ATLANTIC RICHFIELD HANFORD COMPANY
QUARTERLY REPORT
TECHNOLOGY DEVELOPMENT FOR LONG-TERM
MANAGEMENT OF HANFORD HIGH-LEVEL WASTE
OCTOBER 1975 THROUGH DECEMBER 1975

Edited By

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ABSTRACT

This document is the sixth in a series of quarterly reports on work in support of long-term management of Hanford high-level wastes. The work reported here was performed during the period October through December 1975. The specific topics discussed are grouped into the subject areas of:

- *Storage System Integrity and Engineered Improvements*
- *Waste Retrieval*
- *Waste Immobilization and Storage*
- *Contaminated Equipment Volume Reduction*

Previous reports were published as ARH-ST-110 A through D and ARH-ST-132 A.

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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. As currently envisioned, long-term Hanford waste management plans are directed toward future removal of waste from underground storage tanks, conversion of the waste to an improved stabilized form, and final storage of the immobilized waste in a location that does not require controlled management.

The entries in this report under Storage System Integrity and Engineered Improvements are directed toward establishing a data base and methodology for determining the length of time that waste can safely continue to remain in the tanks. This information will also be used to evaluate engineered improvements that might extend the safe in-tank storage period. Identification, development, and demonstration of the technology necessary for retrieval of the waste from underground tanks are discussed under Waste Retrieval. The Immobilization and Storage section of the report summarizes technological developments in the conversion of retrieved waste to an immobilized form satisfactory for final storage and evaluates alternative engineered and final storage methods.

Contaminated Equipment Volume Reduction addresses the development and demonstration of methods for reducing the volume of radioactively contaminated metallic items to a size and form suitable for final storage or disposal. The Energy Research and Development Administration, Division of Environmental Control Technology, sponsors this program; others are sponsored by the Division of Nuclear Fuel Cycle and Production.

SUMMARY

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Combustion limit tests were completed for various sodium nitrate - organic material mixtures. Combustion temperatures (approximately 400° C) exceeded any temperatures recorded for the stored salt-cake waste.	5
Portland Cement Association continued tests to determine the effects of waste chemicals on concrete used in Hanford waste-storage tanks. During a three-month testing period with simulated salt cake solutions, no changes in concrete samples were noted.	5
Development continued on computer models designed to predict radiocontaminant distribution patterns in Hanford Reservation soils and groundwater. Study results now indicate that aquaculture activities, adjacent to the reservation, and the start-up of a second Hanford waste evaporator-crystallizer will have no adverse effects on groundwater flow beneath areas where high-level waste is stored.	9
Preliminary conceptual design of a mechanical system for retrieval of tank-stored waste was completed by Programmed and Remote Systems Corporation.	12
An agitator-pump being studied as a hydraulic waste-retrieval device successfully slurried and pumped synthetic salt cake containing up to 70 weight percent included solids. Interstitial liquor associated with sodium nitrate slurry solids was found to be 50 percent water.	13

SUMMARY (continued)

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Conversion of salt cake to crystalline albite was evaluated as a waste-immobilization alternative. Product leach rates indicated that cesium and strontium are not incorporated into the albite crystalline lattice. Albite was therefore judged an impractical crystalline form for immobilized waste.	22
Tests comparing the leachability of pure synthetic Redox sludge to a clay calcination product made with sludge revealed that reaction with clay reduces leachability significantly.	25
Tests to determine cesium volatility during calcination reactions of synthetic salt cake and clay produced volatility values similar to those obtained for salt cake - silicate melt products manufactured at higher temperatures.	27
Work continued in support of the effort to immobilize waste in silicate-based glasses. The effect of chemical additives on Redox sludge-glasses was evaluated. Tests indicated that feasible glasses containing 30 weight percent sludge can be formed at low temperatures. Chemicals that improve the durability of low-temperature glasses were found to have different effects on high-temperature glasses.	28
Preliminary heat-up began for a laboratory-scale glass melter and work was postponed on an engineering-scale, one-ton-per-day glass melter being built by Battelle-Northwest Laboratories.	32
Sintering of synthetic Redox sludge into a glass matrix was studied as an alternative waste-immobilization concept. Initial experiments with synthetic Redox sludge powder and various crushed glasses yielded products that were very hard and less friable than glass waste forms.	34

SUMMARY (continued)

	<u>Page</u>
In continuing studies of radionuclide removal from synthetic waste liquors, efficiency of ^{137}Cs sorption by resin was observed to increase with higher liquor concentrations of hydroxide and lower concentrations of sodium. Work in actinide removal revealed that the efficiency of americium removal by scavenging and ion exchange tends to increase as sodium nitrate concentration in liquor decreases.	36
Satisfactory removal of ^{90}Sr from actual salt cake was consistent with results obtained for synthetic salt cake, but ^{90}Sr removal from actual terminal liquor was hindered by the presence of an unidentified ligand.	40
Solvents were investigated as a means of extracting sodium from synthetic salt cake solution. Favorable levels of sodium extraction, without appreciable extraction of strontium or cesium, were achieved.	45
The plasma arc furnace torch was demonstrated as a size-reduction device for use in contaminated equipment volume reduction. Preliminary conceptual design of a vacuum meltdown furnace was initiated.	48

STORAGE SYSTEM INTEGRITY AND ENGINEERED IMPROVEMENTS

The objectives of this program are:

- Creation of a data base and methodology for use in periodically evaluating the decision to continue in-tank storage of solidified waste.
- Identification, development, and testing of engineered improvements which could be used to extend the safe storage period of underground tanks.

- Definition of the Hanford groundwater flow system and determination of the extent of groundwater management necessary to control rate and direction of radionuclide movement in the high-level-waste storage areas.

SALT CAKE STABILITY - G. A. Beitel and L. E. Bruns

The potential for exothermic reactions between salt cake nitrates or nitrites and organic materials is critical to the safe storage of Hanford high-level wastes. Studies and tests have been initiated to determine if such reactions are possible.

Shock sensitivity tests, conducted by Poulter Laboratory of Stanford Research Institute, using a standardized U. S. Navy test have shown no evidence of shock-initiated detonation susceptibility.

Combustion limit tests conducted in the Atlantic Richfield Hanford Company laboratories on mixtures of sodium nitrate and organic material (resin or charcoal) have shown that the ease of combustion varies depending on mixture and moisture content.

Combustion limit tests were completed at the end of December. Temperatures required to start combustion exceeded any recorded temperatures for the stored waste and were in the region of 400° C.

These combustion test results will be evaluated and reported during the next report period.

CONTAINMENT INTEGRITY - E. L. Moore and F. R. Vollert

The extended use of Hanford waste-storage tanks will greatly depend on how seriously corrosion and elevated temperatures affect the tanks. Experimental programs have been developed to investigate corrosion of the mild steel

liner and reinforcing bars and deterioration of concrete exposed to the variety of waste compositions found in Hanford tanks. Study of the effects of elevated temperatures on the elastic properties of concrete used in the tanks is also in progress.

The first quarterly report was received from the Portland Cement Association Laboratories on the effects of simulated salt cake solutions on Hanford concrete. No changes were noted in the three-month testing period. The thermal effects testing program was delayed about four months to allow negotiation of contractual agreements. The first tests will be performed during the next report period.

Concrete cores have been removed from the dome of the twenty-year-old 102-A Tank and decontaminated in preparation for shipment to Portland Cement Association for examination. Tests will evaluate the elastic properties of the concrete and will include petrographic sampling, a technique used to examine the concrete's microstructure.

Soil stabilization techniques used in the construction of dams and tunnels are being considered as a way to provide an impervious envelope around a storage tank. In past tests, asphalt emulsion has successfully sealed a joint leak in a waste transfer pipe. Silicate grout, cement grout, and acrylamide organic fixing agent are also being considered and will be tested on a laboratory scale. During the report period, preparations and equipment purchasing continued for scale-up testing of the asphalt emulsion technique and for testing of the vibratory earth drill used to inject the emulsion. Initial tests are planned to begin during the fourth quarter of fiscal year 1976.

RADIONUCLIDE MIGRATION IN GROUNDWATER (formerly RADIONUCLIDE
MIGRATION IN SOILS) - R. A. Deju and R. E. Gephart

The objectives of this program are:

- To conduct the field research necessary to better define the potential migration pathways of radionuclides leaving the high-level-waste storage areas through groundwater.
- To evaluate principal interactions between waste, sediment, and groundwater that are significant in the long-term isolation and/or transport of radioactive waste solutions.
- To determine the extent of radionuclide contamination in the Hanford groundwater environment.

This program involves a three-prong study. First, a geophysical gravity model is being developed and analyzed to identify the transmissive character of various geologic units below the water table. Second, the geophysical study is being complemented by the preparation of strip logs for approximately 100 wells. These strip logs are being used to prepare cross sections along portions of the Hanford Reservation. Using these cross sections, the hydrologic properties of each hydrologic unit will be identified. Third, past hydrologic records of water level, contaminant, and chemistry patterns will be used to determine the extent of contaminant migration through the groundwater pathway and the various sedimentary units that will be delineated with geophysics and strip logs.

During the report period, effort continued on interpreting the results of gravity readings taken at 350 stations on the Hanford Reservation. This geophysical work will form the basis for three-dimensional gravity modeling of the Hanford

Basin. Data corrections have been assembled and compiled for each gravity station. The terrain and regional corrections applied are based upon data reported in "A Regional Gravity Investigation of the Hanford Reservation." The work to date reveals that the anticlinal structure near Gable Mountain is a double anticline with a minor intervening syncline. The relief of this structure, from the crest of the anticlines to the trough of the syncline, appears to be about 30 meters (100 feet). Other anomalies appear to be buried basalt cliffs 3 to 17 meters (10 to 50 feet) high. This information will be compiled to determine the position of paleochannels (thick sedimentary deposits resulting from ancestral pathways of the Columbia River) in the Reservation, especially south of Gable Mountain and between Gable Butte and Gable Mountain. These permeable paleochannel deposits afford the shortest travel times for radiocontaminants to the river through the groundwater pathway.

Samples of sediment materials from wells on the Hanford Reservation have been prepared into strip logs. A strip log consists of well samples, taken at various depths, that are attached to a sheet of cardboard in a continuous strip showing the vertical distribution of sedimentary material. A series of such strip logs from many wells will permit evaluation of stratigraphic variations. The sedimentary strip logs of the Ringold Formation and the glaciofluviatile material will therefore permit study of the movement of groundwater and associated radionuclides in the unconfined aquifer. Preparation of these strip logs was completed during this quarter. This work was coupled with microscopic analyses of the samples. Using the strip logs, work is under way to determine the hydrologic and geologic properties of the unconfined aquifer.

By the end of the next report period, the modeling of gravity data should be well advanced, and the preliminary

stratigraphic and hydrologic correlations using strip logs should be completed. Work to determine the chemistry of contaminant migration will be initiated during the fourth quarter of FY 1976.

LONG-TERM GROUNDWATER MANAGEMENT - R. C. Arnett, R. A. Deju,
R. E. Gephart, R. K. Ledgerwood

The objectives of this program are:

- To identify potential ways in which the groundwater can come into contact with the high-level waste.
- To identify existing computer codes and models useful in predicting consequences of events identified in the objective above.
- To determine the data-gathering requirements needed for long-term prediction of subsurface contaminant migration from high-level-waste storage areas into and through the groundwater flow system.
- To examine potential impact to the high-level-waste storage areas resulting from past, present, and projected activities at Hanford; potentially hazardous contamination accidents; and potential or existing agricultural development adjacent to or within the Hanford Reservation.

A program has been initiated to evaluate computer models and data required for long-term groundwater management of waste areas. A rather comprehensive analysis of finite element techniques as applied to groundwater flow problems is being made. Groundwater flow models available commercially are being examined for their usefulness at Hanford and are being compared

to existing models developed onsite. Areas where significant deficiencies are noted in the computer modeling effort will be slated for additional development work. By recognizing all data requirements and having available the most suitable computer systems to handle this information, maximum credibility should be achieved in predictive efforts.

The initial phase of the nonisothermal vadose zone computer model developed by Boeing Computer Services Richland, Inc. (BCSR) and Dr. Bruce Finlayson, University of Washington, was completed. A report on this work was prepared and is being reviewed. The report describes a computer model which predicts the movement of air and water in desiccated soils. The equations used are a combination of those used in the oil industry for multi-phase fluid movement in porous media and those specialized to the air water system in soil science technology. The report will summarize the computer program and show calculated results for both steady-state and transient conditions. The model shows that water flow is upward in the top of the open lysimeter while at steady state, thus helping to protect the groundwater from contamination.

Work was conducted by BCSR staff in developing methods that summarize the extensive hydrologic analysis results needed to evaluate the environmental consequences of groundwater contamination. A fourth-order Runge-Kutta solution technique was formulated for solving the simultaneous pathline differential equations. This technique will be used in calculating streaklines and arrival time distributions of specific radiocontaminants.

Work was completed on evaluating the hydrologic impact on the high-level-waste storage areas of the Columbia Aqua Products Company aquaculture operation located along the Reservation's northwestern boundary. A report will be issued in January 1976.

Results indicate that these operations will have no major impact on the areas where high level waste is stored. Travel time calculations indicate an actual benefit from the operations, since buildup of a groundwater mound near Umtanum Ridge would slow down travel times of radiocontaminants to the Columbia River through the pathway between Umtanum Ridge and Gable Butte.

A research plan was outlined and the first groundwater well was drilled for the geohydrologic study of the Cold Creek Valley. Irrigation activities in this valley will affect the hydrologic flow regime underlying the Hanford high-level-waste storage areas. The drilling specifications for three additional research wells were completed. The first well will be 30 cm (12 inches) in diameter and will serve as a pumping well site for a multiple observation network. The other two research wells will be located approximately 2.4 kilometers (1.5 miles) north and south of the pumping test site. All wells will be used to characterize the hydrogeology of the Cold Creek Valley and to evaluate the extent of recharge through the valley into the aquifers underlying the high-level-waste storage areas.

Work was completed to evaluate the impact of added water discharges to Gable Mountain Pond resulting from start-up of the second Hanford waste evaporator-crystallizer (the 242-A Evaporator). Its possible effect on the water-table surface appears to be small.

During the next report period, the offsite computer model inventory will be continued with emphasis on the finite element techniques. Work will also continue on concise methods of summarizing and presenting Hanford hydrologic data. Sensitivity tests will be conducted for the arrival time technique. Drilling and coring of wells in the Cold Creek Valley should be completed.

WASTE RETRIEVAL

CONCEPT AND EQUIPMENT DEVELOPMENT - I. E. Reep

The objectives of this task are:

- The definition of areas of the waste retrieval program which will require technology development and evaluation.
- Identification of potential retrieval techniques.
- Preliminary testing of the identified retrieval techniques to establish feasibility.
- Evaluation and reporting on engineering studies and designs performed in support of this subtask.

The concept and equipment development subtask of the Waste Retrieval Program is scheduled to end at the close of FY 1976. Potential retrieval methods have been identified and their feasibility has been established in "bench scale" tests.

A number of engineering study reports were received from consultants during the report period. These included an engineering study and cost estimate for a waste retrieval system; a study evaluating the adaptability of standard mechanical, hydraulic, and pneumatic devices to salt cake and sludge retrieval at Hanford; and a study on the high-level waste management technology development program. This information will provide a basis for the design of a full-scale waste retrieval system.

Mechanical Retrieval - H. A. Wallskog

The objective of this subtask is to complete the conceptual design of in-tank waste retrieval subsystem

components (mechanical mining arm, remote viewing, and material-handling subsystems). The design information provided by this subtask will be used as part of a Conceptual Design Description of a Waste Retrieval System.

A final conceptual design report including cost estimates for a salt cake retrieval system was received from Programmed and Remote Systems Corporation, St. Paul, Minnesota. The report was reviewed by ARHCO engineers. The PaR design is based on a remotely operated, hydraulically activated, articulated mechanical arm.

A final engineering report on the usefulness of standard mechanical, hydraulic, and pneumatic devices for salt cake and sludge retrieval at Hanford was completed. This report presents a summary of the major accomplishments of the bench-scale testing effort, and presents conclusions and recommendations regarding the applicability of "off-the-shelf" equipment to waste retrieval systems. Final review of this report is in progress.

Hydraulic Retrieval - N. M. Arnold

The objective of this subtask is to evaluate the feasibility of in-tank waste retrieval using hydraulic techniques. The concept presently under consideration is the use of a Scumbuster[®] (Vaughan Company, Inc., Montesano, Washington) pump to slurry salt cake in its own interstitial liquor and pump the resulting slurry out of the tank. This technique could also be used for the retrieval of sludge if the moisture content is sufficiently high. Two agitator pumps and their hydraulic power units have been procured for testing. A hydraulic retrieval test loop has been installed for use with the larger pump.

Two series of tests of a modified Model 300 Vaughan Scumbuster® pump (rated at 100 hp) were successfully completed during the report period. Synthetic salt cake, with up to 70 weight percent included solids and an average specific gravity of 1.45, was pumped at rates of up to 200 gallons (757 liters) per minute in a test loop as illustrated in Figure 1. The test series had to be modified because of excessive hydraulic fluid temperatures in the pump motor. Modifications to the pump hydraulic system to eliminate this problem are currently being studied.

Supportive equipment for testing a modified Model 150 Vaughan Scumbuster® centrifugal pump (rated at 60 hp) was purchased and will be delivered during the next quarter. A mobile test rig is being fabricated for pump tests expected to begin late in the next report period.

Waste Material Properties - C. H. Delegard

The objective of this subtask is the characterization of the static and dynamic properties of salt cake, sludge, and other waste forms under conditions proposed for the retrieval operation. Data from this program and the Salt Cake Characterization program will aid in the selection of retrieval concepts and in the formulation of realistic simulated salt cake for testing retrieval equipment.

Previous work has revealed that significant quantities of interstitial liquor may be present in all forms of drained salt cake and that recent salt cake may retain more interstitial liquor than early salt cake. Simulations of sludge and diatomaceous earth combined with salt cake have been formulated.

Several synthetic salt cake slurry samples obtained during the October 1975 test of the Model 300 Vaughan Scumbuster® pump were analyzed for particle size distribution of slurry

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FIGURE 1

HYDRAULIC RETRIEVAL TEST SETUP

solids. The solids were separated from the liquor, washed with isopropanol, dried, and analyzed by screening. As an aid in interpreting the data, the weight ratio of particles larger than 10 mesh (2000 μ m) to particles smaller than 35 mesh (500 μ m) was plotted versus elapsed slurry agitation time (Figure 2). The proportion of larger particles in the slurry samples increased as sodium nitrate content of the salt cake was increased.

In its last run, the Scumbuster[®] successfully pumped a slurry sample containing approximately 70 weight percent sodium nitrate solids. Interstitial liquor associated with the sodium nitrate slurry solids was found to be 50 percent water.

COLD DEMONSTRATION - I. E. Reep

The objectives of this task are:

- Design, fabrication and functional testing of a full-scale waste retrieval system.
- Design and construction of a prototype testing facility that will allow complete testing of waste retrieval subsystem components.
- Testing of subsystem components in order to develop operating techniques and procedures for use during hot demonstration and to obtain design data for modification of components.

PaR In-Tank Waste Retrieval Subsystems - H. A. Wallskog

Preparation of Functional Design Criteria and the Conceptual Design Description for a Waste Retrieval System will begin during the next report period. These documents will be used to support an authorization request to start

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FIGURE 2
 PARTICLE WEIGHT RATIO VERSUS
 PUMPING TIME FOR A
 SYNTHETIC SALT CAKE

preliminary (Title I) design of a waste retrieval system.

Prototype Testing Facility - N. M. Arnold

The prototype testing facility will be included in the Functional Design Criteria and Conceptual Design Description of the full-scale waste retrieval system described above. It was determined that the metal stand for testing mining equipment, formerly known as the cold test facility, will be inadequate for currently planned tests of waste retrieval subsystem components and the complete waste retrieval system. For this reason work on the cold test facility (stand) was stopped and conceptual design of a prototype testing facility is scheduled to begin during the next report period. The prototype testing facility will permit thorough testing of subsystem components and the complete, full-scale waste retrieval system.

Gradall[®] Mechanical Retrieval System - I. E. Reep

Vitro Engineering's design of modifications to the Gradall[®] mechanical mining system (manufactured by Warner and Swasey Company, Gradall Division, New Philadelphia, Ohio) was stopped during the first quarter of FY 1976 to permit an evaluation of overall program priorities. Modification of the Gradall[®] system was suspended indefinitely during the report period when it was determined that PaR's salt cake retrieval system, designed specifically for use at Hanford, will meet program requirements.

IMMOBILIZATION AND STORAGE

The objectives of this program are:

1. Identification, development, and demonstration of technologies for converting high-level waste to an immobilized form satisfactory for long-term or final storage.
2. Evaluation of alternative engineered and final storage methods.

AQUEOUS SILICATE PROCESS

The conversion of fission product wastes to solid, insoluble products suitable for long-term or final storage is being investigated through the Aqueous Silicate process. This process utilizes reactions of clay with waste to form stable products. Basically, three processing options are available in the Aqueous Silicate process. The first option, called the Rich Clay process, features low-temperature aqueous reaction of a stoichiometric excess of clay with waste solution or sludge. For the second option (the Lean Clay process), powders resulting from the stoichiometric aqueous reaction (again at low temperature) of waste solution with clay can be formed, by addition of binder, into products harder and of smoother surface than rich clay products. In the third option, called the Clay Calcination process, dry waste materials (such as salt cake) or other dehydrated waste solutions are reacted with clay at 600 to 800° C to form water- and nitrate-free sodium aluminosilicate powders. These powders may then be incorporated with binders or sintered to form clay calcination products. Aqueous silicate development during the report period was directed exclusively toward this third option.

Crystallinity of Salt - Clay Calcination Products - G. S. Barney

Experiments were continued to determine the effect of reaction variables on the identity of crystalline products from the Clay Calcination process. Clay type, waste composition, and temperature were varied and the products examined by X-ray diffraction. The results of these experiments, given in Table I, show that:

- Changing reaction temperature from 750° to 1000° C did not generally affect the product identity.
- Waste composition and clay type were the most important factors in determining the crystal structure of the products. The anion in the salt evidently has a strong influence on the type of crystalline product obtained.
- Most of the products from kaolin reactions gave intense X-ray patterns indicating good crystallinity, but bentonite reactions yielded products with much poorer crystallinity and, in one case, a glass.

The products obtained from calcined clays were identical to those from uncalcined clays and are not, therefore, reported in Table I.

The influence of crystalline structure on the leach rates of radionuclides from sodium aluminosilicate waste forms is not yet known. If the radionuclide is bound in the sodium aluminosilicate framework, the effect of crystalline structure should be large. If the radionuclide forms a separate crystalline phase different from the host phase, the effect of the host phase crystalline structure will be small.

TABLE I
EFFECTS OF CLAY TYPE, WASTE COMPOSITION
AND CALCINATION TEMPERATURE ON PRODUCT IDENTITY [a]

Waste Composition [b]	Temp., °C	Clay Type	
		Kaolin	Bentonite
NaNO ₃ -NaNO ₂ -NaOH	750	Very good NEP	Medium SCAS
	1000	Very good NEP	Poor SCAS
NaNO ₃	750	Very good CAR	Poor NOS
	1000	Very good CAR	Poor NOS
NaNO ₂	750	Good NEP + SAS + SOD	Medium SOD
	1000	Good NEP + SAS	Poor SOD
NaOH	750	Medium NEP + SAS	Medium NEP + SAS + SMS
	1000	Medium NEP + SAS	Non-Crystalline

- [a] NEP = nepheline (NaAlSiO₄)
 CAR = carnegieite (NaAlSiO₄)
 SOD = sodalite (Na₄Al₃Si₃O₁₂(OH))
 SAS = Sodium aluminum silicate (Na₆Al₄Si₄O₁₇)
 NOS = noselite (Na₈Al₆Si₆O₂₄SO₄)
 SMS = sodium metasilicate (Na₂SiO₃)
 SCAS = sodium calcium aluminum silicate sulfate (Na₆Ca₂Al₆Si₆O₂₄(SO₄)₂)

- [b] 40% waste salt in clay-waste mixture. The NaNO₃-NaNO₂-NaOH-clay mixture was 20% NaNO₃, 10% NaNO₂, 10% NaOH, and 60% clay.

Evaluation of Crystalline Albite as a Product Form - G. S. Barney

Natural albite is known to be more stable toward leaching than nepheline, and thus it is being considered as a possible matrix for the immobilization of radioactive waste. Synthetic salt cake waste was converted to crystalline albite ($\text{NaAlSi}_3\text{O}_8$) by reaction with a mixture of $\text{Al}(\text{OH})_3$ and $\text{SiO}_2 \cdot x \text{H}_2\text{O}$ (Si/Al mole ration = 3). The reaction mixture contained various percentages of the synthetic salt waste in order to determine the effect on leach rate and crystallinity. The salt cake (NaNO_3) was spiked with cesium and strontium in order to test the leachability of albite. Cylindrical samples of the reaction products were prepared by pressing and sintering. Leach rates of these cylinders are shown in Table II.

Leach rates for these albite products are not significantly lower than for nepheline products obtained previously, a result which suggests that cesium and strontium are present in the above samples as separate phases and are not incorporated into the albite crystalline lattice.

Since leach rates are not improved over nepheline, albite is probably not a practical crystalline form for immobilized waste. The volume of albite would be larger than nepheline and the silicate reagents more expensive.

Leach Rate Determinations for Sludge - Clay Calcination Products G. S. Barney

Results of leach rate measurements were obtained for sintered clay calcination products made by reacting synthetic Redox or Purex sludge (see compositions given in Table III) with various clays.

TABLE II

LEACH RATES OF ALBITE SAMPLES

Percentage NaNO ₃	Crystallinity	Sintering Temperature* C°	Leach Rates, g/cm ² -day			
			Based on Cs		Based on Sr	
			1 Day	28 Days	1 Day	28 Days
10	Good	1000	2.9×10^{-3}	1.8×10^{-4}	$< 1.8 \times 10^{-4}$	$< 2.6 \times 10^{-5}$
20	Medium	900	$< 7.3 \times 10^{-5}$	2.4×10^{-4}	$< 1.8 \times 10^{-4}$	$< 2.5 \times 10^{-5}$
30	Medium	700	3.0×10^{-3}	4.5×10^{-3}	$< 1.8 \times 10^{-4}$	2.7×10^{-3}
40	Poor	600	1.0×10^{-2}	6.1×10^{-3}	$< 1.8 \times 10^{-4}$	1.5×10^{-3}

* The optimum sintering temperatures (determined earlier) were used for these samples.

TABLE III

COMPOSITIONS OF REDOX AND PUREX SLUDGES*

<u>Component</u>	<u>Weight Percent of Component in</u>	
	<u>Synthetic Redox Sludge</u>	<u>Synthetic Purex Sludge</u>
H ₂ O	15.3	15
NaOH	7.1	5
NaNO ₃	16.7	7
NaNO ₂		10
Al(OH) ₃	54.0	7
Fe(OH) ₃	5.0	13
Cr(OH) ₃	1.9	
Sr(OH) ₂		7
Na ₂ CO ₃		13
Na ₂ SO ₄	<hr/>	<hr/> 20
	100.0	97

* Small amounts of CsOH and Sr(OH)₂·8 H₂O were spiked into the mixtures so that leach rates could be measured.

Reactions of both bentonite and kaolin clays with synthetic sludge at 1000° C yielded powdered products. These were mixed with a small amount of dilute Na_2SiO_3 solution and pressed into cylindrical shapes. The cylinders were air-dried and sintered at 900° C for two hours. The resulting sintered products were then leached according to the standard International Atomic Energy Agency method. Leach rates of these cylinders varied from 4.0×10^{-6} to 1.2×10^{-3} g/cm²-day (at 20 days based on cesium).

Few trends could be observed in these data. Surprisingly, the concentration of sludge in the product appeared to have little effect on the observed leach rate. However, products made from Redox sludge had slightly higher leach rates than those from Purex sludge. One likely explanation for the scatter in leach rate values is that the porosities of the samples vary significantly, thus affecting the actual surface areas relative to the geometric surface area (i.e., the basis upon which leach rate values are expressed). Compacting pressure, composition, firing temperature, bloating, and other factors could affect porosity.

Evaluation of Clay Calcination Immobilization for Sludge

G. S. Barney

Leach rates of a sample of pure sludge were measured and compared to that of sludge reacted with clay (Clay Calcination process) in order to determine any change in leachability. Synthetic Redox sludge was spiked with cesium and strontium and then fired at 1000° C. The leach rate of this material is compared to that of a typical clay calcination product in Table IV.

TABLE IV

LEACH RATES OF UNTREATED SLUDGE
AND A CLAY CALCINATION PRODUCT
(g/cm²-day)

Leaching Time Days	Untreated Sludge Based on		Clay Calcination Product Based on		R* for	
	Cesium	Strontium	Cesium	Strontium	Cs	Sr
1	1.1×10^{-1}	2.8×10^{-2}	1.9×10^{-3}	2.7×10^{-3}	58	10
2	1.2×10^{-1}	1.4×10^{-2}	1.3×10^{-3}	3.0×10^{-3}	92	5
6	3.8×10^{-2}	7.2×10^{-3}	2.1×10^{-4}	6.5×10^{-4}	181	11
12	1.1×10^{-2}	3.4×10^{-3}	1.3×10^{-4}	3.0×10^{-4}	85	11
19	3.1×10^{-3}	2.3×10^{-3}	4.2×10^{-5}	4.2×10^{-4}	74	5

$$* R = \frac{\text{Leach Rate of Untreated Sludge}}{\text{Leach Rate of Clay Calcination Product}}$$

These results show that the clay calcination product has significantly lower leach rates than those of the untreated sludge. The cesium leach rate is lowered more than the strontium leach rate. Reaction with clay, therefore, has a beneficial effect on leaching properties of sludge waste.

Cesium Volatility During Clay Calcination Reactions

C. H. Delegard

Evaluation of the Clay Calcination process relative to glass-forming processes requires a knowledge of the disposition of volatile radionuclides (e.g., cesium) during the clay calcination reaction. During the report period, the first two of a planned series of cesium volatility determinations were made. One experiment utilized synthetic salt cake with a nonradioactive cesium spike. The second utilized actual salt cake from the 105-S waste tank. In both experiments, a reaction charge which was 40 percent salt cake and 60 percent kaolin by weight was reacted for four hours at temperatures beginning at 650° C and ending at 1000° C.

For the nonradioactive salt cake product, ~ 1.8 percent of the original cesium volatilized and reported to the off-gas train. For the 105-S salt cake product, however, only ~ 0.2 percent of the radioactive cesium volatilized. In both cases, ~ 80 percent of the cesium condensed on the first thermally cool surface encountered in the off-gas train. These cesium volatility values are comparable to those obtained for salt cake - silicate melt products manufactured at 1100 - 1300° C.^[1]

Further determinations of cesium volatility in clay calcination reactions are planned to provide data on the effects of varying clay/waste ratios, reaction times, and temperatures.

SILICATE MELT PROCESS

The objective of this task is to develop and demonstrate processes for incorporation of Hanford high-level wastes into immobile silicate-based glass forms. Present laboratory-scale glass making activities are (a) development and demonstration of suitable processes for conversion of Hanford sludges to glasses, and (b) construction and operation of a small-scale (10 to 25 kg of glass per day) all-electric, continuous melter for eventual hot-cell use with high-level waste.

In previous work, screening experiments for fixation of synthetic Redox sludge were performed to define various temperature and composition regions where satisfactory glasses could be prepared. An equipment development program has also been under way with construction of a one-ton-per-day continuous electromelter to process simulated wastes.

Development of Glass Formulations for Hanford Sludge

M. J. Kupfer, C. W. Hobbick, W. W. Schulz

During the report period, the effect of various chemical additives on the viscosity and durability of low-temperature ($< 1000^{\circ}\text{C}$) Redox sludge-glass melts was evaluated. Based on the results of earlier glass-making experiments, two reference glass formulations were prepared by melting at 1000°C the mixtures given in Table V.

Other glasses were prepared by additions of either Li_2O , LiF , Na_2SiF_6 , ZnO , CaO , BaO , ZrO_2 , or TiO_2 to the 40 percent sludge-glass formulation; or by addition of Li_2O or ZnO to the 30 percent sludge-glass formulation. The viscosities of the melts at 900°C and 1000°C were estimated from visual observations. Solidified products were leached in deionized water at 25°C , with leach rates being determined after 24 hours and 120 hours of leaching.

TABLE VREFERENCE FORMULATIONS OF
REDOX SLUDGE GLASS

<u>Component</u>	<u>Wt. % Composition (Premelt)</u>	
	<u>30%</u> <u>Formulation</u>	<u>40%</u> <u>Formulation</u>
Sludge *	30	40
B ₂ O ₃	27	18
Na ₂ O	13	18
SiO ₂	30	24
	<u>100</u>	<u>100</u>

* Composition of Synthetic Redox Sludge:

<u>Component</u>	<u>Wt. %</u>
Al ₂ O ₃	53.5
Na ₂ CO ₃	22.4
SiO ₂	11.1
Fe ₂ O ₃	4.4
Cr ₂ O ₃	2.8
MnO ₂	1.5
CaO	1.2
SrO	0.16
Trace Elements	2.94
	<u>100.0</u>

Table VI summarizes the experimental conditions and results:

- Viscosity at 1000° C was reduced most effectively for both reference formulations by 5 weight percent replacement of Na₂O by Li₂O. (Workers at the E. I. du Pont de Nemours and Company Savannah River Laboratory have observed similar results using their high-alumina sludge.)
- Addition of fluoride to the 40 percent sludge formulations also reduced viscosity markedly.
- Additions of 5 - 10 weight percent ZnO resulted in slight reduction of melt viscosity, increased product homogeneity, and ensured prevention of a Na₂CrO₄ phase which often segregated during melting of the 40 percent sludge formulations.

The leach rate (based on strontium) of the reference 40 percent sludge glass without additions was 2.0×10^{-5} g/cm²-day after 120 hours leaching. Leach rates for glasses containing Li₂O, ZnO, Na₂SiF₆, LiF, or ZrO₂ were improved over the base glass rate by up to a factor of ten. The glass containing TiO₂ exhibited the best leach rate - 5×10^{-7} g/cm²-day.

Leach rates for products containing CaO and BaO were very high - about 10^{-3} to 10^{-4} g/cm²-day. These glasses were poorly melted, however, since the CaO and BaO additions made them highly refractory. Leach rates for these glasses would undoubtedly be improved if the melting temperature were increased.

The leach rates for the glasses containing 30 weight percent sludge were, in general, considerably lower than for the 40 weight percent sludge glasses. The only additions evaluated for the 30 percent sludge-glasses, ZnO and/or Li₂O, did not appear to improve leachability over the base 30 percent sludge-glass.

TABLE VI
EFFECTS OF CHEMICAL ADDITIVES ON
SILICATE MELT VISCOSITY AND LEACHABILITY

BASIC INGRED. WT. %				ADDITIVES WT. %	VISCOSITY ^a		LEACH RATE g/cm ² -day		PRODUCT APPEARANCE
Sludge	SiO ₂	B ₂ O ₃	Na ₂ O		900° C	1000° C	24 hours	120 hours	
40	24	18	18	None	5	3-4	9.8×10^{-5}	2.0×10^{-5}	Fair, opaque, much Na ₂ CrO ₄
36	21.5	16	16	10 CaO	4-5	4	3.5×10^{-3}	1.2×10^{-3}	Poorly melted, crusty, Na ₂ CrO ₄
36	21.5	16	16	7 CaO, 3 BaO	4-5	4	3.3×10^{-3}	7.1×10^{-4}	Poorly melted, crusty, Na ₂ CrO ₄
36	21.5	16	16	10 ZnO	4	3	1.3×10^{-5}	1.2×10^{-5}	Good, brown opaque, trace Na ₂ CrO ₄
40	24	18	14	4 Li ₂ O	4	2	1.4×10^{-4}	5.1×10^{-6}	Fair, glassy, much Na ₂ CrO ₄
40	24	18	17	1 Na ₂ SiF ₆	3-4	3	8.1×10^{-5}	1.6×10^{-5}	Poor, incomplete dissolution, Na ₂ CrO ₄
38	23	17	17	5 ZnO	3-4	3	2.6×10^{-4}	5.0×10^{-5}	Good, brown opaque, trace Na ₂ CrO ₄
40	24	24 ^b	12 ^b	See ^b	4-5	3-4	1.2×10^{-5}	2.3×10^{-6}	Fair, glassy, no Na ₂ CrO ₄
38	23	17	17	5 ZrO ₂	5	4	6.1×10^{-6}	1.5×10^{-6}	Fair, partially devitrified, Na ₂ CrO ₄
37	22	17	17	7 TiO ₂	4	3	2.2×10^{-6}	5.7×10^{-7}	Fair, partially devitrified, Na ₂ CrO ₄
40	24	18	17.75	0.25 LiF	3-4	2-3	1.2×10^{-4}	1.4×10^{-5}	Fair, partially devitrified, Na ₂ CrO ₄
36	21.5	16	12	10 ZnO, 4 Li ₂ O	2	2	2.1×10^{-4}	3.8×10^{-5}	Good glass, trace Na ₂ CrO ₄
36	21.5	19 ^b	9 ^b	10 ZnO, 4 Li ₂ O	3	2	1.2×10^{-5}	6.3×10^{-6}	Good glass, no Na ₂ CrO ₄
36	21.5	16	12	10 CaO	3	3	1.4×10^{-3}	1.2×10^{-5}	Fair, partially devitrified, Na ₂ CrO ₄
38	23	17	17	5 NaH ₂ PO ₄ ·H ₂ O		3	1.5×10^{-5}	2.7×10^{-6}	Fair, partially devitrified, trace Cr
30	30	27 ^b	13 ^b	None	4-5	3-4	3.6×10^{-6}	9.1×10^{-7}	Fair, two-phased, no Na ₂ CrO ₄
27	27	24 ^b	12 ^b	10 ZnO	4	3	9.5×10^{-6}	2.7×10^{-6}	Good, no Na ₂ CrO ₄
30	30	23.5 ^b	11.5 ^b	5 Li ₂ O	2-3	2	2.4×10^{-6}	$<4.7 \times 10^{-7}$	Good, glassy, no Na ₂ CrO ₄
27	27	18	18	10 ZnO	4-5	4	8.0×10^{-6}	4.1×10^{-6}	Fair, opaque, no Na ₂ CrO ₄
27	27	21 ^b	10 ^b	10 ZnO, 5 Li ₂ O	3	2-3	5.6×10^{-6}	1.0×10^{-6}	Fair, glassy, no Na ₂ CrO ₄

a - Viscosity: 1-runny; 2-very pourable; 3-pourable; 4-hardly pours; 5-melted, but thick

b - Source of Na₂O and B₂O₃ is Na₂B₄O₇

The leach results and appearance of the products noted in Table VI indicate that immobilization of 40 weight percent Redox sludge, using a low melting ($< 1000^{\circ}\text{C}$) formulation may be only marginally successful because of the highly refractory nature of the sludge. Immobilization of 30 weight percent sludge is highly feasible at 1000°C , however; and homogeneous, fairly low viscosity, durable products can be formed.

Work continued on development of high melting ($> 1000^{\circ}\text{C}$) Redox sludge-glass formulations in which reactant proportions were varied over the ranges 25 - 43 weight percent synthetic Redox sludge, 5 - 20 weight percent B_2O_3 , 13 - 20 weight percent Na_2O , and 27 - 48 weight percent SiO_2 . Several of these formulations were modified by the addition of 10 weight percent CaO or 10 weight percent ZnO as aids to increasing durability. The CaO additions did not visibly affect the product appearance or melt viscosity at 1200°C . Zinc oxide additions, however, increased melt viscosity slightly, and in several instances, resulted in production of a separate crystalline phase segregating to the surface of the specimens. The effects of the CaO and ZnO additions to the high-temperature glasses are thus much different from those observed above for the low-temperature glasses.

Tests are presently under way to determine the leachability of the products in deionized water.

Continuous Laboratory-Scale Glass Melter - C. W. Hobbick

During the report period, the final construction phases of the pilot scale continuous melter were completed. A safety review for initial heat-up of the melter was completed and heat-up began in late November. Typical start-up problems occurred during this period (mainly problems with radiant

heating elements), but were expediently corrected. The conductive heating system was operated for ~ 5 hours, when operation was terminated by a blown fuse on the main power line. Initial heating will be continued and completed in the early portion of February 1976. No insurmountable mechanical or heating problems have been encountered during the Phase I heating of the melter.

Engineering-Scale Glass Melter Construction - R. A. Watrous

This task is intended to demonstrate the feasibility of the silicate melt process on a pilot-plant scale, develop suitable process equipment and systems, and obtain scaleup and design data.

On October 31, 1975, with an estimated five weeks of installation work remaining, construction of the one-ton-per-day continuous glass melter by Battelle-Northwest was stopped in order to curtail FY 1976 direct expenditures and permit a review of project costs and funding availability. This review has resulted in the decision that construction should not be resumed until early FY 1977, when the level of funding should permit continuity in construction, start-up, and operating activities.

OTHER IMMOBILIZATION CONCEPTS

The objective of this task is to identify, develop, and evaluate alternative processes (other than the aqueous silicate or silicate melt processes) for conversion of Hanford high-level waste to immobile forms suitable for long-term storage.

The primary immobilization techniques to be investigated in the laboratory include, but are not limited to:

- Glass sintering.
- Concrete with and without addition of monomers.
- Pressed concrete (at hot and ambient temperatures).

Glass Sintering - M. J. Kupfer

Scouting studies were initiated to determine the application of a process for sintering synthetic Redox sludge into a glass matrix. Optimum sintering temperatures were defined for cold-pressed (20,000 psi) pellets of synthetic Redox sludge powder mixed (50:50) with various crushed glasses. Zinc borosilicate, Corning 8870, and Corning 1990 lead glasses (Corning Glass Works, Corning, New York), and soda-lime glass powders (- 325 mesh) were used.^[2] The percent shrinkage of the pellets (Figure 3) was measured as pellet temperatures were raised from 500° to 1100°C in 100° C increments. Shrinkage was determined by measuring the diameter of the pellets with a dial micrometer. The curves indicate continual shrinkage of the pellets up to their fusion points. Little or no bloating occurred, indicating no significant gas generation. This was as predicted, since the thermo-gravimetric analyses for the sludge indicated no significant reactions. Surprisingly, products containing the zinc borosilicate glass and soda-lime glass displayed more shrinkage than did the low-viscosity lead glasses.

All of the sintered products were very hard and less friable than glass waste forms. All began either to crack severely or to fuse (melt) at temperatures above the maximum shown in the Figure 3 curve. Measurements of product porosity, density, and leachability are under way and will be reported after the next report period.

FIGURE 3

V7603-7.1

SINTERING CURVES

RADIONUCLIDE REMOVAL STUDIES

These studies are primarily concerned with devising, developing, and demonstrating processes for removal of all long-lived ($t_{1/2} > 25$ yr) radionuclides from Hanford terminal liquor and salt cake solutions. The overall objective is to develop technology for partitioning such high-level wastes into a small volume of highly radioactive waste requiring further immobilization for long-term storage and a large volume of chemical or very low-level wastes which can be safely stored or disposed of by inexpensive means.

Current laboratory studies continue to be focused on:

- Screening and testing, with synthetic waste solutions containing appropriate radiotracers, various sorption and ion exchange processes and procedures for removal of ^{137}Cs , ^{90}Sr , ^{99}Tc , and now, ^{241}Am .
- Testing radionuclide removal procedures with actual waste solutions as the latter become available.

Scouting experiments have also been started to explore ways of extracting the bulk cation, sodium, from dissolved salt cake as an alternative approach to achieving the volume reduction objective.

Duolite ARC-359[®] Sorption of ^{137}Cs From Synthetic Waste

W. W. Schulz

Tests initiated last quarter were continued to study the effects of various flowsheet parameters (flowrate, temperature, solution composition, etc.) on uptake of ^{137}Cs by Duolite ARC-359[®] (Diamond Shamrock Chemical Co., Cleveland, Ohio) resin from waste liquors. Cesium breakthrough data for runs completed

during the report period are plotted in Figure 4. As noted previously, the slope of these breakthrough curves is a measure of process kinetics.^[2] Qualitatively, efficiency of the Duolite ARC-359[®] resin for sorbing ¹³⁷Cs increased with increased feed hydroxide concentration and with decreased sodium concentration. These latter effects were noted in batch distribution data obtained by ARHCO personnel and by workers at the E.I. du Pont de Nemours and Company Savannah River Laboratory.

Removal of Actinides - W. W. Schulz

What little analytical evidence is currently available indicates that at least some terminal liquors and salt cake solutions contain concentrations of plutonium, americium, and perhaps other actinides in excess of one $\mu\text{Ci/liter}$, our present tentative removal criteria. Recent tests indicate that scavenging (with inert strontium phosphate) and/or sorption (on Sandia Titanate exchangers) procedures used to remove ⁹⁰Sr will also suffice for adequate removal of actinides.

Removal of Am^{+3} by scavenging precipitation and by ion exchange on Titanate exchangers was tested for some 29 synthetic waste compositions in which the concentrations of NaNO_3 , NaNO_2 , NaAlO_2 , Na_2CO_3 , and NaOH were varied parametrically. Americium removal results for three levels of NaNO_3 in NaNO_3 - 1.0 M NaOH solutions are given in Table VII. For this simple (two macro component) system having a relatively low concentration of NaOH (~ 1 M), the americium removal efficiency of both the scavenging and Titanate sorption processes tends to increase as the NaNO_3 concentration decreases. Efficiency data for solutions containing higher concentrations of NaOH and NaNO_3 appear to follow a more

CURVE NO	NaNO ₃ M	NaOH M
1	1.0	6.0
2	3.0	2.0
3	5.0	2.0
4	6.0	1.0

ALL RUNS AT 25°C AT A FLOW RATE OF 2 COLUMN VOLUMES/HOUR
WITH FEEDS CONTAINING $\sim 10^3 \mu\text{Ci } ^{137}\text{Cs/LITER}$

COLUMN SIZE: 2.5 cm DIAMETER
30.5 cm HIGH

V7603-7.2

FIGURE 4

DUOLITE ARC 359[®] RESIN SORPTION OF ^{137}Cs
FROM NaNO₃ - NaOH SOLUTIONS

complicated relationship for which additional data points would be required. Tests to study scavenging and sorption behavior of plutonium, uranium, and neptunium are also scheduled.

TABLE VII
SCAVENGING AND SORPTION BEHAVIOR OF Am^{+3} IN
SYNTHETIC WASTE SOLUTIONS

<u>Synthetic Waste Composition</u>		<u>Sandia Titanate</u> <u>K_d [a]</u>	<u>Scavenging</u> <u>DF [b]</u>
<u>NaNO_3 M</u>	<u>NaOH M</u>		
6.0	1.0	12,000	570
4.0	1.0	175,000	5,000
2.0	1.0	440,000	17,000

[a] Distribution Coefficient - 10 ml solution contacted 48 hours at $\sim 25^\circ\text{C}$ with 0.25g Titanate exchanger; units: (Ci/g resin)/(Ci/ml raffinate).

[b] Decontamination Factor - Solution made 0.025 M H_3PO_4 and 0.0075M $\text{Sr}(\text{NO}_3)_2$; resulting precipitate digested 60 min. at $\sim 25^\circ\text{C}$.

Flowsheet Tests With Actual Salt Cake - W. W. Schulz

Approximately 700 grams of salt cake from the 105-S tank became available late in the report period. This material will be used to test various integrated precipitation - ion exchange flowsheets for removal of ^{90}Sr , ^{137}Cs , ^{99}Tc , actinides, and all other long-lived radionuclides from salt cake solutions. Dissolution of this salt cake in water at 50°C yielded a solution having the composition as listed in Table VIII. This solution also contained approximately 0.1 to 0.2 volume percent undissolved solids of an as yet undetermined composition.

Several initial small-scale experiments were performed with the 105-S salt cake solution to establish scavenging and sorption exchange of ^{90}Sr . In the first two scavenging tests, clarified feed solution (Table VIII) after adjustment to 0.2 M or 2.0 M NaOH was made 0.025 M in H_3PO_4 and 0.0075 M with inert $\text{Sr}(\text{NO}_3)_2$; the resulting strontium phosphate precipitate was digested an hour at 25°C . The final scavenged solution, after centrifugation of the strontium phosphate, contained quantities of ^{90}Sr as given in Table IX along with corresponding values of the decontamination factor (DF). In the third test, waste solution was scavenged by precipitation of $\text{Sr}_3(\text{PO}_4)_2$ in the presence of the small amount of sludge which remained undissolved when the salt cake was treated with water. (The total volume of wet centrifuged solids was 4.0 ml.)

Results of these ^{90}Sr scavenging experiments are in fair agreement with those of tests with synthetic salt cake solutions, thus indicating the absence of any large concentration of ligands which complex ^{90}Sr . Moreover, these results indicate that a single scavenging step will readily reduce the ^{90}Sr concentration to well below the tentative goal of one $\mu\text{Ci/liter}$.

TABLE VIII

COMPOSITION OF TANK 105-S SALT CAKE SOLUTION

<u>COMPONENT*</u>	<u>CONCENTRATION</u>
Na	6.55 <u>M</u>
NO ₃	3.92 <u>M</u>
CO ₃	0.376 <u>M</u>
OH	0.201 <u>M</u>
NO ₂	0.113 <u>M</u>
AlO ₂	0.0983 <u>M</u>
PO ₄	0.0268 <u>M</u>
CrO ₄	0.0138 <u>M</u>
Ni	$< 5.6 \times 10^{-5}$ <u>M</u>
Fe	$< 6.2 \times 10^{-5}$ <u>M</u>
Mn	$< 5.1 \times 10^{-5}$ <u>M</u>
¹³⁷ Cs	5.16×10^4 μ Ci/liter
¹³⁴ Cs	109 μ Ci/liter
¹²⁵ Sb	587 μ Ci/liter
⁹⁰ Sr	28.7 μ Ci/liter

*Analyses for Si, Mg, Ca, Ba, Sr, Zn, Hg, ⁹⁹Tc and actinides are pending.

TABLE IX

SCAVENGING BEHAVIOR OF ^{90}Sr FROM
ACTUAL TK 105-S WASTE SOLUTION

<u>Adjusted Waste Solution Composition [a]</u>			<u>^{90}Sr Removal Results</u>	
<u>NaOH</u>	<u>Clarified?</u>	<u>Quantity of $\text{Sr}_3(\text{PO}_4)_2$ Ppt.</u>	<u>Raffinate ^{90}Sr $\mu\text{Ci/liter}$</u>	<u>DF [b]</u>
0.2 <u>M</u>	Yes	0.0025 <u>M</u>	0.13	220
2.0 <u>M</u>	Yes	0.0025 <u>M</u>	0.59	49
0.2 <u>M</u>	No	0.0025 <u>M</u>	0.26	110

[a] Molarities of other components are approximately as given in Table VIII.

[b] Decontamination Factor = $(\text{Ci/liter feed})/(\text{Ci/liter raffinate})$.

Distributions of ^{90}Sr between the 105-S salt cake solution at 0.2 and 2 M NaOH and Sandia Titanate exchanger were also measured as given in Table X. The high value of these distribution coefficients indicates satisfactory decontamination of ^{90}Sr from the salt cake solution can also be achieved by processing the 105-S salt cake solution through a bed of the Titanate sorbent.

TABLE X

TITANATE SORPTION OF ^{90}Sr FROM
ACTUAL TK 105-S WASTE SOLUTION

<u>Adjusted Solution</u> <u>NaOH Composition</u> ^[a]	<u>Distribution</u> <u>Coefficient</u> ^[b]	<u>Decontamination</u> <u>Factor</u> ^[c]
0.2 <u>M</u>	5060	~130
2.0 <u>M</u>	3240	~ 80

[a] Approximate molarities of other components are given in Table VIII.

[b] Equilibrium distribution (25 °C) of ^{90}Sr between Titanate exchanger and raffinate solutions; units: (Ci/g exchanger)/(Ci/ml raffinate).

[c] Factor = (Ci/liter feed)/(Ci/liter raffinate), based on a single contact of 10 ml of solution with 0.25 g Titanate exchanger.

^{90}Sr Removal from Actual Terminal Liquor - W. W. Schulz

Previously, ^{90}Sr scavenging and sorption tests have been performed with samples of various current Hanford alkaline wastes whose compositions varied from that of near-terminal liquor (10-11 M Na^+ , 3-4 M OH^-) to that of salt cake solution (5 M Na^+ , 0.1 M OH^-). Results of these tests have shown that a small (2-10 percent) fraction of the ^{90}Sr in such solutions, particularly near-terminal liquors from the 102-S and 110-S tanks, is tightly complexed by an unidentified feed ligand and is not readily amenable to removal by either precipitation of inert strontium phosphate or sorption on Sandia Titanate exchanger.^[2]

Data obtained during the report period disproved the hypothesis that the offending ligand was chromate ion. In on series of experiments, the chromate ion concentration of 110-S tank solution (previously adjusted to 6 M Na^+ and 1 M OH^-) was reduced from 0.0091 M to 0.00023 M by precipitation of BaCrO_4 without significant improvement in ^{90}Sr removal by precipitation of strontium phosphate. Further scavenging and sorption removal of radiostrontium from a synthetic 6 M Na^+ , 1 M OH^- waste containing $0.025 \text{ M CrO}_4^{-2}$ was comparable to that from the same solution containing no chromate. Presently, therefore, the complexant(s) in the 110-S and 102-S tank solutions are presumed to be organic compounds but their exact identities are not known.

Thus far, attempts to reduce the ^{90}Sr concentration of four-fold diluted 110-S tank solution (6 M Na^+ , 1 M OH^- , $4,000 \text{ }\mu\text{Ci/liter } ^{90}\text{Sr}$) to $1 \text{ }\mu\text{Ci/liter}$ have been unsuccessful. Approaches tested to date included isotopic dilution with inert strontium, scavenging with iron hydroxide, Sandia Titanate exchanger, and multiple scavenging with 0.0025 M strontium phosphate both with and without added sodium carbonate. The latter multiple scavenging techniques served to reduce the ^{90}Sr concentration to 50 to $200 \text{ }\mu\text{Ci/liter}$. Experiments to determine if the suspected organic complexants can be destroyed by oxidation (at $1\text{-}4 \text{ M OH}^-$) with H_2O_2 , KMnO_4 , $\text{Na}_2\text{S}_2\text{O}_8$, and other oxidizing agents were in progress at the end of the report period.

The full significance to the Radionuclide Removal Program of the presence of some difficult-to-remove ^{90}Sr in some current Hanford waste solutions cannot, of course, be completely evaluated now. It seems only prudent to believe, however, that adequate removal of ^{90}Sr (down, say, to $1 \text{ }\mu\text{Ci/liter}$) from final stored terminal liquor will require development of technology (oxidation, etc.) to overcome the effects of soluble organic

complexants which will accumulate in these solutions. What may be an attractive alternative approach in disposal of terminal liquors - direct immobilization as a source of Na_2O in converting sludges to borosilicate glasses - will also be studied. Very preliminary estimates indicate a good balance between the expected amounts of Hanford terminal liquor and sludge for this blending strategy.

Removal of Sodium by Solvent Extraction - G. S. Barney

As an alternative back-up technology to the radionuclide removal processes discussed above, studies were begun to evaluate solvent extraction as a means of separating inert sodium salts from salt cake and terminal liquor wastes.

It is well known that crown ethers (macrocyclic polyethers) can extract alkali and alkaline earth salts from aqueous solution into organic solvents. Selective extraction of a specific cation is related to the size of the cavity in the polyether ring. Several crown ether - diluent combinations were tested to determine their ability to separate inert sodium salts from radionuclides by solvent extraction. An aqueous, synthetic salt cake solution (5.0 M NaNO_3 , 0.5 M NaNO_2 , 0.1 M NaOH , 0.005 M CsOH , and 0.005 M $\text{Sr}(\text{OH})_2$) was contacted with mixtures of the following crown ethers and diluents:

CROWN ETHERS

dibenzo-18-crown-6
dicyclohexyl-18-crown-6
18-crown-6
t-butylbenzo-15-crown-5
Kryptofix 222[®] (EM Laboratories)
Kryptofix 221[®] (EM Laboratories)

DILUENTS

chloroform
dichloromethane
butyl alcohol
benzene
toluene
o-dichlorobenzene

After equilibration, each of the crown ether - diluent mixtures (18 total) which contained chloroform, dichloromethane, or butyl alcohol as diluents were nearly saturated with Na^+ $\{[\text{Na}^+] \approx [\text{crown ether}] \approx 0.03 \text{ M}\}$. However, those containing benzene, toluene, or o-dichlorobenzene (18 total) extracted Na^+ very poorly and these diluents were therefore eliminated from further consideration. The ability to extract Na^+ appears to be related to the dielectric constant of the diluent. The affinity of the solvent for Na^+ decreases in the order:

($\epsilon = 17.1$)	(9.08)	(4.81)	(9.93)
butyl alcohol	> dichloromethane	> chloroform	> o-dichlorobenzene
	(2.28)	(2.38)	
	benzene	> toluene	

where the numbers in parentheses are dielectric constants for the diluent. Extraction coefficients for Cs^+ and Sr^{++} were lowest for the t-butylbenzo-15-crown-5 extractant ($E_a^0 < 0.0032$ and < 0.0048 , respectively) under these conditions. As expected the 15-crown-5 polyether ring is specific for Na^+ extraction and does not appreciably extract Cs^+ and Sr^{++} . The 18-crown-6 ring does extract Sr^{++} ; however, EDTA is a very effective masking agent for preventing Sr^{++} extraction by the organic solvent.

CONTAMINATED EQUIPMENT VOLUME REDUCTION

The objective of this program is to develop and demonstrate methods for reducing the volume of radioactively contaminated metallic items to a size and form suitable for interim or final storage. Although the problem of disposition of contaminated equipment exists throughout the nuclear industry, this program is focusing its attention on the contaminated decommissioned equipment presently located in the 200 Areas at Hanford.

The Contaminated Equipment Volume Reduction Program has been transferred from the Hanford Waste Engineering Section to the Commercial Waste Engineering Section, both part of the Advanced Waste Engineering Department. The main effect of this transfer is to ensure compatibility of the program's technical approach with commercial fuel cycle waste even though all techniques will be demonstrated first with Hanford waste.

DECONTAMINATION EVALUATION - G. A. Beitel

The purpose of this task is to evaluate costs and secondary waste generation associated with equipment decontamination as a precursor to volume reduction. A decontamination test on a Purex dissolver has been planned to provide this information.

There was no action on this task during the report period because of higher priority work at the decontamination facility. Current plans are to begin decontamination of the dissolver during January 1976. The decontamination work will take about one month, after which the collected data will be evaluated.

SIZE-REDUCTION EVALUATION - G. A. Beitel

Several tools have been identified as size-reduction alternatives. These include the plasma arc furnace torch, the arc saw, and the radio-frequency plasma arc torch.

An equipment size-reduction demonstration was conducted by Technology Application Services Corporation, Raleigh, North Carolina, during the second week of October 1975. The plasma arc furnace torch used in the test had a power output capacity of 2,000 kilowatts continuous operation. The arc flame had a maximum length of about 1.5 meters. The primary objective of the test was to demonstrate that a complex stainless steel heat exchanger (2.6 m long, 1.3 m in diameter, weighing 2600 kg, and filled with 0.6-cm-wall stainless steel tubes) could be cut in two indiscriminately, regardless of torch or vessel motion or the vessel's geometry, individual components or clamping. The torch quite easily cut a gash in the vessel 36 cm wide and 40 cm deep, with a material removal rate of 6 kg per minute. Penetration beyond 40 cm was possible but required much more energy. It was tentatively concluded that such a torch could be developed for size reduction of exceptionally large vessels, but that it would be too inefficient for general use.

A proposal was received from Schlienger, Inc., San Rafael, California, to conduct a demolition demonstration on the remaining half of the vessel used in the plasma arc demonstration. A contract has been written and is being approved. Schlienger proposes to use an innovative tool known as an arc saw, a high power (low voltage, high current) spark erosion machine. The demonstration is tentatively scheduled for February 1976.

Discussions have been held with Energy Systems, Inc., Toledo, Ohio, developer of the Energy Beam[®], a radio-frequency torch. They are in the process of building a 60 kilowatt unit and are interested in leasing it to ARHCO to test its metal-cutting capability.

VOLUME REDUCTION EVALUATION (formerly MELTDOWN EVALUATION)

G. A. Beitel

This task attempts to determine whether radioactively contaminated equipment can be safely melted and cast as a product acceptable for long-term storage. One objective, experimental meltdown of contaminated stainless steel pipe samples, has yielded promising decontamination results. Another objective is design of a low-maintenance, remotely operated meltdown system with maximum fume control.

Hot laboratory meltdown studies, using pieces of contaminated stainless steel pipe, continued during the report period, and additional samples provided results similar to those reported previously. These studies will continue.

Discussions with vacuum furnace owners have led to the conclusion that a vacuum furnace is the ideal meltdown system for optimum fume containment. Furthermore, use of a water-cooled copper crucible and a batch operation may possibly solve both the furnace-liner replacement problem and operational problems such as charging, pouring, casting, and ingot cooling. The preliminary conceptual design of a furnace based upon this concept is proceeding. Contract negotiations will be initiated during the next report period to retain a design consultant to assist with melting-furnace design.

ENGINEERING TEST LABORATORY - G. A. Beitel

The Energy Research and Development Administration - Richland Operations Office has requested that a conceptual design be prepared for a general purpose engineering test laboratory that will be used by all ARHCO waste management programs for which equipment prototypes must be developed and tested. To be known as the Waste Management Engineering Prototype and Test Facility - 200 Area, this facility would be budgeted as an FY 1978 major line item.

Program budget reductions postponed the conceptual design phase of this program; therefore this task was removed from the Contaminated Equipment Volume Reduction Program. Conceptual design will be initiated next quarter using an alternative means of funding.

The Conceptual Design Plan was written and transmitted to ERDA-RL for approval. The architect-engineer for conceptual design work will be Vitro Engineering.

Personnel began preparation of Functional Design Criteria that will be submitted to ERDA-RL during January 1976.

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