ATLANTIC RICHFIELD HANFORD COMPANY
QUARTERLY REPORT
WASTE MANAGEMENT AND TRANSPORTATION
TECHNOLOGY DEVELOPMENT
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ABSTRACT

This document is the first in a series of quarterly progress reports on activities in support of long-term management of Hanford high-level waste. A variety of specific topics are discussed in some technical depth. These topics can be grouped in the areas of: salt cake retrieval, tank reliability, equipment decommissioning, and increased waste immobilization.

ATLANTIC RICHFIELD HANFORD COMPANY
QUARTERLY REPORT

WASTE MANAGEMENT AND TRANSPORTATION
TECHNOLOGY DEVELOPMENT

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 titled Fault Tree Analysis, Tank Corrosion, and Analysis of Explosive Hazards are responsive to this mode. The second alternative provides for adding engineered improvements such as the Radionuclide Transport studies and Equipment Decommissioning reported here. The third alternative involves removal of the waste from tanks followed by further immobilization and storage in an onsite repository. The fourth alternative differs from the third in that storage could be in an offsite repository. The activities listed under Salt Cake Retrieval and Waste Immobilization support these alternatives.

SUMMARY

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Salt Cake Retrieval activities have centered around identifying the equipment units that will comprise a retrieval system and setting up a test stand for evaluating these units.	5
Fault Tree Analysis for the proposition, "Radio-active material is released from high-level waste tank farms," has been completed; a draft-form report will be issued in the next quarter.	14
A critical review of waste tank corrosion tests has been completed in support of the Waste Tank Stability task; a document on this topic is in preparation.	17
Combustion limits for mixtures of nitrates and degraded organics will be determined in a study of salt cake stability.	22
Waste tank contents' characterization has started with salt samples from the 242-S evaporator program and sludge samples from Tank 104-A.	25
A highly selective and sensitive spectrophotometric method using PADAP has been developed for the determination of trace uranium in Hanford nuclear waste. The method is capable of detecting 1 µg of uranium; and only Pd was found to interfere significantly.	32
Two holes 61 cm x 183 cm have been made in basalt in preparation for an Equipment and Facility Decommissioning metal consolidation test.	35
Cost estimate data relative to high-level waste storage modes are being reviewed in preparation for an economic evaluation of immobilization and storage alternatives using principles of discounted cash flow.	42

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An Aqueous Silicate process-scale flowsheet has been calculated; the flowsheet assumes the use of United Technology Center's inert carrier process for mixing waste and clay at a design rate of 22.7 liters per minute waste and 19 kilograms per minute clay.	44
The United Technology Center's inert carrier process for mixing is described and evaluated.	49
An aqueous silicate product with superior leach characteristics and mechanical strength can be obtained by reacting a less-than-stoichiometric amount of calcined clay (kaolin or bentonite) with the waste, washing the cancrinite crystals, and adding a binder.	68
The heat of reaction of uncalcined kaolin with synthetic waste is lower (-49.5 ± 3.6 calories per gram) than that of calcined kaolin (-190.7 cal/g). The reaction is also slower and more complex than with calcined kaolin.	72
Calcined clays react 5 to 30 times faster with standard waste solution than uncalcined clays.	77
The cumulative fraction of cesium leached up to 177 days from massive cancrinite samples varies from 0.0045 to 0.0223 for cancrinite with concrete binder and from 0.0196 to 0.0201 for cancrinite with organic polymer binders.	80
A synthetic commercial caustic waste was immobilized to a cancrinite product by reacting with clay. Cancrinite forms only when additional caustic is introduced, however.	82
Heating of some aqueous silicate products past 100° C dramatically increases their mechanical strength.	83
A variety of powdered aqueous silicate products were subjected to approximately 10^9 rads of ^{60}Co radiation to determine their radiolytic stability. Differential thermal and thermogravimetric analyses of irradiated and nonirradiated control	85

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products were nearly identical from ambient to 1000° C temperatures.

Synthetic salt cake waste is effectively immobilized to a long-term storage form by conversion to a soda-lime or borosilicate glass. Leach rates (after 4 days in deionized water at 25° C) based on cesium of these products range from 3.9×10^{-7} to 6.7×10^{-5} g/cm²-day. 87

Application of the Silicate Melt process to immobilization of Hanford incinerated plutonium-bearing ash was successfully demonstrated. 90

A silicate melter design has been selected and the performance of an operating model has been observed. 93

Glasses containing iron cool rapidly at the surface and a large thermal gradient is established within the cooling mass. This can give rise to stresses in the cast glass. 95

Tests with synthetic, dilute (2M NaNO₃; pH 12) salt cake solution indicate a "Strontium Phosphate Anion Resin" column may be an effective tool for removing ⁹⁰Sr from actual salt cake solution. 99

Additional ion exchange experiments were completed to study removal of ¹³⁷Cs and ⁹⁰Sr from solutions resulting from dissolution of actual salt cake in water. 103

The use of beta-aluminum as a separative membrane for decontaminating high-sodium waste was tested with inconclusive results due to leaks in the membrane. 111

HIGH-LEVEL WASTE MANAGEMENT

SALT CAKE RETRIEVAL (N. C. Rodewald and D. O. Schuler, [ARHCO]; D. Ells, R. D. Lawrence, L. Schwendiman, and S. Sutter [PNL]); and J. Baldridge and L. Ufkes [Vitro])

Objective

Develop and demonstrate technology for removing the high-level waste from storage tanks should this become necessary.

Prior Work

A planning document was prepared; effort on the first phase was initiated. Specifically, past effort centered on developing probes to make *in situ* measurements of hardness, radiation, and temperature in Tank 105-B. Hard forms of waste likely to be found in the tanks were synthesized and crushed to measure fracture strengths. A site was selected for bench-scale testing and chemical makeup and tanks were ordered and received. A pneumatic retrieval system--a truck-mounted vacuum system--was tested at a vendor's shop. This system was capable of removing synthetic salt cake from a 55-gallon drum located 6 meters below the suction point.

Progress During Report Period

During the first quarter of fiscal year 1975, the first activities were further defined to meet a limited objective of developing the most viable dry mining scheme for cold-testing in FY 1975. Table I gives a proposed budget and task breakdown required to develop a dry-mining system consisting of a hydraulic crane-clamshell bucket with a barrel elevator. A conceptual drawing of this system appears in Figure 1. Responsibilities have been assigned to

TABLE I
PROPOSED BUDGET AND TASK BREAKDOWN FOR FISCAL YEAR 1975

<u>Responsible Person(s)</u>	<u>Task</u>	<u>Possible Expenditure</u>	
Schuler (ARHCO)	Hydrocrane and bucket		
	Vendor design study	\$15,000	
	Purchase	<u>35,000</u>	\$50,000
Ufkes and Baldridge (Vitro)	Cold test stand		
	Design study	15,000	
	J. A. Jones purchase and construction	<u>35,000</u>	50,000
Schuler (ARHCO)	Drum elevator		
	Purchase and construction	<u>20,000</u>	20,000
Lawrence and Ellis (BNW)	<i>In situ</i> measurement and sampling	<u>25,000</u>	25,000
Schuler and Rodewald (ARHCO)	Bench-scale testing	<u>10,000</u>	10,000
Sutter and Mishima (BNW)	Resuspension	<u>10,000</u>	10,000
Rodewald (ARHCO)	Pneumatic retrieval	<u>5,000</u>	5,000
Cooper (ARHCO)	Hydraulic retrieval feasibility study	<u>5,000</u>	5,000
-	Handling and containment system	-	-
-	Lighting and TV viewing system	-	-
Total			\$175,000
Surplus contingency			38,000

SECTION THRU TYPICAL 75' DIA TANK

FIGURE 1
CONCEPTUAL MINING TECHNIQUE

various Atlantic Richfield Hanford Company; Battelle Pacific Northwest Laboratories; and Automation Industries, Inc., Vitro Engineering Division, employees. All monies are to be committed during fiscal year 1975 with as much equipment as possible purchased and erected.

During the first quarter of fiscal year 1975 significant progress was made in most of the tasks listed in Table I.

Hydrocrane and Bucket

An equipment search was completed and a small clamshell bucket (sized to fit through a 107-cm riser) was ordered; only one supplier was found. Delivery time runs 10 weeks. Three possible suppliers (designers and fabricators) of custom hydraulic booms have been located. The function of the hydraulic boom is to provide a means of remotely guiding and operating mining equipment. It is a piece of equipment critical to all defined mining systems applicable to salt cakes. Three possible suppliers of this item were found. Evaluation and comparison of customer products and capabilities are scheduled.

A set of equipment specifications describing the hydrocrane boom are being prepared. These specifications have been requested by three vendors who are interested in designing and manufacturing our hydraulic booms.

Cold Test Stand

Significant progress was made on engineering and selecting a site for a cold test stand. A test stand was conceptualized and if built is estimated to cost \$75,000. This stand consists of a 6-meter superstructure supporting two 107-cm risers spaced ~6 meters apart. Underneath this stand is a 9.1-meter deep trench 10.7 meters wide and 12.2 meters long.

Construction personnel estimated that this structure could be built in three months. Two existing structures are possible alternatives to the conceptual test stand--both may be satisfactory. One structure is located inside the 277-T Building which is adjacent to the bench-scale testing site. A Battelle representative has informed us that they will probably want to release this building. The second is referred to as the 190-D Reuse Basin; this facility consists of a cement basin ~4.6 meters deep, 15.2 meters long, and 10.7 meters wide with a steel structure and walkway extending 9.2 meters vertically. Vitro personnel have been retained to study the adaption of these stands and to prepare engineering drawings for J. A. Jones Construction Company. Use of these stands may save \$50,000 to \$75,000.

Drum Elevator Plus Handling and Containment System

Effort was initiated on the task of designing a drum elevator system and a packaging system. The elevator is a rather simple design and construction problem. This work will be done in-house by Process Design and Development Engineering. The packaging system which is designed to seal the drum, install a shielding container, and move the drum from a containment structure is very complex. A similar system was recently designed and constructed for use in B Plant encapsulation. That experience should provide a useful basis from which to start this work.

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

Battelle Pacific Northwest Laboratories personnel have been assisting on the problem of characterizing synthetic and hot waste. In July efforts culminated with the *in situ* measurements of hardness, temperature, and radiation of salt cake under two adjacent risers in Tank 105-B. Salt cake

temperature through a depth of 4 meters was measured at 20° C (68° F). The corresponding radiation level as measured by a 500 R/hr high-range T-P inside a 5-cm pipe ranged from 4.7 R/hr at the bottom to 0.7 R/hr at the waste surface. [The probe was probably 61 centimeters from the tank bottom and was resting on a hard sludge layer.] Seventy-five centimeters above the surface the radiation level inside the pipe was 600 mR/hr as compared with an equivalent unshielded reading of 1.5 R/hr. The pointed probes are an effective way of determining depth of super-hard, impenetrable layers or rocks. Such layers were encountered under the 30.5-cm riser at a depth of 16.5 cm and under an adjacent 10-cm riser near the surface. It was concluded that salt cake or liquid under risers used for liquid level measurement are quite likely to be nonrepresentative of tanks' contents. However the pointed probes show good potential of giving relative hardness profiles when the number of blows required to drive the probe per meter are compared.

In August several more tanks were selected for probing to determine hardness, radiation, and temperature profiles. A string of passive neutron detectors was lowered into the 105-B Tank probe and retrieved after an exposure time of about one week. The detectors were given to the BNW laboratories for analysis. Preliminary indications from these probes are that the transuranic levels in the waste in Tank 105-B are 100 times greater than the limit for burial of transuranic waste. However to insure accuracy these passive wafers must be calibrated with known accuracy.

In September development was completed of two heated-tip probes for penetrating the salt cake and making *in situ* measurements.

Bench-Scale Testing

Two significant tests were accomplished. First, a feasibility test was conducted of a vacuum, pneumatic retrieval system. An attempt was made to suck two barrels of compacted wet salt cake through 33.5 meters of 15-cm hose and pipe up a vertical rise of 15 meters. The vacuum system was found to be capable of sucking water, diatomaceous earth-caustic liquid, sand (wet and dry), and even 7- to 10cm diameter rocks up a 15 meter rise without plugging. However it was found that air forces at the nozzle could not break down wet compacted salt cake. The salt cake seemed to act like a "ball of jelly" which deformed only slightly under the suction forces. A shovel was used to break up the salt cake into discrete chunks. At this point the vacuum increased in the containment vessel indicating that the suction hose was plugging. Continued operation completely plugged the hose. It was necessary to allow the hose to drain and use a water rinse to unplug the hose. It may be wise to delay further testing of vacuum systems until we have preliminary results from alternative mining schemes and a better characterization of actual tank wastes.

As part of the bench-scale testing it is necessary to prepare tanks of synthetic waste which simulates hot waste. Toward accomplishing this goal, various waste forms were mixed and allowed to set up (react or dried, for example) in standard American Society for Testing and Materials (ASTM) forms and fractured in hydraulic presses. The approximate results are shown in Table II.

As a result of these tests 46 x 46 x 122 cm (1.5 x 1.5 x 4') tanks of solid slurry, sludge, and clay were prepared for baking. To date one similar-sized tank of unreacted caustic liquor and clay was baked at 90° C for five

TABLE II
SYNTHETIC SALT CAKE FRACTURE TESTS

<u>Material</u>	<u>Fracture Pressure</u> psi	<u>Observations</u>
Solid slurry	2310	Higher than some cements.
Sludge (dried)	350 to 550	Crumbly but very, very hard.
Na ₃ PO ₄ •12H ₂ O crystal composition	161 to 453	Very hard, but sample crumbled upon setting.
Clay + liquid--fully dried	139 to 146	Drying increases strength.
Diatomaceous earth--dried	304	One sample.

weeks in metallurgical ovens and allowed to dry. Retrieval tests will be conducted on this material when the clamshell bucket becomes available. In addition a 55-gallon drum of hydrated tri-sodium phosphate identical in composition to a 105-B Tank "salt whisker" crystal was synthesized for mining tests.

Resuspension (J. Mishima and S. Sutter)

A salt cake resuspension study is being scoped. During September sources of information on all aspects of the salt cake and its airborne release potential were collected and reviewed.

Other

In August two Atlantic Richfield Hanford Company personnel attended an American Institute of Chemical Engineers short course on "Storage and Flow of Solids." This course was taught by Drs. Jenike and Johanson of Jenike and Johanson, Inc.

These instructors agreed to review at no cost our mining plans with view to solids flow techniques.

Recommendations have been received about how solids flow testing information could assist in designing and selecting mining equipment. The flow properties of the various radioactive salt cakes should be characterized 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.

Summary

Progress was made in the first phase of the project. Tasks I and II have been set up to result in the timely design and procurement of a hydraulic crane plus bucket, a cold test stand, and a barrel elevator.

Technology studies were set up to characterize hot waste, to synthesize waste for cold-testing, and to study materials movement.

Future Work

One or more custom designers and fabricators of a hydraulic crane will be selected.

A design and a site for a cold test stand will be selected.

In situ waste measurements of radiation, hardness, and temperature will be made in several tanks.

Bench-scale testing of material movement by a clamshell bucket will commence.

A barrel elevator will be designed. Bench-scale testing will be conducted as needed.

A resuspension planning document will be issued.

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.

More recently the emphasis has shifted to obtaining bottom event failure probability and duration data, to completing the analysis of the fault tree diagram and its data, and to ranking the cutsets found in decreasing order of importance.

Progress During Report PeriodAnalysis

During this period the detailed analysis of the fault tree diagram and its data were completed. Some 3600 cutsets were identified, each one outlining a unique way in

which the system failure, "Radioactive Material from the High-Level Waste Tank Farms Moves to Offsite," might occur. The analysis provided estimated probability and probable duration of existence for each cutset as well as the identifying code name and descriptions of the bottom events of each cutset.

Many of the cutsets proved to have estimated probabilities far too low to justify their further consideration regardless of the consequences if they were to occur. The remaining cutsets, having the higher estimated probabilities from the multiple sub-tree computer analysis runs, were combined to make a master list of cutsets arranged in order of decreasing estimated probability. Probability-importances were calculated for the bottom events appearing in a group of these cutsets having estimated probabilities above a still higher arbitrary cutoff probability. The probability-importance of a bottom event is defined as the sum of the probabilities of all the cutsets in which the bottom event appears. Only 52 of the total of 149 bottom events appeared in this group, implicitly identifying the remaining 97 bottom events as being of lesser importance, at least from the standpoint of estimated probability of occurrence. The 52 bottom events identified were further classified into seven groups by virtue of common characteristics; and these groups were also ordered by group probability-importance.

These steps are preliminary to obtaining risk-importances where risk-importance for a bottom event is defined as the sum of the risk index values for all the cutsets in which the bottom event appears. Risk index is the sum of the base ten logarithm of the cutset estimated probability and the hazard index for the amount of

radioactive material represented by the cutset. A relative risk index may be calculated, with some qualifications, as the sum of the base ten logarithm of the cutset estimated probability and the base ten logarithm of the weight of radioactive material represented by the cutset.

Evaluation

A substantial fraction of the tasks to be accomplished prior to finishing the preliminary report were successfully completed. The results obtained to date are providing guidance in structuring the remaining tasks.

Problem Areas

The work early in the report period was hindered by the continuing overload of the Cyber-74 computer. Later, the work required to combine the sub-tree analyses into a single group of cutsets ordered by decreasing probability proved tedious and time-consuming. Plans are being made to further upgrade the fault tree analysis computer program to permit it to find all the cutsets of interest in a single pass and to provide a single ordered listing of the cutsets by decreasing probability.

Change in Plan

None.

Summary

Evaluation of the results of the current fault tree analysis effort is in its final phase and the preliminary report will be completed in draft-form during the next report period.

Future Work

Future work planned is summarized by the following major items:

- Complete the current analysis effort to identify the most important events in the fault tree.
- Complete the preliminary report, now in preparation.
- 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 of the work accomplished.

CORROSION BY HIGH-LEVEL WASTE (D. C. Lini)

Objective

The primary objective is to evaluate the effects of corrosion 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

This task was initiated during the prior quarter. During that period the work was concerned with scoping the broadest aspects of the problem. Based on the materials of construction and the types of wastes stored, a search was made to determine what modes of corrosion would lead to loss of tank integrity. Stress corrosion cracking (SCC), pitting, and general corrosion are the major failure modes. Information contained in prior Hanford reports indicates that the mild steel liners are susceptible to SCC. Most of

the earlier experimental efforts at Hanford have investigated the effects of corrosion, especially SCC, on the mild steel liners. Essentially nothing has been reported on the corrosion of the concrete storage tanks in the presence of liquid waste, sludge, or salt cake.

Progress During Report Period

Prior to proposing a corrosion project it was necessary to determine if additional experimental work was warranted. The prior corrosion experience at Hanford and, to a lesser extent, Savannah River was reviewed to learn what studies were made and what they showed. This also indicated what work is currently being conducted.

In searching the literature particular attention was paid to determine what information was obtainable from laboratory experiments and how this applied to evaluating and predicting tank failures. An added contingency to the potential program was that the experimental techniques be applicable to study a variety of environmental variables. Since it is planned that the program be initiated quickly, this necessitates that the initial cold experiments be contracted out.

Contacts were made with offsite corrosion experts to determine what type of experimental program is applicable to our needs and what laboratories could conduct the initial study.

The outgrowth of these efforts has been the determination that additional experimental work is warranted. The scoping of the overall program has been completed. The details of an experimental program and laboratories to conduct the initial cold studies are presently being considered.

A short review of the corrosion research carried out at Hanford has been written. All the corrosion work documented dealt with corrosion studies on the mild steel liner. The predominate waste-form for most of the experimental studies was simulated liquid waste. The predominate waste-form that will be considered in the projected work will be salt cake. However the initial work conducted by Battelle Pacific Northwest Laboratories has indicated that while the rates of corrosion are different, the same types of corrosion are encountered with salt cake as were found with the 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 leading to a premature failure has been SCC. Documentation of actual leaks at Savannah River and the subsequent investigations at Hanford and Savannah River has confirmed that the tanks are susceptible to SCC as a result of the residual stress in the steel liner, the concentration of nitrate ion in the waste solution, and the temperature of the radioactive waste. The evidence for pitting corrosion and accelerated corrosion at the air-liquid and liquid-sludge interface is not as well documented and falls in between general corrosion and SCC as a failure mode.

A second aspect of this program was that of opening lines of communication with offsite corrosion experts. The purpose was to make them aware of our needs, to insure that all aspects of the problem were recognized, to determine what additional experimental techniques are available, to verify that the experimental data would provide information needed to predict tank integrity, and to learn which

laboratories were capable of conducting a cold experimental program.

The program will indicate the propensity for corrosion and tank failure, and will define the conditions which should give the longest-lived tanks. However it cannot not predict when a particular tank will fail. Because of the variety and range of concentrations of wastes to be stored in the tanks, an electrochemical experimental program to study the effects of corrosion on the steel liner is applicable for our needs. The experimental program will be highly dependent on analytical data to determine the corrosive environment. There is considerable mild steel corrosion information in the literature and this program will be able to utilize these data. Also these tests will provide information that will be useful to the current corrosion studies on cathodic protection.

The best method for evaluating the effects of corrosion on the concrete storage tanks in the presence of salt cake has not been determined. This aspect of the program has not been as fully investigated as has been the part on the corrosion of mild steel. While it will be necessary to conduct such a study, just what techniques would provide the most information are still being sought.

In summation, the proposed program will consider corrosion studies on mild steel and concrete. The corrosion studies on mild steel will be predominately electrochemical and will include polarization studies and slow strain experiments to determine the propensity for corrosion and cracking tendency, respectively. This aspect of the program is similar to the approach being conducted at Savannah River. The cold studies on both the mild steel and concrete will be contracted out, while the hot studies will be conducted at

Hanford. This program is highly dependent on analytical support to determine as accurately as possible the actual chemical environment in the waste storage tanks. An in-depth literature survey of corrosion tests is also included in the program.

Evaluation

Several subgoals have been achieved. A review of the Hanford corrosion research has been written. It indicates what has been done and what the experimental studies showed. From this and other studies it is concluded that an experimental program is warranted. It is now possible to launch an effort to determine the details of this program and begin arranging for the contracting out of the cold experiments.

Problem Areas

Since we do not have the in-house capability to carry out all aspects of this program at this time, reliance is going to have to be made on offsite advisors and contractors. The experimental program is highly dependent on analytical support to determine the chemical environment that will be encountered.

Summary

The work this period has dealt with scoping of the program. A review of the corrosion research conducted at Hanford has indicated which types of corrosion have been encountered and how they have been studied. An investigation has been made to determine what additional information would result from an experimental program on the corrosion of the waste storage tanks. The results indicate that additional corrosion studies should be made.

Corrosion studies on both the mild steel liner and the

concrete storage tank are planned. The cold corrosion studies will be contracted out. Hot corrosion studies will be made onsite. The corrosion studies on the mild steel liners will utilize electrochemical techniques. The best approach to evaluating concrete corrosion has not been established at this time.

Future Work

The outline of the experimental program has been formulated. The details of the various aspects will now be worked out. Contact will be made with potential offsite contractors to determine actual experimental programs as well as cost and timing of a program. Separate contractors will be used to conduct the concrete and mild steel studies.

SALT CAKE STABILITY

(G. A. Beitel and L. E. Bruns)

Objective

Identify the conditions under which explosive reactions between carbonaceous matter and salt cake nitrates are possible.

Prior Work

As early as 1964 it was recognized that combinations of organic material and sodium nitrate may exist in the waste tanks which could, in the event of complete dehydration of the salt cake, present potential for thermal explosion. Although detailed studies were recommended, any which may have been undertaken were not reported.

Interest in the subject was again revived in early 1973. Procedures for testing the combustibility of NaNO_3 -organic resin mixtures were developed and approved, but

execution of these tests was deferred.

In September 1973 discussions were initiated between Stanford Research Institute (SRI) and Atlantic Richfield Hanford Company which led to the shock sensitivity tests of NaNO_3 -organic resin mixtures. Preliminary tests conducted in July, 1974, showed no evidence of shock-initiated detonation.

Progress During Report Period

Except for the preliminary effort spent on shock sensitivity studies, this quarter marks the beginning of this task.

During this report period continued gap tests at SRI with an "average" simulated salt cake and varying amounts of resin in various forms of deterioration, all gave negative results. Thus far, with 25 detonations, no hazardous reactions have occurred--a bulged witness plate detected in an earlier test was determined to be due to faulty equipment. Further consideration of the problem showed that the worst cases were not covered. Two things need to be done: (1) higher oxidizing power than previously tested has been detected in crystallizer evaporator waste salts (as high as 70 to 95% NaNO_3); and (2) the 5-cm gap tests initially tried may have a favorable surface area-to-volume ratio; and a larger gap test (15-cm diameter) should be used for a "worst" case. Planned are tests of 70% NaNO_3 -30% resin, 80% NaNO_3 -20% resin, 85% NaNO_3 -15% resin, and 90% NaNO_3 -10% resin using a 15-cm diameter gap test system.

It was initially believed that the primary hazard would arise from detonatable nitrated organics. This belief was based upon experiences with explosions of nitrated ion exchange resins during the course of processing actinides.

Seven such occurrences have been described (*Nuclear Safety*, Vol. 9, No. 5, p. 394). All seven incidents occurred with resins being treated with strong HNO_3 ($\geq 7N$).

On the other hand, any resins which may exist in the waste tanks have been neutralized with NaOH . It is reasonable to assume that any potentially detonatable nitrated organics would be degraded after a long residence in a highly caustic solution rather than for a stable organic to be nitrated to a state of detonatability. Although detonation is certainly the most serious hazard associated with exothermic reactions, it is also the most improbable. In addition to the detonation hazard, any exothermic excursion within the salt cake which results in the generation of gaseous species and rapid pressure increases, even though it is technically neither a detonation nor an explosion, is an unacceptable event. Therefore this investigation is not concerned with detonation alone, but will consider the more general problem of any self-sustained exothermic reaction.

Conceptually, the task is simply to establish combustion limits as a function of water, fuel, and oxidant concentrations. The principle difficulty is identifying or specifying the "fuel", that is, the variety of organic materials which may be present in the salt cake.

This investigation will proceed upon the following assumptions:

- Organic materials have been added to the waste tanks.
- Chemical changes, if any, have been in the direction of a more stable, tar-like or coal-like state.
- Under certain conditions (probably low water content and high temperature), the carbonaceous material can

be oxidized exothermally by the nitrate present.

- Exothermic reactions, if any, will range from slow combustion to thermal explosions comparable to low-grade black powder.

Summary

Emphasis in this area has changed from viewing detonation of nitrated organics as the major hazard to the broader aspect of placing combustion limits on mixtures of nitrates and degraded organics.

Future Work

Several additional shock sensitivity tests on simulated salt cake/organic resin mixtures will be conducted by SRI. Literature review in the area of combustible carbon-nitrate mixtures will be continued. An experimental program which will establish combustion limits of interest will be designed and conducted.

A program is currently being initiated to assay and characterize the salt cake. This characterization will provide invaluable input to the explosive hazards study by determining the organic and inorganic carbon content and distribution of the salt cake. One of our immediate tasks is to specify sampling requirements to be included in the assay procedure.

WASTE TANK CONTENTS CHARACTERIZATION (J. E. Horton and J. S. Buckingham)

Chemical Composition of Salt Cake Produced in the 242-S Evaporator

Objective

Determine the qualitative composition of salt cakes stored in the 242-S evaporator salt cake slurry receiving

tanks and find their quantitative range in typical salt cake.

Prior Work

Tanks 105-S and 106-S received slurry early in the 242-S evaporator program when recycle was about 40% and fresh dilute waste was about 60%. Tank 111-S was the tank receiving slurry in early August from the 242-S evaporator.

As noted in Table III, salts from Tank 105-S and 106-S are mostly sodium nitrate. The salts pick up some moisture in a 75% relative humidity chamber as 23° C but do not deliquesce; their caustic content is 1% or less. Salt from Tank 111-S is ~70% sodium nitrate, 6.6% sodium hydroxide, 10.8% sodium carbonate with small amounts of sodium aluminate and sodium nitrite. The salt from Tank 111-S deliquesced in six days; *i.e.*, it gained 22% of its weight when placed in the 75% relative humidity chamber.

TABLE III
ANALYSIS OF 105-S, 106-S, AND 111-S SALT

	<u>105-S</u>	<u>106-S</u>	<u>111-S</u>
Bulk density, g/cc	1.26	1.27	1.70
H ₂ O, %	3.4	4.2	18.4
NaAlO ₂ , %	0.1	0.6	2.3
NaNO ₂ , %	0.3	0.1	2.7
NaNO ₃ , %	100.3	90.1	69.7
NaOH, %	0.5	1.0	6.6
Na ₂ CO ₃ , %	2.5	4.1	10.8
Na ₂ PO ₃ , %	-	-	1.2
Total, %	107.1	100.0	110.7
¹³⁷ Cs, μCi/g	8.9	17.2	96.
⁸⁹⁺⁹⁰ Sr, μCi/g	-	-	7.54

Analyses of mother liquors associated with the 106-S and 111-S salts are presented in Table IV. Interstitial

liquor is currently being pumped from 105-S; therefore the salt sample was well drained and did not contain sufficient mother liquor which could be analyzed.

TABLE IV
ANALYSES OF 106-S AND 111-S MOTHER LIQUOR

	<u>106-S</u>		<u>111-S</u>	
Density	1.428		1.414 g/cc	
H ₂ O		55.0%		54.4%
NaAlO ₂	1.56M	8.9%	1.34M	7.8%
NaNO ₂	0.66M	3.2%	1.65M	8.1%
NaNO ₃	2.49M	14.8%	2.90M	17.4%
NaOH	5.33M	14.9%	3.80M	10.7%
Na ₂ CO ₃	0.1M	<u>1.0%</u>		
Total		97.8%		98.4%
¹³⁷ Cs	3.39 x 10 ⁵ μCi/liter		4.48 x 10 ⁵ μCi/liter	

The hygroscopicities of the salt samples were measured by placing a weighed portion of the salt in a humidity chamber and observing the increases in weight over a period of time. The relative humidity of the chamber was 75% at 23° C. Figure 2 shows the percent gain in weight of specific salt samples in the humidity chamber. The point at which "free," "flowable" liquid was observed is also indicated.

Thermal conductivity measurements for the 105-S salt are shown in Table V.

FIGURE 2

HYGROSCOPICITY OF SALT FROM 105-S, 106-S, AND 111-S

TABLE V
THERMAL CONDUCTIVITY OF 105-S SALT

Conditions	Temperature	Btu/hr-ft ²
	°C	°F/ft
As-received firmly packed dry crystals	21.8	0.251
Held overnight at 62.1° C	62.1	0.247
Held overnight at 80.0° C	80.0	0.235
Held overnight at 115° C	144.9	0.216
Held over weekend at 156° C	156.0	0.205

Sludge Characterization

Objective

Determine the composition and physical properties of sludge and find their quantitative range from tank-to-tank.

Prior Work

None of record; samples of sludge have just become available.

Progress During Report Period

Tank 104-A was used to store Purex Sludge Supernatant (PSS) generated during the sluicing of Tanks 106-A, 101-A, and 103-A. Much of the sludge in the tank consists of material that did not settle in Tank 002-AR when 106-A, 101-A, and 103-A were sluiced.

A sample of sludge from 104-A showed that the material was quite fluid, having a consistency similar to heavy cream. The ⁸⁹⁺⁹⁰Sr content of the sludge was 43.9 Ci/liter. The "as-received" 104-A sludge was analyzed by fusing 1.7 milliliters with KOH, dissolving the melt with HCl, and diluting to 320 ml. Density and moisture contents were measured on a separate portion of the sludge. Results are shown in Table VI.

TABLE VI
ANALYSIS OF 104-A SLUDGE

	<u>Analysis</u>	<u>Wt%</u>
Density	1.64 g/cc	
H ₂ O		42.3
Al	2.82 moles/liter	4.6
Si	0.83 moles/liter	1.4
Fe	4.99 moles/liter	17.0
Mg	0.11 moles/liter	0.2
Ca	0.41 moles/liter	1.0
Ba	0.009 moles/liter	0.1
Mn	0.71 moles/liter	2.4
Sr	<0.055 moles/liter	
⁸⁹⁺⁹⁰ Sr	4.39×10^7 μ Ci/liter	
¹³⁷ Cs	1.15×10^6 μ Ci/liter	
¹³⁴ Cs	3.33×10^4 μ Ci/liter	
⁶⁰ Co	5.94×10^4 μ Ci/liter	
¹²⁵ Sb	5.95×10^5 μ Ci/liter	
¹⁵⁴ Eu	1.30×10^5 μ Ci/liter	

Particle size distribution of the 104-A sludge, as determined on a particle counter is shown in Table VII. Particle size distribution for sludges from 102-A, 102-AX, and 106-C are also shown for comparison.

TABLE VII
PARTICLE SIZE DISTRIBUTION IN SLUDGES

<u>Particle Size</u> <u>m</u>	<u>Average Diameter</u> <u>m</u>	<u>Weight Percent</u>				
		<u>102-A</u>	<u>103-A</u>	<u>104-A</u>	<u>102-AX</u>	<u>106-C</u>
5						
10	8.2	1.7	9.6	4.3		
20	16.5	33.3	46.7	34.7	35.0	11.7
30	25.9	34.0	14.1	32.5	45.7	22.8
40	35.7	17.6	0.0	7.0	14.3	21.4
50	45.5	11.1	17.0	12.3	3.1	12.4
60	55.4	1.4	5.2	4.7	1.1	15.3
70	65.4	0.7	3.3	3.1	0.4	5.0
80	75.3	0.0	2.0	1.0	0.3	3.8
90	85.3	0.1	1.0	0.5	0.2	2.4
100	95.3	0.1	0.9	0.1	0.1	1.8
<100						3.5

Acidification does not dissolve all of the sludge. Previous work has shown a considerable amount of strontium associated with the insoluble sludge. Treating the acid-insoluble sludge with an equal volume of 50% NaOH, then acidifying with 12M HNO₃ removes additional strontium. Tables VIII and IX show the amount of strontium dissolved by acid for Batches 1 and 2, respectively. Table IX shows the amount of strontium removed by caustic acid treatment. Unfortunately solids remaining after the caustic acid treatment were lost; however the data indicate that the caustic acid treatment removed almost all of the remaining strontium.

TABLE VIII
LOCATION OF STRONTIUM IN BATCH 1 DURING TREATMENT

	<u>Volume</u> <u>ml</u>	<u>Vol%</u>	<u>⁸⁹⁺⁹⁰Sr</u> <u>μCi</u>	<u>Ci</u> <u>%</u>
Storage (feed)	3	100	1.32×10^5	100
PAS (liquid)	12		1.14×10^5	86
(solid)		83		
Caustic-acid (liquid)	5.5		2.02×10^4	15
(solid)	2.5	83		

TABLE IX
LOCATION OF STRONTIUM IN BATCH 2 DURING TREATMENT

	<u>Volume</u> <u>ml</u>	<u>%</u>	<u>⁸⁹⁺⁹⁰Sr</u> <u>μCi</u>	<u>Ci</u> <u>%</u>
Sludge (feed)	3	100	1.32×10^5	100
PAS (liquid)	11.5	-	9.19×10^4	70
(solid)	1.5	50	2.61×10^4	20

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN NUCLEAR
MATERIALS WITH 2-(2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL (PADAP)
(W. I. Winters)

A highly selective and sensitive spectrophotometric method using PADAP has been developed for the determination of trace uranium in solvent extraction streams, PuO_2 , $\text{Pu}(\text{NO}_3)_4$, and Hanford nuclear waste. The method is capable of detecting 1 μg of uranium and only Pd was found to interfere significantly. Using a new brominated derivative of PADAP, it will be possible to improve the sensitivity and selectivity of the procedure.

Two different variations of the uranium procedure using PADAP were evaluated. In the direct method potential interfering ions are complexed with a mixture of (1,2-cyclohexylenedinitrilo)tetraacetic acid (CyDTA), NaF, and sulfosalicylic acid. After adjusting the pH between 7.8 and 8.7 with a triethanolamine buffer, the color is developed with PADAP in a water-ethanol matrix. This approach is the simplest and applicable to environmental samples where interfering ions and acid conditions are at low concentrations. In more complicated matrices such as PuO_2 and nuclear waste it is necessary to separate the uranium away from the matrix using such reagents as tri-octylphosphine oxide (TOPO) and the quaternary amine Aliquat-336[®] (General Mills Company) and then develop the color using an aliquot of the organic phase.

The optimum extraction and color development parameters were established for the method. The most stable colored solutions were formed using a 44% ethanol- H_2O mixture for the direct method and a 68% mixture for the extraction technique. Two milliliters of 1.5 g/liter PADAP were required to provide linear calibrations from 10 to 200 μg of

uranium. The direct method required 30 minutes for full color development and 1.5 hours for the extraction procedure.

One of the first applications studied for the extraction procedure was the determination of trace U in PuO_2 used in the FFTF program. Initial studies to separate U from Pu with TOPO were not adequate; however the selectivity of the method in nitrate systems makes it directly applicable to waste tank analyses. Aliquat-336 extractions with fluoride were found to provide the necessary 10^4 - 10^5 decontamination of factors of U from Pu after reducing the plutonium to Pu(III) in a 4M HCl-2M $\text{NH}_2\text{OH}\cdot\text{HCl}$ matrix. The precision and accuracy for spike recoveries of 10 uranium analyses in $\text{Pu}(\text{NO}_3)_4$ was $97.3 \pm 7.0\%$.

Before applying the method to PuO_2 the effect of the concentrated HCl and HF used in the dissolution on the extraction had to be evaluated. Varying amounts of HCl and HF cause small variations in the uranium extracted. Tests of three different dissolution techniques in which the excess HCl and HF were removed by evaporating to dryness and residual fluoride complexed with Al showed that the removal of HCl and HF by evaporation and complexing would provide the most reliable results and was the most consistent with calibration conditions. A study on the effect of the organic-to-aqueous ratio on the extraction into Aliquat-336 showed no differences over the range of 0.02 to 0.3.

The Aliquat-336 extraction proved to be directly applicable and offered several advantages over the TOPO used in the X-ray analysis of U in Pu described in ARH-2835.^[1] A comparison of the X-ray and PADAP spectrophotometric uranium analyses in PuO_2 was performed since the two methods are normally subject to different interferences. Eight uranium-spiked samples were analyzed. The X-ray gave spike

recoveries of $108.3 \pm 2.5\%$ compared with $100.4 \pm 8.4\%$ for the spectrophotometric method. Before applying the methods to the analysis of the FFTF PuO_2 standard, a new uranium standard and calibrations were prepared to remove the possibility of bias results and to improve the precision of the spectrophotometric results. The average X-ray result for three FFTF standard analyses was 433.3 ppm (117%) compared with 451.6 ppm or 122% for the spectrophotometric technique. Three additional analyses by X-ray gave an average 119% recovery. No good explanation can be found for the high results. X-Ray scans showed no evidence of other cations and the two methods of measurement are independent of each other. Based on these and earlier results both methods should be applicable to the determination of trace U in Pu at the 100 ppm level. Better standards and more accurate and sensitive methods are required for lower level uranium analyses.

The effect of 34 ions on the Aliquat-336 extraction PADAP spectrophotometric method was evaluated at a 10:1 μg ratio of ion-to-uranium. This is significant ($>10\%$) only at uranium levels less than 100 ppm. Palladium was the only ion found to interfere at the 10:1 and 1:1 μg ratio level. This interference could be overcome by using a TOPO extraction. Nitric acid at the 8-milliequivalent level did not affect the extraction of uranium.

Attempts to extend the detection limit of the direct method to 0.1 μg uranium met with limited success. The large overlap in the PADAP spectra and U-PADAP spectra causes poor precision on low absorbance measurements. The PADAP concentration was reduced to 0.5 g/liter for less than 10 μg U to minimize this problem. Attempts to extract the U-PADAP complex failed; however CCl_4 appeared to wash the

excess PADAP reagent away from the U complex. This approach resulted in a 10-fold decrease in the intercept and a 30-fold improvement in the precision of the calibration slope and intercept. Attempts to measure uranium at the 0.25- μ g level resulted in poor yields ($\pm 25\%$) and therefore a 1- μ g U level is considered the limit for this method. This should permit analyses of samples with U concentrations near 1×10^{-4} g/liter. In order to lower the detection limit a more sensitive reagent and better control of spectrophotometer conditions will be required.

Recently a more sensitive and selective brominated derivative of PADAP (Br-PADAP) has been tested. This reagent improved the sensitivity by 30% and is purer with much less overlap of reagent and U complex spectra. This reagent should improve the applicability of the spectrophotometric method in characterizing Hanford's nuclear waste. The accuracy of the spectrophotometric method makes it more desirable than fluorescent uranium analysis techniques and its sensitivity makes it more applicable than X-ray methods. Future work will be directed at using Br-PADAP to reduce the lower detection limit and applying this method to the characterization of Hanford's waste.

EQUIPMENT DECOMMISSIONING

(B. B. Harshbarger)

Objective

To develop and demonstrate processes for consolidating contaminated equipment or other metal components--emphasis is on significant bulk volume reduction with a reduction of hazard to the biosphere.

Prior Work

Meltdown was identified as the unit operation producing the minimum volume-to-weight-ratio product. Besides conventional melting electric furnaces which require size-reduced charge stock, a melter using a thermite-type reaction for fusion heat had been proposed. Two configurations of the thermite-type furnace were identified--the "hole-in-the-ground" melter (Figure 3) and the continuous "autogenous" melter (Figure 4).

Other potential processing steps prior to meltdown; *e.g.*, size-reduction and decontamination, had been identified and the possible means of accomplishing these processes had been specified.

Progress During Report Period

The discovery of one more potential melting technique was made at Schlienger, Inc., in San Rafael, California. Using a nonconsumable, water-cooled, rotating copper electrode, Schlienger arc melts metals and drips them into a skull (water-cooled copper) crucible for solidification. Copper electrode and crucible are used by Schlienger because a high-purity product is desired with no impurities introduced from the processing system.

By gimbal mounting (X-Y-Z mobility) a graphite electrode, it should be possible to drip melt intact failed process equipment into either a water-cooled steel boat mold or into a water-filled shotting basin. Graphite would be used instead of water-cooled copper because:

1. Carbon would be an acceptable containment in steel melts.
2. The complexities of a rotating, water-cooled electrode would be eliminated.

FIGURE 3
HOLE-IN-THE-GROUND MELTER

FIGURE 4
AUTOGENOUS MELTER
Side View

3. Graphite has more mechanical durability than does copper.
4. Graphite electrodes are remotely renewable by screwing another section onto the existing electrode.

The drip melting technique will allow simultaneous size-reduction and consolidation. The product from a drip melter could be further processed in more conventional melters to alter product form or in an attempt to effect meaningful decontamination.

A "hole-in-the-ground" melter two feet in diameter by six feet deep has been dug in basalt on Gable Mountain for prototype testing on a cold basis of this concept. Necessary materials for the test (except oxygen) were ordered. The test will probably take place in December.

Laboratory hot cell melting tests were designed to determine the distribution of radionuclides when contaminated steel is melted. Personnel in T Plant have been seeking cesium-contaminated pipe to be used in the tests. They report only β contamination on jumpers coming to them from B Plant, and cesium contamination in the melt needs to be identified since it is more volatile than strontium and probably will represent the biggest off-gas handling problem.

Full-scale decontamination tests on failed equipment now await identification of a suitable piece of equipment which will not completely deplete the operating budget on a single test. In 1970 the reported cost of decontaminating a Purex Dissolver Tower was \$60,000. No other readily available equipment in the Purex canyons can be handled in T Plant. The search is under way to find an alternate

candidate for decontamination among equipment that has been laid-by in T- or U- canyons.

Summary

A "hole-in-the-ground" thermite-type melting test should be conducted this next quarter. Melting using a mobile graphite electrode arc system (Figure 5) has been - postulated as an alternative to thermite-type melting.

Decontamination of a full-sized piece of equipment for generation of cost-benefit profiles awaits identification of an equipment piece that can be handled within the constraints of our budget. Hot cell laboratory-scale melting tests are planned as soon as ^{137}Cs -contaminated equipment can be obtained and scheduled into the hot cell.

Future Work

More specific information about the viability of the graphite electrode arc melting system will be gathered from informed sources like furnace manufacturers, electrical power source manufacturers, etc.

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.

An inventory of the potential metal feedstock to a decommissioning plant is under way. Such an inventory will include the size, weight, materials of construction, contamination level, and location of material.

FIGURE 5
GIMBAL MOUNTED ELECTRIC ARC MELTER

WASTE IMMOBILIZATION

ECONOMIC STUDIES (J. E. Hammelman)

Objective

The results of this particular study and similar future studies are intended to help

- Establish engineering and laboratory development priorities.
- Identify promising strategies for achieving minimum cost immobilization, solidification, and storage of high-level waste.
- Indicate major cost areas.
- Provide a standard cost comparison methodology for evaluating various waste processing and storage options.

Prior Work

A previous study evaluated the penalty for volume increase associated with Aqueous Silicate versus Silicate Melt processing. The results of this study showed storage costs to be a significant factor in overall cost and thus prompted this more detailed study of processing-storage options.

Progress During Report Period

Data Collection

The initial estimates of chemical and major utility costs have been prepared to allow comparative evaluation of processing costs. Capital requirements for various storage modes have been approximated with the help of Process Design and Development personnel. An example of the

design detail involved in these estimates is shown in Figure 6. Other options being evaluated are waste cylinders in a vault and waste cylinders on the ground surface.

Laboratory immobilization programs are being closely followed because of their effects on chemical and utility cost estimates.

FIGURE 6
PELLET VAULT CONCEPT

Evaluation

These costs are being reviewed and revised in an attempt to assure equitable comparison of alternatives and to keep abreast with demonstrated laboratory technology. In this study, differences in dose-to-man risk for the various alternatives is being assumed negligible because of current inability to evaluate this parameter (risk). This assumption could make option evaluation based on study results subject to some uncertainty.

Summary

Cost estimate data relative to high-level waste storage modes is being reviewed in preparation for an economic

evaluation of immobilization and storage alternatives using the principles of discounted cash flow.

Future Work

The economic evaluation of cost estimate data is expected to begin in the near future. This will be followed by documentation of the study, including: option considered, cost estimates, economic evaluation, conclusions and usage of study results. Upon completion of this report, studies involving volume reduction and actinide removal are expected to begin.

AQUEOUS SILICATE PROCESS: PILOT-PLANNING (R. A. Watrous)

Objective

Various processes for immobilizing High-Level Wastes (terminal liquor, salt cake, sludges) need to be demonstrated on a pilot-plant scale. Current planning is aimed at providing a new facility in which terminal liquor processing as well as Aqueous Silicate, Silicate Melt, and Volume Reduction pilot-plant operations could be conducted using actual wastes. The immediate objective of this work is to define a process flowsheet and guidelines upon which a fiscal year 1977 budget item design for Phase I of the facility can be based. Conceptually, this first phase of the facility will provide the capability to immobilize and store terminal liquor wastes using the Aqueous Silicate process plus subsequent product packaging operations.

Prior Work

None reported relative to pilot-plant planning. [Laboratory development programs are reported elsewhere in this report.]

Progress During Report Period

A proposed flowsheet has been formulated for the aqueous silicate pilot-plant and is shown in simplified form in Figure 7. The example flowsheet is of interest primarily for its definition of clay-waste mixing; in regard to product "packaging" and the addition of binders, however, this flowsheet is perhaps the more simplistic of several alternatives--i.e., no binder other than excess clay is added.

Several characteristic features of this flowsheet are described below:

- Clay-Waste mixing via the United Technology Center (UTC) inert carrier process (see p. 49). Uniformity of mixing, ability to dissipate reaction heat, ease of equipment startup and cleanout, and amenability for remote maintenance are advantages assumed to be gained by use of the inert carrier mixing process as opposed to conventional mechanical mixing equipment.
- Product packaging by "casting in drums". This flowsheet proposes the use of steel drums as (1) the mold for product casting, (2) the means of minimizing dusting problems, (3) the primary "device" for product handling, and (4) a containment barrier.
- Formation of cancrinite (curing) at 90-100° C, by use of a controlled temperature processing oven.
- Removal of entrained organic (heptane) and free water from the solid product by drying in a second oven stage, operating at temperatures equal to

FIGURE 7
AQUEOUS SILICATE PROCESS FLOWSHEET
HOT PILOT-PLANT - PHASE I

the hottest conditions expected in possible future storage situations. The objective of this drying step is to produce a thermally stable product which, in turn, becomes the key to achieving a passive storage mode.

- Storage of product drums in a passive vault. No forced cooling is envisioned other than natural convection within the vault and conduction through the vault walls and surrounding soils. Likewise, the control of humidity or radiolytic hydrogen in the vault atmosphere should be simplified owing to the stable nature of the drummed product.

The proposed design capacity of the flowsheet (six-gallon-per-minute feed rate) represents a compromise between the following possible campaign requirements and the uncertainties in scale-up of the UTC mixing system shown on the following page.

Obviously the 22.7 liters per minute (6 gallons per minute) [feed] capacity plant would require more than two years to process the 30 to 38 million liters (8 to 10 million gallons) of terminal liquor which is estimated to be accumulated if partial neutralization is not added to the current evaporator flowsheet. If scaleup of the mixing equipment proves not feasible, dual processing lines (at least through the step of drum filling) may be necessary.

<u>Processing Campaign Objective</u>	<u>Required Feed Rate (Waste)</u>
1. Solidify all terminal liquor accumulated through FY 1981 in two years (FY 1982, FY 1983).	
Case a ~5 Mgal, if partial neutralization is used	22.7 liters/min (6. gal/min)
Case b 8-10 Mgal, if partial neutralization is not used	36-45 liters/min (9.5-12 gal/min)
2. Demonstrate immobilization of actual salt cake (600,000 gal assumed from the retrieval demonstration)	
Constraint a Processing 600,000 gal salt cake in 1 yr	12.9 liters/min (3.4 gal/min) dissolved salt cake
Constraint b Processing at a rate commensurate with mining capacity of one hydraulic crane arm*	17 liters/min (4.5 gal/min)

*18,144 kg (20 tons) per day assumed as maximum.

Future Work

Waste product and storage system criteria need to be quantified and/or defined in more detail before certain design decisions can realistically be made. Limit for product leach rate and (wind) erosion rate under accident conditions need to be calculated, reviewed, and endorsed. The required life time of the primary containment barrier (drums in the case of this initial flowsheet concept) needs to be studied in considerable detail.

Pending the outcome of these criteria studies, flow-sheet variations may be developed which incorporate the use of binders and surface hardeners (possibly in lieu of steel drum containers) to optimize the leaching and erosion

characteristics of the waste product versus cost.

Summary

An Aqueous Silicate process-scale flowsheet has been calculated for solidification and storage of terminal liquor as the Phase I operation in the proposed waste immobilization hot pilot-plant. The flowsheet assumes the use of the United Technology Center's inert carrier process for mixing waste and clay at a design rate of 22.7 liters per minute waste and 19 kilograms per minute clay.

INERT CARRIER PROCESS EVALUATION (M. H. Campbell)

Objective

Evaluate mixing systems that could be used in the Aqueous Silicate process to mix the solid clay feed material with caustic terminal liquors or with caustic salt slurries. This information is the needed prerequisite to designing a demonstration plant.

Prior Work

During fiscal year 1974 mixing tests were conducted at two vendors' plants under the direction of ARHCO engineers who were assigned the chemical solidification activity funded by the AEC Division of Production and Material Management. One mechanical mixer was judged able to make a satisfactory product, but a test with caustic salt slurry produced an aqueous silicate product with crystalline sodium nitrate.

Progress During Report Period

The United Technology Center (UTC) was engaged by Atlantic Richfield Hanford Company under special agreement SA-179 to determine the feasibility of using their unique

Inert Carrier process for intimately mixing the ingredients of the Aqueous Silicate process, clay and radioactive waste material.

Instructions for conducting the test were that all pilot-plant runs would be performed on the basis that 55-gallon drums would be used to receive the mixed product. The full-scale mixer would be capable of blending liquid solutions or slurries up to 151 liters per minute with clay. Simulated radioactive feed materials would have the makeup shown in Table X. The recommended pilot-plant runs are shown in Table XI.

TABLE X
WASTE MAKEUP COMPOSITION

<u>Composition</u> <u>Wt%</u>	<u>Liquid Feeds*</u>	
	<u>Solution</u>	<u>Slurry #2</u>
H ₂ O	50	44
NaNO ₃	20	17
NaNO ₂	10	10
NaOH	10	22
NaAlO ₂	10	7
TOTAL	100	100
Physical Properties		
Solids, vol%	0	30
Wt%	0	14
Density, g/cc	~1.4	
Viscosity, cp	3 @ 50 °C	272 @ 25° C

*All feeds shall be made up starting with hot caustic. Solution may be stored at ambient conditions if desired. Slurry #2 should be used as quickly as possible after being made up.

TABLE XI
SUGGESTED PILOT-PLANT RUNS

<u>Run Number</u>	<u>Type Clay</u>	<u>Liquid Clay</u>	<u>Temperature °F</u>	<u>Clay-to-Liquid Feed Ratio, g/ml</u>
1	Kaolin (calcined)	Solution	120	0.75
2	Kaolin (calcined)	Solution	120	1.0
4	Kaolin	Solution	120	0.74
5	Kaolin	Solution	120	1.0
13	Kaolin (calcined)	Slurry #2	120	0.50
14	Kaolin (calcined)	Slurry #2	120	0.75
15	Kaolin (calcined)	Slurry #2	120	1.0
17	Kaolin	Slurry #2	120	1.0

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ARRH-ST-110 A

In July 1974, UTC personnel advised that they had prepared mixtures at clay addition rates up to 5.4 kilograms per minute and over a range of clay-to-synthetic radioactive waste ratios of 0.5 to 1.25 g/cc. At this point a demonstration test was arranged. Personnel participating in this test at Coyote, California, on August 9, 1974, were:

<u>UTC</u>	D. D. Ordahl, Manager - New Products Development
	E. L. Watt, Head - Development Operations Branch
	R. D. Sheeline, Program Manager
	J. F. Schimscheimer, Chemist
	C. H. Carlton, Head - Mechanical Properties Research Group
	E. N. Bemis, Process Engineer
<u>ARHCO</u>	A. E. Smith, Manager - Research Department
	M. H. Campbell, Manager - Waste Processing and Storage Technology Section
	D. A. Turner, Manager - Solid Waste Process Design
	G. S. Barney, Senior Chemist - Chemical Technology Laboratory

During the briefing session Mr. Ordahl described the mechanical system, operating principles, and the problems encountered in applying the Aqueous Silicate process. The initial problem concerned selecting an internal surface finish for the system--stainless steel or glass cumulated coatings of clay that caused notable reduction in flow rates. When Teflon inserts were used, flows were not restricted and no cumulation of clay occurred. A second concern was related to maintaining the optimum reactive surface on the clay. When clay alone was recycled in the disperser unit, the inert carrier would wet the clay and prevent rapid mixing of clay particles with caustic solutions. However when clay and caustic solutions were immediately contacted in the disperser, the result was an aqueous silicate product with some apparently superior qualities.

The hardware can best be described in the attached series of photographs. The first photograph shows all system components except the slurry or solution feed tank and the product separations column. Dr. Schimscheimer is adjusting the clay addition belt (a calibrated unit good to ± 0.5 percent) and immediately above that belt is the clay feed tank. A more detailed view is shown in the second picture. Directly in front of the clay metering unit (Photographs 1 and 2) the disperser is evident. The top section of this disperser appears in the third picture, giving a feeling for the mixing action. Again returning to Photograph 1, below and to the right of the disperser and only partially visible, is a pump that provides the solution movement for the disperser. A better view of this pump is provided in Photograph 4. The simulated radioactive feed material was added by a second similar pump shown in the right foreground of Photograph 1. The simulated radioactive material feed tank for this test was installed later and does not appear in these pictures. The separations column where the solid aqueous silicate product is removed from the inert organic diluent stream is shown in the right foreground of Photograph 5. Located at the bottom of the column is a pneumatic valve which provides control for removing the solid product. Not evident in the photographs was a heat exchanger attached to the dispenser loop and the feed tank. In all pictures the floors appear wet because UTC has a standard procedure for discharging the heat exchanger water to the floor.

The operating concept for the Inert Carrier process is based on dispersal of the reactants in an inert matrix to reduce viscosity and provide the maximum surface area for a solid-liquid reaction mechanism. Additionally, the separations column provides for a clean separation of the reaction

PHOTOGRAPH 1
PILOT-PLANT--INERT CARRIER PROCESS

PHOTOGRAPH 2
CLAY METERING UNIT

PHOTOGRAPH 3
TOP SECTION OF DISPERSER

PHOTOGRAPH 4
DISPERSER PUMP

PHOTOGRAPH 5
SEPARATIONS COLUMN

product from the inert organic matrix. An additional advantage of this mixing system is that the inert carrier will rapidly remove heat from exothermic reactions, affording an added degree of control (this is not required in the aqueous silicate reaction). Such a mixer provides a most desirable continuous (and controlled) mixing process from the Aqueous Silicate process. The inert organic diluent for the tests described below was the Normal Paraffin Hydrocarbon (NPH) used in the Purex process at Hanford (specifications appear in Table XII). The product material was not solidified until it had been placed in an oven at 75° C for two hours. This agrees with ARHCO laboratory kinetic studies.

The flowsheet for the demonstration test is shown in Figure 8. The clay feed rate was fixed at 1800 grams per minute (four pounds per minute) and the simulated radioactive feed material was operated in a variable mode to provide ratios of clay/radioactive feed of 0.5 to 1.25 g/cc. A kaolin clay was used for this test. On examining the equipment setup, two loops that permit rapid process adjustments and shutdown with a maximum of control can be identified. The "Feed Heat Control Loop" provides for instantaneous shutdown of liquid feed material which, coupled with stopping clay addition, terminates the process within three minutes. The Disperser Loop provides the reactor and product separator with a bypass that assures operating flexibility.

The process test based upon a clay-to-feed ratio of 0.75 was operated flawlessly for 20 minutes. The following observations are pertinent:

- Process startup required less than five minutes (nothing was operating on arrival).

TABLE XII
 MATERIAL SPECIFICATIONS
 NORMAL PARAFFIN HYDROCARBON (NPH)

<u>Purchase Specifications</u>	<u>Value, wt%</u>	<u>Test Requirements</u>	
		<u>Method</u>	<u>Frequency</u>
a. N-paraffin hydrocarbon	Min. 98 vol%	Zy-28	ES
b. C ₁₀ to C ₁₄ components	Min. 99 vol%	Zy-28	ES
c. Aromatics as 1,2,3,4-tetrahydronaphthalene	Max. 0.2 wt%	Zz-9	ORPE
d. Iodine number (olefins as wt% 1-tetradecene)	Max. 0.1 wt%	Zx-21	ORPE
e. Alcohol	Max. 0.05 wt%	Zx-22	ORPE
f. Sp. gr. @ 20/20° C	Max. 0.76	Zy-10	ES
g. Viscosity @ 25° C	Max. 1.8 centipoises	Zy-9	ES
h. Flash point	Min. 158° F	Zy-6	ES
i. Interfacial tension between hydrocarbon and 0.1M NaOH	Min. 12 dynes/cm	Zy-32	ORPE
j. Solids	None visible	Visual	ES
k. Color	Colorless	Visual	ES

NOTE: Vendors whose products meet the above specifications may submit a one-gallon sample for laboratory evaluation of compatibility with plant processing conditions.

Sampling Procedure: Method C. A 32-oz sample of each tank car should be taken.

ES = Each shipment

ORPE = On request Process engineers

Present Vendor: South Hampton Company
 Sillsbee, Texas

FIGURE 8

ICP PILOT-PLANT SETUP FOR WASTE DISPOSAL DEMONSTRATION

- The separations column was cloudy with dispersed clay for only the first minute; after that the organic at the top of the separator was visibly clear.
- The product in the column seemed to agglomerate, looking like one-inch diameter cornflakes that fell to the bottom.
- The product discharged into five-gallon buckets had the appearance of peanut butter and filled the can without any shaking.
- Equilibrium operation was reached in less than four minutes.
- Organic diluent trapped in the product during discharge came to the surface and could be poured off. Supposedly less than 1% was trapped permanently.
- Process shutdown was accomplished in three minutes. The system was visibly clean.

Observations of tests at clay-to-feed ratios of 1.0 and 1.25 were substantially the same as above with the following additions:

- At a ratio of 1.0, the product material did not settle readily in the receiver drum until the drum was tapped with a mallet. At a ratio of 1.25, the product was too stiff to settle.
- The separations column appeared to operate even better at these higher ratios.

Product materials cured at 75° C for two hours from previous tests were examined. Calcined kaolin clay especially seemed to provide a less porous product than we have been able to obtain by ordinary laboratory mixing techniques.

The surface had a glazed appearance. Kaolin mixed with a caustic/salt slurry also had a less porous appearance than we have achieved. A series of samples were brought back to our laboratories for chemical and physical comparison to products made here. Naturally one of these tests was to measure the amount of entrained NPH diluent. In addition to these smaller samples, five-gallon buckets of product material representative of the various tests performed are being shipped to us for further examination.

Product Evaluation

Samples from the UTC mixer test were analyzed in ARHCO laboratories. The density, hardness, and percent NPH diluent retained in the product are presented in Table XIII. Keeping in mind that this was a scouting test, some generalizations for further confirmation are suggested by these results.

- Higher density and improved hardness are observed with a calcined kaolin feed.
- Under similar conditions calcined kaolin entrains less NPH diluent.
- The Kaolin-Slurry entrains less NPH diluent than Kaolin-Solution.

X-Ray diffraction patterns were made for each sample. The presence of cancrinite was confirmed in every instance. Surprisingly there were no sodium nitrate crystal diffraction patterns in the slurry samples.

Electron microscope examination of each product confirmed the presence of cancrinite. Again, no sodium nitrate crystals were observed. Representative SEM photographs (6, 7, and 8) are attached. The familiar small spheres of the cancrinite crystal can be identified.

Kaolin/Caustic Salt Cake Slurry = 1 g/cc

SEM magnification: x400

Kaolin/Caustic Salt Cake Slurry = 0.75 g/cc

SEM magnification: x5,000

Kaolin/Caustic Salt Cake Slurry = 0.75 g/cc

SEM magnification: x 10,000

SCANNING ELECTRON MICROSCOPE PHOTOGRAPH OF UTC TEST MATERIAL

PHOTOGRAPHS 6, 7, and 8

Quality of this product appears to exceed that made in bench-scale laboratory tests. Data are presented in Table XIII.

The results point up the need to demonstrate improved diluent removal. United Technology Center personnel have already recommended several techniques that would accomplish this; *e.g.*, sloped vibrating belts and improved design on the separating column. Thermal analyses were performed for each sample. Results show no exothermic events below 760° C. From 760° to 900° C an exothermal event was measured. This test implies a definite degree of safety even though organic was entrained.

The apparent success in reacting slurry with clay must be further verified and parameters for assuring complete reaction should be defined. This aspect will have impact on flowsheet design. This product was compared with that of the mechanical mixer tests done last February; it is much more homogeneous. In the case of the slurry and mechanical mixer, crystals were visible to the naked eye.

Future Plans

Success of the initial program leads to the next phase of tests that are directed to providing the detailed information needed for:

- Equipment design.
- Flowsheet design.
- Product quality.
- Reduced organic diluent entrainment.

Equipment design work will be directed to a 40-pound per minute clay addition rate prototype. This prototype would be built by UTC in such a way that the clay metering

TABLE XIII
 PROPERTIES OF AQUEOUS SILICATE PRODUCTS
 Prepared by the Inert Carrier Process*

<u>Product Mixtures</u>	<u>Clay/Waste Ratio</u> <u>g/ml</u>	<u>Density</u> <u>g/ml</u>	<u>Hardness</u> <u>kg/cm²</u>	<u>Wt% NPH</u> <u>in Product</u>
Kaolin - Slurry	1.0	1.52	140	1.33
Kaolin - Slurry	0.75	1.58	8	1.89
Kaolin - Solution	1.21	1.67	28	3.38
Kaolin - Solution	1.00	1.65	10	3.25
Kaolin - Solution	0.75	1.58	1	2.48
Calcined Kaolin - Solution	1.00	1.83	180	1.63
Calcined Kaolin - Solution	0.75	1.64	100	1.79

*United Technology Center, Coyote, California.

system, the radioactive solution/slurry feed tank, and the deentrainment column would be separate from all the remaining mixing equipment mounted in a rack no larger than 10 feet on a side. Prototype criteria will be developed by Atlantic Richfield Hanford Company.

Flowsheet design will require further and more definitive tests of operating modes. The effect of various flow rates, operating temperatures, clay types, and binders need careful attention. The intimate mixing achieved by the subject technique potentially affords new and improved product properties. An investigation of what range of salt cake slurry compositions could be used in this mixing system must be conducted.

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 reaction are 1, 9, and 60 hours.

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)(ft)(°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.

Bulk leach rates for massive aqueous silicate products 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 μm in diameter.

Progress During Report Period

Quantitification of the Aqueous Silicate Process

(G. S. Barney)

A quantitative description of the Aqueous Silicate process is needed as a basis for designing and operating a pilot-plant. Several alternative processing modes have been proposed and are summarized in reference 2. The simplest mode consists of mixing the clay with the waste and allowing the mixture to react to form the product (cancrinite plus excess clay). The quantitative description of this alternative process has been reported previously for many different

A more complex process which yields a product with lower leach rates and greater mechanical strength has also been described. This product consists of almost pure cancrinite crystals bound together with an additive to form a massive block. In order to obtain the pure cancrinite crystals, a less-than-stoichiometric amount of clay is added to the waste and reacted at 100° C. The cancrinite crystals (~1 μ m in diameter) are then filtered and washed to remove excess sodium salts. A binder is added and the mixture is pressed into a mold. The binder is then allowed to cure.

The above process was performed in the laboratory using two clays--calcined kaolin (Georgia Kaolin Astra-Glaze®) and calcined bentonite (Georgia Kaolin MC-101®). The synthetic standard waste solution was reacted with a slightly less than stoichiometric amount of each clay. The volume and composition of each stream was measured and the results are given in Figures 9 and 10.

The required amount of NaOH to be added to the recycle stream will, of course, vary depending on the amount of NaOH, NaNO_3 , and NaNO_2 in the original waste and the type of clay used. These calculations are based on the reactions:

For the standard waste solution used in these experiments (100 ml) about 75 grams of NaOH would be required in order to completely fix all the NaNO_3 and NaNO_2 in cancrinite. This would result in volumes of about 260 ml for the kaolin

FIGURE 9
QUANTIFICATION OF AQUEOUS SILICATE PROCESS
(Using Calcined Kaolin)

FIGURE 10
QUANTIFICATION OF AQUEOUS SILICATE PROCESS
(Using Calcined Bentonite)

product and about 320 ml for the bentonite product. These volumes would, of course, be much less with higher initial concentrations of NaOH in the waste and lower concentrations of NaNO_3 and NaNO_2 . Volumes of cancrinite products for 100 ml of waste solution with a total of 10.0M Na at several different $\text{OH}^-/(\text{NO}_3^- - \text{NO}_2^-)$ mole ratios are given in Table XIV.

TABLE XIV
VOLUMES OF PRODUCTS AS A FUNCTION OF
 $\text{OH}^-/(\text{NO}_3^- - \text{NO}_2^-)$ MOLE RATIOS

<u>Mole Ratio of</u> <u>$\text{OH}^-/(\text{NO}_3^- - \text{NO}_2^-)$</u>	<u>Volume of Kaolin Product, ml</u>
4.0	89
3.0	111
2.0	147
1.0	221

Heat of Reaction of Clays with Synthetic Waste Solution
(G. S. Barney)

Calorimetric measurements of the heat of reaction of kaolin clays with synthetic waste solution (2.0M NaNO_3 -10.0M NaOH) were made using the Model 550 Tronac, Inc., calorimeter. The heat evolved, Q, in calories per gram of clay versus time is shown for Astra-Glaze uncalcined kaolin in Figure 11. This curve indicates that a minimum of at least three steps are involved in the reaction of uncalcined kaolin with waste solution. The very rapid initial heat evolution is due to heat of adsorption and amounts to approximately 2.5 calories per gram of kaolin. The second portion of the curve is probably due to destruction of the kaolin crystal structure and formation of a gel phase. The portion of the curve after the inflection is due to crystallization of the gel to form cancrinite. The reaction

FIGURE 11
HEAT EVOLVED FROM REACTION OF UNCALCINED KAOLIN WITH SYNTHETIC WASTE

again consists of spherical crystals. Figure 11 also indicates that nearly three hours were required for the reaction to go to completion. The average heat of reaction value for three runs with the uncalcined kaolin was -49.5 ± 3.6 cal/g.

Figure 12 shows that the reaction using calcined Astra-Glaze clay is complete in ~25 minutes. There is a very rapid initial exothermic reaction due to adsorption of waste solution on the clay. This heat of adsorption is approximately -10 calories per gram of clay. The overall heat of reaction is -190.7 ± 3.5 calories per gram of clay (average of four runs). Scanning electron microphotographs of the reaction product from these runs show spherical crystals of 0.5 to 3 μ m in diameter. No unreacted clay or gel could be observed.

The above data show the heat of reaction of uncalcined kaolin to be considerably lower than for calcined kaolin. This is expected because of the larger heat of formation for uncalcined kaolin.

Heat of reaction measurements were completed for the two other commercially available calcined kaolins--PAB (J. R. Simplot Company) and Satintone (Engelhard Industries). These measurements should be considered preliminary because of problems encountered with the calorimeter. Further measurements will be made when the instrument problems are corrected. A summary of the results are given in Table XV.

These values are significantly lower than those obtained for calcined Astra-Glaze (-190.7 ± 3.3 cal/g). The differences are probably due to different crystallinities (related to calcination temperature and time) and different impurities present in the clays.

FIGURE 12

HEAT EVOLVED FROM REACTION OF CALCINED KAOLIN WITH SYNTHETIC WASTE

TABLE XV
HEAT OF REACTION* WITH PAB AND SATINTONE
CALCINED KAOLINS WITH STANDARD WASTE

Calcined PAB			Calcined Satintone		
Run #	Sample wt, g	ΔH cal/g	Run #	Sample wt, g	ΔH cal/g
1e	0.50980	-122.5	2g	0.61716	-107.8
1f	0.50531	-169.9	4g	0.47719	- 90.0
3e	0.45492	-139.9	3h	0.52360	-154.6
Average = -144.1 $\pm$ 24.0			Average = -117.5 $\pm$ 33.7		

*At 70° C.

The accuracy of the calorimetric measurements depends on completeness of the reaction. In order to determine whether or not a significant amount of clay is unreacted in these experiments, the solid products were analyzed for Na, Al, and Si. These analyses were compared with those for pure cancrinite and are given in Table XVI.

TABLE XVI
COMPARISON OF ANALYSES FOR CALORIMETER
REACTION PRODUCTS AND PURE CANCRINITE

Sample	Wt% of Element		
	Na	Al	Si
Pure cancrinite*	16.5	15.4	15.9
Run #3 product	15.6	15.8	15.0
Run #4 product	15.6	15.8	15.2
Run #5 product	16.7	15.3	14.5

*Based on the formula,
 $2(\text{NaAlSiO}_2) \cdot 0.52\text{NaNO}_3 \cdot 0.68\text{H}_2\text{O}$,
for pure cancrinite.

According to these analyses the product has a formula very close to that of pure cancrinite. This observation is consistent with the fact that no unreacted clay can be seen in scanning electron photographs of the products.

Kinetics of Calcined Clay-Waste Reactions (G. S. Barney)

Previous work on the kinetics of clay-waste reactions was confined to uncalcined clays. Calcined clays (clays heated to $\sim 700^{\circ}\text{C}$) have recently proved to give superior products when reacted with waste solutions. These products have lower volume, greater hardness, and will not crumble when contacted with water. It is, therefore, necessary to define the kinetics of cancrinite formation from calcined clays.

Rate experiments were performed using both calcined kaolin (Astra-Glaze[®], Georgia Kaolin) and calcined bentonite (MC-101[®], Georgia Kaolin). Calcined clay (10 grams) was reacted with 20 milliliters of standard synthetic waste solution at 100° , 75° , and 60°C . Eight samples of each calcined clay were reacted at each temperature. The samples were filtered and washed after being reacted for a specified length of time. The filtrate and solid product were then analyzed by atomic absorption, X-ray diffraction, and thermal analysis.

Percent of cancrinite in the solid product as a function of time for calcined kaolin is given in Figure 13. A smaller temperature effect is observed than for reactions of uncalcined kaolin. Therefore there is a lower activation energy. The rate of reaction for the calcined kaolin is, however, much greater. Half-times for the reaction at 100° , 75° , and 50°C are 0.2, 0.7, and 4 hours, respectively; and make calcined kaolin very desirable from the operating standpoint. These half-times are 5 to 30 times shorter than corresponding half-times for uncalcined kaolin reactions.

Figure 14 gives rates of cancrinite formation from calcined bentonite at 100° , 75° , and 50°C . The rate curves are very similar to those of Figure 13. The half-times at

FIGURE 13
EFFECT OF TEMPERATURE ON REACTION RATE (CALCINED KAOLIN-WASTE)

FIGURE 14
EFFECT OF TEMPERATURE ON REACTION RATE (CALCINED BENTONITE-WASTE)

100°, 75°, and 50° C are ~0.1, 0.6, and 6 hours, respectively, and are much less than for uncalcined bentonite. A summary of rate data for calcined and uncalcined clays is given in Table XVII.

TABLE XVII
COMPARISON OF REACTION HALF-TIMES*
FOR UNCALCINED AND CALCINED CLAYS

Temperature, °C	Kaolin		Bentonite	
	Uncalcined	Calcined	Uncalcined	Calcined
100	1	<0.2	1	0.1
75	10	0.7	9	0.6
50	150	4	60	6

*All half-times are given in hours.

Leach Rates of Massive Aqueous Silicate Products

(G. S. Barney)

Data for long-term leaching have now been acquired for a 177-day time span using a proposed tentative standard leach test procedure which follows the International Atomic Energy Agency's suggested method.^[3] These data, shown as cumulative fraction of cesium leached, are given in Figure 15 for six different samples. The sample numbers correspond to sample preparations given in Table XVIII.

The leach curves clearly show the effect of decreasing the frequency of changing the leach water. The measured leach rate decreases dramatically when the frequency changes from weekly to monthly. This is due to an approach to equilibrium between the cesium in the sample and the cesium in the leachate. Leach rates at the end of 177 days are approximately 10^{-4} to 10^{-5} g/cm²-day.

The fraction leached for calcined bentonite products is significantly less than for calcined kaolin products.

FIGURE 15
FRACTION OF CESIUM LEACHED FROM MASSIVE SAMPLES

TABLE XVIII
SAMPLES USED IN LEACHING EXPERIMENTS

<u>Sample #</u>	<u>Cancrinite Type</u>	<u>Binder*</u>	<u>Wt Cesium, g</u>
10	Calcined kaolin	30% PMMA	0.0378
11	Calcined kaolin	20% PS	0.0424
13	Calcined kaolin	10 g C-III, 8 g H ₂ O	0.0508
14	Calcined kaolin	5 g C-III, 4 g H ₂ O	0.0330
17	Calcined bentonite	10 g C-III, 8 g H ₂ O	0.1027
18	Calcined bentonite	5 g C-III, 8 g H ₂ O	0.1450

*10 g of cancrinite were used in each sample; PMMA = polymethylmethacrylate; PS = polystyrene; C-III = portland cements.

The product with the smallest fraction leached was made by reacting calcined bentonite with synthetic waste and binding the cancrinite product with portland cement.

Application of the Aqueous Silicate Process to Immobilization of Neutralized Nuclear Fuel Services' Waste -
 (C. H. Delegard)

Determination of the applicability of the Aqueous Silicate process to immobilization of neutralized commercial Nuclear Fuel Services (NFS) waste was determined recently. At NFS there are approximately two million liters of the neutralized waste of the approximate composition shown in Table XIX.

As can be seen, this NFS waste is low in the caustic necessary as reactant for the Aqueous Silicate process. Various amounts of solid NaOH were thus added to aliquots of the synthetic waste before reacting them with clay. Aqueous silicate reactions of the synthetic waste and PAB calcined kaolin (J. R. Simplot Company) were performed at 80° C (the temperature of the stored waste) using various clay/waste ratios. The experimental conditions and results

of the runs are shown in Table XX.

TABLE XIX
COMPOSITION OF THE NUCLEAR FUEL SERVICES'
RADIOACTIVE WASTE SOLUTION

<u>Component</u>	<u>Concentration</u>
OH ⁻	0.18M
NO ₃ ⁻	7.91M
SO ₄ ⁼	0.28M
PO ₄ [≡]	0.094M
AlO ₂ ⁻	0.11M
C ₂ O ₄ ⁼	0.069M
Na ⁺	8.17M
Ni ⁺⁺⁺	0.040M
Fe ⁺⁺⁺	0.31M
¹³⁷ Cs	4.951 Ci/liter
¹³⁴ Cs	0.6297 Ci/liter

X-Ray diffraction evidence shows that the caustic addition was necessary to form cancrinite from the synthetic NFS waste and calcined kaolin reactants. The volume increase for hard products in this process ranges from 70 to 85%. Clearly the NFS waste requires the additional hydroxide to form satisfactory aqueous silicate products.

Mechanical Strength of Baked Aqueous Silicate Products

(C. H. Delegard)

If aqueous silicate products are ultimately cast into waste tank-size blocks, radiolytic heating could raise center-line temperatures to 300° C. A laboratory test was carried out to determine the effect of heating on the mechanical strength of aqueous silicate products since this could be an important criteria for evaluating the retrievability of the product.

A series of aqueous silicate products in the form of cubes were made by reacting a calcined kaolin with a

TABLE XX
 PROPERTIES OF AQUEOUS SILICATE PRODUCTS
 OF NUCLEAR FUEL SERVICES' WASTE

<u>Clay/Waste Ratio, g/ml</u>	<u>NaOH Concentrated Waste, M</u>	<u>Total Volume Increase Including Waste on Reaction, %</u>	<u>Liquid Not Sorbed, %</u>	<u>Hardness kg/cm²</u>
0.75	0.18	50	0	0
1.0	0.18	60	0	0
0.65	1.90	75	10	0
0.87	1.90	50	0	0.8
0.65	4.50	70	5	32
0.87	4.50	75	5	45
0.60	6.54	70	0	32
0.80	6.54	85	0	18

synthetic waste solution. One cube was not heated and was used for a control. The other cubes were baked at various temperatures from 100° to 400° C. The control cube had a failure point of less than 400 newtons. The cubes heated at 100° C and higher resulted in dehydration and cracking. These heated cubes failed at loads between 11,100 and 17,800 newtons, therefore showing significant strength despite their cracked appearance.

Radiolytic Stability of Aqueous Silicate Products

(C. H. Delegard)

A variety of powdered aqueous silicate products were subjected to approximately 10^9 rads of ^{60}Co radiation to determine their radiolytic stability. The dose received was the calculated upper limit anticipated for aqueous silicate products with an initial, ^{137}Cs concentration of one curie per liter. Typical terminal liquors contain 0.3 to 0.5 curies of ^{137}Cs per liter. X-Ray diffraction analyses of the irradiated products compared with nonirradiated control samples showed no differences in diffraction patterns or peak intensities.

Differential thermal and thermogravimetric analyses (DTA and TGA) were recently obtained for the irradiated and nonirradiated control products. Both traces are virtually superimposable from ambient to 1000° C temperatures. These results indicate radiolysis of chemically bound water and nitrate salts in aqueous silicate products is negligible.

Future Work

1. Determine application of the Aqueous Silicate process to various actual salt cake and sludge samples.

2. Make additional heat of reaction determinations for commercial clays.
3. Test various binders for cancrinite crystals.
4. Obtain additional leach rate data for massive aqueous silicate products.
5. Determine leach rate and hardness of products heated to various temperatures (to 1000° C).
6. Measure vapor pressure of clay products at various temperatures so that pressure increase during storage can be predicted.

SILICATE MELT PROCESS

Objective

The purpose of this task is to develop a process for immobilizing high-level radioactive waste by melting a mixture of radioactive waste solids and basalt or sand to form nonvolatile and nondispersable rock-like products of low leachability suitable for long-term storage.

Prior Work

Hot cell tests showed that the Silicate Melt process could effectively immobilize several actual radioactive wastes including salt cake from Tank 116-TX, Pu-bearing soil from 216-Z-9 Trench, contaminated soils from near Tanks 106-T and 102-S, and Redox neutralized sludge. A two-step procedure for immobilization of spent fuel cladding hulls involving conversion to oxides in a gaseous HF-O₂ mixture at 600° C followed by melting with SiO₂ to form silicates was partially tested with actual irradiated zircaloy and stainless steel. Dense silicates of low-water leachability were produced in all cases.

Round-robin tests of tentative standard leach test procedures proposed by the AEC-sponsored Subcommittee on Leach Rate Testing Methods were begun.

Sea sand (99.7% SiO_2) was successfully substituted for basalt in formulations to immobilize synthetic salt cake waste. Scouting studies of the use of sand indicated products containing greater than 33 wt% waste exhibited lower leach rates than comparable products made with basalt. In addition, charges containing 55 wt% salt cake waste were immobilized to products which exhibited satisfactory leach rates when sand was used as the source of silica. Highly significant was the fact that the volume of a product containing 50 wt% waste was 36% less than the volume of the original waste.

Progress During Report Period

Immobilization of Salt Cake with Sand (A. L. Dressen)

During the present reporting period experiments were performed to establish effects on product quality of incorporating varying percentages of waste and boron trioxide in formulations with sand. The conditions and results of these tests are summarized in Table XXI. Significant features of these data are as follows:

- Product densities ($\sim 2.4 \text{ g/cm}^3$) are not significantly affected by addition of B_2O_3 . Charges containing up to 30 wt% synthetic salt cake waste (composition shown in Table XXII) and 0 to 5 wt% B_2O_3 do not completely melt at 1400°C . Formulations of 30 wt% or higher waste content produce glassy silicates.

TABLE XXI
CONDITIONS AND RESULTS OF SALT CAKE WASTE-SAND-B₂O₃ STUDIES

Composition, wt%			Furnace Temperature °C	Density g/cm ³	State	Leach Rate Based on Cs		Leach Rate Based on Sr	
ITS-2*	Sand	B ₂ O ₃				g/cm ² -day		g/cm ² -day	
						24 hr	96 hr	24 hr	96 hr
20	80		1400	-	Did not melt	-	-	-	-
20	75	5	1400	-	Did not melt	-	-	-	-
20	65	15	1400	2.31	Glassy	8.6 x 10 ⁻⁵	2.0 x 10 ⁻⁵	4.2 x 10 ⁻⁶	2.1 x 10 ⁻⁶
30	70		1400	-	Did not melt	-	-	-	-
30	65	5	1400	2.48	Glassy	1.2 x 10 ⁻⁵	4.5 x 10 ⁻⁶	5.2 x 10 ⁻⁶	1.3 x 10 ⁻⁶
30	60	10	1400	2.37	Glassy	2.2 x 10 ⁻⁶	3.2 x 10 ⁻⁶	5.8 x 10 ⁻⁵	1.1 x 10 ⁻⁵
30	55	15	1400	2.47	Glassy	1.0 x 10 ⁻⁵	1.7 x 10 ⁻⁶	6.7 x 10 ⁻⁶	8.4 x 10 ⁻⁷
40	60		1400	2.30	Glassy	2.4 x 10 ⁻⁵	3.8 x 10 ⁻⁶	9.5 x 10 ⁻⁶	1.8 x 10 ⁻⁶
40	55	5	1400	2.40	Glassy	4.5 x 10 ⁻⁶	1.5 x 10 ⁻⁶	1.5 x 10 ⁻⁵	3.2 x 10 ⁻⁶
40	45	15	1400	2.48	Glassy	3.3 x 10 ⁻⁶	1.7 x 10 ⁻⁶	2.3 x 10 ⁻⁶	5.8 x 10 ⁻⁷
50	50		1400	2.50	Glassy	2.0 x 10 ⁻⁵	9.6 x 10 ⁻⁶	2.4 x 10 ⁻⁵	1.4 x 10 ⁻⁵
50	45	5	1400	2.43	Glassy	3.1 x 10 ⁻⁶	7.7 x 10 ⁻⁷	4.0 x 10 ⁻⁴	1.1 x 10 ⁻⁶
50	35	15	1400	2.43	Glassy	2.4 x 10 ⁻⁶	2.9 x 10 ⁻⁶	8.1 x 10 ⁻⁷	5.3 x 10 ⁻⁶
60	40		1400	2.58	Glassy	3.8 x 10 ⁻⁶	3.9 x 10 ⁻⁷	2.2 x 10 ⁻⁶	5.6 x 10 ⁻⁷
60	35	5	1400	2.52	Glassy	9.7 x 10 ⁻⁷	7.2 x 10 ⁻⁷	6.6 x 10 ⁻⁶	8.3 x 10 ⁻⁷
60	30	10	1400	2.26	Glassy	<1.1 x 10 ⁻⁶	7.4 x 10 ⁻⁷	3.3 x 10 ⁻⁶	8.3 x 10 ⁻⁷
60	25	15	1400	2.47	Glassy	1.8 x 10 ⁻⁶	1.6 x 10 ⁻⁶	1.2 x 10 ⁻⁶	3.0 x 10 ⁻⁷

*Salt cake waste.

TABLE XXII
COMPOSITION OF SYNTHETIC
SALT CAKE WASTE

Component	Composition
	Weight Percent
NaNO ₂	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

- The leach rates based on cesium (after four days' leaching in deionized H₂O at 25° C) of the products which contained no B₂O₃ actually decrease as the percentage of salt cake waste in the charge formulation is increased. The product containing 60 wt% waste and 40 wt% sand leaches at a rate of only 3.9×10^{-7} g/cm²-day.
- Leach rates based on cesium (four days) of products containing >40 wt% salt cake waste are nearly identical for products containing 5 and 10 wt% B₂O₃ but increase with further additions of B₂O₃. Similar behavior occurs when leach rates are based on strontium.
- For products containing B₂O₃, a plot of leach rate versus percentage of waste appears to be a parabola with a minimum rate at *ca.* 50 to 60 wt% waste. Incorporation of this quantity of waste results in a volume reduction of at least 36% from the volume of the original waste.

The effect of additions of varying amounts of B_2O_3 and/or lime (CaO) to silicate melt mixtures of sand and salt cake waste on product quality was also investigated. Conditions and results of these tests are shown in Table XXIII and summarized as follows:

- Glassy products resulted from all of the runs when ≥ 30 wt% salt cake waste was used. Crystalline, incompletely melted products resulted when 20 wt% waste was used. [Melting at a higher temperature than $1200^\circ C$ could modify these results.]
- The leach rates of products containing CaO and no B_2O_3 as additive were very nearly constant (1.3×10^{-6} to 4.3×10^{-6} g/cm²-day based on Cs) for formulations containing 20 to 60 wt% waste (Table XXIII, Figure 16). For products containing 5 wt% B_2O_3 and 5 wt% CaO, a plot of leach rate versus percentage of waste is a parabola with a minimum rate at about 50 wt% waste (Figure 16). Products containing CaO: B_2O_3 percentages of 15:5 and 10:10 (20 wt% total additives) leach at rates which are about 10 times higher than products containing 5 wt% CaO:5 wt% B_2O_3 or 10 wt% CaO:0 wt% B_2O_3 .

Immobilization of Incinerated Ash by the Silicate Melt Process (C. W. Hobbick)

The first application of the Silicate Melt process to immobilization of Hanford incinerated plutonium-bearing ash was demonstrated recently. The 500-gram charge consisted of 2.2 wt% ash, 5.0 wt% boric oxide, 10.0 wt% sodium carbonate, and 82.8 wt% crushed basalt rock. All charge

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TABLE XXIII

CONDITIONS AND RESULTS OF SODA-LIME-SILICA SILICATE MELT PROCESS TESTS

Composition, wt%				Furnace Temperature °C	Density g/cm ³	State	Leach Rate Based on Cs g/cm ² -day		Leach Rate Based on Sr g/cm ² -day	
ITS*	Sand	CaO	B ₂ O ₃				24 hr	96 hr	24 hr	96 hr
20	70	5	5	1200	2.1	Crystalline	3.6 x 10 ⁻⁵	2.7 x 10 ⁻⁵	6.8 x 10 ⁻⁵	4.7 x 10 ⁻⁵
20	70	10		1200	1.9	Crystalline	1.2 x 10 ⁻⁵	2.6 x 10 ⁻⁶	9.4 x 10 ⁻⁵	2.9 x 10 ⁻⁵
20	60	15	5	1200	2.3	Crystalline	2.2 x 10 ⁻⁵	2.2 x 10 ⁻⁵	6.2 x 10 ⁻⁵	6.2 x 10 ⁻⁵
30	60	10		1200	2.2	Glassy	1.2 x 10 ⁻⁵	2.5 x 10 ⁻⁶	1.9 x 10 ⁻⁵	3.4 x 10 ⁻⁶
30	50	10	10	1200	2.6	Glassy	3.9 x 10 ⁻⁶	1.4 x 10 ⁻⁶	6.8 x 10 ⁻⁶	2.6 x 10 ⁻⁶
30	50	15	5	1200	2.5	Glassy	1.3 x 10 ⁻⁵	2.4 x 10 ⁻⁶	1.6 x 10 ⁻⁵	7.7 x 10 ⁻⁶
40	50	5	5	1200	2.5	Glassy	2.0 x 10 ⁻⁶	1.5 x 10 ⁻⁶	3.2 x 10 ⁻⁵	6.5 x 10 ⁻⁷
40	50	10		1200	2.4	Glassy	1.9 x 10 ⁻⁶	2.7 x 10 ⁻⁶	4.5 x 10 ⁻⁶	8.8 x 10 ⁻⁶
40	50	10	10	1200	2.7	Glassy	3.1 x 10 ⁻⁵	2.1 x 10 ⁻⁵	2.0 x 10 ⁻⁵	3.3 x 10 ⁻⁵
40	40	15	5	1200	2.2	Glassy	3.8 x 10 ⁻⁵	3.2 x 10 ⁻⁵	3.7 x 10 ⁻⁵	4.4 x 10 ⁻⁵
50	40	5	5	1200	2.6	Glassy	1.4 x 10 ⁻⁶	1.1 x 10 ⁻⁶	7.1 x 10 ⁻⁶	9.9 x 10 ⁻⁷
50	40	10		1200	2.5	Glassy	4.9 x 10 ⁻⁶	2.1 x 10 ⁻⁶	2.2 x 10 ⁻⁵	1.4 x 10 ⁻⁵
50	35	15		1200	2.7	Crystalline	7.6 x 10 ⁻⁶	1.3 x 10 ⁻⁶	7.4 x 10 ⁻⁵	4.6 x 10 ⁻⁵
50	30	5	15	1200	2.5	Glassy	6.4 x 10 ⁻⁵	1.3 x 10 ⁻⁵	1.8 x 10 ⁻⁴	7.4 x 10 ⁻⁵
50	30	10	10	1200	2.3	Glassy	7.1 x 10 ⁻⁵	2.6 x 10 ⁻⁵	1.8 x 10 ⁻⁴	1.2 x 10 ⁻⁴
50	30	15	5	1200	2.6	Glassy	8.1 x 10 ⁻⁵	3.6 x 10 ⁻⁴	1.6 x 10 ⁻⁴	4.7 x 10 ⁻⁵
60	35	5		1200	2.5	Glassy	6.3 x 10 ⁻⁶	2.5 x 10 ⁻⁶	2.4 x 10 ⁻⁶	2.2 x 10 ⁻⁶
60	30	5	5	1200	2.8	Glassy	1.7 x 10 ⁻⁵	7.5 x 10 ⁻⁶	2.1 x 10 ⁻⁶	1.9 x 10 ⁻⁶
60	30	10		1200	2.5	Glassy	1.6 x 10 ⁻⁶	4.3 x 10 ⁻⁶	2.2 x 10 ⁻⁵	5.9 x 10 ⁻⁶

*Salt cake waste..

FIGURE 16
PRODUCT LEACH RATES

constituents were blended except the incinerated ash, which was double-bagged in plastic, placed in a graphite-clay crucible, and covered by the blended ingredients. Upon heating the mixture inductively, black smoke and some flaming resulted from the combustion of the plastic coverings. A maximum melting temperature of 1300° C was maintained for one hour.

The solidified product was black and glassy with a micro-thin, rust-colored layer on the exposed surface. The density of the glass was 2.44 g/cm³. The final product contained 0.002 g Pu per gram of glass. The leach rate based on ²³⁹Pu was 2.0 x 10⁻⁸ g/cm²-day after seven days of leaching. This extremely low leach rate is characteristic of other silicate melt products containing plutonium-bearing soil from the Z-9 trench.

Silicate Melt Process Development (D. J. Bradley, H. H. Irby, and J. D. Kaser - Battelle Pacific Northwest Laboratories)

Objective

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

Prior Work

A short pilot-plant test was conducted at Penberthy Electromelt Company, Seattle. This test revealed that the development of a reliable discharge valve should be emphasized and that elemental iron can be produced if basalt is used as the source of silica.

Progress During Report Period

A 1.1 ton/day all-electric glass melter, designed by Penberthy Electromelt Company for Evans Specialty Product Company, was selected as the basis for designing a pilot-plant unit for the Silicate Melt process, since few modifications will be required.

Personnel from PNL and ARHCO visited Evans Specialty Products in Corvallis, Oregon, to inspect the melter. On the whole, the melter operates satisfactorily, but the following improvements could be made:

1. The glass discharge stream wavers and is erratic because the glass wets the walls of the drain opening. Carbon sleeves have been tried to avoid wetting, but the carbon burns up rapidly and frequent replacements are time-consuming. The wavering discharge stream may be a drawback for our application. They suggested using an electrically heated, air-cooled freeze valve.
2. The forehearth power supply has a voltage control system which is inherently unstable. A power control system would be inherently more stable.
3. Water-cooled yokes, which prevent glass leaking from the forehearth seams, developed leaky welds. It was suggested that the welds be X-rayed or simply eliminated completely.
4. The forehearth bricks should interlock with the melter bricks to avoid glass leakage.

The installed cost of this particular melter was about \$90,000.

The glass batch material is delivered to the melter through a screw feeder. The discharge barrel is water-cooled and moves back and forth to distribute the batch. The feeder works very smoothly with -70 mesh material. Jamming occurs when the batch material is larger than 30 mesh. The batch material is dry and delivery rate is controlled by a glass level probe in the forehearth.

No significant electrode or refractory wear have been observed during the two months the melter has been operated.

Detailed design drawings have been obtained and are being reviewed for design modifications.

Future Work

The design of the pilot-plant melter will be completed; then procurement and construction will begin.

Infrared Absorption by Melts Containing Iron Oxide

(D. M. Strachan)

Large concentrations of iron(II) oxide (FeO) in glass-making formulations have been reported to cause low thermal conductivity and thus large thermal gradients in glass melters. Iron within a glass absorbs infrared radiation and reduces the influence of radiation heat transport which is the normal mode of heat transport in molten commercial glasses. Since silicate melt formulations which contain basalt as the source of SiO_2 can contain from 1 to 6 wt% FeO , a literature search was carried out to determine the effect of the presence of FeO on the melter operation.

Studies have been made by several authors on the effect of iron content on the thermal gradient in a glass melter.^[4-6] Weyl^[4] described one experiment. A long tank

furnace was divided into two parallel compartments--one holding a glass with iron and the other a glass without iron. The glass was heated from overhead by gas burners. Temperature gradients were higher for the iron-containing melts. Due to a lack of thermal conduction, temperatures at the tank bottoms were lower in melts containing iron. Thermal conduction is poor due to absorption of infrared radiation by Fe(II). This is substantiated by varying the Fe(II)/Fe(III) ratio. An example of how the thermal gradient varies with Fe(II) is shown in Figure 17 (taken from reference 6). In this Figure the Fe(II) content is shown as an intensive variable with the total iron content in parenthesis. Commercial glasses show even steeper slopes than these control samples. It is also shown that these thermal gradients are up to 2 to 3 times those in glasses containing no iron.

In all the studies discussed above heating was accomplished using gas-fired burners above the melt. Since electrical heating by immersed electrodes will probably be the technique used for melting radioactive waste, the thermal gradient will certainly be modified. Thermal convection will also arise due to the eddy currents set up by the electric fields. In the literature reviewed to date no data seem to be available on thermal gradients in electric furnaces.

Iron(II) poses yet another problem which is independent of the furnace type used. Since glasses containing Fe(II) absorb IR radiation during the melting process, they must also emit IR radiation while cooling. Glasses containing iron cool rapidly at the surface and a large thermal gradient is established within the cooling mass. This can give rise to stresses in the cast glass.

FIGURE 17

PLOT OF TEMPERATURE (°C) VERSUS DISTANCE
GLASS SURFACE (INCHES)

[Original in °F versus inches]

In the design of the ARHCO prototype electric glass melter, thermocouples are being positioned so that thermal gradient information can be obtained for silicate melt formulations containing varying amounts of FeO.

SALT CAKE VOLUME REDUCTION (W. W. Schulz)

Objectives

This work 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 long-lived radionuclides which will permit a 10- to 100-fold reduction in the volume of nonradioactive material which must be immobilized and/or stored.

Prior Work

Methods for reducing the volume of salt cake were investigated. Initial tests were designed to determine behavior of salt cake when treated with water and to establish the amount and nature of any undissolved residue. Applicability of nickel ferrocyanide and calcium phosphate scavenging techniques for removing ^{137}Cs and ^{90}Sr , respectively, from the water leachate were investigated. Dissolved Tank 105-S salt cake was scavenged twice by coprecipitation of $0.002M \text{ Ni}_2[\text{Fe}(\text{CN})_6]$ and $0.0025M \text{ Ca}_3(\text{PO}_4)_2$; these scavenging steps removed 99.95% of the ^{137}Cs and 97% of the ^{90}Sr . The concentration of ^{90}Sr in the doubly-scavenged liquor was only about eight-fold higher than the MPC_w value for ^{90}Sr in water in a controlled area.

Precipitation of inert strontium phosphate was found to be more effective than precipitation of either calcium

phosphate or iron hydroxide in scavenging radiostrontium from salt cake solutions.

Cesium-137 was found to be effectively removed from salt cake solutions by sorption on Duolite ARC-359[®] (Diamond Shamrock Company) resin.

Experiments with Synthetic Salt Cake

Experiments were performed this month to compare loading behavior of Duolite ARC 359 resin with that of Zeolon 900[®], a zeolite-type exchanger made by the Norton Company. Breakthrough data for these runs are shown in Figure 18. [The feed for these runs was a solution of the composition:

2.0M	NaNO ₃
0.2M	NaOH
0.05M	NaAlO ₂
0.04M	NaNO ₂
0.03M	Na ₂ CO ₃
0.008M	Na ₃ PO ₄
0.0012M	Na ₂ SO ₄

containing 272 Ci/liter ¹³⁷Cs.] Following the loading cycle in each run the bed was washed (upflow; 25° C, 1 column volume/hour) with 2M (NH₄)₂CO₃-2M NH₄OH solution.

The data in Figure 18 show that the Zeolon 900 resin sorbs ¹³⁷Cs more strongly than the Duolite resin. Correspondingly, it is more difficult to elute ¹³⁷Cs from the Zeolon resin than from the Duolite material. For example, 6 column volumes of the (NH₄)₂CO₃-NH₄OH eluent removed 98.9% of the ¹³⁷Cs from the Duolite column but only 75.5% of the cesium from the Zeolon column.

Japanese workers^[7] reported previously that macroreticular anion exchange resins treated successively with Na₂HPO₄ and calcium acetate solutions (so-called

FIGURE 18

SORPTION OF ^{137}Cs FROM SYNTHETIC SALT CAKE SOLUTION BY
DUOLITE ARC 359 AND ZEOLON 900 EXCHANGERS

"Calcium Phosphonate-Anion Exchange Resin") efficiently sorb radiostrontium from river and drinking water. Our preliminary data, discussed below, indicate a similar "Strontium Phosphate-Anion Exchange Resin" sorbs ^{85}Sr very effectively from synthetic dilute salt cake solution.

To prepare a "Strontium Phosphate-Anion Exchange" column a 25-ml bed (1.5-cm diameter) of Dowex MSA-1^R macroreticular resin (Dow Chemical Company) was converted from the as-received chloride-form to the hydroxide-form by flowing 4M NaOH solution until the effluent was free of Cl^- . After washing with water, two liters of 1M H_3PO_4 and one liter of 0.25M $\text{Sr}(\text{NO}_3)_2$ were passed through the bed. The final bed was then again washed with water.

A synthetic salt cake solution of the composition

6.0M	NaNO_3
0.59M	NaOH
0.14M	NaAlO_2
0.11M	NaNO_2
0.10M	Na_2CO_3
0.026M	Na_3PO_4
0.0036M	Na_2SO_4

was prepared. Except for a slightly higher NaOH concentration, this composition corresponds, approximately, to that of a solution obtained by dissolving actual salt cake from the 105-S Tank in a near-minimum volume of water.

For use with the "Strontium Phosphate-Anion Exchange Resin" a portion of the synthetic salt cake solution was diluted to one-third its volume with water and then spiked to 30 $\mu\text{Ci/liter}$ ^{90}Sr . This solution was passed down flow at 25° C and at one column volume per hour through the resin bed; hydraulic characteristics were excellent as expected from the Japanese work. A total of 38 bed volumes of effluent were collected before the feed supply was exhausted.

Samples of the effluent from the load cycle were analyzed by gamma energy spectrometry using an NaI(Tl) detector. Only very meager results are available at report time but such data as are at hand indicate excellent removal of radiostrontium. Thus effluent after passage of 37 column volumes of feed contained $0.047 \mu\text{Ci/liter } ^{90}\text{Sr}$. [The value $0.047 \mu\text{Ci/liter}$ is the lower detection limit with the NaI system.]

The results of this first test of the "Strontium Phosphate Anion Exchange" column are, of course, very encouraging. If successful with the actual salt cake solution, the "Strontium Phosphate Anion Exchange Resin" approach could be of great advantage in reducing the volume of salt cake without generating new solids.

A comprehensive set of experiments is in progress to determine optimum conditions for scavenging of ^{90}Sr from salt cake solutions by single or multiple precipitation of $\text{Sr}_3(\text{PO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$, or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. These experiments involve addition of varying amounts of stock $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, or $\text{Fe}(\text{NO}_3)_2$ solutions to synthetic salt cake solutions (spiked with ^{85}Sr) containing 0.0, 0.25, or 0.5M Na_2CO_3 and previously adjusted to pH 8, 10, 12, and 12.8 (the base salt cake solution composition is 6.0M NaNO_3 -0.1M NaNO_2 -0.004M Na_2SO_4 -0.025M Na_3PO_4). Detailed tabulation of results of these experiments will be deferred until the experimental program has been completed. Tentative findings from results presently available for solutions at pH's 12.0 and 12.8 include the following:

- At all pH's and carbonate concentrations tested, $\text{Sr}_3(\text{PO}_4)_2$ is more effective than either $\text{Ca}_3(\text{PO}_4)_2$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ in scavenging radiostrontium.

- Effectiveness of any of the three precipitate types in scavenging radiostrontium increases with increasing pH.
- Scavenging of radiostrontium by any of the three precipitates decreases with increasing carbonate concentration of the salt cake solution.

Experiments with Actual 105-S Salt Cake

Two salt cake solutions from Tank 105-S salt cake were prepared for volume reduction experiments by dissolution of the salt cake in water. One portion (105-S-1) of the salt cake was first air-dried for four to six weeks before it was dissolved. Another portion (105-S-2) was dissolved without previous air-drying.

The dissolution procedure for the air-dried 105-S-1 sample was as follows: 85.4 g (100 ml) were mixed in 131 ml of water to yield 158 ml of solution and 9 ml of white, difficultly centrifugable solids. Table XXIV lists the composition of the salt cake solution insofar as it was determined. After air-drying, the solids volume was 3.0 ml and their weight was 1.96 g. Composition of the dried solids as determined by fusion with KOH and subsequent analysis of an HCl solution of the melt is shown in Table XXV.

Significant about the 105-S-1 solution was its high carbonate content and relatively low pH and aluminum content (Table XXIV). Evidently during prolonged exposure of the Tank 105-S salt cake to air most of its NaOH content was converted to Na_2CO_3 . Subsequent dissolution of the resulting material in water produced a pH 10 solution from which the aluminum precipitated as $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

TABLE XXIV
SALT CAKE SOLUTION--TANK 105-S SALT CAKE

Component	Concentration	
	105-S-1**	105-S-2**
Na ⁺	6.4M	6.68M
NO ₃ ⁻	NA†	5.35M
OH ⁻	NA	0.091M
CO ₃ ²⁻	0.46M	0.074M
NO ₂ ⁻	0.082M	0.028M
SO ₄ ²⁻	NA	0.0087M
PO ₄ ³⁻	0.0076M	0.0025M
Al ³⁺	<6.7 x 10 ⁻³ M	0.026M
Cr ³⁺	NA	0.0046M
Ni ²⁺	<0.0002M	0.00010M
Mn ²⁺	<3.6 x 10 ⁻⁵ M	<0.00011M
Fe ³⁺	4.3 x 10 ⁻⁵ M	2.4 x 10 ⁻⁵ M
¹³⁷ Cs	27,000. μCi/liter	7,050. μCi/liter
¹⁰⁶ Ru- ¹⁰⁶ Rh	NA	~300. μCi/liter
¹³⁷ Cs	NA	22.1 μCi/liter
⁹⁰ Sr	11.3 μCi/liter	10.9 μCi/liter
Pu	NA	<9.4 x 10 ⁻⁷ g/liter
pH	10	12

†NA = no analysis.

*105-S salt cake sample air-dried 4 to 6 weeks before dissolving.

**105-S damp salt cake not air-dried.

The data in Table XXV show that about 99.5% of the ¹³⁷Cs in the mixture of 105-S-1 salt cake and sludge is soluble in water. On the other hand, only 10% of the ⁹⁰Sr reported to the salt cake solution. These results are in excellent agreement with previous data for a solution made from salt cake from the 116-TX Tank.

TABLE XXV
COMPOSITION OF UNDISSOLVED SOLIDS--
TANK 105-S SALT CAKE^a

Component	Concentration (wt%)	
	105-S-1	105-S-2
Na	7.0	13.1
Al	22.0	2.0
Si	0.9	NA
Fe	0.3	NA
Cr	0.35	NA
Pu	NA [†]	0.0015 ^b
Ni	0.2	0.05
Mn	0.02	0.074
⁹⁰ Sr	9 $\mu\text{Ci/g}$	97 $\mu\text{Ci/g}$
¹³⁷ Cs	9 $\mu\text{Ci/g}$	18.2 $\mu\text{Ci/g}$
¹⁰⁶ Ru	8 $\mu\text{Ci/g}$	NA
¹⁵⁵ Eu	3.3 $\mu\text{Ci/g}$	NA
⁶⁰ Co	NA	8.9 $\mu\text{Ci/g}$

[†]NA = no analysis.

^aWashed.

^b1000 $\mu\text{Ci/g}$.

To prepare portions of 105-S-2 for volume reduction experiments, 167 g (140 ml) of the damp solids were dissolved in 255 ml of water to yield 315 ml of yellow-colored solution and 0.25 ml of easily centrifugable brown-colored solids. Table XXIV lists the composition of this salt cake solution insofar as it has been determined. After air-drying, the solid residue weighed 0.0405 g. The dried solids were completely soluble in 6M HCl; composition of the brown solids from 105-S-2 insofar as it has been determined is listed in Table XXV.

The composition for 105-S-2 listed in Table XXIV is typical of solutions produced by water dissolution of damp salt cake. As expected, the carbonate concentration is much lower and aluminum concentration and pH are higher than for the solution prepared from the 105-S-1 sample.

Only a small volume of brown-colored solids remain undissolved when damp salt cake is dissolved in water. In contrast, a large volume of gelatinous $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ solids precipitates when air-dried salt cake is dissolved in water to yield a pH 10 solution.

The salt cake solution and the HCl solution obtained by dissolution of the dried brown solids from 105-S-1 were analyzed for plutonium by existing analytical methods. With appropriate reservations about the accuracy of data obtained by these methods it appears that the salt cake solution free of sludge may be a nonactinide waste (~ 0.05 nCi/g), while the sludge clearly is an actinide waste (~ 1000 nCi/g). [For calculational purposes the density of the salt cake solution was taken as 1.2 g/ml and all the plutonium was taken as ^{239}Pu .] No information is yet available as to the concentration of other actinides in either the solutions or solids.

In agreement with data from earlier studies, very little of the radiocesium is retained by the sludge. According to the available analytical data, the ^{90}Sr split about equally between solution and sludge phases. This result is at variance with results for 105-S-1 and previous results which show that only about 10% of the ^{90}Sr reports to the salt cake solution.

Removal of Cesium

From 105-S-1 Salt Cake Solution. Fifty ml of the salt cake solution, at pH 12, resulting from three consecutive scavenging operations for removal of ^{90}Sr (see "Removal of Strontium," p. 108) were diluted to 150 ml with water. The resulting material was passed downflow at 25° C and one column volume per hour through a 10-ml bed of Duolite ARC 359[®] (Diamond Shamrock Company) resin. The feed solution

to the Duolite resin bed contained 8400 $\mu\text{Ci/liter}$ ^{137}Cs ; the composite loading effluent contained only 12 $\mu\text{Ci/liter}$ ^{137}Cs . Subsequently all the effluent from the first loading cycle contained <0.015 $\mu\text{Ci/liter}$ ^{137}Cs .

From 105-S-2 Salt Cake Solution. Approximately 60 ml of the 105-S-2 salt cake solution were diluted to 180 ml and passed in succession through two Duolite 359 and two Zeolon 900[®] (Norton Company) resin beds. Results of these tests are summarized in Table XXVI.

TABLE XXVI
ION EXCHANGE REMOVAL OF ^{137}Cs
FROM DILUTED 105-S-2 SALT CAKE SOLUTION

Conditions: Portion of salt cake solution listed in Table XXIV diluted to three times its volume with water and passed (1 col vol/hr, 20° C, downflow) successively through ion exchange beds listed.

Bed No. ^a	Exchanger Type ^b	Total Bed Volumes	^{137}Cs , $\mu\text{Ci/liter}$	
			Influent	Effluent ^{c,d}
1	Duolite ARC 359	18.8	2420.	78.5
2	Duolite ARC 359	16.6	78.5	10.8
3	Zeolon 900	15.1	19.0	0.626
4	Zeolon 900	13.8	0.626	0.362

^aAll resin beds were 1.14-cm diameter by 9.8-cm high (10.0 ml).

^bUnused resin each run.

^cEffluent also contained about 100 $\mu\text{Ci/liter}$ ^{106}Ru - ^{106}Rh .

^dComposite effluent.

The MPC_w for ^{137}Cs in water in a controlled zone according to the latest U. S. Atomic Energy Commission guidelines is 0.4 $\mu\text{Ci/liter}$. Effluent from the fourth (second Zeolon 900) column contained less ^{137}Cs than this value. Indeed effluent from the third resin column contained

only 1.5 times the ^{137}Cs MPC_w (48 hour/week exposure) value.

Even though the resin treatment outlined in Table XXVI yielded effluent containing less ^{137}Cs than the MPC_w (48-hr) value, the two Duolite ARC 359 resin columns used with 105-S-2 salt cake solution were not nearly as effective in removing ^{137}Cs as those used with 105-S-1 salt cake solution. The reason for the poor cesium sorption behavior is not known; it may be associated with pH or Na/Cs ratio effects. The Duolite ARC 359 beds used with 105-S-2 solution were allowed to stand, after equilibration with NaOH, two to three weeks before use; such standing may have affected their capacity for sorbing ^{137}Cs . In any event, these results point up the need for a series of ion exchange column runs to define effects of pH, Na/Cs ratio, and other variables on Duolite ARC 359 and Zeolon 900 sorption of Cs from synthetic and actual salt cake solutions.

Removal of Strontium

From 105-S-1 Salt Cake Solution. Attempts to scavenge ^{90}Sr from the as-prepared Tank 105-S-1 salt solution (Table XXIV) by precipitation of either $\text{Sr}_3(\text{PO}_4)_2$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ were uniformly unsuccessful (Table XXVII) even with added phosphate. Failure to remove ^{90}Sr by these scavenging techniques is attributed to extensive carbonate complexing of ^{90}Sr at pH 10. In line with this belief, double precipitation of $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ effected substantial removal of ^{90}Sr . This experiment again showed that nickel ferrocyanide scavenging effectively removes ^{137}Cs from salt cake solutions.

Results from a 10-ml scale experiment also showed that $\text{Sr}_3(\text{PO}_4)_2$ scavenging of ^{90}Sr from the Tank 105-S-1 salt cake solution was significantly improved when the solution was adjusted to pH 12. Subsequently the large volume of

TABLE XXVII
ATTEMPTS TO SCAVENGE STRONTIUM FROM 105-S-1 SALT CAKE SOLUTION

Operation	Total Solids	Initial		Scavenged, $\mu\text{Ci/liter}$	
	ml	^{90}Sr	^{85}Sr	^{90}Sr	^{85}Sr
A. <u>Total Leachate</u>					
1. 3 successive 0.0025M $\text{Sr}_3(\text{PO}_4)_2$ scavengings at pH 10, $\text{PO}_4 = 0.0076M^a$	0.4	11.3	-	9.4	-
2. 3 successive 0.0025M $\text{Sr}_3(\text{PO}_4)_2$ scavengings at pH 12, $\text{PO}_4 = 0.0076M^b$	0.45	-	43.7	-	17.9
3. 3 successive 0.0065M $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ scavengings at pH 12 ^c	1.8	-	17.9	-	29.2
B. <u>Separate 10-ml Portions Leachate</u>					
1. Scavenge with 0.0025M $\text{Sr}_3(\text{PO}_4)_2$ at pH 10 and 0.033M PO_4	0.2	11.3	-	10.0	-
2. Scavenge with 0.0050M $\text{Sr}_3(\text{PO}_4)_2$ at pH 10 and 0.0076M PO_4	0.15	11.3	-	8.5	-
3. 3 successive 0.0075M $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ scavengings at pH 10	1.15	11.3	-	5.8	-
4. 3 successive 0.0025M $\text{Sr}_3(\text{PO}_4)_2$ scavengings at pH 12.1	0.3	11.3	-	$<4.7 \times 10^{-4}$	-
5. 2 successive scavengings with 0.0019M $\text{Ni}_2[\text{Fe}(\text{CN})_6] - 0.0025M \text{Sr}_3(\text{PO}_4)_2$ at pH 8 ^d	0.75	11.3	-	0.38	-

^a100 ml leachate.

^b55 ml leachate from 1.

^c52 ml leachate from 2.

^dInitial ¹³⁷Cs = 27,000 μCi/liter, final ¹³⁷Cs = 7.0 μCi/liter.

leachate which had been scavenged at pH 10 was spiked with Sr, adjusted to pH 12, and scavenged by precipitation of $\text{Sr}_3(\text{PO}_4)_2$. Based on ^{85}Sr analyses, such scavenging was ineffective as was also scavenging by $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ at pH 12. It is important to note, however, that the leachate contains Rh which interferes badly with accurate measurement of low concentrations of ^{90}Sr . There is a possibility, therefore, that large-scale scavenging with $\text{Sr}_3(\text{PO}_4)_2$ at pH 12 was successful.

The abortive attempts to scavenge ^{90}Sr from this actual salt cake solution point up the need for more detailed knowledge of the interrelationships of pH, carbonate, and phosphate concentrations to scavenging of ^{90}Sr by $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Experiments to define these relationships are in progress as mentioned earlier.

From 105-S-2 Salt Cake Solution. The effluent from the four-column ion exchange treatment described previously under "Removal of Cesium from 105-S-1 Salt Cake Solution," p. 108, contained 0.94 $\mu\text{Ci/liter}$ ^{90}Sr compared with an influent concentration of 3.6 $\mu\text{Ci/liter}$. Thus the combination of Duolite ARC 359 and Zeolon 900 resin beds removed only about 30% of the influent ^{90}Sr .

The effluent from the ^{137}Cs removal step was passed in succession through two 10-ml beds of "strontium phosphate anion resin" prepared as described on p. 101 of this report. Solution was passed downflow at 25° C and at a rate of about one column volume per hour. The composite effluents from the first and second strontium resin beds contained, respectively, 0.81 and 0.55 $\mu\text{Ci/liter}$ ^{90}Sr . [For comparison, the MPC_w for ^{90}Sr in water in a controlled zone is 0.01 $\mu\text{Ci/liter}$.] Failure of the strontium phosphate resin beds to remove any appreciable ^{90}Sr from this

particular actual salt cake solution is discouraging after the excellent results obtained with synthetic salt cake solution. Here again the important variable may be solution composition since the synthetic salt cake solution contained appreciably more NaOH (0.59 versus 0.09M) and Na_3PO_4 (0.026 versus 0.0026M) than the actual salt cake solution. Additional column tests with both synthetic and actual salt cake solutions are needed to define suitable feed composition ranges for successful operation of a strontium phosphate anion resin bed.

Future Work

1. Complete batch scavenging tests with synthetic salt cake solutions to establish effects of pH and solution composition on scavenging of radiostrontium by various precipitates; confirm results by tests with actual salt cake solutions.
2. Determine effects of pH and solution composition on removal of ^{137}Cs and ^{90}Sr by various ion exchangers.

Salt Cake Volume Reduction: Sodium Removal

(J. D. Kaser, 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.

Progress During Report Period

Further work is required to determine the validity of this approach.

J. D. Mackenzie of University of California, Los Angeles, a consultant to PNL, suggested that as a way to decontaminate the large volumes of high-sodium waste currently stored at Hanford and Savannah River we might make use of the idea that sodium beta-alumina preferentially conducts sodium ions. The energy required to effect the separation by electrodialysis could theoretically be much lower than the energy required to convert all the waste to glass. Furthermore, the resulting reduction in radioactive waste volume could substantially reduce waste storage costs.

To test this idea a beta-alumina sample was obtained from Corborundum Company of Falconer, New York, in the form of Monofrax HR fused cast brick. Square plates approximately 2" x 2" x 1/4" were cut from the brick to form test membranes. The beta-alumina plates were cemented to short sections of 7/8" ID glass tubing.

The membranes were tested for holes or leaks by inverting the glass tubes with the membranes attached into water and observing whether the trapped air volume decreases with time. Most pieces of beta Al_2O_3 leaked. One apparently leak-tight piece was obtained by cutting the brick to retain the fused surface of the brick as one membrane surface.

The apparatus for measuring the conductivity of the membrane is shown in Figure 19. The glass tube and beaker were filled with test solution in which graphite electrodes were immersed. A constant voltage was applied across the electrodes and the current flow was measured with a d.c. milliammeter.

Since radiocesium is the chief contaminant of the high-sodium wastes, the conductivity of cesium and sodium ions through membrane was measured and compared. The

FIGURE 19
APPARATUS FOR MEASURING IONIC CONDUCTIVITY OF $\beta\text{-Al}_2\text{O}_3$

electrodes were immersed. A constant voltage was applied across the electrodes and the current flow was measured with a d.c.. milliammeter.

Since radiocesium is the chief contaminant of the high-sodium wastes, the conductivity of cesium and sodium ions through membrane was measured and compared. The membranes were in contact with 1N solutions of Cs_2CO_3 and Na_2CO_3 .

The results for two beta-alumina samples are tabulated below.

Membrane	<u>Cs⁺ Conductivity</u>	<u>Na⁺ Conductivity</u>
	<u>(ohm-cm)⁻¹</u>	<u>(ohm-cm)⁻¹</u>
1	4.8×10^{-4}	3.0×10^{-4}
2	2.1×10^{-4}	1.8×10^{-4}

Membrane 1 was slightly permeable to air, while membrane 2 seemed to be impermeable. It is obvious from the result that the conductivity of beta Al_2O_3 is apparently not much different for either ion. This is quite different from what one might expect from limited published data. Yao and Kummer^[8] found that the self-diffusion coefficients in beta-alumina were much greater for Na^+ ions than the K^+ or Rb^+ ions and only 20% of Na^+ could be displaced from beta-alumina by immersion in molten CsNO_3 . The lack of sensitivity may have been due to the many small pores through the membrane which may not leak much air but nevertheless conduct appreciable number of ions. This explanation seems plausible since the air leak rate should be proportional to the square of the diameter.

Two preliminary experiments were made to test the separation of sodium from a solution containing both sodium carbonate and cesium carbonate. The amount of separation

observed was not large. Sodium passed through the membrane 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 the permeation experimental results are so far inconclusive and should be repeated with a leak-free membrane.

Future Work

Several beta-alumina thimbles are being sent to us by Dr. Atsuo Imai of Toshiba Company, Japan. These thimbles were specially designed for use as solid electrolyte membranes and should be leak-free, but will be tested for leaks before use. If necessary an attempt will be made to seal the pores with a resin or polymer. The excess sealant would be removed from the membrane surface by grinding. Experiments described above will be repeated and will also be tried with some solutions containing radiocesium to test separation at very low cesium concentrations. Later the effect of anions on separation will be investigated. Finally, if there is an incentive based on experimental results, separation from molten salt mixtures may be studied.

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