rate and low cohesion of the cancrinite particles. This product relies on excess clay to bind the particles together. Leach rates

FIGURE 12
A CONCEPTUAL FLOW DIAGRAM FOR THE CONVERSION OF
RADIOACTIVE WASTES TO ALUMINOSILICATE MINERALS

are improved significantly when using the Lean Clay process alternative, because the actual surface area is reduced by binding the crystals together. Stoichiometric amounts of clay are added in this process so that there is no unreacted clay. The washing step in this alternative is necessary to remove any unreacted salts that might be present in the cancrinite after reaction. These salts are then recycled and reacted with more caustic and clay. In the Clay Calcination process alternative, a clay-salt cake mixture is heated to 700-800° C which converts it to the mineral form nepheline. Leach rates are again improved with this alternative because the actual surface area is reduced.

Recently tests for immobilization of actual terminal liquor solution from Tank 110-BX were performed using the process flowsheet alternatives in Figure 12. J. P. Simplot Company's calcined PAB® kaolin and Interpace Company's mixed kaolin-bentonite Indian Hill® were reacted at a 1.0 g/ml clay/waste ratio for four days at 60° C with 110-BX recycle waste solution. The composition of the 110-BX solution is shown in Table IX. The resulting rich clay products were then subjected to leaching by deionized water at room temperature.

Another set of products was reacted at stoichiometric clay/waste ratios (0.61 g/ml for PAB calcined and 0.66 g/ml for Indian Hill) to form the mineral cancrinite. The products were crushed, washed and dried, and the dried powders were compounded on a 1:1 weight basis with Type III portland cement binder (lean clay alternative). Using a minimum of water, 700 µl per gram of mixture, the cement with clay product aggregates were cured three days at room temperature and 100% relative humidity. These products were cast in 1.5-cm diameter cylindrical forms, and leached as

TABLE IX
COMPOSITION OF TANK 110-BX SOLUTION

Density: 1.4402 g/ml
 Viscosity: 14 to 17 centipoises
 ^{134}Cs : 2.39×10^3 $\mu\text{Ci/liter}$
 ^{137}Cs : 3.45×10^5 $\mu\text{Ci/liter}$

Constituent	Concentration	
	<i>M</i>	wt%
NaOH	3.42	9.5
NaNO ₃	2.84	16.8
NaNO ₂	1.67	8.0
NaAlO ₂	1.99	11.3
Na ₂ CO ₃	8.7×10^{-2}	0.6
Na ₃ PO ₄	7.12×10^{-3}	0.1
Na ₂ SO ₄	6.51×10^{-2}	0.6
H ₂ O		52.9
TOTAL		99.8

described above.

Clay calcination products were prepared as follows: the calcined PAB kaolin and the mixed kaolin-bentonite Indian Hill were reacted as above for the rich clay product with 110-BX full-level waste liquor. Once reacted, pellets of each waste product were fired at 700° C for two hours to form nepheline.

The leach rates of all products (Table X) were based on the geometric surface area and were determined by counting the ^{137}Cs in the leachate. The results in Table X show leach rates for products prepared by the Lean Clay process to be considerably lower than products prepared by the Rich Clay path, especially during the initial (24-hour) stage of leaching. Clay calcination products prepared from calcined PAB kaolin showed even lower leach rates. The Indian Hill clay calcination product, however, shows slightly higher leach rates than its rich clay product. The

TABLE X
LEACH DATA FOR PRODUCTS MADE FROM
VARIOUS FLOWSHEET ALTERNATIVES

<u>Flowsheet Alternative</u>	<u>Leach Rate (g/cm²-day)</u>	
	<u>24 hours</u>	<u>504 hours</u>
Rich Clay Process		
a. PAB, calcined	2×10^{-1}	1×10^{-2}
b. Indian Hill	3×10^{-3}	7×10^{-4}
Lean Clay Process		
a. PAB, calcined	1×10^{-2}	4×10^{-4}
b. Indian Hill	1×10^{-3}	9×10^{-5}
Clay Calcination Process		
a. PAB, calcined	8×10^{-3}	2×10^{-4}
b. Indian Hill	2×10^{-2}	6×10^{-4}

dehydration of the ion-exchanging bentonite structure may account for the higher leach rates for the Indian Hill clay-calcination product. In general the leach trends for products prepared from actual waste correlate quite closely with trends for products prepared from synthetic waste when using the various Aqueous Silicate flowsheet alternatives.

Clay Calcination Alternative (G. S. Barney)

Comparison of the Aqueous Silicate alternative processes (Figure 12) shows that the Clay Calcination process has several important advantages. It can be applied to sludges in addition to salt cake and terminal liquor. The product volume is lower (0.8 x terminal liquor; 1.4 x salt cake) and the thermal and radiolytic stability of the product are improved. These advantages appear to justify further study on this option.

The conceptual flow diagram for the Clay Calcination process is given in Figure 13. There now appear to be

FIGURE 13

CONCEPTUAL FLOW DIAGRAM FOR TWO OPTIONAL
PROCESS ROUTES OF THE CLAY CALCINATION PROCESS

two possible routes--one in which the clay-waste mixture is molded into bricks and fired, and the other in which the loose mixture is fired, then mixed with a binder and formed into bricks. Advantages of the latter route are that the volume of product is less and firing the loose mixture allows facile release of gases (NO_x , H_2O , CO_2) before molding into bricks, thus preventing cracks in the final product. Some cracking results from firing the molded bricks because of internal pressure from release of the gases.

The product of the Clay Calcination process is crystalline nepheline. The stoichiometry of the reaction with salt cake or terminal liquor can be represented by the equation

The reaction with sludge would obviously be much more complex and would probably result in more than one crystalline phase.

Prior work on this process involved firing a cancrinite product at 700 to 900° C to form nepheline. The cancrinite intermediate step is not necessary, however, according to recent results. Therefore an aqueous reaction step is avoided and the solid waste is reacted directly with clay. In order to test Alternate B (Figure 13) of the clay calcination process, synthetic salt cake spiked with cold Sr and Cs was reacted with kaolin and bentonite clays at 900° to 1000° C. The clay and waste were previously mixed thoroughly with an electric blender. The composition of the synthetic salt cake used is shown in Table XI.

The effects of reacting various amounts of synthetic salt cake with the clays on the product crystallinity

TABLE XI
COMPOSITION OF SYNTHETIC SALT CAKE

<u>Component</u>	<u>Percent by Weight</u>
NaNO ₃	60
NaNO ₂	20
Al(OH) ₃	10
NaOH	10

is given in Table XII. The Table shows that increasing the amount of synthetic waste in the clay-waste mixture from 10 to 40% resulted in improved crystallinity of the nepheline product. The theoretical limit for formation of pure nepheline from kaolin is 40% salt cake in the mixture (assuming salt cake to be pure NaNO₃).

TABLE XII
EFFECT OF CLAY/SALT CAKE RATIO ON PRODUCT

<u>Run No.</u>	<u>Clay Type</u>	<u>Salt Cake in Mixture %</u>	<u>Weight Loss %</u>	<u>Product Identity</u>
1	Kaolin	10	21	Poor nepheline
2	Kaolin	20	20	Poor nepheline
3	Kaolin	30	24	Good nepheline
4	Bentonite	10	18	Poor nepheline
5	Bentonite	20	22	Poor nepheline
6	Bentonite	30	22	Good nepheline
7	Bentonite	40	24	Good nepheline
8	Kaolin	40	26	Good nepheline

The compositions of several products are compared with that of pure nepheline in Table XIII. These data show that the composition of Sample 8 is very close to that of pure nepheline, while Samples 1 and 4 are deficient in sodium. Samples 4 and 7 are deficient in aluminum. The compositions of Samples 8 and 7 confirm the theoretical limit of 40 wt% of salt cake in the product. The effect of

TABLE XIII
COMPOSITION OF SEVERAL PRODUCTS
COMPARED WITH PURE NEPHELINE*

<u>Sample No.</u>	<u>N₂O</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>Total</u>
Pure nepheline*	21.81	35.89	42.30	100.0
1	6.37	41.83	51.86	100.1
8	21.64	33.89	40.62	96.2
4	8.54	18.95	56.58	84.1
7	21.95	16.98	44.13	83.1

*Formula is assumed to be NaAlSiO₄.

variable composition on the leach rate will be discussed later.

The volume of the nepheline product (Route B, Figure 13) is significantly less than cancrinite products made from salt cake. The theoretical volume increase is just 45% for salt cake (assuming again pure NaNO₃ as salt cake and pure nepheline as the product). Measured values for products 7 and 8 are 53 and 65%, respectively.

Scanning electron photomicrographs of nepheline products 7 and 8 are shown in Figure 14. Nepheline particles made from bentonite appear to be partially fused, with some smooth melted surfaces apparent. According to the Na₂O-SiO₂-Al₂O₃ phase diagram, the higher silica content of bentonite would indeed result in a lower melting point for the product. The nepheline product from kaolin consists of clusters of very small crystals.

Massive samples were prepared by adding binders to the powdered products, pressing the mixtures into cylindrical shapes, and then allowing the binders to cure. Two binders were studied: ZnO-Na₂SiO₃ mixtures and Type III portland cement. Thirty grams of fired product were mixed with either 4.0 g ZnO + 100 ml 41 Be' Na₂SiO₃ or 15 g

Sample 7 1000X
NEPHELINE FROM BENTONITE

Sample 8 1000X
NEPHELINE FROM KAOLIN

FIGURE 14
SEM PHOTOGRAPHS OF NEPHELINE PRODUCTS

portland cement + 10 ml H₂O. The ZnO-Na₂SiO₃ binder was cured by heating at 200° C for 30 minutes and the cement binder was cured by allowing the mixture to sit in a sealed container for about one week.

The compressive strengths of the massive samples were measured after leaching and the results are given in Table XIV. The nepheline made from kaolin and bound with ZnO-Na₂SiO₃ formed a relatively weak product; whereas nepheline from bentonite with the same binder formed products with compressive strengths comparable to those made with portland cement binder. There appeared to be no trends in compressive strengths of products bound with portland cement.

TABLE XIV
COMPRESSIVE STRENGTH OF MASSIVE SAMPLES

Sample No.	Compressive Strength*, lb/in. ²	
	ZnO-Na ₂ SiO ₃ Binder	Portland Cement Binder
1	-	-
2	-	6,300
3	<200	7,200
4	8,000	5,900
5	2,500	4,100
6	6,200	4,400
7	<200	7,000
8	<200	6,200

*Samples were cylinders 28 mm in diameter x 10 mm long.

The massive samples were leached for 32 days using a leach test procedure which follows the proposed International Atomic Energy Agency (IAEA) method.^[2] These experiments were designed to demonstrate the effects on leaching of (1) the type of clay used to make the nepheline product, (2) the amount of salt cake used, and (3) the type of binder used. Both cesium and strontium were measured in the leachates (the 30.0-g samples contained 0.2 g strontium

and 0.5 g cesium). Leach rates based on cesium are given in Table XV.

Leach rates based on the fraction of Cs leached vary from 3.3×10^{-2} to 7.8×10^{-6} g/cm²-day. Based on the fraction of Sr leached, leach rates are smaller by factors of 1.5 to 10. Each of the three variables studied has an appreciable influence on the leach rate. This can be seen from plots of fraction Cs(Sr) leached after 25 days versus fraction of salt cake waste in the product (Figures 15 and 16). Conclusions which can be drawn from these Figures are:

- Samples prepared with ZnO-Na₂SiO₃ binder have lower leach rates than those with the portland cement binder.
- Nepheline products made from bentonite are less leachable than those made from kaolin.
- Cesium leach rates rise significantly as the fraction of waste in the products becomes greater than 0.3. Strontium leach rates actually decrease with increasing waste content.

Leach rates of products from the Clay Calcination process are significantly lower than for products from either the Lean Clay or Rich Clay processes. This advantage, in addition to those of lower product volume and improved thermal and radiolytic stability, seems to justify additional study of this option.

TABLE XV
LEACH RATES* OF MASSIVE SAMPLES OF CLAY CALCINATION PRODUCTS

Sample No.	Product Formulation			10 ⁴ Leach Rate, g/cm ² -day after			
	Clay Type	% Salt Cake	Binder	1 day	4 days	18 days	32 days
1	Kaolin	10	ZnO-Na ₂ SiO ₃	6.9	6.9	0.74	0.36
2	Kaolin	20	ZnO-Na ₂ SiO ₃	22	16	2.8	1.2
3	Kaolin	30	ZnO-Na ₂ SiO ₃	22	17	3.1	1.2
8	Kaolin	40	ZnO-Na ₂ SiO ₃	164	58	7.4	2.6
4	Bentonite	10	ZnO-Na ₂ SiO ₃	0.70	1.3	0.93	0.71
5	Bentonite	20	ZnO-Na ₂ SiO ₃	0.29	0.20	0.089	0.078
6	Bentonite	30	ZnO-Na ₂ SiO ₃	2.4	3.1	1.7	1.6
7	Bentonite	40	ZnO-Na ₂ SiO ₃	327	110	18	30
1	Kaolin	10	portland cement	132	49	17	11
2	Kaolin	20	portland cement	133	31	9.9	5.8
3	Kaolin	30	portland cement	82	21	5.6	2.5
8	Kaolin	40	portland cement	166	52	7.6	2.8
4	Bentonite	10	portland cement	53	32	4.1	0.66
5	Bentonite	20	portland cement	17	14	5.4	2.5
6	Bentonite	30	portland cement	77	21	2.5	1.8
7	Bentonite	40	portland cement	173	44	18	10

*Based on fraction of cesium leached.

FIGURE 15

EFFECTS OF BINDER, CLAY TYPE, AND WASTE CONTENT
ON THE FRACTION OF CESIUM LEACHED AFTER 25 DAYS

FIGURE 16

EFFECTS OF BINDER, CLAY TYPES, AND WASTE CONTENT
ON THE FRACTION OF STRONTIUM LEACHED AFTER 25 DAYS

Immobilization of Purex Sludge (C. H. Delegard)

Application of the Aqueous Silicate process to immobilization of the water-soluble portion of a salt cake/sludge mixture was described in the previous progress report.^[1] Recently, experiments to immobilize water-insoluble Purex sludge were performed using a procedure similar to the Rich Clay process shown in Figure 12. Purex sludge consists of a mixture of various hydrated metallic oxide precipitates (primarily aluminum and iron) resulting from neutralization of high-level acid waste. The principal insoluble radionuclides associated with the sludge are ^{239}Pu and ^{90}Sr . Water-soluble salts (containing some ^{137}Cs) are also associated with unwashed moist sludge.

Earlier attempts to immobilize sludge with Indian Hill[®] kaolin-bentonite clay (Interpace Corporation) resulted in a crumbly product. It was suspected that this low cohesiveness was a result of insufficient caustic in the sludge to promote complete formation of cancrinite.

In the current experiments, varied amounts of Indian Hill clay, moist Tank 104-A sludge and 50% NaOH solution were mixed using clay/sludge weight ratios of 4:1, 4:3, and 2:3 (Table XVI). The mixtures were cast into cylinders 1 cm high and 1.4 cm in diameter. The castings were reacted for five days at 70° C. The cylindrical products were leached with deionized water at room temperature.

TABLE XVI
FORMULATION OF AQUEOUS SILICATE SLUDGE REACTIONS

<u>Product</u>	<u>Clay Weight, g</u>	<u>Sludge Weight, g</u>	<u>50% NaOH Volume, ml</u>
A	4	1	4
B	4	3	3
C	4	6	2

Surprisingly the leach rates based on ^{137}Cs were similar for all of the products despite the varied clay/sludge ratios; they ranged from 1.5×10^{-5} to 2.9×10^{-5} g/cm²-day after 552 hours of leaching (Table XVII). Leach rates based on ^{90}Sr ranged from 4.6×10^{-6} to 7.5×10^{-6} g/cm²-day; leach rates based on ^{239}Pu ranged from 1.3×10^{-4} to 5.3×10^{-5} g/cm²-day. The plutonium leach data are tentative, however, until alpha energy counting results are obtained.

TABLE XVII
LEACH RATES BASED ON ^{137}Cs , ^{90}Sr , AND ^{239}Pu
FOR AQUEOUS SILICATE SOLIDIFIED SLUDGE PRODUCTS

Element	24 hours		552 hours	
	Leach Rate g/cm ² -day	Fraction Leached	Leach Rate g/cm ² -day	Fraction Leached
A/Cs	1.4×10^{-3}	0.0042	1.6×10^{-5}	0.0074
B/Cs	1.4×10^{-3}	0.0045	2.9×10^{-5}	0.0092
C/Cs	3.5×10^{-4}	0.0012	1.5×10^{-5}	0.0055
A/Sr	1.7×10^{-4}	0.00052	7.5×10^{-6}	0.0033
B/Sr	1.3×10^{-4}	0.00045	5.7×10^{-6}	0.0022
C/Sr	7.0×10^{-5}	0.00023	4.6×10^{-6}	0.0018
A/Pu	3.4×10^{-3}	0.010	2.9×10^{-4}	0.038
B/Pu	2.1×10^{-3}	0.0069	1.3×10^{-4}	0.019
C/Pu	2.2×10^{-3}	0.0074	5.3×10^{-5}	0.012

The leach rates based on strontium and plutonium increase slightly with increasing clay/sludge ratios. The reason for this unexpected trend has not yet been determined. It is also important to note that leach rates based on ^{239}Pu (although data are still preliminary) are higher than rates based on ^{137}Cs or ^{90}Sr . A possible explanation is that plutonium is not trapped by bentonite or cancrinite. Since plutonium is present as an insoluble compound in the sludge, it is possible that it may not participate in an aqueous (silicate) reaction. Instead, fixation of ^{239}Pu could be through mere physical entrapment. Thus the

clay/cancrinite may simply act as a binder to the finely particulate insoluble compound.

The underwater mechanical stability of the products varied depending on the clay/sludge ratio. The product with the highest clay/sludge ratio showed no flaking or fracturing on soaking. Approximately 5 wt% of the product with the lowest clay/sludge ratio became flaky and separated from the casting.

Mechanism of Cesium Entrapment (C. H. Delegard)

In an effort to further understand the nature of cesium's retention in the bentonite/cancrinite reaction, a series of tests were conducted to follow the course of cesium in that reaction.

Two parallel 100° C reaction runs were performed using synthetic terminal liquor. Cesium-137 tracer was added in one run. For both runs reaction times were set at 5, 10, 15, 20, and 30 minutes and at 1, 2, 3, and 24 hours. The reaction solids were filtered, washed, and immediately dried to terminate the reaction. The dried solids were then weighed. The radioactive solids were analyzed for ^{137}Cs and their nonradioactive counterparts were examined for crystallinity using X-ray diffraction techniques. The course of cesium entrapment in the bentonite/cancrinite solids is detailed in Figure 17.

As can be seen in Figure 17, cesium entrapment rapidly reaches a maximum at 15 minutes, declines rapidly, and then reaches a plateau. X-Ray diffraction spectra of the corresponding nonradioactive products showed the steady diminution of the bentonite peaks with the concurrent growth of the cancrinite peaks. Thus the cesium entrapment maximum occurs when the solids are essentially all bentonite. The

cesium entrapment level declines slightly and plateaus as the cancrinite crystallizes.

The weight versus time curve for the solids produced, as shown in Figure 18, increases rapidly for the first several hours and gradually levels out over 24 hours. The weight-time curve is smooth except for a small hesitation at 15 minutes. This hesitation may signal the beginning of cancrinite crystallization. X-Ray diffraction data show that at 15 minutes the first faint emergence of the cancrinite pattern occurs. This observation concurs with earlier observations reported in ARH-ST-110 A.^[3]

SILICATE MELT PROCESS

Objectives

The purpose of this work is to demonstrate and evaluate, on a laboratory-scale, a high-temperature Silicate Melt process for immobilization of high-level radioactive wastes to low-solubility silicate glass or mineral forms.

Increased immobilization of Hanford simulated salt cake waste is a specific objective. Application of the Silicate Melt process to radioactive sludges, contaminated soils, spent cladding hulls, and incinerator ash is also being evaluated.

Prior Work

Hot cell tests have demonstrated that the Silicate Melt process could effectively immobilize several radioactive wastes, including salt cake from Tank 116-TX, Pu-bearing soil from the 216-Z-9 Trench, contaminated soils from near Tanks 106-T and 102-S, Redox neutralized sludge, and incinerator ash. A two-step process for immobilization of spent fuel cladding hulls involving conversion to oxides by

FIGURE 17
CESIUM ENTRAPMENT VERSUS TIME FOR SOLIDS OBTAINED
FROM ALUMINUM REMOVAL USING BENTONITE

FIGURE 18
WEIGHT GAIN VERSUS TIME FOR SOLIDS OBTAINED
FROM ALUMINUM REMOVAL USING BENTONITE

treatment with gaseous HF-O₂ mixtures at 500 to 600° C followed by melting at 1200 to 1400° C with silica to form silicates was partially tested with actual irradiated Zircaloy and stainless steel. In all cases dense silicates of low-water-leachability were produced.

Synthetic salt cake waste was effectively immobilized to a long-term storage form by conversion to a soda-lime or borosilicate glass. Mixtures of 20 to 60 wt% synthetic salt cake, 30 to 70 wt% sea sand (99.7% SiO₂), and 0 to 15 wt% boron trioxide (B₂O₃) or lime (CaO) were melted at 1200 to 1400° C. Leach rates based on cesium of these products (after four days in deionized water at 25° C) ranged from 3.9×10^{-9} to 6.7×10^{-5} g/cm²-day. A plot of leach rate versus percentage of waste in the borosilicate product was a parabola with a minimum rate at about 55 wt% waste. Leach rates of soda-lime glasses were nearly constant for products containing 20 to 60 wt% waste and 10 wt% lime. Highly significant was the fact that the volume of a borosilicate or soda-lime glass containing 50 to 60 wt% salt cake was less than the volume of the original waste. Furthermore, no sacrifice in leach rates occurred for products incorporating 50 to 60 wt% salt cake as compared with those containing 30 to 40 wt% salt cake.

The first application of the Silicate Melt process to immobilization of Hanford incinerated plutonium-bearing ash was demonstrated. The 500-gram charge consisted of 2.2 wt% ash, 5.0 wt% boric oxide (B₂O₃), 10 wt% sodium carbonate (Na₂CO₃), and 82.8 wt% crushed basalt rock. The leach rate, based on ²³⁹Pu, was only 2×10^{-8} g/cm²-day after seven days of leaching.

Progress During Report PeriodCesium Volatility (C. W. Hobbick)

The volatility of ^{137}Cs from Hanford salt cake upon conversion to soda-lime and borosilicate glasses was determined. Earlier^[4] studies showed that from 1 to 5% of the cesium in synthetic salt cake volatilized when 10 to 40 wt% waste was melted with basalt. Addition of boron trioxide (B_2O_3) to such mixtures reduced cesium volatilization to 1% or less.

The experiments with actual salt cake reported here will help provide parameters for operation of a continuous, pilot-scale glass melter. Attempts were made to relate cesium volatility to operating conditions such as charge formulation, furnace temperature, and melting time.

Mixtures of 30 to 50 wt% Tank 105-S salt cake (containing about 50 μCi ^{137}Cs per gram of salt cake) and appropriate amounts of sea sand (99.7% SiO_2) or basalt, B_2O_3 , lime (CaO), and TiO_2 were melted in graphite-clay crucibles by resistance or induction heating techniques. The crucible was housed in a quartz container which was connected to a vacuum-drawn off-gas collection system located outside the furnace. Gases evolved (NO_x , SO_2 , ^{137}Cs , and H_2O) from the charge were drawn, as indicated in Figure 19, through a water-cooled condenser, two dry traps, and two scrubbers filled with distilled water. After reaching the molten state, a static off-gas system consisting of a primary and secondary loop (Figure 20) was used to collect any remaining ^{137}Cs . At the completion of each run the various parts of the gas train were leached with hydrofluoric acid. The leachates were analyzed for ^{137}Cs concentration by gamma energy pulse height methods using a lithium drifted germanium [$\text{Ge}(\text{Li})$] detector.

FIGURE 19
VACUUM DRAWN CESIUM VOLATILITY APPARATUS

FIGURE 20
STATIC CESIUM VOLATILITY APPARATUS

The effect of the time required for melting was determined by heating the mixture from ambient temperature to 1200° C over various time periods ranging from 0.5 minutes (induction heating) to 3.5 hours. In order to determine cesium volatility after reaching the molten state, the furnace temperature was maintained at 1200° C for 26.5 hours. Table XVIII summarizes the experimental conditions and results. Cesium volatility for the formulations tested became substantial only when the ingredients were melted very rapidly. It is surmised that under these conditions insufficient time was allowed for any solid-state reactions to occur between cesium and silica--consequently 14 to 35% of the ^{137}Cs volatilized from the mixtures. There was little discernable difference in ^{137}Cs volatility between samples heated to 1200° C for 30 minutes versus those heated to 1200° C in 3.5 hours.

TABLE XVIII
EFFECT OF MELTING TIME ON ^{137}Cs VOLATILITY

<u>Formulation</u>	<u>wt%</u>	<u>Time Required for Melt</u>	<u>% of Total</u>
ITS waste	30	3.5 hr	4.65
Basalt	60	0.5 hr	1.25
B ₂ O ₃	10	0.5 min	23.85
ITS waste	50	3.5 hr	1.46
Sea sand	40	0.5 hr	1.80
B ₂ O ₃	10	0.5 min	13.56
ITS waste	50	3.5 hr	7.56
Sea sand	45	0.5 hr	6.25
CaO	5	0.5 min	34.85

Of the total ^{137}Cs volatilized, greater than 98% evolved below 1200° C. Less than 1% of the total ^{137}Cs volatilization occurred below 450° C. Greater than one-half of the ^{137}Cs evolved between 450° and 650° C.

The greatest concentrations of volatilized cesium were found in the lid of the reactor vessel which extended outside the furnace and experienced temperatures of 500° to 600° C. Decreasing levels of ^{137}Cs were found from the condenser to the final dry trap (Figure 20).

The effects of variations in the charge formulation are summarized in Table XIX.

TABLE XIX
EFFECT OF CHARGE FORMULATION
ON ^{137}Cs VOLATILITY

Charge Formulation wt%						^{137}Cs Volatility*
Salt Cake	Basalt	Sand	B_2O_3	CaO	TiO_2	
30	70					5.4
30	65		5			3.9
30	60		10			4.7
50		40	10			1.5
50		45		5		7.6
50		40		5	5	4.4

*Melting time (ambient to 1200° C) was 3.5 hr for all runs.

Fewer experiments were run than desired because of the limited quantities of salt cake available. From the limited data, however, the following observations were made:

- The cesium volatility was lowest for the borosilicate formulations even though a greater percentage of salt cake was incorporated than in the basalt formulations. Cesium volatility was highest in the soda-lime formulation.
- The addition of B_2O_3 to formulations containing basalt as the source of silica does not affect cesium volatility. This is in disagreement with previous experiments^[4] with synthetic waste which showed additions of B_2O_3 to reduce

cesium volatility by approximately a factor of 5.

- The addition of TiO_2 to soda-lime formulations resulted in a substantial lowering of the melting temperatures which, in turn, resulted in lower volatility of ^{137}Cs .

In summary, the ^{137}Cs volatilities exhibited by borosilicate and soda-lime formulations are considered within the manageable range for large-scale continuous melters. Under typical operating conditions about 1.5 to 7% in the salt cake will volatilize. Utilization of the "cold cap" melting technique used by Industry (a cap of unmelted ingredients maintained over the melt at all times) could result in even lower volatility. The ability of ^{137}Cs to be precipitated easily on surfaces (below 650°C) is advantageous to recycling the cesium.

Devitrification Studies (A. L. Dressen)

Some of the glasses obtained by solidifying high-level Purex process waste are known to crystallize (devitrify) when stored at high temperatures.^[5] Devitrification is often accompanied by an increase in leach rate of one or more particular elements. Results of earlier scouting studies showed the silicate glasses made by the Silicate Melt process do not devitrify readily.^[4]

Recently more extensive experiments were performed to determine devitrification behavior of the various silicate glass-making formulations under investigation at ARHCO. Glasses were obtained by melting synthetic salt cake with crushed basalt and B_2O_3 , or with silica sand and B_2O_3 or CaO . The resulting melts were heated for a total of two months at both 500° and 700°C to promote devitrification.

The samples were examined after the first month and again after the second month by X-ray diffraction for the presence of crystalline components. The samples were then leached in deionized water. Leach rates of the heated samples were compared with those for samples of the same glasses stored at room temperature.

A summary of the charge compositions and results of the leach tests are given in Tables XX and XXI. The results in Table XX show that heat treatment at 500° C did not cause any of the glasses to devitrify. Leach rates based on cesium for samples stored at 500° C for two months increased from factors of 1.3 to 3.0. Leach rates for these samples when based on Sr were actually improved by the heat treatment in two cases--they increased from factors of 1.2 to 6.5 for the other cases.

All of the glasses made by melting salt cake with basalt crystallized when stored for one month at 700° C. X-Ray diffraction patterns have not been indexed to any specific mineral or compound. Leach rates based on cesium for these products increased from one to almost three orders of magnitude. Leach rates based on strontium remained low--increasing by at most 10 times.

Only one glass made with sand devitrified after two months at 700° C. The leach rate (based on Cs) of this glass increased by about only a factor of three. None of the products made by melting salt cake with sand exhibited more than a 10-fold increase in leach rate based on Cs after storage at 700° C for two months.

Emphasis should be placed on the fact that, because of their low radioisotopic content, center-line temperatures of glasses made with actual salt cake are

TABLE XX
DEVITRIFICATION BEHAVIOR OF GLASSES STORED AT 500° C

Charge Composition, wt%					Leach Rate (96 hr), g/cm ² -day								
Salt Cake	Basalt	Sand	B ₂ O ₃	CaO	State			Based on Cs			Based on Sr		
					Initial	1 Month	2 Months	Initial	1 Month	2 Months	Initial	1 Month	2 Months
30	60		10		G1 ^a	G1 ^a	G1 ^a	1.2 x 10 ⁻⁶	4.4 x 10 ⁻⁵	5.7 x 10 ⁻⁶	2.2 x 10 ⁻⁶	1.1 x 10 ⁻⁵	5.9 x 10 ⁻⁷
40	50		10		G1	G1	G1	8.3 x 10 ⁻⁶	8.6 x 10 ⁻⁶	1.1 x 10 ⁻⁵	2.4 x 10 ⁻⁶	5.5 x 10 ⁻⁶	4.2 x 10 ⁻⁶
40	60				G1	G1	G1	1.2 x 10 ⁻⁶	9.2 x 10 ⁻⁵	b	2.9 x 10 ⁻⁶	4.5 x 10 ⁻⁵	b
40		50	10		G1	G1	G1	2.8 x 10 ⁻⁶	9.5 x 10 ⁻⁷	7.4 x 10 ⁻⁶	4.2 x 10 ⁻⁶	7.9 x 10 ⁻⁷	4.8 x 10 ⁻⁶
40		55		5	G1	G1	G1	5.7 x 10 ⁻⁷	1.0 x 10 ⁻⁵	1.7 x 10 ⁻⁵	9.1 x 10 ⁻⁷	1.1 x 10 ⁻⁶	5.9 x 10 ⁻⁶
40		50		10	G1	G1	G1	8.7 x 10 ⁻⁷	6.8 x 10 ⁻⁷	9.2 x 10 ⁻⁶	1.4 x 10 ⁻⁶	2.9 x 10 ⁻⁶	1.5 x 10 ⁻⁶
50		45		5	G1	G1	G1	1.7 x 10 ⁻⁶	6.0 x 10 ⁻⁷	3.0 x 10 ⁻⁶	3.9 x 10 ⁻⁶	6.7 x 10 ⁻⁷	4.0 x 10 ⁻⁷
50		40		10	G1	G1	G1	4.5 x 10 ⁻⁶	2.0 x 10 ⁻⁶	b	6.8 x 10 ⁻⁶	1.6 x 10 ⁻⁵	b

^aG1 = glassy.
^bNot determined.

TABLE XXI
DEVITRIFICATION BEHAVIOR OF GLASSES STORED AT 700° C

Charge Composition, wt%					Leach Rate (96 hr), g/cm ² -day								
Salt Cake	Basalt	Sand	B ₂ O ₃	CaO	State			Based on Cs			Based on Sr		
					Initial	1 Month	2 Months	Initial	1 Month	2 Months	Initial	1 Month	2 Months
30	60		10		G1 ^a	Crys ^a	Crys ^a	1.2 x 10 ⁻⁶	4.8 x 10 ⁻³	7.3 x 10 ⁻⁴	2.2 x 10 ⁻⁶	1.9 x 10 ⁻⁴	1.3 x 10 ⁻⁵
40	50		10		G1	Crys	Crys	8.3 x 10 ⁻⁶	1.8 x 10 ⁻⁴	6.2 x 10 ⁻⁵	2.4 x 10 ⁻⁶	2.4 x 10 ⁻⁴	4.6 x 10 ⁻⁶
40	60				G1	Crys	Crys	1.2 x 10 ⁻⁶	9.1 x 10 ⁻⁵	4.2 x 10 ⁻⁴	2.9 x 10 ⁻⁶	3.8 x 10 ⁻⁵	3.3 x 10 ⁻⁵
40		50	10		G1	G1	G1	2.8 x 10 ⁻⁶	3.5 x 10 ⁻⁷	5.6 x 10 ⁻⁶	4.2 x 10 ⁻⁶	1.8 x 10 ⁻⁶	6.1 x 10 ⁻⁷
30		55		5	G1	G1	G1	5.7 x 10 ⁻⁷	2.8 x 10 ⁻⁶	1.4 x 10 ⁻⁵	9.1 x 10 ⁻⁷	9.9 x 10 ⁻⁶	2.5 x 10 ⁻⁶
40		50		10	G1	G1	G1	8.7 x 10 ⁻⁷	8.2 x 10 ⁻⁷	5.6 x 10 ⁻⁶	1.4 x 10 ⁻⁶	2.7 x 10 ⁻⁶	9.2 x 10 ⁻⁷
50		45		5	G1	G1	G1	1.7 x 10 ⁻⁶	4.9 x 10 ⁻⁶	1.1 x 10 ⁻⁵	3.9 x 10 ⁻⁶	1.2 x 10 ⁻⁴	6.5 x 10 ⁻⁶
50		40		10	G1	Crys	Crys	4.5 x 10 ⁻⁶	1.5 x 10 ⁻⁶	1.4 x 10 ⁻⁵	6.8 x 10 ⁻⁶	5.6 x 10 ⁻⁶	1.1 x 10 ⁻⁵

^aG1 = glassy; Crys = crystalline.

expected to be only about 23° to 30° C. The storage temperatures used in this study were selected to determine minimum temperatures for crystallization and to evaluate the effect of devitrification on leach behavior.

Effects of Addition of CaO to Soda-Lime-Type Formulations (A. L. Dressen)

Initial studies to evaluate the use of soda-lime-type glass formulations for immobilization of Hanford salt cake were presented in ARH-ST-110 A.^[3] Soda-lime glasses are prepared by melting mixtures of salt cake, sea sand (99.7% SiO₂) and lime (CaO). During the present report period the effect of varying the amounts of CaO added to the formulation on the product leach rates was determined and the results are summarized in Table XXII and Figures 21 and 22.

TABLE XXII
VARIATION OF LEACH RATES WITH CaO ADDITION

Charge Composition			Leach Rate Based on Cs		Leach Rate Based on Sr	
wt%			g/cm ² -day		g/cm ² -day	
Salt Cake	Sand	CaO	24 hr	96 hr	24 hr	96 hr
30	70		7.8 x 10 ⁻⁵	3.1 x 10 ⁻⁵	3.3 x 10 ⁻⁵	2.0 x 10 ⁻⁵
30	65	5	2.3 x 10 ⁻⁵	2.4 x 10 ⁻⁶	6.1 x 10 ⁻⁵	1.7 x 10 ⁻⁵
30	60	10	2.2 x 10 ⁻⁵	4.7 x 10 ⁻⁶	2.3 x 10 ⁻⁵	4.1 x 10 ⁻⁶
30	55	15	2.1 x 10 ⁻⁵	3.0 x 10 ⁻⁶	6.4 x 10 ⁻⁵	2.8 x 10 ⁻⁵
40	60		8.9 x 10 ⁻⁶	1.9 x 10 ⁻⁶	4.4 x 10 ⁻⁶	1.1 x 10 ⁻⁶
40	55	5	2.0 x 10 ⁻⁵	4.0 x 10 ⁻⁶	1.2 x 10 ⁻⁵	2.3 x 10 ⁻⁶
40	50	10	2.2 x 10 ⁻⁶	4.6 x 10 ⁻⁶	1.2 x 10 ⁻⁶	7.2 x 10 ⁻⁶
40	45	15	1.1 x 10 ⁻⁵	2.0 x 10 ⁻⁶	9.2 x 10 ⁻⁵	6.0 x 10 ⁻⁶
50	50		1.7 x 10 ⁻⁵	3.7 x 10 ⁻⁶	2.0 x 10 ⁻⁶	2.0 x 10 ⁻⁷
50	45	5	2.5 x 10 ⁻⁵	3.6 x 10 ⁻⁶	1.1 x 10 ⁻⁵	2.0 x 10 ⁻⁶
50	40	10	8.7 x 10 ⁻⁶	3.8 x 10 ⁻⁶	2.2 x 10 ⁻⁵	1.4 x 10 ⁻⁵
50	35	15	1.9 x 10 ⁻⁵	3.3 x 10 ⁻⁶	7.1 x 10 ⁻⁵	4.4 x 10 ⁻⁵
60	40		2.2 x 10 ⁻⁵	7.7 x 10 ⁻⁶	3.6 x 10 ⁻⁶	1.6 x 10 ⁻⁶
60	35	5	1.0 x 10 ⁻⁵	4.1 x 10 ⁻⁶	2.9 x 10 ⁻⁶	2.7 x 10 ⁻⁶
60	30	10	2.9 x 10 ⁻⁵	1.4 x 10 ⁻⁵	7.9 x 10 ⁻⁵	6.1 x 10 ⁻⁵
60	25	15	8.9 x 10 ⁻⁵	4.1 x 10 ⁻⁵	2.1 x 10 ⁻⁴	6.4 x 10 ⁻⁵

FIGURE 21
VARIATION OF LEACH RATE (BASED ON CESIUM)
WITH CaO ADDITION

FIGURE 22
VARIATION OF LEACH RATE (BASED ON STRONTIUM)
WITH CaO ADDITION

Leach rates based on Cs (96 hours) appear to be independent of the amount of CaO in formulations containing up to 50 wt% salt cake (Figure 21). However addition of 10 to 15 wt% CaO somewhat increases the leach rates of products made with greater than 50 wt% waste. Interestingly, glasses containing 50 wt% salt cake and 0 to 15 wt% CaO exhibit equal leach rates (based on Cs) of 4.0×10^{-6} g/cm²-day.

As much as 100-fold increase in leach rates based on Sr (96 hours) occurs as the amount of CaO added to charges containing 50 wt% salt cake rises from 0 to 15 wt% (Figure 22). Similar behavior is seen for glasses made with other amounts of waste.

Addition of 5 wt% CaO to formulations containing 40 to 60 wt% salt cake produces glasses with fairly constant leach rates of 4.0×10^{-6} and 2.0×10^{-6} g/cm²-day based on Cs and Sr, respectively. However further addition of CaO appears detrimental to the leachability of glasses immobilizing salt cake.

Microstructure and Composition of Silicate Melt
Products Containing Simulated Hanford Waste

(J. L. Daniel, Battelle Pacific Northwest Laboratories)

Specimens of silicate melt glasses containing simulated Hanford waste were studied by microscopy and microprobe methods to determine microstructural and compositional characteristics. The two glass specimens were representative of glasses prepared with Hanford basalt and with sea sand as the source of SiO₂ (Figure 23 and Table XXIII).

FIGURE 23

HALF-SECTIONS OF SILICATE MELTS READY FOR SAMPLING

Upper: Basalt glass, approximate 5.5 cm thick.
Samples were taken from near top, center, and bottom
at side (interface with crucible) and axis.

Lower: Sand glass, about 3 cm thick, after samples
were removed from top and bottom regions along axis.
Two other samples were taken from side near crucible.

TABLE XXIII
NOMINAL COMPOSITION OF SILICATE MELTS
(COMPONENT MATERIALS)

Component	wt%	
	Basalt Glass	Sand Glass
Simulated salt cake waste	30	50
Crushed basalt	60	-
B ₂ O ₃	10	-
Sea sand	-	50

The glass specimens were examined first by optical microscopy at magnifications to 50X to obtain a general picture of homogeneity, possible crystallinity, and the presence of inclusions. The same or nearby areas on the same specimens were examined in considerable detail by the use of the scanning electron microscope at magnifications to 1000X. Concurrent with the scanning electron microscopy, an X-ray microprobe analysis was conducted on selected regions of each specimen for both detailed elemental analysis and mapping of individual elements. The resulting X-ray maps then could be compared directly with electron micrographs of the same regions to determine the physical distribution of the element in question.

The basalt glass was black in color and uniformly glassy throughout. Thin sections of the glass were gray-green by transmitted light. Pores, scattered randomly across all sections (Figure 24), ranged in diameter from about 20 μ m to 1 mm. The highest pore concentration occurred near the top of the casting.

The elemental composition of the basalt glass was very uniform throughout with the exception of small variations in Si content and the presence of metallic iron inclusions. Silicon immediately surrounding the larger pores was

8X

50X

Side of middle section, showing glass/crucible interface.
Metallic (iron) inclusions are common, and porosity
is randomly distributed throughout.

FIGURE 24
BASALT GLASS

in slightly higher concentrations than in the matrix generally (Figure 25). However the differences were estimated to be about 1% or less, and occurred only in the vicinity of the pores.

Bright metallic inclusions, composed primarily of iron with a trace of phosphorus, occurred along the outside edges near the interface with the graphite clay crucible and at the upper surface (Figure 24). The largest inclusions, approximately 1 to 4 mm in diameter, occurred primarily on the sides and top; smaller inclusions, approximately 0.5 mm in diameter, were found along the bottom edges.

No metallic or other inclusions were observed on the interior of the specimen. However, small bright spots approximately 1 μ m in diameter were observed scattered randomly over all polished surfaces and on the as-fractured surfaces as well. X-Ray fluorescence analysis showed no difference between those spots and the surrounding matrix, indicating that the spots were either fragments or a second phase of matrix material or contained only light elements not detectable by X-ray fluorescence methods. The latter possibilities include primarily Na, B, C, and O.

Within the limits of sensitivity of the X-ray fluorescence analyses no systematic or significant variation in the Cs or Sr content was detected relative to location.

The sand glass casting was amber in color and uniformly glassy throughout. Pores averaged somewhat smaller in size and fewer in number than in the basalt glass. Most of the largest pores are along the edges of the crucible (Figure 26).

The primary difference in composition of this glass compared with the basalt glass is the absence of iron

100X

A. Interior region about 3/4 mm from crucible interface.

100X

B. Silicon X-ray map of A; Si is slightly higher concentrations around pores.

FIGURE 25
BASALT GLASS

8X

50X

FIGURE 26
SAND GLASS, POLISHED SECTION OF BOTTOM REGION OF CASTING

and the very low concentration of calcium--both of which are among the main constituents of the basalt. Also missing in the sand glass are the low- or trace-quantities of Ti, Mn, P, and S, presumably also constituents of the basalt raw material. The Cs concentration in the sand glass appears to be slightly higher than was detected in the basalt glass.

No metallic deposits or inclusions were found in the sand glass, consistent with the absence of iron in the sand glass. No detectable variation in composition was detected from one location to another in this glass [e.g., Al, Cs, (Figure 27)]. As in the basalt glass, the sand glass also contained a random distribution of the small ($\sim 1 \mu\text{m}$) bright spots whose compositions appear to be similar to that of the matrix or which contain only light elements which cannot be detected by X-ray fluorescence techniques.

It can be concluded that the sand glass is slightly more uniform in composition and microstructure than the basalt glass because of the absence of contributions of the impurities from the basalt. Except for the metallic iron inclusions found in the basalt glass, nothing was noted in either microstructure or microcomposition to indicate a significant lack of homogeneity either in thickness or on a horizontal plane.

A. Aluminum

100X

B. Cesium

100X

FIGURE 27

SAND GLASS, TYPICAL X-RAY MAPS. ALL COMPONENTS ARE UNIFORMLY DISTRIBUTED.

Silicate Melt Pilot-Plant Development (D. J. Bradley,
H. H. Irby, and J. D. Kaser - Battelle Pacific North-
west Laboratories)

Objective

This engineering task is intended to demonstrate the feasibility of the Silicate Melt process on a pilot-plant scale, develop suitable process equipment and systems, and obtain scale-up and design data.

Prior Work

After selection of the glass melter design, contacts were made with vendors to select refractories for melter construction. Monofrax K-3[®] was chosen as the glass contact refractory, TZB Zircon[®] as secondary paving material. The remainder of the refractories will be K-23, K-26, and K-28 insulating firebrick from Babcock and Wilcox and Superduty[®] firebrick from Banner.

An analysis was completed of the electrical resistivities of three simulated waste glasses. From this study, specifications for the melter power supply system were to be derived.

Progress During Report Period

As a result of the electrical conductivity analysis performed on three simulated Hanford waste glasses,^[1] the design specifications for the power supply system of the glass melter were completed.

The system consists of three separate power supplies. They are silicon controlled rectifier (SCR) power controller-types, controlling the power to the 480 volt tapped primary of the step-down power transformer. Tap

switches on the primary allow changes in secondary voltage in 20 volt steps. Voltage and current on the primary is only indicated; while voltage, current, and kilowatts on the secondary are indicated and recorded.

The SCR power controller is controlled by a kilowatt controller which operates as a closed loop controller. Output power is transduced and returned as feedback information to the kilowatt controller which will automatically adjust power to the load to agree with the present level of the setpoint.

Load capabilities of the three supplies are as follows:

- Main or starter electrodes: 150 kVA.
Volts: 80 V to 480 V in 20 volt steps.
Current: 312.5 to 1875 amperes.
- Riser and forehearth electrodes: 37.5 kVA.
Volts: 140 V to 480 V in 20 volt steps.
Current: 78 to 268 amperes.

The off-gas system for the melter has been designed and all the equipment is in order. This system is sketched in Figure 28. There will be two different operational modes in the off-gas system. The first is that which will handle gas-fired startup. Approximately 10^6 Btu/hr will be required during startup. This will be provided by the combustion of propane with air. The heat of combustion for propane (C_3H_8) is 19,774 Btu/hr, which gives a requirement of 51 lb/hr of propane. The off-gas that results from the use of 10% excess air for complete combustion is given in Table XXIV.

FIGURE 28
OFF-GAS SYSTEM FOR SILICATE MELT PROCESS PILOT-PLANT

TABLE XXIV
STARTUP OFF-GAS DESCRIPTION

Product	lb/hr	ft ³ /hr at	
		1832° F (1000° C)	212° F (100° C)
a. N ₂	761	45,497	13,331
b. CO ₂	152	5,783	1,694
c. H ₂ O	83	7,719	2,262
d. O ₂	18	961	282
	1,104	59,960	17,569
	ft ³ /min	999	293

These gases, because of their large volume, will be handled by a water-fed Venturi scrubber and separator supplied by a 12" conduit system. The balance of the piping will be 4".

The second method of operation will be when the melter is in the all-electric melting mode. During this operation mode the off-gas will be handled by the packed scrubber. The actual melter off-gas rate is expected to be approximately 17 ft³/min at 800° F (estimated exit temperature from melter) and 8 ft³/min at 100° F, when in this mode.

The off-gas system blower is capable of creating a vacuum of 10" water. The pressure drop in the piping system was calculated to insure that this blower would handle the estimated load.

Pressure taps are located at six points on the off-gas system for the purpose of regulating and monitoring the operating pressures in the system. Manometers are used to indicate the operating pressures on the hood, main melter cavity, forehearth, and inlet to exhaust blower. Manual valves are used to adjust the pressures on the main

melter cavity, forehearth, and hood. A manually adjusted damper is used on the exhaust blower inlet to keep the pressure less than the design pressure. Pressures across the packed scrubber inlet and outlet and between packed scrubber and atmosphere are electronically detected and recorded. The scrubber recirculation tank is equipped with specific gravity and weight factor services.

Recent discussions with Penberthy Electromelt, Inc., Seattle, Washington, and a visit to Evans Products Company, Corvallis, Oregon, by PNL personnel have resulted in at least two design changes to the melter.

The first change calls for removal of 4" of insulating firebrick from the Monofrax K-3 riser block-forehearth channel interface. Also a cooling yoke will be added at the above interface to provide extra cooling. This will insure a frozen glass seal between melter and forehearth and therefore prevent glass leakage.

Another change in the present design concerns the water-filled catch basin located underneath the melter to retain glass in event of a melter bottom failure. It is not a recommended practice to use water in this basin. Instead a basin lined with insulating firebrick is the approach taken by the glass industry. This provides the advantages of easier removal of glass and no steam formation in case a spill does occur, easier maintenance and general housekeeping, and far better access to the melter bottom area.

A possible design change will be to use 2" instead of 1.25" molybdenum electrodes. This would give much less electrode wear (due to lower current density) and allow greater operating flexibility. The cost-benefit aspects of this change are currently being examined.

Future Work

A run plan for the melter will be drawn up and approved and feed chemicals will be ordered. A system for handling and mixing the raw batch chemicals for the melter will be finalized. A safe operating procedure for the Silicate Melt process melter will be drafted and approved.

RADIONUCLIDE REMOVAL STUDIES (SALT CAKE VOLUME REDUCTION)

(W. W. Schulz)

Objectives

When the present Hanford Waste Management Program is completed approximately 140 million liters of solid salt cake will be stored in underground mild steel tanks. This material will contain at most only a few hundred milligrams of long-lived ($t_{1/2} > 25$ y) radionuclides. Some 30 to 40 million liters of terminal liquor will also have accumulated when currently scheduled waste evaporation operations have been completed. This latter high-caustic waste contains substantial concentrations of Cs and, as yet, undefined small amounts of other radionuclides (e.g., ^{90}Sr , ^{99}Tc , ^{129}I , actinides, etc.). The objective of these studies is to devise, demonstrate, and evaluate chemical procedures for removing all long-lived radionuclides from these wastes. Motivation to realize this objective is provided by the strong economic incentive to reduce by a factor of 10 to 100 (hopefully more) the volume of such waste requiring expensive immobilization and/or storage for its safe long-term containment.

Prior Work

Radiocesium can be effectively removed from salt cake solutions by precipitation of $\text{Cs}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ at pH 8-10. A major disadvantage of this method of removing cesium is that large amounts of aluminum precipitate when the salt cake solution is adjusted to pH < 11 . A much more acceptable way of removing ^{137}Cs from both salt cake solutions and terminal liquors is to sorb it on Duolite ARC 359[®] resin, a phenol-based exchanger made by the Diamond Shamrock Company. The ^{137}Cs content of actual salt cake solution in one test was reduced from 8400 $\mu\text{Ci/liter}$ to ~ 0.13 $\mu\text{Ci/liter}$ by passage through a series of Duolite ARC 359 resin beds.

Various precipitation procedures for removal of radio-strontium from salt cake solutions were scouted. Tests with synthetic salt cake solutions spiked with ^{85}Sr showed that effective strontium removal can be accomplished by precipitation of $\text{Ca}_3(\text{PO}_4)_2$, $\text{Sr}_3(\text{PO}_4)_2$, or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; a series of experiments to determine effects of solution pH and composition on removal of strontium by these precipitates was begun.

Sorption of strontium on a bed of "Strontium Phosphate"-form ion exchange resin was also briefly studied with generally encouraging results. This exchanger was prepared by passing solutions of H_3PO_4 and $\text{Sr}(\text{NO}_3)_2$ over a bed of Dowex MSA-1[®] (Dow Chemical Company) macroreticular strong-base resin.

Discussion

Introduction

Considerable progress was made during the quarter toward formulating and testing integrated schemes for

removing long-lived radionuclides from Hanford salt cake solutions and terminal liquors. Reported here are data relating to Duolite ARC 359 resin uptake of ^{137}Cs and ^{90}Sr from both synthetic and actual salt cake solutions and to scavenging of ^{90}Sr from such solutions by precipitation of hydrated iron oxides, calcium phosphate, or inert strontium phosphate. A new analytical procedure for determining low levels (0.001 to 0.01 $\mu\text{Ci/liter}$) of ^{90}Sr in salt cake solutions is also described.

Conceptual Radionuclide Removal Scheme

Figure 29 depicts a conceptual approach for reducing by a factor of 10 or more the volume of Hanford high-level waste which must be immobilized and/or stored by expensive means. The approach shown in Figure 29 is patterned closely after that presently being followed at the Savannah River site. The potential benefits of removing radionuclides from Hanford waste were recognized, however, as early as 1972.

The overall objective of the Radionuclide Removal (Volume Reduction) approach is to partition Hanford wastes into two fractions: (1) a large volume of decontaminated waste which can be safely and adequately contained in a relatively inexpensive storage mode and (2) a small volume of high-level waste requiring more expensive immobilization and storage procedures. To achieve these objectives the scheme shown in Figure 29 involves:

1. Treatment of salt cake-sludge mixtures with water to dissolve the salt cake part.
2. Centrifugation-filtration of the resulting mixture to separate the highly radioactive

FIGURE 29
CONCEPTUAL SCHEME FOR REMOVAL OF RADIONUCLIDES FROM
HANFORD HIGH-LEVEL WASTE

sludge from the less-active salt cake solution.

3. Removal of all long-lived (>25 year-half-life) radionuclides from salt cake solutions, terminal liquors, and mixtures thereof by means of well-known ion exchange and/or precipitation techniques.
4. Solidification and disposal (storage) of the decontaminated liquor.
5. Combination of the sludge and isolated fission products, drying, and immobilization-storage as a high-level waste.

Simple physical separation of the sludge from the dissolved salt cake will separate the waste mixture into an actinide-containing fraction and, hopefully, a non-actinide (<10 nCi/gram) waste or at least one that can be made so by subsequent ion exchange and/or precipitation techniques.

Cost-benefit and other studies are needed to establish which radionuclides require removal and to what level. We know that ^{137}Cs and ^{90}Sr should be removed from salt cake solutions and that ^{137}Cs and, very likely, ^{99}Tc should be removed from terminal liquors. Tentatively, our goal is to devise procedures for reducing the concentration of all long-lived radionuclides to the maximum permissible concentration (MPC_w) stated in 10 CFR 20 for these radionuclides in an insoluble form in water in a controlled zone. More stringent removal criteria may be desirable and may be defined later.

Cost-benefit studies are also needed to define the optimum method of disposal of decontaminated salt cake solutions and terminal liquors. We envision that, if

adequately freed of long-lived radionuclides, such solutions might simply be evaporated (vacuum crystallizer, wiped film evaporators, even solar ponds) and stored as a chemical waste. Alternatively, it may be desirable to immobilize the decontaminated solutions by a simplified, inexpensive modification of the Aqueous Silicate process and store them in existing tanks as a very low-level radioactive waste.

Analytical data obtained both here and at Savannah River demonstrates that 99+% of the plutonium in Hanford waste is associated with the sludge. Our conceptual Radionuclide Removal plan (Figure 29) involves laboratory and engineering studies to determine technical feasibility and economic benefits of removing actinides from the sludge fraction.

Laboratory studies will also be performed to determine applicability of the Silicate Melt process to immobilization of Hanford sludges. Such studies will address themselves not only to immobilization of sludges but also to mixtures of sludge and long-lived fission products removed from salt cakes and/or terminal liquors. We also plan to determine applicability of low-temperature processes (e.g., Aqueous Silicate, Cement, etc.) to immobilization of sludges and, possibly, aqueous solutions thereof.

Duolite ARC 359 Resin Sorption of Cesium and Strontium

The process (cf. Figure 29) presently favored for removal of long-lived radionuclides from salt cake solutions, terminal liquors, and mixtures thereof involves sorption of radiocesium on beds of Duolite ARC 359 resin. Proper design of these resin beds and specification of feed compositions requires knowledge of the equilibrium distribution of cesium as a function of aqueous phase composition

and, likely, temperature. Equilibrium cesium distribution ratio data obtained to date with Na-form Duolite ARC 359 resin and both NaNO_3 -NaOH and synthetic salt cake solutions are collected in Table XXV and plotted in Figures 30 and 31. As anticipated, equilibrium uptake of cesium by Duolite ARC 359 resin is determined primarily by the hydroxide and total sodium ion content of the equilibrating solution and is independent, or almost so, on the nature and concentration of other anions. This behavior means that for a good first approximation we can use distribution data obtained with simple NaOH- NaNO_3 solutions to design resin beds and specify feed composition and operating conditions.

The distribution ratio data in Table XXV show that Duolite ARC 359 resin removes ^{137}Cs more efficiently from dilute salt cake solutions than from concentrated solutions. To minimize the volume of solution which must be processed for removal of radioisotopes, however, it is desirable to operate with concentrated solution. A suitable compromise, perhaps, is to use 7-8M Na^+ solutions containing 2-3M OH^- .

Higgins and Phillippi^[6] in 1963 at the Oak Ridge National Laboratory studied use of Duolite C-3 resin for removal of ^{137}Cs , ^{90}Sr , and rare earths from synthetic low-level alkaline wastes of nearly the same compositions as dissolved Hanford salt cake. [Duolite ARC 359 resin is an improved version of Duolite C-3 resin.] Higgins and Phillippi reported the Duolite C-3 resin to be quite efficient in removing ^{90}Sr and rare earths as well ^{137}Cs , of course, from such wastes.

Our initial results (Table XXVI and Figure 31) confirm that Duolite ARC 359 resin does indeed sorb strontium although not quite as strongly as cesium, from alkaline salt solutions. Just as observed for cesium, strontium

TABLE XXV

SORPTION OF Cs BY DUOLITE ARC 359 RESIN -
DISTRIBUTION RATIOS

Ten-ml portion of each listed solution contacted 48 hr at 25° C with 0.25 g of air-dried Na-form Duolite ARC 359 resin

Aqueous Phase Composition^a

Total Sodium	OH ⁻	Cs
<i>M</i>	<i>M</i>	<i>K_d</i> ^d
7.13 ^b	1.0	78.2
5.40 ^b	1.0	101.
4.60 ^b	1.0	116.
3.42 ^b	0.99	184.
2.52 ^b	0.96	253.
2.60 ^b	0.51	169.
3.1 ^c	1.0	180.
3.9 ^c	1.0	129.
6.0 ^c	1.0	78.4
7.0 ^c	1.0	71.2
7.0 ^c	0.5	52.4
7.0 ^c	2.0	104.
7.0 ^c	3.0	157.
7.0 ^c	4.0	269.
4.0	4.0	525.

^aAll solutions contained ~2300 $\mu\text{Ci/liter}$ ^{137}Cs .

^bSolutions prepared by diluting appropriate amounts of synthetic salt cake solution of the composition 6.36M NaNO₃-0.09M NaOH-0.074M Na₂CO₃-0.028M NaNO₂-0.026M NaAlO₂-0.0087M Na₂SO₄-0.0025M Na₃PO₄ to 500 ml with water and 23.2 ml of 20.2M NaOH.

^cSolutions contained only NaNO₃ and NaOH.

^d $K_d = \mu\text{Ci } ^{137}\text{Cs/g resin} \div \mu\text{Ci } ^{137}\text{Cs/ml solution.}$

FIGURE 30

BATCH DISTRIBUTION DATA FOR UPTAKE OF RADIOCESIUM
AND RADIOSTRONTIUM BY DUOLITE ARC 359 RESIN

FIGURE 31

VARIATIONS OF $C_s K_d$ WITH FEED HYDROXIDE CONCENTRATIONS

TABLE XXVI
SORPTION OF Sr BY DUOLITE ARC 359 RESIN -
DISTRIBUTION RATIOS

Ten-ml portions of each listed solution contacted 48 hr at 25° C with 0.25 g of air-dried Na-form Duolite ARC 359 resin

Aqueous Phase Composition ^a		
Total Sodium	OH ⁻	Sr
<u>M</u>	<u>M</u>	<u>K_d^b</u>
7.17 ^c	1.02	47.8
5.53 ^c	0.99	50.6
4.61 ^c	0.99	71.2
3.78 ^c	0.94	85.6
2.50 ^c	0.96	109.
4.00 ^d	1.0	103.
3.18 ^d	1.0	112.

^aAll solutions contained 15 Ci/liter Sr.

^b $K_d = \mu\text{Ci } ^{85}\text{Sr/g resin} \div \mu\text{Ci } ^{85}\text{Sr/ml solution.}$

^cSolutions prepared by diluting appropriate amounts of synthetic salt cake solution of composition listed in Table XXV with water and 23.2 ml of 20.2M NaOH.

^dSolutions contained only NaNO₃ and NaOH.

distribution ratios are strongly inversely dependent upon the total sodium concentration of the equilibrating solution; dependency of strontium distribution ratios upon the hydroxide concentration of the waste solution has not yet been determined. It also appears, contrary to the behavior of cesium, that strontium sorbs slightly more strongly onto the Duolite resin from NaNO₃-NaOH solutions than from synthetic salt cake solutions of the same hydroxide and total sodium concentrations. More data are required, however, to substantiate or refute this latter observation.

In addition to obtaining equilibrium distribution

ratios we also have performed column tests to study uptake of cesium and strontium by Duolite ARC 359 resin. These tests (Figures 32 and 33) were made with synthetic salt cake solution (Table XXV) spiked with ^{137}Cs or ^{90}Sr and diluted with water and NaOH to 1M NaOH and indicated total sodium concentrations. Not surprisingly, breakthrough behavior of both cesium and strontium followed that predicted from distribution data listed in Tables XXV and XXVI. The slope of breakthrough curves such as those plotted in Figures 32 and 33 is known to be a measure of process kinetics and to be a complex function of the ion exchanger properties and operating conditions. Other than to note the absence of any peculiarities in the shape of the breakthrough curves, no attempt is made here to calculate slopes or to derive quantitative information about the kinetics of uptake of cesium and strontium by Duolite ARC 359 resin. Such information will be obtained when flowsheet conditions have been better defined.

Scavenging of Strontium from Synthetic Salt Cake Solution

The bulk (>90%) of the ^{90}Sr in the mixture of sludge-salt cake stored in underground tanks is associated with the sludge. However when such mixtures are treated with water, the ^{90}Sr in the salt cake and probably part of that in the sludge dissolves.

We are investigating both precipitation and ion exchange methods for removing ^{90}Sr from salt cake solution. A comprehensive set of experiments to study effects of salt cake NaOH, Na_2CO_3 , and Na_3PO_4 concentrations upon scavenging of ^{90}Sr by precipitates of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Sr}_3(\text{PO}_4)_2$, and $\text{Ca}_3(\text{PO}_4)_2$ is approximately 90% complete. These experiments

FIGURE 32

SORPTION OF ^{137}Cs ON DUOLITE ARC 359 RESIN--
 BREAKTHROUGH BEHAVIOR AS A FUNCTION
 OF FEED SODIUM CONCENTRATION

FIGURE 33

SORPTION OF Sr ON DUOLITE ARC 359 RESIN--
 BREAKTHROUGH BEHAVIOR AS A FUNCTION
 OF FEED SODIUM CONCENTRATION

are being performed with synthetic salt cake solutions spiked with ^{85}Sr ; principal conclusions derived from these experiments will subsequently be verified in tests with actual salt cake solutions.

Earlier^[1] data obtained with synthetic salt cake solutions adjusted to pH's in the range 10 to 12.8 showed that inert $\text{Sr}_3(\text{PO}_4)_2$ precipitates scavenge radiostrontium more efficiently than do either $\text{Ca}_3(\text{PO}_4)_2$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ precipitates. At 1.0M NaOH (Table XXVII), however, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ scavenges strontium slightly more efficiently than does $\text{Sr}_3(\text{PO}_4)_2$. Comparison of the data in Table XXVII with the earlier results also shows that all three precipitates scavenged more radiostrontium from pH 12.8 salt cake solution than from salt cake solution adjusted to 1M NaOH.

TABLE XXVII
SCAVENGING OF ^{85}Sr FROM SYNTHETIC
SALT CAKE SOLUTION

Conditions: 30-ml portions of synthetic salt cake solution, traced with ^{85}Sr , adjusted to indicated concentrations of $\text{Fe}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, or $\text{Ca}(\text{NO}_3)_2$, stirred 30 min at $\sim 25^\circ \text{C}$, and centrifuged.

Scavenging Agent Concentration <i>M</i> ^a	$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$		$\text{Sr}_2(\text{PO}_4)_2$		$\text{Ca}_3(\text{PO}_4)_2$	
	Sr	Solids ^b	Sr	Solids ^b	Sr	Solids ^b
	DF	vol, ml	DF	vol, ml	DF	vol, ml
0.029	139	1.5	110	1.5	58	1.4
0.015	91	1.0	57	0.8	32	0.7
0.0075	54	0.7	36	0.6	30	0.3
0.0037	35	0.5	16	0.3	29	0.3

^aSynthetic salt cake solution: 6M NaNO_3 -0.1M NaNO_2 -0.04M Na_2SO_4 -0.025M Na_3PO_4 -1M NaOH.

^bCentrifuged wet volume.

We recognize that inclusion of a scavenging step in the overall radionuclide removal flowsheet has both some advantages and some disadvantages. Such a scavenging step provides not only a way of removing the bulk of the ^{90}Sr from the salt cake solution but may also provide a valuable and desirable way of removing other long-lived radionuclides, particularly actinides. Precipitation of $\text{Sr}_3(\text{PO}_4)_2$ prior to separation of the sludge from the salt cake solution may greatly aid centrifugation of the finely divided sludge.

Disadvantages to a headend (or, possibly, tailend) scavenging step include generation of more radioactive solids requiring immobilization. Admixture of sludge with inert $\text{Sr}_3(\text{PO}_4)_2$ may produce a solid not amenable to incorporation in glass and/or concrete. Scavenging is basically a batch process whose use may make for unwieldy time cycles.

For the present we plan to continue development of scavenging procedures. We also expect, however, to continue our studies of sorbents (*e.g.*, "strontium phosphate" anion exchange resin, Sandia Laboratories' titanate exchanger, etc.) suitable for removal of strontium and other multivalent cations from salt cake solutions.

Improved ^{90}Sr Analytical Method

As stated in the last quarterly report,^[1] attempts to determine the efficiency of various scavenging and sorption techniques for removing ^{90}Sr from actual waste solutions have been largely frustrated by the inadequacy of the presently available (at ARHCO) methods for determining low ^{90}Sr concentration. We have now completed development of what appears to be a satisfactory method for analyzing for small concentrations (0.01-0.1 $\mu\text{Ci/liter}$) of ^{90}Sr in

salt cake solutions and terminal liquor.

The new Sr analytical procedure involves:

- a. *Bis*(2-ethyhexyl)phosphoric acid (HDEHP) extraction of ^{90}Sr from a pH 4.5 sodium acetate buffer solution containing diethylenetriaminepentaacetic acid (DTPA) to complex and prevent extraction of inert and radioactive contaminants including ^{106}Ru , ^{90}Y , and rare earths.
- b. The HDEHP extract is then scrubbed three times with fresh one-fifth volume portions of 0.75M hydroxyacetic acid-0.035M NaOH-0.005M ethylenediaminetetraacetate to remove ^{137}Cs and other coextracted impurities.
- c. Following the scrub steps, ^{90}Sr in the HDEHP phase is stripped into a 1M HNO_3 solution.
- d. All the HNO_3 strip solution is diluted with pH 10 NH_4Cl solution, and the pH adjusted, if necessary, to pH 10. Strontium-90 is then extracted into a TTA (thenoyltrifluoroacetone)-TBP solution.
- e. Duplicate 2-ml samples of the TTA-TBP extract are pipetted onto stainless steel beta dishes, dried under a heat lamp, flamed, and beta-counted for 20 minutes. These mounts are also gamma-counted [NaI(Tl)] and any gamma correction is subtracted from the beta count.

Parallel samples spiked with a known amount of gamma-emitting ^{85}Sr are carried through the entire procedure to determine ^{90}Sr recovery. Recoveries typically are in the 50 to 60% range.

This analytical procedure has been applied with good success to actual salt solutions containing from 0.01 to 16 $\mu\text{Ci/liter}$ ^{90}Sr and from <3 to 10,000 $\mu\text{Ci/liter}$ ^{137}Cs and 10 to 100 $\mu\text{Ci/liter}$ ^{106}Ru . In all instances the final mounts for beta-counting have been free of gamma emitters. Tests with synthetic solution spiked with ^{88}Y and ^{144}Ce indicate this procedure provides good decontamination from radioyttrium and radiocerium.

Flowsheet Tests with Actual Salt Cake Solution

In addition to resin and precipitation tests with synthetic salt cake solutions we are also testing various parts of the radionuclide removal flowsheet with actual salt cake solutions and terminal liquors as these become available to us.

Strontium-90 Scavenging Tests

Results of tests in which $\text{Sr}_3(\text{PO}_4)_2$ was precipitated from solutions obtained by dissolution of salt cake from the 105-S and 108-S Tanks are presented in Table XXVIII. Portions of these salt cakes were dissolved in water using a salt cake/water ratio of 0.66 g/ml. Portions of the resulting salt cake solutions containing $\sim 0.1M$ NaOH and $10^{-3}M$ PO_4^{3-} were butted to about $1M$ NaOH and $0.025M$ PO_4^{3-} . Subsequently, varying amounts of $1.5M$ $\text{Sr}(\text{NO}_3)_2$ solution were added; the resulting precipitates were digested, with stirring, for 60 minutes at 25°C and then centrifuged. Strontium-90 in centrifugates was determined by the analytical procedure described earlier. Tests with the 105-S salt cake solution were performed with solution previously freed of sludge. Both tests with the 108-S solution were made by precipitating $\text{Sr}_3(\text{PO}_4)_2$ before centrifugation of the sludge.

TABLE XXVIII
 $\text{Sr}_3(\text{PO}_4)_2$ SCAVENGING OF ^{90}Sr FROM ACTUAL SALT CAKE SOLUTION

Salt Cake Solution		$\text{Sr}(\text{NO}_3)_3$ <i>M</i>	Sr, $\mu\text{Ci/liter}$ Scavenged Solution	Sr, DF		Vol Precipitated <i>ml</i> ^a
Tank No.	vol <i>ml</i>			Actual Salt Cake Solution	Synthetic Salt Cake Solution ^b	Actual Salt Cake Solution
105-S ^c	10	0.0037	0.245	72	36	0.10
	10	0.0075	0.163	109	57	0.10
	10	0.015	0.123	144	110	0.15
	10	0.0073	0.0087	<i>d</i>	-	-
108-se	15	0.0048	0.241	130	-	0.275 ^f
	208	0.0050	0.288	109	-	2.09

^aCentrifuged wet volume.

^bComposition before scavenging was: 6M NaNO_3 -0.1M NaNO_2 -0.004M Na_2SO_4 -0.025M Na_3PO_4 -1M NaOH , and 100 $\mu\text{Ci/liter}$ ^{85}Sr .

^cComposition before scavenging was: 7.47M Na^+ -5.89M NO_3^- -1.27M OH^- -0.116M AlO_2^- -0.048M PO_4^{3-} -0.00233M Si -0.000095M Ni^{2+} -0.0243M Cr -0.00011M Fe -33000 $\mu\text{Ci/liter}$ ^{137}Cs -355 $\mu\text{Ci/liter}$ ^{106}Rh -254 $\mu\text{Ci/liter}$ ^{135}Cs -17.7 $\mu\text{Ci/liter}$ ^{90}Sr -6.2 $\mu\text{Ci/liter}$ ^{99}Tc ; concentration of NO_2^- , SO_4^{2-} , CO_3^{2-} , and actinides not determined.

^dAfter three scavengings with 0.0073M $\text{Sr}_3(\text{PO}_4)_2$.

^eComposition before scavenging (insofar as presently known): 7.43M Na^+ -0.031M PO_4^{3-} -0.0233M AlO_2^- -5230 $\mu\text{Ci/liter}$ ^{137}Cs -31 $\mu\text{Ci/liter}$ ^{90}Sr .

^fIncludes 0.175 ml sludge.

^gVolume sludge plus $\text{Sr}_3(\text{PO}_4)_3$ precipitated.

Strontium decontamination factors (DF) obtained with actual salt cake solutions are in fair to good agreement with data obtained with synthetic salt cake solutions. [Strontium-90 DF's quoted in Table XXVIII are regarded as conservative values because in our analytical method part of the beta-count we ascribe to ^{90}Sr could be due to a small amount of ^{106}Ru "leaking" through the procedure.] Results in Table XXVII show, therefore, that scavenging techniques can be used successfully to remove ^{90}Sr from salt cake solutions.

Cesium-137 Removal Tests

A portion of the Tank 108-S 7.4M Na^+ -1M OH^- salt cake solution, after the $\text{Sr}_3(\text{PO}_4)_2$ scavenging headend treatment described in Table XXVIII, was passed successively through three fresh 10-ml beds of 20 to 50 mesh, Na-form Duolite ARC 359 resin. The diameter of each bed was 1.14 cm. All downflow loading operations were performed at 25° C and one column volume per hour. Feed to the first column contained 5166 $\mu\text{Ci/liter}$ ^{137}Cs and 0.288 $\mu\text{Ci/liter}$ ^{90}Sr . Results of these tests are summarized in Table XXIX.

TABLE XXIX
DUOLITE ARC 359 RESIN SORPTION OF ^{137}Cs
FROM TANK 108S SALT CAKE SOLUTION

Column No.	Composite Loading Effluent		Cs DF
	Column Volumes	^{137}Cs , $\mu\text{Ci/liter}$	
1	14.0	500	10
2	13.9	15.5	33
3	14.0	0.45	33

The composite effluent from the third Duolite resin column contain 0.14 $\mu\text{Ci/liter}$ ^{90}Sr and, as indicated in Table XXIX, 0.45 $\mu\text{Ci/liter}$ ^{137}Cs . For reference the MPC_w

values for soluble ^{90}Sr and ^{137}Cs in water in a controlled zone are 0.01 and 0.4 Ci/liter, respectively, while the MPC_w values for insoluble ^{90}Sr and ^{137}Cs are both 1.0 $\mu\text{Ci/liter}$.

Future Work

Activities planned for the next quarter include:

1. Continue acquisition of equilibrium distribution ratio data for Duolite ARC 359 resin sorptions of radiocesium and radiostrontium as a function of solution composition and temperature.
2. Conduct column tests to study effect of flow rate on uptake of ^{137}Cs by duolite ARC 359 resin.
3. Begin studies of Dowex 1 resin sorption of ^{99}Tc from salt cake solutions and terminal liquors; start acquisition of equilibrium distribution data.
4. Continue studies of scavenging of strontium from synthetic and actual salt cake solutions.

The Use of Beta-Alumina Membranes to Decontaminate High Sodium Waste (J. D. Kaser and H. Hollis - Battelle Pacific Northwest Laboratories)

Objective

This project was undertaken to explore methods for reducing the volume of radioactive salt cake by separating the nonradioactive sodium, which makes up the bulk of the waste, from the radioisotopes by selective conduction of sodium ions through sodium beta-alumina.

Prior Work

Special beta-alumina tubes were received from Toshiba Company, Japan. These tubes are nonporous and were specially fabricated for use as solid electrolyte membranes. Single ion conductances and separation factors were measured for cesium and sodium from aqueous carbonate and nitrate solutions. Separation factors of about 10 were obtained. However membrane resistances as high as 2×10^5 ohms were encountered and the membrane finally cracked after approximately 100 hours.

Three unsuccessful attempts were made to decontaminate radioactive salt cake solution. Each attempt failed because the beta-alumina tube cracked shortly after an electromotive force was applied.

Progress During Report Period

Since the incentive for decontamination or volume reduction of salt cake waste is economic, processing cost should be less than the expected savings in storage costs. A significant processing cost for the proposed electrolytic separation of sodium-form salt cake is the cost of electric power. The cost of electricity required to remove the sodium in one gallon of salt cake through a single beta-alumina membrane is estimated to be \$0.08 using the following assumptions:

Sodium in 1 gal of salt cake:	5.56 lb
Electrochemical equivalent of sodium:	529 amp hr/lb
Overall emf across membrane:	10 volts
Electric energy cost:	\$0.003/kW hr

Atlantic Richfield Hanford Company personnel have estimated that decontamination of salt cake will save about \$1.70/gal in storage cost for the final product. If the power consumption can be kept low by keeping the voltage drop low across the membrane, and by being able to carry out the separation with few separation stages and little reflux, the process might be attractive.

On the other hand it is not hard to imagine a situation where the electric cost can wipe out the savings in storage cost. For example, if five separation stages and 50% reflux are required, the electric energy cost will be about \$1.60/gal.

As a result of our past experimental work, communications with offsite experts and published research of others, the use of beta-alumina membranes with aqueous solutions does not appear feasible because beta-alumina cracks in aqueous solution and the sorption of hydrogen ions drastically reduces the conductivity of the beta-alumina. Present plans are to investigate molten salt systems and stop further work with aqueous solution unless a good way of avoiding these difficulties is identified.

Future Work

Plans are being made to evaluate the performance of beta-alumina membranes in molten salt.

EQUIPMENT DECOMMISSIONING

(G. A. Beitel and B. B. Harshbarger)

Objective

The objective of this program is to develop and demonstrate processes for consolidating contaminated equipment or other metal components. The emphasis is on decontamination and significant bulk volume reduction without hazards increase to the biosphere.

Prior Work

Meltdown using a thermite-type reaction for fusion heat was identified as the simplest means of obtaining volume reduction since intact equipment could be charged to the melter, obviating the need for independent size-reduction. A batch small-scale (1800-kg) melt to demonstrate the concept was planned using a 76-cm hole in basalt rock as the refractory vessel. Additionally, a size-reduction and melting technique for intact equipment employing a sweeping graphite electrode arc melter was discussed with furnace manufacturers and deemed feasible.

Other potential processing steps prior to meltdown (e.g., size-reduction and decontamination) had been identified along with methods of doing them.

Progress During Report Period

Lectromelt Corporation of Pittsburgh presented a conceptual design for a sweeping graphite electrode arc melter. They were the only furnace vendor to express interest in the concept, and are still working on the finalized design and its estimated cost. Building 277-T has been tentatively identified as the location for the arc melter test.

To check the viability of the hole-in-the-ground melter systems, a small-scale test was run using a few hundred pounds of steel. While all test components functioned properly when checked independently, problems were encountered when the integrated test was attempted. An analysis of the problems resulted in modifications which have yet to be tested.

In conjunction with the hole-in-the-ground melter test, contracts were let to Battelle Pacific Northwest Laboratories to analyze the properties of the resulting metal ingot and to determine the particulate concentration in the off-gas from the reaction. Midwest Research Institute proposed studies to make a more precise analysis of atomic and molecular species in the off-gas from a thermite reaction; final approval of this contract is still pending.

As part of a contract with Norman Engineering, approved in February, a preliminary design will be provided for a facility to handle the equipment decommissioning on a "hot" basis.

Atlantic Richfield Hanford Company's Chemical Technology Laboratory now has charge of stock coupons for induction melt studies but is hindered by the analytical difficulty of determining the radioactivity because of the irregular coupon geometries involved. Melts should take place in April.

Discussions with the Solar Programs Section of BNW to assess the possibility of substituting a solar melter for the arc melter appear to rule out such a possibility. While power requirements (one megawatt) are within existing technology, the configurations require the piece being melted to be either above or partially surrounded by the

solar collection system. In addition, the solar energy must be transmitted into a sealed chamber through a fail-safe window with high transmittance--no mean task.

In accordance with this program's timetable, a document on "Preliminary Criteria for Acceptable Terminal Product Form" was written in March and will be distributed after reproduction.

Full-Scale decontamination tests on a failed Purex dissolver await the construction of handling dunnage so it can be moved from Purex to T Plant.

Future Work

The hole-in-the-ground melter test will be completed either by using the silicon-oxygen fuel system as originally envisioned except that silicon will be fed batch-wise, or by using the conventional sodium nitrate-silicon reaction to supply the heat fusion. Battelle Pacific Northwest Laboratories will assess the physical and metallurgical properties of the ingot made to determine its corrosion resistance, mechanical integrity, and friability (for potential recovery purposes).

We will continue to work with Norman Engineering in supplying the information needed to design an operable hot decommissioning facility.

Demonstrating the viability of a sweeping arc melter will take over a year based on the minimum construction time for the melter itself. We shall make a concurrent effort to remodel 277-T Building to make it suitable for accepting the melter once it is built.

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