ATLANTIC RICHFIELD HANFORD COMPANY
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WASTE MANAGEMENT AND TRANSPORTATION
TECHNOLOGY DEVELOPMENT
October 1974 through December 1974

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ABSTRACT

This document is the second in a series of quarterly progress reports on activities in support of management of Hanford high-level waste. It covers the period October through December 1974. A variety of specific topics are discussed. They can be grouped in the areas of: salt cake retrieval; tank integrity; storage system improvements; waste immobilization; and conversion of failed, contaminated equipment to safe storage forms.

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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

	<u>Page</u>
Salt cake retrieval work moved ahead with contract approval for mechanical mining cold test prototype design and construction. Mining using a combined agitator-pump may permit hydraulic retrieval with no added liquids. Pneumatic retrieval was tested using vendor-owned vacuum pneumatic truck-mounted equipment. Potential mechanisms are being studied for radioactive particle suspension and release during mining operations. Solids flow properties are being evaluated by offsite experts.	6
Thermodynamic calculations for salt cake stability indicate low probability of any dangerous reactions within the salt cake.	21
Mathematical analysis of soil-water transport mechanisms has proven more difficult than expected but is proceeding toward a projected March 1975 completion date. Soil-salt cake interaction experiments have been postponed pending the availability of salt cake samples.	25
Corrosion studies to date for mild steel predict increased corrosion rates in tanks with salt cake and concentrated liquors relative to rates in tanks which contain dilute liquor. Concrete deterioration studies are planned.	29
The fault tree analysis preliminary report was completed this quarter and will be issued in January. The analysis identified important system flaws which may be candidates for engineered improvements. Most of the postulated system faults were identified as unimportant.	32
Engineered responses considered to date fall into the categories of salt cake characteristics modification, improvements to the containment system, or retrieval and transformation into a new product containment configuration. Feasible options for salt cake modification or <i>in situ</i> containment repair are presently difficult to identify.	36

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Groundwater management studies are directed toward control of groundwater transport of nuclides. An improved model of the Hanford groundwater is being obtained from current measurements of soil parameters. Control of the groundwater might be effected by altering soil parameters, altering groundwater viscosity, or by altering groundwater flow potential gradients.	39
Analytical methods for determining the actinide content of various Hanford high-level wastes such as salt cake, sludges, and terminal liquor are being established in order to determine acceptable long-term management alternatives for the wastes.	41
Equipment decommissioning efforts have identified meltdown as virtually the only feasible size-reduction technique for equipment. Alternatives are movable electric arc melting and modified thermite <i>in situ</i> melting. Lectromelt Corporation has agreed to make a design proposal for a gimbal-mounted, graphite-electrode arc melter. Hole-in-the-ground melting tests were delayed by lance fabrication and steel availability. Laboratory hot cell melting tests and full-scale decontamination tests will be run next quarter.	43
A set of waste immobilization tests using an immiscible liquid carrier mixing process were judged a qualified success. Organic carrier removal constitutes potential economic and safety obstacles to the successful implementation of the process.	46
Engineering preliminary cost studies of waste immobilization alternatives have identified storage structure as a major cost variable. This conclusion places a large incentive on minimizing the final waste-form storage volume, suggesting that greater emphases should be placed on silicate melt product-form; and especially on separation of radioactive isotopes from the bulk of the inert material in the waste. Separate processing seems desirable if the inert fraction can be adequately decontaminated.	58
The maximum permissible leach rates (MPLR) for solidified radioactive waste forms were calculated	63

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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. 65

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. 72

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) for ¹⁰⁶Ru. 73

The fraction of ¹³⁷Cs leached from cancrinite products was about two times higher when leached by Hanford groundwater rather than deionized water. 74

To effectively pour molten glass from a continuous melter, melt viscosities should be in the range 50 to 200 poises. Optimum furnace operating temperatures for achieving such viscosities in formulations to immobilize salt cake are 1000° to 1100° C when using basalt as the source of silica and 1250° to 1350° C when using sea sand as the silica source. 78

Application of the Silicate Melt process to immobilization of salt cake from Tanks 105-S and 106-S was demonstrated. In one experiment 50 wt% salt cake was incorporated into a glass formulation; the product exhibited a leach rate of only 3.4×10^{-6} g/cm²-day. 83

The electrical conductivities for molten glasses containing simulated salt cake were obtained. As a result, the specifications for the melter 86

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electrode power supplies for the Silicate Melt process pilot-plant have been completed.

A safety review has been initiated to determine whether a high-temperature glass-making process has inherent risks which cannot be reduced to acceptable levels at reasonable costs.

95

Studies to scout ion exchange and precipitation techniques for removal of ^{137}Cs and ^{90}Sr from dissolved salt cake have been hampered by the inadequacy of the presently available analytical procedure for determination of trace-levels of ^{90}Sr . Recently a new analytical procedure was successfully developed for determination of low (0.01 to 0.1 $\mu\text{Ci/liter}$) levels of ^{89}Sr using a solvent extraction technique which utilizes bis-2-ethylhexylphosphoric acid as the extractant.

108

Experiments were performed on the separation of sodium from cesium by electrodiffusion of sodium through sodium beta-alumina. Measured separation factors are encouraging; however lower membrane conductivity in contact with nitrate solutions and membrane cracking are problems.

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HIGH-LEVEL WASTE MANAGEMENT

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

A proposed Budget and Task Breakdown to meet the limited objective of developing the most viable dry mining scheme for cold testing during fiscal year 1976 was presented in the first quarterly report.

Progress During Report Period

The proposed budget and task breakdown as reported in the first quarterly report and Tasks I and II of a previous assignment were updated to incorporate the following items:

1. Give full consideration (as requested by the U. S. Atomic Energy Commission Waste Management and Transportation Director) to hydraulic mining schemes.
2. Provide a subcontract to Program and Remote Systems Corporation (PaR) for preliminary design of a mechanical miner, elevator system, lighting and TV system, and a portable packaging system.

3. Subcontract to Jenike and Johanson, Inc., (J&J) for the study of solid material flowability of solid waste.

During December a review of the Project was started to formulate short-term optional plans that would lead to more full-scale hardware for cold testing.

Problem Areas

Proper staffing of the Project to give adequate attention to all tasks remains a problem. It would be desirable to issue more subcontracts to architectural and engineering firms.

Future Work

A list of short-term, optional plans will be prepared and issued.

During the third quarter of fiscal year 1975 Task I, "Concept Development," is to be essentially completed.

Mechanical Mining and Cold-Test Stand (D. O. Schuler)

Objective

Design and build, for mining salt cake, a mechanical miner comprised of a hydraulic boom, digging device, barrel elevator, and portable packaging system.

Prior Work

A search was conducted for engineering and architectural firms to design and build a mechanical miner. Three vendors were tentatively selected to visit; a set of equipment specifications better describing the necessary

application was prepared.

A list of potential sites and structures for cold testing was compiled. Personnel of Automation Industries, Inc., Vitro Engineering Division, were retained to prepare conceptual engineering drawings and cost estimates for identified alternatives.

A small clamshell bucket and hydraulic system were ordered for bench-scale testing, but delivery has been delayed.

Progress During Report Period

In October two members of the Solid Waste Design Subsection visited four hydrocrane manufacturers. They observed that PaR of St. Paul, Minnesota, has good expertise in the design and manufacture of remote manipulators and television cameras for the nuclear industry.

In November ARHCO received proposals from three of the four vendors visited in October: (1) Programmed and Remote Systems Corporation, St. Paul, Minnesota (PaR); (2) FMC Corporation, Engineered Systems Division, Santa Clara, California; and (3) Hydrasearch Company, Annapolis, Maryland.

Programmed and Remote Systems Corporation's proposal was selected over the other two because of the Company's experience in fabricating remote handling equipment for use in a nuclear environment and the ability to supply prototype hardware in a reasonable length of time. During December a letter of justification and a memorandum to prepare a contract were prepared and forwarded to the ARHCO legal counsel.

Vitro Engineering personnel did not complete a detailed test stand design as scheduled. They would prefer

to complete mining system design first so that loads on the stand would be known. With the PaR contract this information will become known in March 1975. There does not appear to be any problem in completing the cold test stand starting from this date for use in the third quarter of FY 1976 when the PaR miner is to be delivered.

The hydraulic clamshell bucket for use in bench-scale testing was completed and delivered in December--this is 1.5 months later than scheduled. The mobile hydraulic power unit for use with the bucket was received; but the main control valve was back-ordered and will not be shipped until December 28. Thus bench-scale mining tests with a clamshell bucket will not begin until next month.

In lieu of the test with a clamshell bucket, observations were made on the ability of a tractor-mounted backhoe to dig and dump salt cake. This appears to be the best method tested to date for moving salt cake. Other observations are that the backhoe's digging can result in enough agitation that the salt cake can be turned into a semi-fluid state. Dumping of salt cake into a barrel results in kinetic forces being applied to the elevator over and above the weight of the salt cake. This phenomenon results in excellent packing of salt cake within the drum. Under ideal mining conditions when the backhoe and barrel elevator are near each other, the mining rate could approach *ca.* 50 barrels/hr.

A specification sheet and description were prepared for a barrel elevator and were submitted to about 10 vendors for bids. Four "no-bids" have been received to date. The design and fabrication effort on this task has been included in the PaR contract.

Problem Areas

Long delays in equipment delivery continue to be a problem in the area of bench-scale and feasibility testing.

Future Work

A contract will be placed with the vendor. Clam-shell bucket performance will be evaluated in various synthetic waste forms. A suitable site will be selected for the cold test area, and cold test design of the equipment will be started.

Hydraulic Mining (J. V. Cooper)

Objective

Evaluation of feasibility of semihydraulic and hydraulic methods for retrieval of salt cake.

Prior Work

ARH-1338, "Study--Pseudo Hydraulic Mining of SX Sludge and Salt Cake," by H. A. Reading reports a conceptual idea for mining SX Tank Farm sludge using water sprays for sludge breakup, coupled with pneumatic retrieval.

Progress During Report Period

Various ARHCO personnel have been consulted about the possibility of hydraulically mining salt cake. All felt the idea is worth pursuing.

On November 12, 1974, a representative of Picatti Brothers of Yakima, Washington, presented films demonstrating the use of the Scum-Buster[®]--a centrifugal pump with a patented impeller design which enables it to pump a slurry of up to 80% solids. In a telephone conversation on December 12,

1974, Picatti Brothers indicated they would make a bid on a 2" pump; this bid was received in late December and is being reviewed.

A high-pressure water system was designed and is being fabricated in ARHCO Shops.

Problem Areas

Selecting a suitable power source to drive the pump may be a problem. Uncontrolled liquid within a tank and air filtration are potential technical problems.

Future Work

Bench-scale testing of both high-pressure (10,000 psi), low-volume water streams and the Scum-Buster pump will take place when the necessary equipment is available.

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

Objective

Evaluate feasibility of pneumatic means for retrieval of salt cake.

Prior Work

Several tests were made with the Supersucker[®], a large, truck-mounted vacuum system. Numerous problems such as plugging of hose and break up of salt cake at nozzle were observed.

Progress During Report Period

A meeting was held November 14, 1974, with Frank Espinosa of the Vacuum Industrial Pollution

Corporation of Portland, Oregon, to discuss the application of the Vactor® Jet-Rodder® vacuum truck to salt cake mining. This truck has several interesting features which we would like to test; namely, a variable pressure, variable flow, water pump with "exclusive jack hammer" action which overcomes obstructions. Another version of their vacuum truck comes with a mechanical digger attached to the suction nozzle. Both devices show promise in solving the problem of breaking up salt cake at the suction nozzle.

As part of the preparation work at Hanford, hard samples of simulated waste such as salt cake and sludge were prepared in 55-gallon drums for testing with the Jet-Rodder vacuum truck.

Problem Areas

A considerable length of time is required to prepare hard samples of waste. Sample size is currently limited to 55-gallon drums or to 0.46 m x 0.46 m x 1.22 m tanks.

Future Work

Conduct tests January 6, 7, and 8; and analyze results.

Potential Airborne and Resuspension Release of Radioactive Salt Cake During Mining (S. Sutter, L. C. Schwendiman, and J. Mishima - Battelle Pacific Northwest Laboratories)

Objective

To ascertain possible airborne hazards presented by salt cake mining.

Prior Work

Background material relating to possible airborne

release was gathered.

The information sources tapped were ARHCO and BNW technical documents, scientists in both ARHCO and BNW who are engaged in various phases of the salt cake retrieval program, Nuclear Information Center at Oak Ridge, Tennessee, and sources in the BNW Technical Library referring to mining of nonradioactive materials.

Progress During Report Period

This time was spent studying the documents, assimilating and then organizing the collected material. Initially an outline of a document was scoped, then a first document was submitted as a draft. After review, changes in the document are now in progress.

As the document is revised, the fault tree analysis (made by others) will be used to indicate potential accident situations. This will help to specify the places where the accident potential is the greatest.

Since the exact mining method has yet to be selected, this document is addressing the problem of potential release from all of the schemes under consideration.

The requested evaluation of the American Society for Testing and Materials (ASTM) Standard Test 245-51, "Abrasion Resistance of Stone Subjected to Foot Traffic," was completed and forwarded as a letter report.

Future Work

During the next reporting period the document should be completed. The document will be titled "Background Information and Proposed Research Relating to Inadvertent Release of Airborne Contamination in Salt Cake Retrieval Operations."

Materials Flow Properties (C. H. Delegard, N. C. Rodewald, and D. O. Schuler)

Objective

The purpose of this task is to characterize the to flow properties of salt cake, sludge, and other waste forms.

Previous Work

The Jenike and Johanson, Inc., short course on "Storage and Flow of Solids" sponsored by the American Institute of Chemical Engineers was attended.

Dr. Johanson reviewed our planning document. He gave us the following quoted recommendations:

"Proposal for characterization of the flow properties of salt cake material for the evaluation of various mining and packaging equipment.

"A. Measurement of properties of existing simulated (nonradioactive) materials and interpretation of test results.

"B. Modification of test equipment for remote testing and purchase by ARH of modified test equipment.

"C. Development of remote test technique and training of ARH personnel for running tests.

"D. Interpretation of test results for bin design parameters.

"E. Interpretation of test results for evaluation of various proposed mining equipment and other materials handling and packaging devices.

"The goal of this work is to provide a means of characterizing the flow properties of the various radioactive salt cakes in such a way as to provide an accurate simulation of the salt for mining studies and to provide a preevaluation of proposed mining techniques.

"Based on our standard testing fees, consulting fees and test equipment sale price, we estimate the project cost to be on the order of \$30,000 to \$50,000 depending on the relative amounts of testing done by J&J and ARH, and the amount of work involved in part E."

Progress During Report Period

Meetings and conversations with ARHCO personnel and Dr. Johanson were held to further define Task A. It was concluded that simplified screening tests should be run on approximately 10 waste forms. Based on these results, two samples are to be selected for detailed tests. Total cost of Program A is \$5,000. At this point a decision will be made on Program B which is estimated at about \$12,000.

In addition to getting approval on a Purchase Order for Task A, 10 samples were selected, packaged, and shipped to Jenike and Johanson, Inc. Samples of waste included salt cakes of various composition and moisture content, diatomaceous earth-caustic liquid, sludge, reacted clays, and trisodium phosphate. Jenike and Johanson, Inc., will run the simplified tests in December 1974.

Salt Cake Models. A simplified model for salt cake materials has been suggested by members of Waste Management Process Engineering and Design Section. This model described salt cake solids as exclusively sodium

nitrate crystals of various sizes. The interstitial liquor associated with these crystals is saturated in sodium nitrate, or course, but has varying concentrations of sodium hydroxide and sodium aluminate. In connection with the J&J investigations into solids flowability, some data were gathered (using this model) on salt cake drainability.

Jenike and Johanson, Inc., has made it clear that solids flowability is extremely dependent on the moisture content of the salt cake. Two properties of the salt cake which may affect its moisture content are the interstitial liquor base concentration (which affects the liquor's viscosity) and the crystal size of the salt cake solids. Thus some correlation is sought between the interstitial base (NaOH and NaAlO_2) concentration and the amount of interstitial liquor retained in the salt cake. Also, a correlation is sought between the crystal size of the salt cake solid phase and the amount of interstitial liquor retained in the salt cake.

Using Millipore[®] filter presses operated at 3.6×10^{-3} Newtons/meter² (25 psi), the amount of liquor retained for various sodium nitrate crystal sizes was determined. Large crystals of NaNO_3 were grown by the slow cooling of a saturated solution. These crystals were sieved (U. S. Series scale) to five size ranges: <10 mesh (>1.98 mm), 10 to 14 mesh (1.40 to 1.98 mm), 14 to 20 mesh (0.833 to 1.40 mm), 20 to 25 mesh (0.070 to 0.833 mm) and >25 mesh (<0.707 mm).

Twenty grams of sodium nitrate in each of the five crystal size ranges were contacted with 40 milliliters of synthetic terminal liquor (roughly 50% H_2O , 20% NaNO_3 , 10% NaNO_3 , 10% NaOH , and 10% NaAlO_2). The slurries were then pressure-filtered as described and the weight gain of the

sodium nitrate crystals recorded. Table I details these results. This experiment was performed twice with good reproducibility. At this time no rationale can be offered for the sawtooth behavior.

In a similar experiment ability of >25 mesh NaNO_3 to retain liquids of various viscosity liquors was tested. Three 20-gram portions of >25 mesh sodium nitrate crystals were each slurried with three sodium nitrate-saturated synthetic waste liquors containing roughly 3, 5, and 7M NaOH. The viscosities of these liquors were 17.9, 25.3, and 37.3 centipoises at room temperature in order of increasing caustic concentration. As might be expected, when the caustic concentration of the liquors increased (and thus their viscosities), the liquor retention of the sodium nitrate increased. These data may also be found in Table I.

Future Work

Further work will be done on modeling salt cake materials as sodium nitrate solids with terminal liquor-type interstitial liquors.

Jenike and Johanson, Inc., solids flow testing equipment will be evaluated for its utility in characterizing salt cake materials.

In Situ Measurements (R. C. Lawrence, D. Ells, and N. C. Rodewald)

Objective

Develop probes for making *in situ* measurements of radiation, hardness, and temperature in several waste tanks.

TABLE I
RETENTION OF SYNTHETIC WASTE LIQUORS BY SODIUM NITRATE CRYSTALS

<u>Mesh Size</u> <u>U. S. Series</u>	<u>Viscosity Liquor</u> <u>Centipoise</u>	<u>Weight</u> <u>NaNO₃</u> <u>g</u>	<u>Weight Pressed</u> <u>NaNO₃</u> <u>g</u>	<u>Fraction</u> <u>Weight Gain</u>
<10	17.9	20	27.7	0.36
10-14	17.9	20	38.2	0.91
14-20	17.9	20	28.0	0.40
20-25	17.9	20	37.0	0.85
>25	17.9	20	31.5	0.58
>25	17.9	20	30.9	0.54
>25	25.3	20	33.9	0.70
>25	37.3	20	33.0	0.65

Prior Work

Probes were developed and used in Tank 105-B; probes were further modified to improve performance.

Progress During Report Period

Penetration tests were made on synthetic waste to test a 1.9-cm pipe probe driven with a slide hammer and a heated-tip 5.1-cm pipe probe driven with a 1.3×10^2 Newtons/m² air jack hammer.

Slide Hammer Penetration Test. The slide hammer driven-1.9-cm pipe probe was tested on synthetic waste with the approximate results:

	<u>No. of 0.9-m Drop Blows</u>
Blow sand (200 West Area near site where vacuum truck dug a trench)	30
Reacted clay-caustic barrel #3	40
Synthetic salt cake barrel #16	10 at top to 30 near bottom (need larger depth of consistent salt cake)
Trisodium phosphate synthetic composition simulation of 105-B salt whisker	3 at top to ∞ at depth of 33 cm
Hot probe of Tank 105-B	30 to 60 assisted blows until impene- trable layers were hit

Modifications have been made to prevent the collar from slipping and tips from bending. Tests are being made with several over-sized tips in an effort to reduce the effect of shaft resistance. Probes with oversized tips are hard to remove. A possible solution that will be tested is a reverse bevel on the exit shoulder.

Heated Tip Probe. The initial testing of the heated tip 5.1-cm pipe probe in the simulated waste material was rather unsuccessful because of the small driving force of an electric impact hammer. In the current tests we were able to obtain the use of a 41-kg jack hammer. These tests were again carried out in a drum of trisodium phosphate salt. The probe was placed in the same hole that was used in the electric impact hammer tests. The probe was first driven with heaters off for approximately 2.1 cm. At this point 200 V were applied to both heaters, giving a combined power level of about 2 kW. After the heater had been on for about 30 minutes a pool of boiling liquid (106° C) was observed surrounding the tip.

The heater was disconnected and by driving on probe for 30 seconds, 3.2 cm was gained in penetration. This method of heating and driving was continued six times with a result in penetration of approximately 18 cm.

The ability to drive the 5.1-cm pipe probe in a drum of "clay caustic" was tested. It was possible to drive the probe cold--heater off--to the bottom of the material (71 cm) in 40 seconds.

In salt cake the heated-tip probe was observed to cause the salt cake to boil at approximately 130° C.

In an attempt to establish an easy method of penetrating the simulated salt whisker (trisodium phosphate) it was attempted to use a 3.8-cm star drill driven with a rotary air impact hammer. Penetration was 20 to 50 times faster than with the heated-tip probe. The test was terminated with the bit stuck in the waste. It is believed some of the problem lies in the fact that the air passageway which is supposed to blow out the pulverized material was plugged. This problem also caused the rotation of the drill

to be impeded to the point where it finally failed to rotate. It was concluded that a common star drill (used for cement drilling) when affixed to the tip of a probe may provide an improved technique for penetrating the concrete-hard layer commonly found in our waste tanks.

Future Work

Additional calibration tests will be performed and hopefully several tanks such as 116-TX and/or 101-SX will be probed.

STORAGE SYSTEM INTEGRITY

Salt Cake Stability (G. A. Beitel)

Objective

Identify the conditions under which explosive 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 quarter a literature survey was begun.

Progress During Report Period

Theoretical computations were performed which establish an upper limit to the temperature which could be reached if a mixture of NaNO_3 , carbon, and water were to undergo a sudden and complete reaction. Figures 1 and 2 show the most significant results of these computations.

FIGURE 1
PEAK THEORETICAL FLAME TEMPERATURES FOR DRY NaNO_3 MIXTURES

FIGURE 2
INFLUENCE OF MOISTURE ON PEAK FLAME TEMPERATURES OF NaNO_3 MIXTURES

Detailed discussion of the assumptions behind these computations will appear in the Hazardous Reactions Status Report, due June 1, 1975. Figure 1 shows that peak temperatures would occur when the carbon-sodium nitrate mixture contains approximately 85% NaNO_3 and the temperatures will drop rapidly with increasing carbon content. If the carbon is present as an organic compound, higher concentrations of NaNO_3 are allowable. Figure 2 shows the sensitivity to moisture content in the region of low carbon content.

The practical importance of these computations is that they provide a framework within which to consider the problem at hand. For example, from Figure 2, with a minimum moisture content of 9.5%, the maximum temperature for a mixture containing 4% carbon is 400°C . Since the ignition temperature is slightly above 400°C , such a mixture could never explode--even if some external mechanism were used to ignite it, it could not propagate. Hence it is a safe mixture.

Although it is known by analogy with other studies on combustible or explosive materials that actual flame temperatures are always less than the theoretical temperatures, no such prior data for the nitrate-carbon system exist. It was hoped that the black-powder industry would be able to provide such information. However it was always so easy to produce a black-powder mixture which performed adequately that tests were not conducted to identify the composition boundary between explosive and nonexplosive mixtures. Therefore we are preparing to conduct these combustion-limit tests.

The initial experiments are planned to be simple, unconfined combustion of pure NaNO_3 plus charcoal mixtures. Pre-ignition temperatures will be controlled. Composition

will be varied to determine combustion limits. As the data base grows, other organic materials will be substituted for charcoal and then the NaNO_3 will be replaced with simulated salt cake compositions.

The end result of the effort described above will be a guideline with which to compare the stability of mixtures of known composition. To apply this knowledge to the salt cake, it is necessary to identify the organic carbon content of the salt cake. To insure that the necessary information is available, we are presently making arrangements with the Atlantic Richfield Hanford Company Chemical Technology Laboratory to make total carbon and total organic-carbon determinations a routine part of the salt characterization program.

Future Work

Based upon the results of the above tests, selected compositions will be tested in the kilogram-size quantities. These actual "explosive" tests will be conducted out-of-doors behind a suitable protective barrier. If after the above tests it is desirable to obtain quantitative data on the reaction kinetics, consideration will be given to subcontracting for molten salt reaction tests.

A status report on the thermodynamic studies will be started during the coming quarter so that it will be completed by June 1, 1975, as scheduled.

Radionuclide Transport Studies for Salt Cake Stored Underground (D. J. Brown)

Objectives

The objectives of this subtask are (1) to identify all radionuclide transport mechanisms and to evaluate

relative rates of radionuclide movement in the Hanford environment by each mechanism identified; (2) to develop an efficient and accurate computer model for assessing the rate and direction of radionuclide movement from its underground storage site to points of potential uptake by man; and (3) to assess the potential impact of radionuclide movement through the Hanford environment on man.

Prior Work

Three primary mechanisms have been identified by which radionuclides could be transported through the Hanford environment. These are biologic, atmospheric, and hydrologic. A significant number of technical reports have been published on some specific aspects of each mechanism, but as yet there is not sufficient knowledge about any of the ones included in these reports to accurately predict the rate and direction of radionuclide movement.

Work in fiscal year 1975 has been directed toward hydrological transport. Mathematical equations were written to describe liquid vapor and gas movement through sediments under non-isothermal conditions. It was discovered that the numerical solution of the system of partial differential equations describing combined liquid, vapor, gas, and temperature induced flow is best accomplished using orthogonal collocation on finite elements for the first numerical reduction to a system of ordinary differential equations. Experience showed that a six-fold savings in computer time was achieved using the orthogonal collocation method.

Progress During Report Period

A question concerning the system of partial differential equations now formulated was raised during the

report period: which of two variables (capillary pressure or liquid water pressure) should be used in the dynamic equation of the liquid phase, and in the expression for fugacity (escaping tendency of the liquid)? Significant insight was gained by considering the more general expression for capillary pressure rather than that defined by Philip and Devries. Careful evaluation of the general expression has led Dr. B. Finlayson, mathematical consultant, University of Washington; and Mr. R. W. Nelson, Computer Sciences Corporation, to accept the liquid water pressure as the correct variable to use. Laboratory studies by Dr. R. Jackson, Tempe, Arizona, during the past year have tended to confirm this choice.

Evaluation

Progress toward formulation of the system of partial differential equations has progressed along a single line of development rather than through parallel path efforts. Accordingly, each problem encountered on the single line effort often means a direct delay. It is now estimated that the acceptable form of the partial differential equations will be completed by March 1975.

Progress on the numerical solution aspects of the system continue on schedule, and will be completed by the end of this fiscal year.

Problem Areas

There has been a four-month delay in the developing of drilling and sampling tools needed for obtaining hot salt cake samples from the underground storage tanks. When these are completely developed and the samples delivered to the laboratory, work will begin on testing salt cake-sediment reactions and radionuclide migration.

The biologic and atmospheric transport aspects of this subtask will be started in fiscal year 1975 as funds are made available.

Future Work

A system of mathematical equations and solution methods will be completed this fiscal year and will form the basis for the development of a computer model capable of predicting radionuclide transport in the sediments surrounding the underground storage tanks.

A responsible evaluation will be made of the transport mechanisms which might cause an unacceptable long-term migration of radionuclides from a breached storage tank. Work will continue toward development of models capable of predicting rate and direction of radionuclide movement via the primary transport modes now identified. Salt cake characterization will be completed and tests designed to determine the reaction of salt cake with Hanford sediments will be evaluated with respect to radionuclide migration.

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

Since corrosion studies have been more or less

continuously conducted at Hanford, it was prudent to review the corrosion experience at Hanford and, to a lesser extent, Savannah River to learn what studies were made, what these studies showed, and what work is currently being undertaken. This report would be the basis to determine what additional effort is warranted and how the proposed work will contribute to the ongoing effort. This task has been completed. A document has been prepared, is being edited, and will be available in the near future for review and critique.

All the corrosion work documented dealt with corrosion studies on the mild steel liner. The predominant waste form for most of the experimental studies was simulated liquid waste.

The key waste forms that will be considered in the projected work will be salt cake, interstitial liquor, and terminal liquor. The initial results obtained by personnel of Battelle Pacific Northwest Laboratories have indicated that while the rates of corrosion are different, the same types of corrosion were encountered using simulated salt cake as were found utilizing the simulated liquid waste.

The findings of the earlier investigators showed that the rate of general corrosion is low and reasonable for mild steel in the presence of caustic-nitrate salt solution. The main corrosion mode causing premature tank failure has been stress corrosion cracking (SCC).

It was concluded that an experimental program is warranted to study waste tank degradation. The program will indicate the propensity for corrosion and deterioration of the storage system. The aim will be to define the conditions which will give the longest-lived tanks. It will not predict when a particular tank will fail.

Progress During Report Period

This activity is still in the planning phases. The first draft of the planning document was completed during this period and a comment draft will be issued in the near future. The proposed project will include: an experimental program utilizing electrochemical techniques to investigate corrosion of the mild steel liner and steel reinforcing bars; an experimental program involving stand immersion tests to investigate the deterioration of the concrete waste storage tanks; and a literature search to evaluate the effect 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. It is the liquid component of the stored waste that will cause the major physical degradation of the waste storage tank. Corrosion and deterioration of the tanks would be minimal, at the most, if the stored waste were completely dry.

The experimental programs are subdivided into "hot" and "cold" phases. The hot phases will be conducted onsite using actual radioactive waste samples in the laboratory and, preferably, also in the actual waste storage tanks. By conducting the experiments in the stored waste in the tanks, the test environment becomes identical with the storage environment and the results will be much more meaningful.

Future Work

It is planned to contract out the cold phases of the program to appropriate offsite laboratories. The first phase of the corrosion studies is being conducted by

Battelle Memorial Institute, Columbus, Ohio. The Portland Cement Association has been contacted about the first phase of the concrete test program. The North Pacific Division of the U. S. Corps of Engineers at Troutdale, Oregon, has also been contacted concerning the possibility of having them make and run evaluation tests on concrete specimens for later actual immersion tests at Hanford of the concrete specimens.

Because of the variety of range of compositions of the wastes to be evaluated, an electrochemical experimental program is being proposed to study the effects of corrosion on the steel liner and the reinforcing steel. Battelle-Columbus Laboratories will conduct potentiodynamic polarization, constant-strain rate, and linear polarization experiments on mild steel exposed to simulated wastes. For the first phase of this study the test liquor will consist of the synthetic liquid components of the waste, primarily supernatant, interstitial liquor, and terminal liquor. As mentioned above, the liquid components of the waste are the primary aggressive elements causing degradation of the waste storage system. By initially considering only the liquid component, some experimental obstacles can be avoided.

Special emphasis will be made to determine the effects of high-caustic concentrations in the presence of nitrate ion on the corrosivity of mild steel, particularly in relation to stress and pitting corrossions. Work by Battelle Pacific Northwest Laboratories has indicated that pitting corrosion of mild steel is enhanced in the presence of simulated salt cake.

The concrete experimental program will consist of immersion tests. Concrete specimens of suitable dimensions will be made using our concrete mix. For the hot phase of.

the program the concrete specimens will be exposed to representative waste in the actual tanks for periods of time up to one year. Laboratory tests using simulated waste will be made to evaluate the effects of specific components of the waste and the effect of temperature. The tests will last approximately one year. Nondestructive tests will be used to measure the extent of deterioration. In this way the same sample can be monitored over the duration of the test period. A literature search will be made to evaluate the long-term effects of irradiation on the structural materials.

The metallurgical cold corrosion test program will be initiated by personnel of the Battelle Memorial Laboratories at Columbus. Contact has been made with the Portland Cement Association and the North Pacific Laboratory of the U. S. Corps of Engineers regarding a cold deterioration program on concrete--the former will submit a proposal.

Approval of the planning document and budgeting at the proper level are of the utmost importance and first concern. The cold corrosion testing program will be initiated immediately. Equipment for the onsite phases of the testing program will be ordered and arrangements for the onsite testing program will be made. Proposals for the cold concrete deterioration program will be solicited.

Fault Tree Analysis (W. J. Van Slyke)

Objective

The main objective of this effort is to identify opportunities for system-engineered improvements for high-level wastes storage. A secondary objective is to provide information useful in determining the length of time for which the existing high-level waste tanks may be considered

adequate containment for salt cake produced by the evaporation of high-level waste liquors. The overall objective is to provide additional pertinent information for improved high-level waste management decisions.

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, on developing computer fault tree analysis techniques demanded by the unique nature of the high-level waste system analysis problem, and on 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, not unexpected in view of the complexity of the high-level waste storage system. Most of the cutsets found had probabilities or consequences too slight to be of concern. The preliminary analysis ranked the causative (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.

Progress During Report Period

Work continued this period in evaluating the results from the preliminary fault tree analysis. Risk indices were calculated for the more probable and consequential cutsets found. These were ranked in order of their seriousness by risk index, the sum of the hazard index (the logarithm of the dilution required to achieve MPC for a given quantity of material) added to the logarithm of the cutset probability. The most serious 15 cutsets were

identified for inclusion in the preliminary fault tree analysis report draft, expected to be out for review in January 1975.

Work continued on both the fault tree analysis computer program (by ARHCO) and the fault tree graphics program (by CSC). The fault tree analysis program is being revised to permit it to simultaneously find all the cutsets as done by the previous program version and to retain the most probable cutsets, printed out in order of decreasing probability. The capability to print out all cutsets, below a given number of events either with or without their computed probabilities, will be retained. The probability computations are being revised, in cooperation with Battelle Pacific Northwest Laboratories users of the program, to conform with the current more flexible methodology present in the Rasmussen report.

The fault tree graphics program is being altered so that it can be used to make fault tree diagrams which have dimensions well suited to report page format. Its capability will include the manual, interactive selection of transfer gates based on program output data to a user terminal. The resultant fault tree sub-diagrams can easily be tailored to fit within a given page size consistent with any preferred photo-reduction factor. It is anticipated that the preliminary fault tree analysis report will have diagrams prepared using this revised graphics program. Each program is thought to represent an advance in the state-of-the-art in fault tree analysis.

Evaluation

Preparations have been completed for timely

issuance of the preliminary fault tree analysis draft report in January.

The fault tree analysis report draft is in typing for issuance early next quarter. It includes preliminary analysis results, conclusions, and recommendations for both engineered response considerations and for input to the "leave or retrieve" subject area.

Computer program revisions now in progress will permit greater versatility and power for fault tree analyses.

Problem Areas

None.

Change in Plans

None.

Future Work

Future work planned is summarized by the following major items:

- Revise the fault tree diagram to incorporate ARHCO internal responses to the preliminary report.
- Complete the current analysis effort to identify the most important events in the fault tree.
- Provide input to the ARHCO efforts on engineered responses.
- Obtain improved estimation of the characteristics for each contributing event identified as important in the initial analyses.

- Modify and extend the fault tree efforts as required by ARHCO and the Atomic Energy Commission continuing requirements.
- Prepare periodic reports and a final report of the work accomplished.

ENGINEERED RESPONSES

Storage Stabilization (L. E. Bruns)

Objective

The objective of this subtask is to study methods of improving high-level waste containment by encompassing the tank with soil stabilization agents. Alternate methods for affixing in-tank contents will be studied. This report starts the first of a series on storage stabilization and hence encompasses a brief review of work initiated in late 1973.

Prior Work

Considerable usage is made throughout the Country for sealing tunnels, dams, etc., by use of stabilization agents. Initial studies consisted of literature reviews and consultation with experts in the field. Some affixing agents found worthy of further investigation were AM-9^R (American Cyanamid Company), asphalt, concrete, silica-type grouts, and various mixtures of these.

Progress During Report Period

To date several different stabilizing agents have been investigated for forming containment around a waste tank. Among them are AM-9 (an organic gel), an asphaltic emulsion, and silica-type grouts. A proposal was received

from one vendor for encompassing a tank or tank farm with a grout. A tank farm test was made about a year ago using AM-9; problems are its high ingestion toxicity and its in-ground, long-term stability. It does appear, by examination of tank farm cores, that AM-9 is resistant to water penetration. Laboratory tests were made with soil-asphaltic emulsion mixtures and these have shown good shear and tensile strength and are almost impermeable to water. Some initial silica-soil tests were conducted using a vendor formula; qualitative observations show that it should be considered for further testing. All three types of soil stabilizing agents are recommended for comparison field testing.

Some work was done with solidification of terminal liquor using Simplot and bentonite clays to absorb the liquor and affixing the clay-terminal liquor with an asphaltic emulsion. Coupons have been prepared and leach tests are in progress.

Future Work

A fast-drilling technique using a vibrating system will be investigated for injecting the stabilizing agent into the ground. If successful, work will begin on a "cold" test, first using the asphaltic emulsion-type grout. The ability to completely "cocoon" a postulated subsurface waste will be investigated.

Product and Containment Improvements (J. E. Hammelman)

Objectives

The goal of this task is to identify and evaluate *in situ* technologies with the potential for providing the high-level waste with an adequate degree of safety.

Progress During Report Period

The technologies to be reviewed must be applied to either (1) decrease the mobility of the in-tank waste or (2) increase the reliability of the waste containment system.

Most of the effort to date has been spent on evaluating technologies capable of decreasing waste mobility. The wastes which are subject to *in situ* immobilization studies are, in order of priority, terminal liquor, non-pumpable liquid heels, salt cake, and, finally, sludge.

Terminal liquor *in situ* fixation processes include neutralization with acid (HNO_3 , H_3PO_4 , H_2CO_3 , etc.) and reaction with silicon compounds (clay, diatomite, water glass, etc.).

Evaluations of these technologies have been initiated. A partial literature search has been completed. In cases where data are missing, laboratory studies will be requested.

Methods for improving waste containment have involved concepts which add an additional layer of containment to the waste. These concepts do not appear to be highly promising.

Summary

Definition of the problem and potential solutions are still developing. Collection of data on processing options are being collected on the basis of study priority. At this point, waste fixation options appear more promising than waste containment ones.

Future Work

Work on data collection, including cost information where possible, will continue. As soon as criteria are available, comparisons will be made and conclusions drawn so that the engineering effort can be better directed.

Groundwater Management (D. J. Brown)

Objective

The objective of this subtask is to develop methods for controlling the rate and direction of radionuclide movement in the Hanford subsurface environment for improving radionuclide immobilization and containment capability.

Prior Work

Preliminary scouting studies were made to identify those parameters which control the rate and direction of groundwater movement. On the basis of the information available, several methods were proposed by which the groundwater could be controlled. One parameter identified was permeability. Methods were proposed by which the permeability of the sediments could be altered. These methods included (1) explosive devices, (2) using an air curtain, and (3) physically grouting the pore space through which the

groundwater moves. A second parameter considered was that of introducing chemicals to alter the viscosity of the groundwater. A third method consists of altering the natural groundwater balance within a given area by ingesting or discharging water into the subsurface environment.

The effort of the scouting studies was directed toward retarding or shifting groundwater flow patterns and/or physically removing the groundwater from one location and moving it to another by pumping.

Progress During Report Period

Work was started to more precisely define the hydrologic parameter of the sediments over the Hanford Reservation. Initial pump tests have been scoped and the equipment ordered to carry out the field testing.

Evaluation

Although a delay has been experienced in the start of the field pumping tests, the objectives of this task should be accomplished on schedule.

Problem Areas

Availability of the pump test equipment has caused a five-month delay in starting the field testing. Equipment has now been identified at various locations throughout the United States, and the vendor contacted.

Future Work

Scouting studies have identified certain parameters and methods of controlling the groundwater flow systems. Field tests will soon be initiated to accurately define hydrologic properties of the sediments which control the groundwater flow rate and direction underlying Hanford.

When additional and improved field data become available, a clearer understanding will emerge as to the flow system's ability to transport and store groundwater. This will permit detailed impact and immobilization studies to be conducted, thus allowing for the proper hydrologic management of the Hanford groundwater flow system.

ACTINIDE ANALYSES IN HANFORD WASTE (S. J. Johnson and W. I. Winters)

Prior Work

None.

Objective

The actinide content of various Hanford high-level wastes such as salt cake, sludges, and terminal liquor must be established in order to determine acceptable long-term management alternatives for the wastes. An actinide analytical method is presently being developed at ARHCO for quantitative determination of actinides at levels ranging from below their maximum permissible concentrations in water to the nanocurie per gram of waste level. The high salt caustic nature of the waste and the expected low levels of actinides create a unique analytical problem. Several different approaches for the isolation of actinides from the waste are being considered, such as

- Group solvent extraction with dihexyldiethylcarbamyldimethylene phosphonate (DHDECMP) or Aliquat-336® (General Mills Company) and selective stripping of individual actinides.
- Selective extraction of individual actinides with tri-iso-octylamine (TIOA) or thenoyl-tri-fluoroacetone (TTA).

- High-pressure ion exchange to isolate either individual actinides or the group.
- Isolation of actinides by carrier precipitation techniques.
- Solvent extraction or ion exchange separations from basic media.

Progress During Report Period

Initial experiments were performed to evaluate DHDECMP as extractant for the actinides. Results showed that plutonium could be quantitatively extracted from a 6M HNO_3 -1M $\text{Al}(\text{NO}_3)_3$ matrix with 30 vol% DHDECMP in xylene. It was necessary to use 100% DHDECMP, however, to effectively extract americium and neptunium from the same matrix. The 100% DHDECMP must then be diluted at least 50% with xylene before the actinides can be stripped.

Plutonium and neptunium were easily stripped with 0.1M HNO_3 -0.1M HF from 50 vol% DHDECMP-xylene. This, however, posed a problem when the neptunium and plutonium concentrations were too low. Direct mounts of the acid on stainless steel discs are necessary for alpha analysis and the HF caused corrosion of the discs which produced interference during counting. It was thus necessary to boil the acid solutions down to dryness to remove volatile HF, and then to re-dilute with HNO_3 .

Preliminary data show that americium can be stripped from 50 vol% DHDECMP-xylene with 0.1M HNO_3 . Experiments are presently under way to further evaluate various agents for stripping Pu, Am, Np, and U from various concentrations of DHDECMP in xylene.

Aliquat-336, a quaternary ammonium extractant, was

found to quantitatively extract greater than 90% ^{241}Am , ^{239}Pu , ^{237}Np , and ^{233}U tracers from a synthetic terminal liquor. Americium-241 was successfully stripped from the organic with 8M HNO_3 . A 1.0M Na_2CO_3 solution was found to quantitatively strip Pu, Np, and U from the organic. After acidification of the Na_2CO_3 solution to 1M HNO_3 , 80% of the Pu was extracted into 0.5M thenoyltrifluoroacetone (TTA) in xylene. Future work will be directed toward obtaining quantitative extraction and separation of Np with TTA. The procedure will then be formalized for testing on actual waste samples.

Future Work

The Aliquat-336 separation will be applied to the analysis of the actinides in actual terminal liquors. If successful separations are obtained, then work will proceed on refining extraction conditions, applying to other waste forms, and decreasing the detection limits for the method.

EQUIPMENT DECOMMISSIONING

(B. B. Harshbarger).

Objective

To develop and demonstrate processes for consolidating contaminated equipment or other metal components--emphasis to be on decontamination and significant bulk volume reduction without hazard increase to the biosphere.

Prior Work

Meltdown using a thermite-type reaction for fusion heat was identified as the simplest means for obtaining volume reduction since intact equipment could be charged to the

melter, obviating the need for independent size-reduction. The batch "hole-in-the-ground" and the continuous "autogenous" melters were postulated as operable configurations for the thermite-type melters. Additionally, a melter for intact equipment employing a gimbal-mounted arcing mobile graphite electrode was proposed.

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

Progress During Report Period

Lectromelt Corporation of Pittsburgh was visited to discuss the feasibility of the gimbal-mounted, graphite-electrode arc melter. They concurred that the concept is feasible and agreed to submit a proposal for a prototype melter capable of covering a melting area 6' x 9'. Their proposal should be forthcoming in February. They suggested that water shotting of the dripping melt would be preferable to collecting it in water-cooled boats because a solid buildup of metal on the walls of the boat may occur before the drips have a chance to run into the collection basin. Remelting of the shot in a conventional furnace will be necessary to make ingots, but materials handling problems of shotted steel are much less complex than those associated with fragmented steel. Lectromelt will make no provision for off-gas treatment facilities in their proposal; an independent design will be required for this problem.

The hole-in-the-ground melter test scheduled for December has been held up by inability to get refractory-coated lances made by Maintenance. Steel planned for use in the test was sold as scrap by excess utilization so the test is now waiting on both steel and lances. It has been

tentatively rescheduled for February.

Laboratory hot cell melting tests await the preparation of the metal coupons needed as feedstock. Preliminary findings on the off-gas problems during meltdown should be available in February.

Full-Scale decontamination tests are planned for the next quarter. The cost of decontaminating a failed Purex dissolver is estimated at \$10,000 for the manpower and materials needed.

The total available feedstock for the program is approximately 150,000 cubic feet with a total weight less than 3,750 tons (basis: 90% void volume and 500 pounds per cubic foot true density).

Future Work

The proposal by Lectromelt Corporation will be evaluated and an independent design firm contacted to design the off-gas treatment facilities as well as to provide engineering evaluation as to a suitable structure (existing or new) in which to house the melter.

Product quality, homogeneity, and distribution of charge stock components will be determined for both the hole-in-the-ground melt and the hot cell crucible melt.

Decontamination of full-scale intact equipment to generate a cost-benefit profile will be carried out as soon as monitoring manpower can be allocated.

WASTE IMMOBILIZATION

INERT CARRIER PROCESS EVALUATIONObjective

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 current work has been to evaluate the UTC mixing process in regard to its being included in the ARHCO cold pilot-plant and subsequently in a hot demonstration-scale immobilization 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 uncalkaolin). The pilot process equipment was piped as shown by the schematic diagram, Figure 3. By observation the mixing results were mostly favorable:

- Rapid startup and attainment of equilibrium operation was possible (~5 to 10 min).

FIGURE 3

INERT CARRIER PROCESS PILOT-PLANT SETUP FOR AQUEOUS SILICATE MIXING DEMONSTRATION

- Equipment shutdown and cleanout was achieved in about three minutes.
- Density of the peanut butter-like product mixture appeared to be somewhat higher (less porosity) than that made by ordinary laboratory mixing techniques.
- Some NPH carrier, however, 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.
- It was determined that Teflon-lined equipment was suitable to prevent wet clay from sticking to equipment surfaces. For similar reasons a polypropylene separator column was used to separate the product from the carrier (Figure 3).

Progress During Report Period (R. A. Watrous)

Under Special Agreement SA-179 a second series of pilot-plant tests were defined and performed using the UTC pilot-plant facility and personnel. The following five major objectives were designed into this second series of mixing tests:

- 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.
- Test the inert carrier mixing concept when a bentonite clay is used.
- Add nonradioactive cesium to the synthetic waste

formulations to permit comparison of cesium retention between the ICP mixed product samples and those mechanically mixed in the laboratory.

- Test the ability of the ICP process to accommodate higher caustic concentration in the synthetic waste, which when mixed with calcined kaolin could potentially result in a temperature excursion.

The equipment arrangement used was essentially as indicated by Figure 3.

Second Mixing Series

In initial tests, UTC personnel conducted tests to improve carrier separation as well as compare NPH with heptane as the carrier. A vibrator was attached to the separator column to help separate the product and the carrier. Several runs were made to check out the operation of the separator with the vibrator as well as to compare carriers.

Some reduction of free carrier in the product resulted with the vibrator on the separator. The least carrier transfer was experienced with a 50.8-cm product height using vibration. This indicated that the height of the product layer had some influence on carrier decanting. However some entrained carrier still remained in the product. Running the product over a moving belt screen removed most of the free, but none of the entrapped, carrier. No difference in mixing characteristics or carrier transfer with the product was found between heptane and NPH. 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.

Second Demonstration Runs

On October 16 and 17, 1974, a second series of demonstration runs was arranged. Personnel participating in these tests at Coyote, California, were:

Atlantic Richfield Hanford Company

M. H. Campbell
C. H. Delegard
W. P. Metz
D. A. Turner
R. A. Watrous

United Technology Center

C. H. Carlton
D. D. Ordahl
J. F. Schimscheimer
R. D. Sheeline

Two synthetic waste formulations (Table UTC-1) were proposed as being representative of dilute and normal terminal liquor.

Table UTC-2 defines the clay type and mixing ratios used in this series of demonstration runs. Some observations regarding product quality are also noted in Table UTC-2.

TABLE UTC-1
NONRADIOACTIVE SYNTHETIC CAUSTIC WASTE FORMULATIONS

<u>Ingredient</u>	<u>Waste No. 1</u> <u>wt%</u>	<u>Waste No. 2</u> <u>wt%</u>
H ₂ O	50	47.4
NaNO ₃	20	21.1
NaNO ₂	10	7.4
NaOH	10	14.2
NaAlO ₂	10	9.8
Cs ₂ CO ₃	0.35	0.35
Total	100.35	100.25

TABLE UTC-2
SECOND DEMONSTRATION TEST SERIES WITH HEPTANE CARRIER

<u>Order</u>	<u>Identification</u>	<u>Clay Type</u>	<u>Calibration</u> <u>g/min</u>	<u>Nominal</u> <u>Ratio</u>	<u>Waste Calibration</u>		<u>Clay/Waste Ratio</u>		<u>Product Appearance</u> <u>Comments</u>
					<u>Start</u> <u>ml/min</u>	<u>Finish</u> <u>ml/min</u>	<u>Start</u> <u>g/ml</u>	<u>Finish</u> <u>g/ml</u>	
1	C1	Bentonite	1,650	0.74	2,230	2,230	0.74	0.74	Soupy.
2	C2	Bentonite	1,650	0.84	1,964	1,980	0.84	0.83	Soupy.
3	C3*	Bentonite	1,650	1.04	1,586	-	1.04	-	Fair-good.
3	D2*	Bentonite	1,650	1.04	-	1,600	-	1.03	Fair-good.
4	C4	Bentonite	1,650	1.24	1,330	1,230	1.24	1.34	Looks like unreacted clay.
5	A1	Kaolin	1,450	0.75	2,013	2,000	0.72	0.72	Good.
6	A2*	Kaolin	1,450	1.0	1,450	-	1.0	-	Excellent.
6	B2*	Kaolin	1,450	1.0	-	1,480	-	0.98	Excellent.
7	F1	Kaolin	1,500	0.67	2,240 [†]	2,240	0.67	0.67	Good.
8	F2	Kaolin	1,500	0.84	1,785 [†]	1,820	0.84	0.82	Good.
9	F3	Kaolin	1,500	1.04	1,440 [†]	1,360	1.04	1.10	Thick.
10	F4	Calcined kaolin	1,500	1.0	1,560 [†]	-	0.96	-	Hung up in separator by solidified chunk from previous run.

Other observed results are summarized as follows:

- Use of normal heptane as the carrier (instead of NPH) showed no difference in mixing characteristics or in the observed amounts of carrier transferred with the product. Product samples were sent to ARHCO laboratories for analyses of entrained carrier and comparison with products made with NPH. Results are expected in January 1975 after completion of current work to develop an analytical method for heptane in clay.
- An apparently serious difficulty in using this mixing process with bentonite became evident. In tests using Federal Bentonite's Wyo-Bond[®] (a 200-mesh, sodium-form uncalcined bentonite) the product as it came out of the separator column was impregnated with bubbles of carrier liquid up to several millimeters in diameter. Little of this organic separated from the clay/waste mixture on setting overnight. Deentrainment of carrier appeared to be a more serious problem with the bentonite reactants than with either the kaolin or calcined kaolin reactants. In tests using synthetic waste #2 (more representative of terminal liquor at its limiting concentration) and a 30° C carrier temperature, no temperature excursions or premature hardening problems were encountered in the separator column. [At higher operating temperature, however, a problem may exist.]
- In Run F4 there was product holdup in the column. It was fairly stiff, packed down readily under

vibration, and extruded very slowly. When the separator column was cleaned out, a large chunk of product from Run F3 had caused major blockage. This material had a reasonable amount of time to harden while clays were being charged in the feeder. If the separator column had been cleaned out after Run F3, product delivery would have been similar to F3.

- Product density and cesium retention results were determined in ARHCO laboratories and are discussed in the following Section, "Evaluation of UTC Products."

Carrier Removal Development

Following demonstration tests, UTC made a further effort to improve the product-carrier separation. A synchronous (vibratory) screen gave satisfactory carrier separation, but the product transfer off the screen was inadequate.

A Syntron feeder was tried with some success. The product spreading did help in separating entrained carrier. Air blowing across the product helped to evaporate a considerable amount of free carrier so that it did not run into the product collection container. Samples taken from the separator and from the end of the Syntron channel indicated some loss of entrained carrier; however no analysis was run as it was believed that a heated system would improve carrier removal.

A belt conveyor was fabricated with 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. As this conveyor system

incorporated the features that were expected to give best removal of the heptane carrier, a series of test runs were made with the three clays as shown in Table UTC-3. 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-min vacuum treatment, weighed, cured at 75° C, and weighed again. The weight losses are shown in Table UTC-4.

Significantly less weight loss is shown for all samples after being treated by vibration, heat, and a flow of air on the belt conveyor. These weight losses represent mostly heptane, but include some water loss. Actual carrier retention is currently being analyzed by ARHCO laboratories and results are expected in January 1975.

Preliminary Evaluations of UTC Products (C. H. Delegard)

Liter-samples of the mixed products formulated during the demonstration tests were shipped to ARHCO's Chemical Technology Laboratory to be examined and analyzed. Meanwhile, UTC continued their efforts to lower the carrier content of the clay/waste mixtures and sent further liter-samples from these later efforts.

These UTC products were compared with similar laboratory mechanically mixed products. The product qualities of concern are density, cesium retention, and extent of cancrinite formation. In comparing unreacted UTC products among themselves, product carrier content is an important quality. The densities and cesium retention abilities of representative UTC products and their mechanically mixed counterparts have been determined. Unfortunately, X-ray

TABLE UTC-3

TEST RUNS AND PRODUCT TREATMENT CONDITIONS FOR HEPTANE DEENTRAINMENT

Clay	Feed Ratio	Sample Location	Treatment		
			No Cure	75° Cure	20-min Vacuum and 75° C Cure
Calcined kaolin	0.77	Separator column	X	X	X
		Carrier removal belt	X	X	X
Kaolin	0.89	Separator column	X	X	X
		Carrier removal belt	X	X	X
Bentonite	1.0	Separator column	X	X	X
		Carrier removal belt	X	X	X

Note: Caustic solution was Waste No. 1, Table UTC-1.

TABLE UTC-4

VACUUM AND HEAT CURE WEIGHT LOSS FOR PRODUCT SAMPLES

Clay	Gross Weight of Sample and Location, g*		
		Separator Column	Conveyor Belt
Calcined kaolin	Initial	1,506.3	1,479.0
	20-min vacuum	1,466.5	1,468.8
	Difference	39.8	10.2
	22-hr, 75° C	1,409.0	1,430.0
	Difference	57.5	38.8
Kaolin	Initial	1,430.0	1,528.0
	20-min vacuum	1,385.6	1,519.5
	Difference	44.4	9.5
	20-hr, 75° C **	1,380.0	1,513.0
	Difference	5.6	8.5
Bentonite	Initial	1,633.9	1,630.5
	20-min vacuum†	1,616.0	1,629.5
	Difference	17.8	1.0
	20-hr, 75° C	1,582.0	1,619.0
	Difference	34.0	10.5

*Gross weight includes can and lid (approximately 139 g).

**This includes the free water on the product after cure.

†Vacuum was limited to 26" to avoid blowing the separator sample out of the container. Others went to 29" vacuum after heptane evaporation.

diffraction data to determine cancrinite formation have been delayed due to installation of new diffractometer equipment. A procedure is now being tested to determine the quantity of carrier still present in UTC mixed products.

Using a method proposed by CTL personnel, the particle densities of UTC produced products and their mechanically mixed analogues were determined. The densities for the UTC mixed products were approximately 5% higher than their laboratory mixed counterparts. The disparity in densities would probably be even greater if UTC mixer and

production mechanical mixer products were compared. The mixed products compounded in Baker-Perkins' Rotofeeder^R mechanical mixer appeared to contain even more air bubbles than the CTL laboratory products. Of course, due to space savings, a denser product is favored. The various products' densities are shown in Table UTC-5.

Also shown in Table UTC-5 are the fractions of cesium washed from the UTC, and laboratory-mixed products. For J. R. Simplot's uncalcined kaolin PAB^R and Federal Bentonite's Wyo-Bond^R bentonite, the products' differences in cesium retention are small. For Engelhard's Satintone 1^R calcined kaolin, however, the UTC process does seem to decrease the cesium retention ability. These data will be checked with results for other UTC-prepared Satintone^R samples.

TABLE UTC-5
CESIUM RETENTION AND PARTICLE DENSITY
OF UTC AQUEOUS SILICATE PRODUCTS

Clay	Waste*	Clay/Waste g/ml	Particle Density g/ml		Fraction Cs Washed	
			UTC	Mechanical	UTC	Mechanical
Satintone	#1	1.00	1.9	1.9		
Satintone	#2	1.00	1.9	1.8	0.17	0.024
PAB	#1	1.00	1.8	1.7	0.20	0.26
Wyo-Bond	#1	1.24	1.8	1.7	0.070	0.045

*#1 = 3.9M NaOH; #2 = 6.2M NaOH.

Future Plans

Laboratory analyses of UTC product samples are expected to be completed early next quarter. At that time it should be possible to make a final evaluation of the feasibility of simple clay/waste mixing using the inert carrier process. However for a more definitive evaluation of mechanical

mixing versus inert carrier mixing, the following additional testing is considered necessary:

- Testing (at vendors' plants) of mechanical mixers under conditions and objectives more identical to those used in the UTC tests described above.
- Scouting runs at both mechanical mixer and UTC pilot-plants to test the addition and co-mixing of binder reagents such as cement.

A proposal has also been 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. Currently this proposal is being analyzed; a decision to enter into contract with UTC for Phase I work may be made early next quarter.

ECONOMIC STUDIES (J. E. Hammelman)

Objectives

The immediate goals of this study are

- To compare waste solidification strategies involving aqueous silicate and silicate melt processing.
- To identify for future study areas which show potential processing cost reductions.

Prior Work

During the previous report period cost data for process

chemicals and utilities were collected and reviewed. In order to obtain an engineering estimate of waste storage capital requirements, rough storage concepts were developed and estimated.

Progress During Report Period

Cost numbers for chemicals, utilities, and storage have been collected, reviewed, and summarized for study purposes. Processing strategy options have also been evaluated and the associated costs defined. The last estimates to be derived before the actual economic analysis are those for the processing plant construction.

A summary of the processing costs and volumes to be used in the economic analysis study are presented in Table II. Drafting of the final study report is approximately one-half complete.

Evaluation

While a present worth analysis is not possible until processing plant capital cost estimates are obtained, it is apparent that the "Lean Clay" process which traps all salts in a cancrinite-type aluminosilicate cage is not economically competitive with the other processes. Further evaluation including present worth analysis has been deferred until plant costs are available.

Summary

All of the cost estimates with the exception of the plant capital have been determined for the study. As soon as plant estimates are determined economic analysis will be performed.

TABLE II
PROCESSING COST AND VOLUME SUMMARY

<u>Feed</u>	<u>Process</u>	<u>Volume Product</u> <u>Volume Feed</u>	<u>Chemical- Utility Cost</u> <u>\$/gal feed</u>
Terminal liquor	Rich clay-bentonite	1.32	0.078
	Rich clay-kaolin	1.26	0.142
	Lean clay-bentonite	2.99	0.730
	Lean clay-kaolin	2.94	1.00
	Silicate melt (bentonite solidification)	1.72	0.149
	Silicate melt (nitric acid addition)	0.65	0.234
Composite waste (salt cake + sludge)	Rich clay-bentonite	1.6	0.115
	Rich clay-kaolin	1.6	0.228
	Lean clay-bentonite	10.2	4.830
	Lean clay-kaolin	10.2	5.616
	Silicate melt	0.96	0.054

60

ARR-ST-110 B

Future Work

The next tasks to be performed are the completion of the processing plant estimates followed by economic analysis and documentation of the study. After study documentation the decision of future studies will be examined.

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 than 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.

Cancrinite products from 49 commercially available clays were tested for hardness, pH, volume increase, and percent liquid not sorbed by the product. Fourteen clays were selected for further study.

A variety of powdered aqueous silicate products were subjected to approximately 10^9 rads of cobalt-60 radiation. That dose is the calculated upper limit anticipated for Hanford aqueous silicate products. X-Ray diffraction, scanning electron photomicrographs, and thermogravimetric studies showed no radiation-induced structural alteration of the products occurred due to irradiation.

The melting range for cancrinite products is about 900° to 1200° C. Zeolytic 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 area of the samples. Leach rates of products strongly depend on the processing mode used.

Scanning electron photographs of cancrinite products show them to be masses of spherical crystals ~ 0.5 to $3 \mu\text{m}$ in diameter.

Progress During Report Period

Leachability Criteria for Immobilized Radioactive Wastes

(G. S. Barney)

Leachability criteria for solidified radioactive wastes have not yet been established. An in-depth analysis of the hazards associated with water leaching of stored, solidified, radioactive wastes is necessary to obtain these criteria. In the absence of such criteria, it may be useful to consider calculation of maximum permissible leach rates (MPLR) based on several simplifying assumptions. The basis for these calculations is that water, after contacting the solid waste, may safely contain radionuclide concentrations less than or equal to maximum permissible concentration (MPC) in an uncontrolled zone. The MPC values for major radionuclides contained in Hanford waste are given in Table III.

TABLE III
MAXIMUM PERMISSIBLE CONCENTRATIONS
(MPC) OF RADIONUCLIDES IN WATER

<u>Isotope</u>	<u>MPC, Ci/liter</u>
Cs	2×10^{-8}
Sr	3×10^{-10}
Ru	1×10^{-8}

The approximate concentration of ^{137}Cs , ^{90}Sr , and ^{106}Ru in the solid waste are 10^{-2} , 10^{-4} , and 10^{-4} curies per liter, respectively. Assuming congruent leaching, the MPLR in $\text{g}/\text{cm}^2\text{-day}$ is given by

$$\text{MPLR} = \frac{d}{\sum \frac{C_i}{(\text{MPC})_i}} \left(\frac{F}{S} \right)$$

where d is the density of the solid-waste form, C_i is the concentration of the i^{th} isotope in the solid, $(\text{MPC})_i$ is the maximum permissible concentration of the i^{th} isotope, F is the flow rate of water, and S is the surface area contacted by that water. This equation is similar to that noted by personnel in Battelle Pacific Northwest Laboratories. It is assumed that there is perfect mixing of the leachate and a constant leach rate. If the density of the waste-form is assumed to be 2.0 g/ml, then

$$\text{MPLR} = \frac{2000 \text{ g/liter(s)}}{8.4 \times 10^5 \text{ liter/liter(s)}} \left(\frac{F}{S} \right) = 2.4 \times 10^{-3} \text{ g/liter} \left(\frac{F}{S} \right)$$

The value of the fraction, (F/S) , depends on the circumstances by which the water comes in contact with the solidified waste. For example, if Hanford wastes are contained in million-gallon spheres and flooded by the Columbia River (flow rate $\sim 2.5 \times 10^{11}$ liters/day) the value for (F/S) is 400 liters/cm²-day. Values calculated for MPLR at various ratios of (F/S) are given in Table IV.

TABLE IV
MAXIMUM PERMISSIBLE LEACH RATE (MPLR)
FOR SOLID WASTES VERSUS (F/S) RATIO

<u>F/S, liters/cm²-day</u>	<u>MPLR, g/cm²-day</u>
10^2	2.4×10^{-1}
1	2.4×10^{-3}
10^{-2}	2.4×10^{-5}
10^{-4}	2.4×10^{-7}

These results show that very low leach rates may be necessary to prevent slow-moving groundwater from becoming

contaminated to an extent greater than MPC. A hazards analysis is necessary to determine the probability of groundwater contacting stored waste.

Leaching of Massive Aqueous Silicate Products

(G. S. Barney)

The effects of water leaching on the surface of massive cancrinite products were studied using the scanning electron microscope (SEM). The products were made by adding various binders to cancrinite crystals. The products were leached for 177 days using a proposed standard leach test procedure which follows the International Atomic Energy Agency suggested method.^[1] The leach results of these tests were graphically shown in the last progress report^[2] and are shown again in Figure 4. Both the leached surfaces and nonleached matrixes of these samples were examined and compared using SEM. Observations to be made were as follows:

- Porosity of sample and effect on leach rate.
- Relative leachability of binder compared with cancrinite crystals.
- Changes in surface features after leaching.
- Surface effects of firing (850° C) cancrinite products.
- Size of discrete particles in sample matrix.

Figure 5 shows SEM photographs of leached and unleached surfaces of cancrinite products with polymer binders. The polymethylmethacrylate product (#10) appears to be very porous with individual cancrinite crystals imbedded in the polymer matrix. After leaching, the surface becomes rough--possibly due to dissolution of the polymer

FIGURE 4
FRACTION OF CESIUM LEACHED FROM MASSIVE SAMPLES

Sample #10 (1000 X)
POLYMETHYLMETHACRYLATE BINDER

Leached Sample #10 (1000 X)
POLYMETHYLMETHACRYLATE BINDER

Sample #11 (1000 X)
POLYSTYRENE BINDER

Leached Sample #11 (1000 X)
POLYSTYRENE BINDER

FIGURE 5
SEM PHOTOGRAPHS OF CANCRINITE - POLYMER PRODUCTS

binder. Sample #11 with the polystyrene binder is less porous. This may be the reason for the lower leach rate observed for the product. Imbedded cancrinite crystals are obvious in the unleached sample. Again, the leached surface appears to be more rough than the unleached surface, possibly due to dissolution of polystyrene binder leaving behind the crystalline cancrinite.

An unusually low leach rate was observed previously for Sample #17 which is cancrinite with a portland cement Type III binder. This is probably due to the very low porosity of this sample as shown in Figure 5. Sample #14 which gave a much higher leach rate is shown in comparison. Leaching appears to fill up the cavities on the surface of both samples. Individual cancrinite crystals cannot be observed because of the fine particle nature of the cement.

Firing the cancrinite products at $\sim 850^{\circ}\text{C}$ significantly decreases leach rates. Leaching for 177 days also appears to have little effect on the surface features of the fired product as shown in Figure 6. There is, however, a large difference in the sample matrix, depending on the type of clay used to make the product. Cancrinite made from bentonite and then fired gives a glassy matrix whereas kaolin yields a crystalline matrix. This is probably due to the higher silica content of the bentonite.

A dramatic change on the surface of Sample #7 occurred during leaching, as shown in Figure 8. This sample was prepared by reacting fired bentonite, synthetic waste, and CaO as binder. The large crystals that form at the surface are probably those of a calcium compound.

In summary, the following general observations were made on the surface effects of leaching cancrinite samples:

Sample #14 (1000 X)

Leached Sample #14 (1000 X)

Sample #17 (1000 X)

Leached Sample #17 (1000 X)

FIGURE 6
SEM PHOTOGRAPHS OF CANCRINITE - PORTLAND CEMENT PRODUCTS

Sample #4 (400 X)
FROM BENTONITE

Leached Sample #4 (400 X)
FROM BENTONITE

Sample #8 (1000 X)
FROM KAOLIN

Leached Sample #8 (1000 X)
FROM KAOLIN

FIGURE 7
SEM PHOTOGRAPHS OF FIRED CANCRINITE PRODUCTS

Sample #7 (1000 X)
CALCIUM OXIDE BINDER

Leached Sample #7 (1000 X)
CALCIUM OXIDE BINDER

Sample #13 (1000 X)
PORTLAND CEMENT BINDER

Leached Sample #13 (1000 X)
PORTLAND CEMENT BINDER

FIGURE 8
SEM PHOTOGRAPHS OF CANCRINITE -
CALCIUM OXIDE (PORTLAND CEMENT)

1. Polymer binders appear to leach faster than the cancrinite.
2. Leach rates are definitely dependent on surface porosity as shown by SEM photographs.
3. Leaching has very little effect on the appearance of fired ($\sim 850^{\circ}$ C) cancrinite products in contrast to products with binders.

Application of the Aqueous Silicate Process to
Immobilization of Salt Cake and Sludge (C. H. Delegard)

Application of the Aqueous Silicate process to immobilization of the water-soluble portion of a salt cake/sludge mixture was determined recently. Eight grams of a mixture of 10 wt% 104-A sludge and 90 wt% Tank 108-S salt cake were partially dissolved in 20 ml of water. Portions of the supernatant composition, shown in Table V were made 5 in hydroxide and were then reacted for five days at 60° with Indian Hill[®] kaolinite-bentonite clay (Interpace Corporation) using a 1:1 clay/waste ratio. The cancrinite products were leached in deionized water at room temperature using the proposed standard leach test. The bulk leach rates after 528 hours were about 1.6×10^{-4} g/cm²-day based on ^{90}Sr and 1.1×10^{-4} g/cm²-day based on ^{137}Cs . The cumulative fraction of ^{90}Sr leached was 0.0087 and of ^{137}Cs was 0.027. Experiments are presently under way to determine the application of the Aqueous Silicate process to immobilization of both water-soluble and -insoluble portions of salt cake/sludge.

TABLE V
COMPOSITION OF SALT CAKE/SLUDGE SUPERNATANT

Component	<u>Salt Cake/Sludge Supernatant</u>	
	<u>Concentration</u>	
OH ⁻	0.250	moles/liter
NO ₃ ⁻	3.29	moles/liter
NO ₂ ⁻	0.0093	moles/liter
AlO ₂ ⁻	0.0918	moles/liter
CO ₃ ⁼	0.400	moles/liter
¹³⁷ Cs	3.35 x 10 ⁴	μCi/liter
⁸⁹⁺⁹⁰ Sr	5.19 x 10 ³	μCi/liter

Immobilization of ¹⁰⁶Ru-Bearing Waste Liquor

(C. H. Delegard)

A study was made to determine the effectiveness of the Aqueous Silicate process for immobilizing ¹⁰⁶Ru. Waste liquor (Tank 109-S) from which nearly all ¹³⁷Cs had been removed as a result of laboratory volume reduction experiments was used as feed. As shown in Table VI, this waste contained 2 x 10⁴ μCi/ml ¹⁰⁶Ru. Enough solid NaOH was added to the waste liquor to bring the caustic concentration to 5M. Portions of the waste solution were reacted for five days at 60° C with Engelhard Company's calcined kaolin Satintone 1® , J. R. Simplot Company's uncalcined kaolin PAB®, and Interpace Company's mixed kaolin-bentonite Indian Hill®. It was found, by water-washing the products, that roughly 99% of the ruthenium reported to the wash. This behavior was anticipated because of the anionic nature of ruthenium in alkaline aqueous solutions, and is not considered serious with respect to long-term immobilization product forms because of the short half-life (about one year) for ¹⁰⁶Ru.

TABLE VI
COMPOSITION OF 109-S

<u>Component</u>	<u>Concentration</u>
NO ₃ ⁻	0.700M
NO ₂ ⁻	1.039M
OH ⁻	1.44M
AlO ₂ ⁻	0.846M
¹⁰⁶ Rh	1.97 x 10 ⁴ μCi/liter
¹³⁷ Cs	<3.3 μCi/liter

Hanford Groundwater Leaching of Certain Aqueous
Silicate Products (C. H. Delegard)

Numerous data on the leach rates of aqueous silicate products have been gathered and reported. Most of these data were obtained using distilled water as leachant. For comparison with leach data from other researchers, pure distilled water leachant is requisite. However for leaching products which could potentially be stored at the Hanford site, it was deemed desirable to evaluate Hanford groundwater as the leachant and to compare leaching results obtained with this leachant with those obtained with deionized water.

Using previously determined Hanford groundwater compositions as a basis, a simulated groundwater was formulated with a pH of 9.4 and containing 1.5 meq/liter Si, 6.5 meq/liter Na, 13 meq/liter CO₃⁼, and 2.7 meq/liter Cl⁻. This solution was used as leachant for two powdered aqueous silicate products. Due to possible cracking or swelling, massive coupon-type leach samples provide little control of leaching surface area and were therefore not used. Instead the powdered products were used to equalize surface area effects and thus provide a better comparison of leaching by the two leachants.

One product was made from Georgia Kaolin's MC-101[®] bentonite and the other with sodium silicate solution; 104-BY waste liquor was used in both instances. X-Ray diffraction of similarly made nonradioactive products showed cancrinite and unreacted bentonite in the MC-101 product. Cancrinite alone appeared in the sodium silicate product.

As shown in Figure 9, the total fraction of cesium leached was higher for both products when using simulated Hanford groundwater as leachant. While Hanford groundwater has a higher pH than the distilled water (thus making it less corrosive to the cancrinite structure), it appears that the sodium in the groundwater ion exchanges the fixed cesium and causes the higher leach rate.

It must be emphasized that the surface area of the powder in contact with the leachant was extremely high because of the small particle sizes of the powder; thus the fractions of cesium leached obtained were much higher than those obtained when leaching typical massive block-like samples.

In summary, the leach data obtained clearly suggest further leach rate determinations for other waste forms using simulated Hanford groundwater as leachant.

Future Work

- Make additional heat of reaction determinations for commercial clays.
- Test various binders for cancrinite crystals.
- Obtain additional leach rate data for massive aqueous silicate products.
- Determine leach rate and hardness of products heated to various temperatures (to 1000° C).

FIGURE 9
CESIUM LEACHING FROM AQUEOUS SILICATE PRODUCTS
USING DISTILLED AND GROUNDWATER LEACHANTS

- Measure vapor pressure of clay products at various temperatures so that pressure increase during storage can be predicted.
- Apply the Aqueous Silicate process to sludge solids.
- Study cesium disposition in the aqueous silicate product.

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 treatment with gaseous HF-O_2 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% SiO_2), and 0 to 15 wt% boron trioxide (B_2O_3) 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^{-7} 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 (B_2O_3), 10 wt% sodium carbonate (Na_2CO_3), and 82.8 wt% crushed basalt rock. The leach rate, based on ^{239}Pu , was only 2×10^{-8} g/cm²-day after seven days of leaching.

Progress During Report Period

Viscosities of Silicate Melt Formulations:

(A. L. Dressen)

To effectively pour molten glass from a continuous melter, melt viscosities should be in the range 50 to 200

poises. Optimum operating temperature for achieving such viscosities in formulations to immobilize salt cake are currently being determined for eight glass compositions previously found to yield satisfactory products (Table VII). Salt cake used in these tests is a synthetic mixture of the composition shown in Table VIII.

TABLE VII
FORMULATIONS FOR VISCOSITY TESTS COMPOSITION,
WEIGHT PERCENT

<u>Sample No.</u>	<u>Salt Cake</u>	<u>Sand</u>	<u>Basalt</u>	<u>CaO</u>	<u>B₂O₃</u>
V-1	40	50			10
V-2	40	55		5	
V-3	40	50		10	
V-4	50	45		5	
V-5	50	40		10	
V-6	30		60		10
V-7	40		50		10
V-8	40		60		

TABLE VIII
COMPOSITION OF SYNTHETIC SALT CAKE

<u>Component</u>	<u>Concentration, wt%</u>
NaNO ₃	38.0
Na ₂ CO ₃	13.8
NaNO ₂	19.9
NaOH	1.8
CsNO ₃	3.6
NaAlO ₂	14.6
Sr(NO ₃) ₂	1.8
SrCO ₃	1.8
NaH ₂ PO ₄	1.3
Na ₂ SO ₄	1.6
NaCl	0.9

Results of viscosity measurements for five of the formulations are summarized in Table IX. These data are plotted as $\log \eta$ (where η is viscosity in poise) versus $\frac{1}{T}$ ($^{\circ}\text{K}$) in Figure 10.

The lowest viscosities occur for the two formulations containing basalt and B_2O_3 . If one makes the assumption that a viscosity of 100 poises or less is necessary to pour the molten glass, these two mixtures containing 30 and 40 wt% salt cake require operating temperatures of only 1000 and 1100 $^{\circ}\text{C}$, respectively.

Glass formulations in which sand (99.8% SiO_2) supplies the silica exhibit higher viscosities when lime (CaO) is substituted for B_2O_3 . Operating temperatures $\sim 100^{\circ}\text{C}$ higher are necessary to pour sand-lime mixtures.

In general, furnace temperatures for formulations containing sand must be in the range 1250 to 1350 $^{\circ}\text{C}$ whereas those for basalt mixtures can be about 250 $^{\circ}\text{C}$ lower. Not surprisingly, however, higher waste content in formulations containing either basalt or sand lowers the temperature required to achieve pourable viscosity.

Future Work

- Complete tests to determine ^{137}Cs and ^{106}Ru volatilization during melting of formulations for immobilization of radioactive salt cake.
- Complete all batch tests with actual and synthetic salt cake.
- Prepare terminal report on batch-scale studies of immobilization of salt cake.

TABLE IX
VISCOSITIES OF SILICATE MELT SAMPLES

Sample No.	Viscosity at Given Temperature (°C), Poise									
	<u>900</u>	<u>1000</u>	<u>1050</u>	<u>1100</u>	<u>1150</u>	<u>1200</u>	<u>1250</u>	<u>1300</u>	<u>1350</u>	<u>1400</u>
V-1		1640		445		162		82		
V-3				1220		405		160		76
V-5			980		300		127		66	
V-6	1600	245		75		32				
V-7	1300	102		37		17

FIGURE 10
VISCOSITIES OF SILICATE MELT FORMULATIONS

- Begin intensive testing of silicate immobilization of actual sludges, contaminated soils, and incinerator ash.
- Complete procurement and fabrication of all equipment for laboratory-scale continuous melter.
- Begin continuous melter tests with salt cake.

Application of the Silicate Melt Process to
Immobilization of Salt Cake from Tanks 105-S and 106-S
 (A. L. Dressen and C. W. Hobbick)

Application of the Silicate Melt process to immobilization of salt cake from Tanks 105-S and 106-S was recently demonstrated. The composition of 105-S and 106-S salt cakes are shown in Table X. In one experiment a mixture of 50 wt% 106-S salt cake, 45 wt% sea sand (99.7% SiO₂) and 5 wt% lime (CaO) was melted at 1200° C. The leach rate of the amber-colored soda-lime glass product (based on ¹³⁷Cs) was 3.4 x 10⁻⁶ g/cm²-day after 29 total days of leaching.

TABLE X
 COMPOSITION OF TANKS 105-S and 106-S SALT CAKE

Component	Concentration	
	105-S	106-S
NaNO ₃	100.3 wt%	90.1 wt%
NaNO ₂	0.3 wt%	0.3 wt%
NaAlO ₂	0.1 wt%	0.6 wt%
Na ₂ CO ₃	2.5 wt%	4.1 wt%
NaOH	0.5 wt%	1.0 wt%
Na ₂ SO ₄	0.2 wt%	-
NaH ₂ PO ₄	0.02 wt%	-
¹³⁷ Cs	8.9 μCi/g	17.2 μCi/g
¹²⁵ Sb	2.2 x 10 ⁻² μCi/g	-

Immobilization of 105-S salt cake was accomplished by melting a mixture of 30 wt% salt cake, 60 wt% crushed basalt rock, and 10 wt% boron oxide (B_2O_3) at $1200^\circ C$. The dense (2.8 g/cm^3), black glassy product exhibited a leach rate (based on ^{137}Cs) of $7 \times 10^{-6} \text{ g/cm}^2\text{-day}$ after 44 days of leaching with deionized water.

The leach rates for both of the silicate melt products are comparable with rates for similar products made from synthetic salt cake.

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

Objective

The general objective during the reporting period was to gain information needed to select the glass contact refractories and to finalize the design of the power supply system needed for the Silicate Melt process pilot-plant unit.

Prior Work

A 1.1 ton per day all-electric glass melter, designed by Penberthy Electromelt Company for Evans Specialty Products Company, Corvallis, Oregon, was selected as the basis for designing a pilot-plant unit for the Silicate Melt process. The few modifications required were incorporated in the design of the melter.

Progress During Report Period

The location of the melter for the Silicate Melt process has been chosen to be the northeast corner of

EDL-147, 324 Building, to facilitate greater ease of placement and construction of the melter. The Building modification drawing has been completed along with the general elevation view, engineering flow diagram, and equipment layout for the Silicate Melt process. Personnel from PNL visited Carborundum and Corhart Refractories Companies and the Federal Glass Company of Columbus, Ohio, to gather information on refractories for use in the Silicate Melt Process and operational aspects of all electric glass melters. Due to recommendations from Carborundum and Corhart personnel and from the operational experience of Penberthy Electromelt and Evans Specialty Products in Corvallis, Oregon, Monofrax K-3[®] will be used for the glass contact bricks in the Silicate Melt process. Monofrax K-3 is on order from the Carborundum Company, as is also the secondary paving material, TZB Zircon[®], from the Chas. Taylor & Sons Company. The latter material was selected on the basis of past performance in glass melters operated by Penberthy Electromelt and Evans Specialty Products.

To complete the final design on the electrode power supplies for the Silicate Melt process melter, the electrical conductivities of simulated Hanford waste glasses at operating temperatures were needed. Three simulated Hanford waste glasses have been recently analyzed by PNL personnel. This analysis is presented in the following Section. As a result of this study the specifications for the melter electrode power supplies have been completed.

Future Work

To gain a better understanding of corrosion rates on refractories in contact with simulated Hanford waste glasses, a batch of simulated waste is being sent to

the Carborundum Company, Niagara Falls, New York. Both the fused cast AZS series (Monofrax S-3, S-4, and S-5) and the fused cast chrome series (Monofrax K-3, and E) will be tested. The design of the off-gas system for the Silicate Melt process will be finalized and the equipment put on order.

Electrical Conductivity of Simulated Salt Cake Waste Glasses (J. L. Bates - Battelle Pacific Northwest Laboratories)

The electrical conductivity of molten glass is important in the design and operation of directly heated electric glass waste melters and in the production of quality controlled simulated salt cake waste products. The electrical conductivity of these simulated waste glasses was studied. The compositions are listed in Tables XI through XIV. Melting was performed in air in platinum crucibles at 1400° C.

The conductivity was measured in air at 1 atm using two parallel platinum plates immersed to a known depth into the molten glass. The platinum plates, 0.300" wide, were inserted into parallel slots cut into the ends of high-purity Al_2O_3 tubes. The platinum plates were rigidly held in the slots with platinum pins and ceramic cement. Connecting platinum wires were welded to each plate and exited from the top of the 18" long Al_2O_3 tubes. The alumina tubes were cemented and clamped together to fix the distance between the plates at 0.300".

Temperatures were measured with a Pt versus Pt-10% Rh thermocouple attached to the alumina tubes 1" above the ends of the platinum electrodes.

TABLE XI
 SILICATE MELT INGREDIENTS (SALT CAKE #1) AND
 APPROXIMATE GLASS COMPOSITION

<u>Component</u>	<u>wt%</u>	<u>mol wt</u> <u>g</u>	<u>mol%</u>
Silicate Melt Ingredients (Salt Cake #1)			
NaNO ₃	9.27	85.	7.02
Na ₂ CO ₃	6.00	106.	3.64
NaNO ₂	5.07	69.	4.73
NaOH	3.38	40.	5.44
CsNO ₃	1.11	194.9	0.36
Sr(NO ₃) ₂	1.13	211.6	0.34
NaAlO ₂	0.93	82.	0.73
NaH ₂ PO ₄	0.20	120.	0.11
Na ₃ SO ₃	0.09	142.	0.04
NaCl	0.09	58.5	0.10
H ₃ BO ₃	18.19	61.8	18.95
SiO ₂ (sea sand)	54.54	60	58.54
Approximate Glass Composition			
SiO ₂	68.9	60.	71.6
Na ₂ O	15.5	62.	15.6
B ₂ O ₃	13.0	69.6	11.6
Al ₂ O ₃	0.7	102.	0.5
Cs ₂ O	1.0	281.8	0.2
SrO	0.7	103.6	0.4
P ₂ O ₅	0.2	141.95	0.1

TABLE XII
 SILICATE MELT INGREDIENTS (SALT CAKE #2) AND
 APPROXIMATE GLASS COMPOSITION

<u>Component</u>	<u>wt%</u>	<u>mol wt</u> <u>g</u>	<u>mol%</u>
Silicate Melt Ingredients (Salt Cake #2)			
NaNO ₃	10.38	85.	7.98
NaNO ₂	5.45	69.	5.12
NaAlO ₂	3.99	82.	3.18
Na ₂ CO ₃	3.77	106.	2.38
CsNO ₃	0.98	194.9	0.32
Sr(NO ₃) ₂	0.98	211.6	0.31
NaOH	0.55	40.	0.89
Na ₂ SO ₄	0.44	142.	0.21
NaH ₂ PO ₄	0.36	120.	0.21
NaCl	0.25	58.5	0.29
H ₃ BO ₃	18.21	61.8	19.54
SiO ₂ (sea sand)	54.64	60.	59.57

Approximate Salt Composition

SiO ₂	68.6	60.	71.9
Na ₂ O	13.6	62.	13.9
B ₂ O ₃	12.9	69.6	11.7
Al ₂ O ₃	3.1	102.	1.9
Cs ₂ O	0.9	281.8	0.2
SrO	0.6	103.6	0.4
P ₂ O ₅	0.3	145.95	0.1

TABLE XIII.

SILICATE MELT INGREDIENTS (SALT CAKE #2A) AND
APPROXIMATE GLASS COMPOSITION

Component	wt%	<u>mol wt</u> g	<u>mol%</u>
Silicate Melt Ingredients (Salt Cake #2A)			
NaNO ₃	22.92	85.	20.68
NaNO ₂	12.00	69.	13.34
NaAlO ₂	8.81	82.	8.23
Na ₂ CO ₃	9.32	106.	6.03
Sr(NO ₃) ₂	2.17	211.6	0.79
CsNO ₃	2.17	194.9	0.85
NaOH	1.09	40.	2.08
Na ₂ SO ₄	0.97	142.	0.52
NaH ₂ PO ₄	0.80	120.	0.51
NaCl	0.54	58.5	0.71
NaCO ₃	10.05	100.	7.71
SiO ₂ (sea sand)	30.16	60.	38.55

Approximate Glass Composition

SiO ₂	44.2	60.	47.4
Na ₂ O	34.9	62.	36.2
CaO	8.3	56.	9.5
Al ₂ O ₃	8.0	102.	5.1
Cs ₂ O	2.3	281.8	0.5
SrO	1.6	103.6	1.0
P ₂ O ₅	0.7	141.95	0.3

TABLE XIV
WASTE GLASS ELEMENTAL COMPOSITIONS

	Salt Cake #1		Salt Cake #2		Salt Cake #2A	
	Glass		Glass		Glass	
	wt%	mol%	wt%	mol%	wt%	mol%
O	50.5	60.6	50.7	61.0	39.3	52.7
Si	32.3	22.1	32.2	22.0	20.7	15.8
Na	11.5	9.6	10.0	8.4	25.7	15.8
B	4.1	7.2	4.0	7.1	-	-
Ca	-	-	-	-	6.0	3.2
Al	0.4	0.3	1.7	1.2	4.3	3.4
Cs	0.7	0.1	0.7	0.1	2.5	0.4
Sr	0.5	0.1	0.5	0.1	1.2	0.3
P	0.05	0.04	0.2	0.1	0.3	0.2

The resistance between the two electrodes was measured using two different techniques and equipment:

- A direct measurement of resistance was obtained using a milliohmmeter. The current leads were attached to the voltage probes. The measurements were made only at 40 Hz. Resistance was read directly to $\pm 3\%$ and no external reference resistor or oscillator was inserted into the measurement circuit. Resistance values were limited to 1000 ohms or less.
- A direct measurement of resistance was obtained using an impedance bridge at 1000 Hz. Resistance values were limited to 1000 ohms or less.
- A direct measurement of resistance was obtained using an impedance bridge at 1000 Hz. Resistance values were accurate to $\pm 1\%$ and measurements could be made from 10^{-3} to 10^6 ohms. Direct current measurements were also attempted, but the high ionic nature of the melt resulted in large transient variations apparently resulting from polarization effects.

The immersion depth of the platinum electrodes was determined at temperature. The probes and Al_2O_3 support tubes were slowly lowered into the molten glass. On contact, the resistance of the system suddenly decreased. The probes were then immersed a known distance into the liquid.

Measurements were made during both decreases and increases in temperature beginning at 1400°C . The probes were subsequently frozen into the glass at room temperature and measurements were then made of the solid and liquid from 400°C and above.

Because the geometry of the molten glass is relatively undefined in the system used for these measurements, it was necessary to calibrate the system and determine a cell constant. The specific conductivity can be obtained from the directly measured resistance of a liquid of known resistivity in the identical system. Calibrating with a liquid of known resistance, a cell constant (K) is obtained which is used to calculate the resistance (R) and the specific conductivity (σ)

$$\sigma = \frac{1}{\rho} = \frac{K}{R}$$

where ρ is the specific resistivity.

A cell constant was determined using 0.01 to 1*N* solutions of potassium chloride. Accurate values of the electrical conductivity for these solutions are known as a function of temperature and with specific conductivities between 0.0012 and $0.1\text{ ohm}^{-1}\text{cm}^{-1}$. The cell constant was determined at 40 and 1000 Hz using the milliohmmeter and impedance bridge.

The electrical conductivity results are illustrated in Figures 11 and 12. The results obtained during

FIGURE 11

ELECTRICAL CONDUCTIVITY OF SALT CAKE WASTE GLASSES

FIGURE 12

ELECTRICAL CONDUCTIVITY OF SIMULATED SALT CAKE WASTE GLASSES

heating and cooling are identical at temperatures above 800° C. The $\log \sigma$ versus $1/T$ curves are approximately linear below 800° C. At higher temperatures the conductivity becomes increasingly less temperature dependent. The Salt Cake-2A glass exhibited some unusual variations above 800° C at 40 Hz as a wavy appearance of the curve. The data were, however, reproducible.

The conductivity values above 800° C are consistently higher at 1000 Hz than at 40 Hz. Higher conduction at higher frequency is frequently observed in ionic conducting systems where polarization near the electrodes can occur. This observation is inconsistent with attempts to measure d.c. conductivity with the impedance bridge. Resistance values varied widely and changed with time, current density, and applied voltage.

The higher conductivity at higher frequency suggest that high frequencies could be utilized in the ceramic melter. Many commercial glass manufacturers now use the higher frequencies to take advantage of these increased conductivity values where increased efficiencies may be possible.

In summary, the electrical conductivity of three simulated salt cake waste glasses were measured from 400 to 1400° C. Conduction in solid and liquid silica systems, such as these simulated salt cake waste glasses, occurs principally by the conduction of alkali ions. The differences in conduction values between simulated salt cake wastes should, therefore, be directly related to the alkali composition of the glass.

The electrical conductivity at both 1000 and 1400° C, and at 40 and 1000 Hz, appears to vary linearly with the mole percent of combined sodium and cesium, as

illustrated in Figure 13. The largest variations in Figure 13 were observed at 1000 Hz.

Safety Review of Silicate Melting Process for Atomic
Energy Commission Wastes (J. D. Kaser - Battelle
Pacific Northwest Laboratories)

Objective

This study is being initiated to determine whether a glass-making process has inherent risks which cannot be reduced to acceptable levels at reasonable costs.

This study will consider in detail only the melting and product forming steps; in other words, only those process steps unique to glass-making.

- The fundamental hazardous event to be investigated is the release of dangerous amounts of radioactive material from the processing cell.
- The initial portion of the study will consist of a conceptual design of the process, equipment, and facility. Next, the various ways fundamental hazardous events can occur will be traced and catalogued with the aid of fault trees and event trees.
- The pathways for release will be ranked in order of probabilities and the effect and cost of design changes to reduce risk will be evaluated.
- A comparison of the hazards related to glass-making should be compared with the hazards of alternative processes, such

FIGURE 13

ELECTRICAL CONDUCTIVITY OF SALT CAKE WASTE GLASSES
AT 1000 AND 1400° C, 40 AND 1000 HERTZ AS A
FUNCTION OF COMBINED SODIUM AND CESIUM CONCENTRATION

as the Aqueous Silicate process and encapsulation in concrete. This final portion of the study implies that a similar safety analysis should be made for the alternative processes.

Prior Work

None.

Progress During Report Period

A preliminary review of the glass-making process uncovered three possible ways dangerous amounts of radioactivity could be released from the processing cell.

1. A glass spill in the cell causing vaporization of radioactive material which forms an aerosol so fine that it passes through cell ventilation filters.
2. A hydrocarbon fuel explosion during fuel-fired startup, causing the filters or the cell to rupture.
3. A steam explosion from a sudden injection of water into the melter, strong enough to rupture the cell or off-gas filters.

The first possible hazard emphasizes the importance of the on-going volatility experiments at ARHCO. Further, the design review and pilot-plant testing of the melter should thoroughly cover fuel-fired startup techniques and perhaps look for other startup techniques. Radiological hazards due to fuel explosions will be minimized by using inactive glass material during startup. Cooling water system design should receive a careful safety analysis. A

scope design of the full-scale melting process has been started as a basis for more detailed analysis.

Future Work

A detailed fault tree analysis will be carried out to pin-point failure mechanisms.

SALT CAKE VOLUME REDUCTION (W. W. Schulz)

Objectives

When the present Hanford Waste Management Program is completed approximately 190 million liters of solid salt cake will be stored in underground mild steel tanks. This material will contain at most only a few milligrams or less of radionuclides per metric ton. A decision to remove the salt cake from the present tanks, immobilize it, and store it elsewhere either onsite or offsite, appears to provide strong incentive to concentrate the radionuclides and thereby reduce significantly the volume of inert material which must be immobilized and/or stored as a high-level waste. The work reported here involves scouting studies to explore the potential of well-known precipitation and/or sorption techniques for removing radionuclides including actinides, if present, from aqueous solutions of dissolved salt cake. The objective is to define processes for removing and concentrating all long-lived radionuclides to permit a 10- to 100-fold reduction in the volume of nonradioactive material which must be immobilized and/or stored.

Volume reduction studies were extended this quarter to include removal of long-lived radionuclides from so-called terminal liquor. Some 8 to 12 million gallons of terminal

liquor will have accumulated when currently scheduled waste evaporation operations have been completed. This high-caustic waste contains substantial concentrations of ^{137}Cs and, as yet, undefined small amounts of other radionuclides (e.g., ^{90}Sr , ^{99}Tc , actinides, etc.). Various methods (e.g., partial neutralization followed by vacuum evaporation, Aqueous Silicate process, etc.) for converting this waste to a solid-form suitable for interim storage are being investigated by others. An alternative way of handling terminal liquor is to reduce the concentration of all long-lived radionuclides to levels where the resulting solution can be handled, immobilized, and stored as, preferably, a non-radioactive chemical waste, or at least as a low-level radioactive waste.

Acceptable levels to which the concentrations of ^{90}Sr , ^{137}Cs , and other long-lived radioisotopes must be or should be reduced have not been defined as yet. Tentatively we are attempting to reduce the concentrations of long-lived radionuclides to the MPC_w values for waters in a controlled zone. It is recognized that these levels may be impractically low to attain and that a better criterion is to reduce the hazard index of the radionuclides to or below that of nitrate ion in the waste.

Discussion

Removal of Cesium from Salt Cake Solutions

Previous tests with both actual and synthetic salt cake solutions have shown that the radiocesium concentration of such solutions can be reduced to MPC_w (48-hr exposure) levels by either (a) multiple precipitation of $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ or (b) by passage through one or more beds of Duolite ARC 359^R resin, a phenolic-type ion exchanger available from

the Diamond Shamrock Company. The former method works but has several disadvantages; namely: (a) it is basically a batch process which uses fairly expensive reagents and which generates solids requiring further handling, (b) solution pH must be adjusted to $\leq$ pH 10 for effective cesium scavenging, and (c) large amounts of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ precipitate, in some cases, when the solution is adjusted to pH 10. For these reasons we are concentrating on the use of ion exchange techniques for removal of radiocesium from both salt cake solutions and terminal liquors.

Duolite ARC 359 resin has been used extensively in Hanford's B Plant to remove $\sim 95\%$ of the radiocesium from alkaline Purex and Redox supernatants. Much is already known about its chemical and physical properties. Scouting studies (results of which have been reported previously) show that, as expected, Duolite ARC 359 resin will also remove radiocesium very effectively from both concentrated ($\sim 6.8M$ total sodium) and dilute ($\sim 2M$ total sodium) actual salt cake solutions. Indeed, in one series of tests diluted salt cake solution (pH 12) containing $8400 \mu\text{Ci/liter } ^{137}\text{Cs}$ was passed downflow (1 col vol/hr, 25°C) in succession through two 10-ml beds of Duolite ARC 359 resin. Effluent from the second column contained $< 0.13 \text{ } ^{137}\text{Cs } \mu\text{Ci/liter}$; the MPC_w for ^{137}Cs in water in a controlled zone is $0.4 \mu\text{Ci/liter}$.

Because of the favorable results obtained in the early scouting studies with Duolite ARC 359 resin, we are now undertaking a comprehensive series of tests with both actual and synthetic salt cake solutions to define optimum operating conditions for removal of radiocesium. Column runs will be made to define effects of hydroxide, total sodium, and Na/Cs ratio on cesium sorption capacity of

Duolite ARC 359 resin. Particular emphasis will be placed on studies of sorption of cesium from concentrated 6 to 7 Na) salt cake solutions; successful removal of ^{137}Cs from concentrated solutions will eliminate the need to dilute and reconcentrate prior to final solidification/immobilization of the decontaminated solution. Mathematical methods for correlating cesium breakthrough data for extrapolation to plant-scale columns will be pursued.

Initial results of studies of the effects of feed sodium and hydroxide concentration on uptake of ^{137}Cs by Duolite ARC 359 resin are plotted in Figure 14. Feed for these runs was prepared by diluting a 6.8M Na-pH 12.6 solution obtained by dissolution of salt cake from the 105-S Tank with water and stock NaOH solution. The breakthrough curves in Figure 14 show, in general agreement with the findings of others, that cesium sorption by Duolite ARC 359 resin varies directly with the feed hydroxide concentration. With feeds containing 3 to 6M Na and 1 to 2M hydroxide, the 1% cesium breakthrough point occurred only after passage of 20 to 23 column volumes of effluent.

The results in Figure 14 have an immediate practical significance with respect to use of Duolite ARC 359 resin to remove radiocesium from salt cake solutions. Because of the desire to produce non-hygroscopic salt cake the 222-S vacuum evaporator is currently being operated to produce salt cake containing only very little NaOH. Preparation of satisfactory ion exchange feed from solutions of such salt cake will require addition of at least some NaOH. A convenient source of this NaOH might be terminal liquor itself!

FIGURE 14.

EFFECTS OF FEED COMPOSITION ON UPTAKE OF ^{137}Cs
BY DUOLITE ARC 359 RESIN FROM SALT CAKE SOLUTIONS.

Removal of Cesium from Terminal Liquor

A sample of recycle liquor from the 106-S Tank was used in the first experiment to study Duolite ARC 359 removal of radiocesium from terminal liquor. [Recycle liquor, as the term is used here, refers to solution approaching expected terminal composition but which may be routed through the evaporator one or more times yet.] Composition of this recycle liquor (insofar as it has been determined) is listed in Table XV.

TABLE XV
COMPOSITION OF RECYCLE LIQUOR FROM 106-S TANK

<u>Component</u>	<u>Concentration</u>
NaOH	5.15M
NaNO ₃	2.32M
NaAlO ₂	1.50M
NaNO ₂	0.75M
Na ₂ CO ₃	0.068M
¹³⁷ Cs	3.56 x 10 ⁵ μCi/liter

In preparation for ion exchange tests a portion of the 106-S solution was arbitrarily diluted 10-fold with water (one volume of recycle liquor diluted to 10 volumes). Such dilution provided a solution whose NaOH and total sodium concentration was known to be in a demonstrated range for ¹³⁷Cs removal by Duolite ARC 359 resin. Satisfactory removal of ¹³⁷Cs may be possible with no or smaller dilution; this remains to be demonstrated.

A total of 42 column volumes of the diluted recycle liquor was passed downflow (at 25° C and one column volume per hour) through a 10-ml bed of Duolite ARC 359 resin. [The resin bed had been previously washed with NaOH and water and classified by upflow of water.] A plot of the ¹³⁷Cs concentration (in μCi/ml) of the effluent as a

function of column volumes of effluent is shown in Figure 15.

These initial data show, as expected, that Duolite ARC 359 resin can be used to reduce the ^{137}Cs concentration of 10-fold diluted recycle (terminal) liquor to the MPC_w level ($0.4 \mu\text{Ci/liter}$) for ^{137}Cs in a controlled zone. For the conditions shown in Figure 15 the ^{137}Cs concentration of the first 30 column volumes of effluent was $<0.86 \times 10^{-4} \mu\text{Ci/ml}$, the lower detection limit of the particular gamma analysis technique used.

As part of the overall program to define operating conditions for use of Duolite ARC 359 resin for removal of radiocesium from both salt cake solutions and terminal liquors it is planned to conduct column experiments with undiluted actual terminal liquor. Material for such tests has been requested. Resin column tests with actual terminal liquors will be performed not only to define conditions for reducing the ^{137}Cs concentrations to drinking water levels but also conditions for removal of sufficient heat-producing ^{137}Cs to permit solidification by one of the methods mentioned earlier.

Removal of Strontium from Salt Cake Solutions

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. The resulting salt cake solutions thus contain 3 to $10 \mu\text{Ci/liter}$ ^{90}Sr . The MPC_w for ^{90}Sr in water in a controlled zone is $0.01 \mu\text{Ci/liter}$.

We are investigating both precipitation and ion exchange methods for removing ^{90}Sr from salt cake solutions.

FIGURE 15

DUOLITE ARC 359 RESIN SORPTION OF
 ^{137}Cs FROM DUOLITE RECYCLE LIQUOR

A comprehensive set of experiments (Table XVI) to study effects of salt cake NaOH and Na_2CO_3 concentration 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 75% complete. Because of the inadequacy of presently available (in ARHCO) methods of analyzing for low levels of ^{90}Sr we currently are conducting such experiments with synthetic salt cake solutions spiked with ^{85}Sr ; conclusions derived from these experiments will subsequently be checked in experiments with actual salt cake solutions.

The efficiency of all three of the scavenging agents tested for removing radiostrontium from salt cake solutions increases with increasing pH again indicating the necessity for adding some NaOH to salt cake solutions. At pH's 12 and 12.8 the strontium decontamination factor (Sr DF) and volume of precipitate both vary directly with the concentration of added Sr^{2+} , Ca^{2+} , or Fe^{3+} . At pH 10 the volume of precipitate also varies directly with concentration of added metal ion but at this pH, for some unknown reason, the Sr DF in some cases falls off at the higher added metal ion concentration.

Results in Table XVI show that over the pH range 10 to 12.8 inert $\text{Sr}_3(\text{PO}_4)_2$ precipitates scavenge radiostrontium considerably 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. The centrifuged volume of $\text{Sr}_3(\text{PO}_4)_2$ precipitates is also considerably less than that of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. For these reasons we will emphasize use of $\text{Sr}_3(\text{PO}_4)_2$ scavenging techniques in further studies of removal of radiostrontium from salt cake solutions.

Strontium scavenging by either $\text{Ca}_2(\text{PO}_4)_2$ or $\text{Sr}_3(\text{PO}_4)_2$ precipitates varies not only with pH and concentration of precipitant ion but also with salt cake solution

TABLE XVI

TYPICAL DATA FOR SCAVENGING OF ^{85}Sr FROM SYNTHETIC SALT CAKE SOLUTION

Conditions: Ten-ml portions of synthetic salt cake solution adjusted to indicated pH, traced with ^{85}Sr , made indicated concentration 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.

pH ^a	Scavenging Agent								
	$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$			$\text{Sr}_3(\text{PO}_4)_2$			$\text{Ca}_3(\text{PO}_4)_2$		
	$\text{Fe}(\text{NO}_3)_3$	Sr	Solids ^b	$\text{Sr}(\text{NO}_3)_2$	Sr	Solids	$\text{Ca}(\text{NO}_3)_2$	Sr	Solids
	M	DF	vol, ml	M	DF	vol, ml	M	DF	vol, ml
10	0.029	2.	1.4	0.029	11.	0.4	0.029	9.	1.1
	0.015	25.	1.0	0.015	277.	0.2	0.015	11.	0.5
	0.0075	27.	0.8	0.0075	139.	0.1	0.0075	10.	0.4
	0.0037	15.	0.4	0.0037	127.	0.05	0.0057	6.	0.3
12	0.029	93.	0.95	0.029	147.	0.3	0.029	49.	0.9
	0.015	56.	0.6	0.015	124.	0.2	0.015	23.	0.5
	0.0075	44.	0.3	0.0075	119.	0.15	0.0075	12.	0.35
	0.0037	24.	0.15	0.0037	102.	0.1	0.0037	6.	0.25
12.8	0.029	464.	0.8	0.029	737.	0.3	0.029	420.	0.7
	0.015	296.	0.6	0.015	441.	0.2	0.015	249.	0.4
	0.0075	215.	0.4	0.0075	240.	0.1	0.0075	74.	0.3
	0.0037	57.	0.25	0.0037	101.	0.05	0.0037	16.	0.2

^aInitial salt cake solution 6M NaNO_3 -0.1M NaNO_2 -0.004M Na_2SO_4 -0.025M Na_3PO_4 -0.25M Na_2CO_3 .

^bCentrifuged wet volume.

carbonate concentration (Figure 16). Actual salt cake solutions contain typically only 0.1M carbonate or less. Experiments to study scavenging of radiostrontium by $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2$ precipitates at this lower carbonate concentration are planned.

We are also investigating various sorbents for use in column-type operation for removal of ^{90}Sr from salt cake solutions and, possibly, terminal liquor. Continuous column operation would be preferable to batch-type precipitation processing. As reported previously, we have had some success in using a "strontium phosphate" resin [macroreticular anion resin in which $\text{Sr}_3(\text{PO}_4)_2$ has been precipitated] for removing ^{85}Sr from synthetic salt cake solution; we plan to extend these studies to actual salt cake solutions when a suitable ^{90}Sr analytical method is available. We also plan to test the use of the "titanate" sorbent currently being developed and tested by Sandia Laboratory personnel. Informal arrangements have been made with Sandia people to acquire some of these sorbents in the next quarter or two.

New ^{90}Sr Analytical Procedure

Attempts to determine the efficiency of various scavenging and sorption techniques for removing ^{90}Sr from actual waste solutions has been largely frustrated, as already mentioned, by the inadequacy of the presently available methods for analyzing low levels of ^{90}Sr . The present analytical method involves extraction of the ^{90}Sr from an NH_4NO_3 solution at pH 10 into a thenoyltrifluoroacetone-hexone solvent and subsequent stripping of the ^{90}Sr into a pH 4.5 sodium acetate solution. Recovery of strontium by this procedure is only fair. A more serious objection is that ^{106}Ru , a beta emitter ordinarily present in low-to-high

FIGURE 16

EFFECT OF SALT CAKE Na₂CO₃ CONCENTRATION ON SCAVENGING OF STRONTIUM BY Ca₃(PO₄)₂ AND Sr₃(PO₄)₂ PRECIPITATES

concentrations in actual waste solutions, coextracts and strips with ^{90}Sr , to some extent at least, and is counted as ^{90}Sr .

We have now developed 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. This new procedure involves bis-2-ethylhexylphosphoric acid (HEDHP) extraction of ^{90}Sr from a pH 4.5 sodium acetate solution containing diethylenetriaminepentaacetic acid (DTPA) to complex and prevent the extraction of inert and radioactive contaminants including ^{106}Ru . The extracted ^{90}Sr is stripped into 1M HNO_3 solution, an aliquot of the strip solution is mounted for direct beta counting of the ^{90}Sr . Extraction-strip recovery of strontium is determined in parallel determinations with the sample spiked with the gamma-emitting ^{85}Sr and is generally in the range 85 to 95%.

Thus far this new method has been used with good success to measure the ^{90}Sr concentration of 3-fold diluted actual salt cake (105-S Tank) solution from which ^{137}Cs had been removed by passage through Duolite ARC 359 resin. Such solutions contain, typically, 0.1 to 1 $\mu\text{Ci/liter}$ ^{137}Cs and 100 $\mu\text{Ci/liter}$ ^{106}Ru - ^{106}Rh and, according to the new analytical procedure, 0.7 $\mu\text{Ci/liter}$ ^{90}Sr . Using our most sensitive Ge(Li) detection equipment, no gamma emitters could be detected in the HEDHP extraction. [The ^{90}Sr value reported here cannot be extrapolated to yield the ^{90}Sr concentration of the original undiluted salt cake solution because the Duolite ARC 359 resin may have removed some strontium.]

The new analytical procedure was also successfully used to determine the ^{90}Sr concentration of 10-fold diluted recycle liquor from the 106-S Tank after prior Duolite ARC 359 resin removal of ^{137}Cs . Duplicate analyses showed

this solution to contain only 0.13 $\mu\text{Ci/liter}$ ^{90}Sr ! Once again this value cannot be extrapolated to the ^{90}Sr concentration of the undiluted recycle liquor because the resin treatment may have removed some ^{90}Sr .

Further development of the new ^{90}Sr method and its application to determination of ^{90}Sr levels in scavenged salt cake solutions will be continued next quarter.

Removal of Other Long-Lived Radionuclides

We are well aware, of course, that salt cake solutions and terminal liquor may contain, in addition to ^{137}Cs and ^{90}Sr , other long-lived fission products (*e.g.*, ^{99}Tc , ^{93}Zr , etc.) and actinides. At this point in time we do not know which of these are present in salt cake solutions and terminal liquors and to what extent. [We know that the bulk of the plutonium in mixtures of salt cake and sludge is associated with the sludge and expect that many other long-lived radionuclides (*e.g.*, ^{93}Zr) have also concentrated in the sludge.] Analytical methods are being developed as rapidly as possible to determine the concentration of these other long-lived radionuclides. Until quantitative data are available no satisfactory assessment can be made of which other long-lived radionuclides must be taken account of in volume reduction studies.

Future Work

- A series of Duolite ARC 359 resin runs will be made with NaOH-NaNO_3 solutions spiked with ^{137}Cs to determine breakthrough curves as a function of feed composition.
- Further tests of the applicability of the newly developed ^{90}Sr analytical procedure to analysis of salt cake

solutions and terminal liquors before and after scavenging will be made.

Salt Cake Volume Reduction: Sodium Removal (J. D. Kaser and H. Hollis - Battelle Pacific Northwest Laboratories)

Objective

This project has been undertaken to explore methods for reducing the volume of radioactive salt cake by separating the nonradioactive sodium from the radioisotopes by selective conduction of sodium ions through sodium beta-alumina.

Prior Work

Membranes were cut from a sample of beta-alumina in the form of fused cast refractory brick obtained from the Carborundum Company. Two preliminary experiments were made to try separating sodium from a water solution containing both sodium carbonate and cesium carbonate. The amount of separation observed was not large. Sodium passed through these membranes about three times faster than cesium. After these experiments the membrane was thoroughly rinsed, dried, and tested for leaks using a mass spectrometer helium leak detector. There was appreciable leakage which appeared to occur uniformly over the membrane surface, indicating many small pores.

This leakage means these initial experimental results were not conclusive and should be repeated with leak-free membranes.

Progress During Report Period

Beta-alumina tubes were received from Dr. Atsuo Imai of the Toshiba Company, Japan. These tubes

are non-porous, fine-grained, and specially fabricated for use as solid electrolyte membranes.

Single Cation Conductances. To measure the approximate conductivity of the membrane for a single cation, 1M carbonate solution was placed both inside and outside the beta-alumina tube. The area of contact with the solutions was not determined but was kept approximately constant. The following relative resistances were determined:

	<u>Current</u> milliamps	<u>emf</u> volts	<u>Resistance</u> ohms
Na ⁺	17.0	40	2.4×10^3
Cs ⁺	2.0	40	2×10^4

These results indicate that sodium should permeate the membrane 8.5 times faster than cesium.

Separation from Carbonate Solutions. A series of batch experiments was made using feed solutions containing both sodium and cesium carbonate. Approximately 200 ml of feed solution were placed outside the beta-alumina tube. A stainless steel anode was immersed in this feed solution. At the beginning of each experiment 14 ml of distilled water were placed inside the beta-alumina tube. The stainless steel cathode was immersed in the distilled water; then 40 volts emf were applied across the electrodes. At the conclusion of each experiment both the feed and product solutions were sampled and analyzed and a separation factor was calculated. The separation factor is defined as follows:

$$S.F. = \frac{[Na^+]_p [Cs^+]_f}{[Cs^+]_f [Na^+]_p}$$

where $[\text{Na}^+]_f$ = sodium concentration in the feed

$[\text{Na}^+]_p$ = sodium concentration in the product

$[\text{Cs}^+]_f$ = cesium concentration in the feed

$[\text{Cs}^+]_p$ = cesium concentration in the product.

Results of the first three experiments are tabulated below:

Experiment number:	1	2	3
Separation factor:	25	4.5	2.0
Duration of the Experiment (hours)	1	22	48

The separation factor decreased as the duration of the experiment increased. This may be due to the fact that initially the membrane contains only sodium ions and some time is required for cesium ions to break through.

Separation from Nitrate Solutions. Experiments were conducted to evaluate the separation of mixtures of cesium and sodium in aqueous nitrate solutions. Measured separation factors ranged from 6.5 to 12. Due to the unexpectedly low conductivity of the beta-alumina in nitrate solutions, these values are not steady-state values since all the sodium ions originally in the membrane have not been completely displaced. The beta-alumina tube cracked after the final experiment while being checked for leaks. Details of these experiments are given as follows:

Experiment number:	11/26	11/27
Separation factor:	11.9	6.5
Current, ma (at constant emf of 40 volts)	0.1-0.2	0.2
Membrane resistance, ohms	~200 K	~200 K
Time, hr	25	25
Temperature, °C	25	25

The experimental data show an unusually high membrane resistance when nitrate feed solutions are used rather than carbonate solutions. The resistance in carbonate solutions is about 20,000 ohms, but is increased 10 times to 200,000 ohms when nitrate solution is used. The pH of the feed solutions after the experiment was 6.5 compared with the very basic carbonate feed solution. Dr. Imai suggested that hydronium ions will substitute for sodium in beta-alumina, causing a decrease in conductivity. The conductivity of the membrane recovered when in contact with 1N Na_2CO_3 solution on both sides of the membrane.

It appears that two new problems have arisen: (1) low conductivity with aqueous nitrate feeds and (2) membrane cracking. However the separation factor values are encouraging.

Future Work

Experiments are planned to separate sodium from radioactive aqueous salt cake solution. Process electric power requirements will be estimated from experimental data for aqueous solutions and tentative plans have been made to investigate separation from molten salt cake.

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