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MASTER

**PRELIMINARY FLOWSHEET FOR THE CONVERSION
 OF HANFORD HIGH-LEVEL WASTE TO GLASS**

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I. INTRODUCTION

The waste processing task for the long-term high-level waste, as described in ARH-LD-142, is to develop processes for converting waste removed from the Hanford underground waste tanks to more immobile form and to develop a cost effective process. The flowsheets in this document describes such a process.

The process involves a chemical separation of the radionuclides from industrial chemicals, then making glass from the resulting small volume of highly radioactive waste. Glass has received serious consideration as a waste form because it can be very durable; the natural glass, obsidian, has been age dated at up to 136 million years⁽¹⁾. The process is specific for the waste found in the tanks (see Figure 1, Hanford Waste). The process for the immobilization of strontium and cesium recovered and encapsulated in recent Waste Management operations is found in Reference 2. The encapsulated waste is of very small volume compared to the waste in the tanks.

FIGURE 1. Hanford Waste

II. PROCESS SUMMARY

The radionuclides are distributed in the Hanford Defense Waste according to solubilities. The strontium and the actinides are found predominantly in the sludge and the cesium and the technetium are found in the water soluble salt cake and the residual liquor. The tasks of the Radionuclide Removal process are to separate radionuclides from the nonradioactive chemical waste (e.g. NaNO_3 , NaOH) and to prepare a dry feed for the glass melter.

The strontium and actinides are removed by a combination of centrifugation, precipitation and ion exchange. Centrifugation removes most of the strontium and actinides. Residual quantities remaining in solution are removed by precipitation and ion exchange on a sodium titanate ion exchanger. The solution species, cesium and technetium, are adsorbed: cesium on cation resin and technetium on anion resin. All radioactive waste separated from the bulk chemicals will be concentrated into a small volume, dried and mixed with glass-making additives. A summary of waste volumes and activity levels entering and leaving the process is shown in Figure 2.

Conversion of the small volume of radioactive waste to a homogeneous glass takes place in a ceramic lined melter which is heated internally by electrical conduction through the molten glass. The melter off-gas produced as the wastes are oxidized goes through an off-gas treatment system where NO_x and SO_x are removed. The molten glass stream overflowing from the melter is either cast directly into 24-inch (0.61m) diameter steel containers or processed via forming machines to 0.87-inch (2.2 cm) diameter glass marbles.

III. CRITERIA AND PROCESS EFFECTIVENESS

The preliminary criteria for the Radionuclide Removal process are:

- a reduction in the volume of waste requiring immobilization. (The saving in storage cost must more than pay for the Radionuclide Removal Plant.)
- a reduction of radioactivity in the salt waste to 10 nanocuries per gram with emphasis on separating radionuclides having half-lives greater than 25 years from non-radioactive waste.*

A sizeable reduction in immobilized waste volume has been achieved (see Figure 2) and the criteria of 10 nCi/g has been met on actinides in laboratory tests.⁽³⁾

The elimination of most radionuclides with half-lives greater than 25 years has proved achievable. The Radionuclide Removal process has a demonstrated effectiveness for the removal of actinides, Sr, Cs and Tc. Samarium-151 is one of probably several radionuclides removed to a large extent by the process although the process was never specifically developed for this purpose. Iodine-129 (half-life 1.6×10^7 years) is one that is unaffected by the process. However, only 47 curies was produced and some of it was lost to the reprocessing plant ventilation air. Assuming all 47 curies leave the Radionuclide Removal plant as a component of the salt then the contribution of iodine-129 to the radioactivity of the decontaminated salt would be 0.5 nanocuries per gram.

*The basic objective is to reduce radioactivity in the bulk salt waste to a level that will permit its disposal as a "chemical waste", without the need for expensive containment or long-term surveillance. Development of such criterion, based on pathway-to-man studies, is currently underway and will be discussed in future reports. In the meantime, however, the 10 nCi/g limit has been adopted as a target for preliminary process development studies.

The short-lived radionuclides in the existing waste inventory will have decayed to a low level by the time Radionuclide Removal plant begins operation in the 1990's. Tritium (^3H) and carbon (^{14}C) are unaffected by the Radionuclide Removal process but these radionuclides are found in very low quantities in the waste. Most of the tritium in the fuel elements was disposed with the process condensate from fuel reprocessing operation, while ^{14}C was released as a component of the reprocessing off-gas.

The failure to remove the radionuclides with short half-lives, less than 25 years, becomes a problem with scheduled reprocessing of N reactor fuel in the Purex Plant. The ruthenium in this waste will cause a significant radiation increase in the decontaminated salt.

The hazard introduced by ruthenium can be eliminated by:

- (1) additional processing steps for ruthenium removal in the Radionuclide Removal process or at the Purex Plant;
- (2) a delay in processing to allow the ruthenium to decay; or
- (3) more rigorous storage of the ruthenium contaminated salt.

Plans for ruthenium removal includes studies of process chemistry on both the caustic neutralized high level waste and Purex acidified waste to determine processes and product forms that are compatible with melter operations. Ruthenium chemistry depends on solution pH. For Purex acid waste, there are at least two possibilities for ruthenium removal. In the Redox Plant ruthenium was removed by ozonation of the ruthenium contaminated solution. Ozonation causes the ruthenium to volatilize, then it is removed from the ozonator off-gas by scrubbing with caustic. A process similar to that used for the vitrification of commercial reactor waste can be applied directly to Purex acid waste without going to the Radionuclide Removal plant. Both processes would require

additions to the Purex plant. Plans for ruthenium removal from caustic solutions includes studies of ruthenium precipitation and adsorption of ruthenium on iron titanate.

A delay in the processing of the N reactor waste to beyond the year 2000 is a secondary alternative to removal by processing. This delay allows sufficient time for the ruthenium to decay to an insignificant level. The waste could be stored in double-shelled tanks until that time, if processing is required before decay is complete, then the added risk of ruthenium in the salt waste can be alleviated by sealing the waste in containers and/or storing it in underground caverns rather than bulk storage in surface trenches.

The Radionuclide Removal process, is not entirely effective in removing all the radionuclides with half-lives greater than 25 years, but it is expected to meet the 10 nCi/g goal on total radioactivity. Any program to remove radioactive constituents, other than those currently targeted for removal, such as antimony and selenium will require a greater technological development effort. Since these exist in relatively small quantities, reduction in the radioactivity of the decontaminated salt will be very small, and probably not justified on the basis of increased storage safety.

IV. BASIS

The average chemical waste composition was taken from Reference 4. The fission products inventory was assumed equal to the fission products production as calculated by United Nuclear Industries (UNI) using computer code RIBD-II described in Reference 5. An exception is the tank inventory values for tritium, which are based on reactor production plus an estimated reduction factor which accounts for losses during the initial fuel element reprocessing. Corrections are made for the strontium and cesium recovered in processing operations at B Plant. The actinide content has been estimated by computer codes corrected for recovery in the reprocessing plants. The correction was based on plant accountability data.

V. RADIONUCLIDE REMOVAL PROCESS

A. Waste Preparation

Waste Preparation includes the receiving of waste from waste retrieval, the dissolution of salt cake, the storage and blending of this waste to obtain a uniform composition, and the separation of the waste into two fractions: a sludge and a waste liquor. The insoluble sludge, which includes most of the strontium and actinides, is dried to a powder. The waste liquor is pumped through the ion exchange and precipitation processes to remove the soluble radionuclides.

Salt cake and sludge shipped to the Radionuclide Removal Plant are transferred to a dissolver where hot water is added to dissolve the salt cake. Enough water is added to make a concentrated salt solution; the sludge remains undissolved. The waste is transferred from the dissolver to storage tanks for blending with other waste. A feed with a consistent composition is desirable. Blended waste is fed to the sludge centrifuge to separate the dissolved salt cake solution from the sludge. The sludge is transferred to a dryer and the salt cake solution flows to an ozonator where it is combined with residual liquor, a recycle stream, and the centrate from the Washed Sludge Centrifuge. Two sludge drying steps are needed to prepare the sludge for immobilization. The sludge is dried, washed, then redried, to make a suitable product. The initial drying step may be eliminated, if current laboratory testing is successful.

The washing process removes soluble chemicals from the sludge. Sulfate ion in concentrations of 0.5 percent or higher causes the glass to separate into two phases: one phase is water soluble and high in cesium and the other is a glass. The washing reduces the sulfate to an acceptable level and also reduces the volume of sludge requiring immobilization. After washing, the insoluble sludge is centrifuged, dried and collected in batch cans.

Strontium and Actinide Removal

Most of the strontium and actinides in Hanford defense waste are insoluble components of the sludge and follow the process path of the sludge. The insoluble components are washed and dried as described in Section V A, Waste Preparation. The remaining strontium and actinides are soluble components of the salt cake solution and residual liquor and are removed by a precipitation and ion exchange.

Salt cake solution, residual liquor, and sludge wash waste are mixed together a batch at a time in a tank. Ozone is bubbled through the solution to destroy any organic that may interfere with precipitation and ion exchange of the strontium and the actinides.

Organic compounds used at Hanford include sodium tartrate, hydroxyacetic acid, sodium ethylenediaminetetraacetate, sodium diethylenetriaminepentaacetate and sodium hydroxyethylenediaminetetraacetate. In the waste tank these organic compounds have formed complexes with the strontium and the actinides. Destruction of the organic ligand by ozonation makes efficient removal of the strontium and the actinides possible from those solutions (primarily residual liquor) where organic carbon is high. The bulk

of the salt cake is low in organic carbon, hence ozonation of the bulk salt cake solution will probably be unnecessary.

Ozonation is considered to be a pretreatment, rather than a process for strontium removal. However, removal of some of the strontium from solution actually does occur; flocs of probably both aluminum hydroxide and ferric hydroxide agglomerate and precipitate some of the strontium and the actinides out of solution.

After ozonation the caustic concentration is adjusted to improve ion exchange selectivity, then nonradioactive strontium nitrate and sodium phosphate, if needed, are added to precipitate the radioactive strontium and the actinides.

Essentially all of the strontium and the actinides in solution are removed by either the precipitation process or by adsorption on a column of inorganic sodium titanate $[\text{Na}(\text{Ti}_2\text{O}_5\text{H})]$ ion exchange media.

The precipitate formed by the precipitation process is removed by centrifugation and the clarified liquor from the centrifuge is filtered through a sand filter. This filtered solution passes through the column of sodium titanate exchanger. The sodium titanate has a large affinity for uncomplexed strontium and other polyvalent cationic radionuclides. Recent laboratory data indicate that ozonation followed only by ion exchange with sodium titanate resin may accomplish essentially complete removal of the strontium and actinides, making the precipitation process unnecessary. Further testing, however, is necessary before the precipitation step can be eliminated.

The strontium and actinide loaded exchange bed is not eluted. Instead, the bed contents are added at a uniform rate to the tank that accumulates the strontium sludge. This is the feed tank for the strontium clarifier centrifuge. The sludge from the strontium clarifier centrifuge consisting of ozonation precipitate, strontium precipitate, and sodium titanate resin is dried and collected in batch canisters. The waste is sampled and blended with other wastes and sent to the glass plant.

C. Cesium Removal

Cesium is water soluble and is found in the salt cake and residual liquor. The salt cake-residual liquor solution made in waste preparation is processed through the strontium removal process and then pumped to cesium ion exchange.

The waste is prepared for adsorption on a column of Duolite ARC-359 ion exchange resin by adding sodium hydroxide to the waste. At moderately high sodium hydroxide concentrations cesium is adsorbed on this strong acid resin. The column is loaded for a predetermined time, then the feed is diverted to a second column while the first column is being washed and eluted. The loaded column contains mostly sodium even though cesium is the desired cation. However, sodium is one of the additives in the immobilization process, hence a wash which would selectively remove the sodium has been eliminated.

The ion exchange bed is prepared for elution by washing with water and dilute caustic. The caustic wash is essential to prevent aluminum hydroxide precipitation in the elution. The sodium and cesium are eluted with

a concentrated solution of ammonia added as ammonium carbonate and ammonium hydroxide. The resin is reconditioned by flushing excess ammonium ion from the resin with a caustic solution. This prevents aluminum hydroxide precipitation in the succeeding cesium loading operation.

The high volatility of the ammonium hydroxide-ammonium carbonate allows easy recovery of the eluent as ammonia and carbon dioxide. The ammonia and carbon dioxide are evolved as gases as the cesium eluate is concentrated. The ammonia and carbon dioxide are reabsorbed in water, enriched with fresh ammonia and carbon dioxide and reused in the next elution. The concentrated carbonate solution of sodium and cesium is dried to a powder and mixed with other dried wastes.

The wash waste from cesium ion exchange is processed in two different systems. The regeneration waste and dilute cesium product is evaporated and the ammonia and carbon dioxide are reabsorbed, concentrated and combined with the eluent recovered in cesium product concentration. The caustic wash is combined with the technetium wash waste in a separate evaporator. The concentrate from both systems, the caustic waste system and the regeneration waste system, are combined and recycled through strontium, cesium and technetium removal processes. The water that is evaporated from these wastes is condensed and recycled for use as salt cake solvent and makeup water for resin washes.

D. Technetium Removal

Technetium is present as the soluble pertechnetate ion and is removed in a final ion exchange operation by a strong base anion resin. Technetium is associated primarily with the residual liquor, hence technetium removal from salt cake solution may not be necessary.

Technetium ion exchange is operated on a five day cycle; technetium is adsorbed on anion resin for approximately four days then flow is diverted to a second column and the first column is eluted on the fifth day. The column is prepared for elution by a caustic and a dilute nitric acid wash. The caustic wash removes carbonate and nitrite ions and the dilute nitric acid gently converts the resin to the nitrate form. The technetium is eluted from the bed with 6M nitric acid and then the bed is prepared for adsorption of more technetium by displacing the acid with water.

The eluent is a very dilute solution of technetium which must be concentrated and neutralized. The nitric acid concentration must be reduced to a low level to reduce the amount of sodium nitrate formed during neutralization because it will be incorporated in the glass product. Thus it is important that most of the nitric acid be separated from the technetium.

First the 12,800 gallons of nitric acid eluent are reduced in acid concentration by formic acid denitration of small batches of about 700 gallons of eluent at a time.

The seven hundred gallon batches are reduced from an acid concentration of 6M HNO_3 to 1M HNO_3 by reacting the acid with the formic acid. Formic acid converts the nitric acid to nitrous oxide. The nitrous oxide is evolved from solution as gas and then recovered in a bubble-cap absorber column.

Upon completion of the reaction about 83 percent of the nitric acid has been destroyed and evolved as nitrous oxide. Most of the remaining nitric acid is evaporated in an acid evaporator and the acid is recovered from the vapor. The technetium waste is neutralized and combined with the sludge, dried and sent in batch cans to the glass plant.

The 1M nitric acid solution from the formic acid reactor is pumped continuously to the acid evaporator. The acid vapors are absorbed and enriched in a rectifying column by a distillate stream that is refluxed from the condenser. The product from the nitric acid rectifying column is approximately 25 percent nitric acid. The distillate from the column condenser contains a trace of nitric acid and is reused in the preparation of fresh eluent.

The 25 percent acid product from the acid rectifier is pumped to the feed plate of the nitrous gas absorption column. This acid is enriched by the countercurrent contact of the nitric acid with the nitrous oxide gas. The acid leaving the nitrous oxide absorber is 13M nitric acid. This concentrated acid is diluted to 6M nitric acid for use in the next elution. Fresh acid is added to make up for any losses.

VI. GLASS PROCESS

The Radionuclide Removal (RR) process produces three feed streams for the glass plant. They are (1) dried sludge plus technetium, (2) dried strontium phosphate plus titanate exchanger, and (3) dried cesium carbonate concentrate. These are contained in batch cans for transfer between the main canyon facility (RR process) and the glass plant. Lag storage of the intermediate product cans provides needed flexibility for blending glass melter feeds to meet melter feed specifications as well as decoupling these two major processing operations.

Batch blending of melter feed will be achieved as follows:

- o Selected batch cans are carried by the in-cell crane and coupled to a system of weigh scales, vibrating feeders and batch mixers.
- o Glass forming ingredients (SiO_2 , B_2O_3 , and Li_2CO_3) are also weighed and blended with the wastes.
- o Lastly, a relatively small quantity of glass frit and oxide dust, being recycled via batch cans from the melter off-gas filter systems, is similarly added to the feed batch. A blended feed batch is discharged from the mixer into batch cans, transferred to the melter cell, and discharged to the melter feed hopper. A batch feeder/distribution mechanism controls the continuous addition of the batch to the melter.

The flow sheet being considered here blends dried waste streams with borosilicate glass formers to effect a product glass with the following composition:

<u>Component</u>	<u>Wt%</u>
waste oxides	37.3
SiO_2	53.8
B_2O_3	6.9
Li_2O	2.0

The addition of Li_2CO_3 (oxidized to Li_2O) lowers glass viscosity, thereby allowing melter operation at temperatures of about 1200°C . Interest is currently centered on borosilicate glasses largely because of their low leachability characteristics in both the vitreous and devitrified states. Evaluation of borosilicate glasses formed by using synthetic waste indicates that the leach rate would increase only by a factor of 10 to 100 if devitrification occurs.

Currently chosen as the melter concept under development for Hanford waste immobilization, the joule-heated, ceramic lined melter offers the potential for long life, high capacity, low off-gas effluent volume, and high glass quality. The ceramic melter is a refractory lined cavity, equipped with electrodes between which electrical energy is dissipated within the molten glass. Power input to the melter is controlled to keep the melt fluid at a temperature of about 1200°C . With multiple sets of electrodes and a "forehearth" melter zone, the discharge glass temperature and, hence, viscosity can be adjusted to optimize conditions for casting.

Glass overflows the melter at a rate of about 2.3 l/min and for the glass monolith option, fills carbon steel canisters in essentially a continuous casting operation. The total weight of glass to be produced in the 9 tonnes per day melter is estimated at 32,500 tonnes, which at a conservatively low specific gravity of 2.45, will fill 17,900 24-inch (0.61m) diameter by 12 foot (3.66m) long canisters. During casting, each canister is held under the glass melter drain, enclosed in a cooling-annealing cart. While hot glass ($\sim 1200^\circ\text{C}$) is being poured into the canister, the canister walls are cooled by forced air to hold them at about 510°C . When the canister

is full, it is moved to the annealing area. There it remains in the cart where a programmed cooldown period (perhaps 10 days) serves to partially anneal the monolith, thereby reducing the degree of cracking that would occur if the canisters were simply allowed to cool by natural convection or were rapidly cooled to room temperature.

To make marbles as the glass product form, the melter is equipped with a forehearth in which the temperature is controlled to about 975° - 1050° C, prior to discharging the glass to four marble forming machines. Such a forehearth will need to be about 10 feet long. The glass stream from the drain is sheared into gobs. Gobs slide down steel chutes (two per marble machine) and enter grooved rollers. After travelling between the rollers, the marbles drop from the ends, slide down cooling chutes beneath the rollers, and fall into canisters where they self cool. The production rate of 0.875-inch (2.2 cm) diameter marbles is 410 per minute or about 200 ft^3 (5.7 m^3) of the bulk product per day. Total campaign production is estimated at $780,000 \text{ ft}^3$ ($22,000 \text{ m}^3$).

Another major area of the process is the off-gas treatment required for removal of cesium and ruthenium as well as inert SO_x and NO_x volatilized from the glass melt. In operation of the melter, the molten pool of glass is covered by a blanket of the waste oxide and glass additives. The cool blanket condenses the bulk of escaping volatiles and returns them to the molten pool. The resulting melter effluent is expected to carry 100 percent of the H_2O , NO_x , and CO_2 present in melter feed, an as yet unknown fraction of the SO_2 present in the melter feed, and (during infrequent periods of abnormal blanket distribution) up to five percent of the cesium contained in melter feed.

This off-gas stream is routed first through a rechargeable filter bed composed of the ground glass frit and maintained at a temperature of about 175° C. Here, dust, cesium, and other volatiles are condensed or filtered and after bed replacement, are recycled to the feed blending system. Next, a sintered metal blowback filter further removes dust from the off-gas. Water vapor, NO_x , and SO_x , are finally removed via a condenser and absorber using a Na_2CO_3 solution. (The absorber also serves as a secondary decontamination step for volatilized cesium). This potentially contaminated solution of nitrate and sulfate salts is recycled to the headend of the Radionuclide Removal process. The salts ultimately leave the process in the decontaminated salt stream.

The final glass product has properties of low dispersibility, low leachability, and relatively high thermal stability. Leach rates based on Cs are expected to range from 2×10^{-6} to 2×10^{-5} gm/cm²-day after 120 hours leaching.

Radionuclide concentrations and heat generation in the glass (decayed to 1990) will be as follows:

	<u>Ci/l</u>	<u>Btu/hr-l</u>
⁹⁰ Sr	4.22	9.79×10^{-2}
¹³⁷ Cs	1.28	2.10×10^{-2}
⁹⁹ Tc	0.0028	3.5×10^{-5}
Transuranics	0.0067	$\sim 6.7 \times 10^{-4}$

The monolithic product form, after being partially annealed via a ten day controlled cooldown, is expected to be moderately stressed and cracked.

VII. FLOW SHEET DEVELOPMENT

The flow sheets presented in this document capture an instant in the continuing development of a better process for radionuclide removal and glass making. Development work is aimed at simplifying the process thus reducing costs and maintenance.

The processing of residual liquor has proven to be an area where improvement is needed. The residual liquor contains the complexing agents and most of the technetium. The complexing agents must be destroyed to permit the reduction of strontium to very low levels.

The current method of adding ozone to destroy the complexing agents has proven very effective but the ozonation takes hours to complete. Currently the development task is to reduce the reaction time which would reduce the reactor size and cost. The reaction time can be reduced by good mixing of the ozone and the solution and by exposing the solution to ultraviolet light.

Technetium removal is the other area of residual liquor processing that could be improved. The removal of technetium from the waste by anion exchange is simply a matter of pumping the solution through a bed of anion resin, but the recovery of the technetium from the eluent is complicated because a large volume of concentrated nitric acid is required for the elution. The eluent is a very weak solution of technetium. The technetium must be concentrated into a small volume and neutralized before it can be dried and made into a glass feed.

Solvent extraction is being actively investigated as a replacement flow sheet for technetium. Preliminary laboratory investigations indicate that cyclohexanone, methylisobutylketone, and pyridine will effectively extract technetium from simulated waste solution. Equilibrium data and bench scale operations are planned. A decision on solvent extraction or ion exchange will depend upon capital cost, safety, pollution, and ease of operation and maintenance.

The flow sheet for strontium removal from the waste solution includes two processes, precipitation and ion exchange. Laboratory tests with sodium titanate ion exchanger have been very successful and future hot cell tests will determine if adequate strontium removal can be achieved without using precipitation. Some additional testing will be required to determine if a column of sodium titanate will plug under the rigors of plant operation. A test column of sodium titanate will be operated at various flow rates, backflushed and run through many cycles of off to full flow. If all testing is successful, precipitation will be dropped.

Development of the glass immobilization flow sheet is continuing in two major areas, glass formulation, and equipment development. Both real and simulated wastes are continually being immobilized at crucible scale in various borosilicate glasses. Effects of glass additives such as SiO_2 , B_2O_3 , TiO_2 , CaO_2 , and Al_2O_3 , on properties including leach rates, abrasion resistance, high temperature viscosity and high temperature electrical conductivity are being determined. Studies to estimate the stability of defense waste glasses in long-term storage are being planned.

A computer program is being written to aid in estimating the variability of glass plant waste feeds, and to calculate glass compositions for testing in the laboratory and in developmental melters. Equipment development for defense waste glass immobilization has largely been delegated to Battelle Pacific Northwest Laboratories. They will begin by testing diverse waste glass compositions in equipment developed for the commercial waste program. Subsequently, they will build and operate a small melter specifically to test defense waste glasses and their effect on high temperature electrode materials. Future developmental melters will be scaled up and will incorporate design features for remote operation and maintenance. Battelle will also develop and test glass product canister designs for defense waste application.

VIII. ACKNOWLEDGMENTS

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APPENDIX A

PROCESS FLOW DIAGRAMS

- P1 Feed Preparation and Storage
- P2 Sludge Washing
- P3 Strontium Precipitation
- P4 Strontium and Cesium Removal
- P5 Residual and Technetium Removal
- P6 Cesium Concentration
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