Removal of Dissolved and Suspended Radionuclides from Hanford Waste Vitrification Plant Liquid Wastes

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REMOVAL OF DISSOLVED AND SUSPENDED RADIONUCLIDES
FROM HWVP LIQUID WASTES

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ABSTRACT

It was determined during Preliminary Design of the Hanford Waste Vitrification Plant that certain intermediate process liquid waste streams should be decontaminated in a way that would permit the purge of dissolved chemical species from the process recycle loop. This capability is needed to ensure proper control of product glass chemical composition and to avoid excessive corrosion of process equipment. This paper discusses the process design of a system that will remove both radioactive particulates and certain dissolved fission products from process liquid waste streams. Supporting data obtained from literature sources as well as from laboratory- and pilot-scale tests are presented.

INTRODUCTION

The primary purpose of the Hanford Waste Vitrification Plant (HWVP), which is now undergoing Detailed Design, is to immobilize Hanford Site liquid high-level and transuranic (TRU) defense waste into a borosilicate glass matrix. The vitrification process and supporting equipment are structured around a joule-heated, liquid-fed ceramic melter from which the molten glass product will be poured into stainless steel canisters. The product glass, consisting of approximately 25 wt% waste oxides and 75 wt% glass-forming frit, will be subject to limitations on chemical composition to ensure acceptable quality.

The HWVP feed slurry, on the other hand, will experience fairly wide variations in its chemical composition, as shown by Table 1.

Incoming batches of HWVP feed will undergo concentration by evaporation, then chemical adjustment and mixing with frit before being continuously fed to the melter as a concentrated slurry. The melter offgas will contain water vapor, noncondensable gases, entrained particulates, and other species such as cesium, strontium, and halides (i.e., fluoride and chloride), which will partially volatilize from the 2100 °F molten glass in the melter.

Wet scrubbing of the melter offgas in a submerged bed scrubber (SBS) will remove most of the particulates, semi-volatiles, and water

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Table 1. Hanford Waste Vitrification Plant Reference
Feed Chemical Compositional Range.

Chemical composition range limits (oxide basis)	Wt% of total nonvolatile oxides	
	Minimum	Maximum
Al_2O_3	2.0	26.0
BaO	0.0	20.0
CaO	0.0	20.0
CdO	0.0	10.0
Fe_2O_3	8.0	60.0
$(La, Nd)_2O_3$	0.0	8.0
MnO_2	0.0	20.0
MoO_3	0.0	8.0
Na_2O	4.5	22.0
NiO	0.0	8.0
SiO_2	0.0	17.5
TiO_2	0.0	4.0
U_3O_8	0.0	32.0
ZrO_2	0.0	40.0
Cr_2O_3	0.0	2.0
Noble metals (PdO, Ph_2O_3, Ru_2O_3)	0.0	1.0
P_2O_5	0.0	4.0
SO_3	0.0	2.0
F	0.0	6.9
Fission product elements and minor components	0.0	5.0
Volatile components	lb/100 lb total waste oxides	
Cl	0.0	0.3
CO_3	2.4	30.0
NO_x (as NO_3)	0.0	36.0
TOC	0.0	11.0
Overall waste loading limits		
lb total nonvolatile oxides/gal	0.21	0.83

TOC = Total organic carbon

vapor. The resulting SBS liquid effluent will contain significant levels of halides and sodium as well as concentrations of dissolved cesium, strontium, and TRU in excess of that permitted in the final HWVP process liquid effluent. Accordingly, this liquid must be treated as an intermediate process waste requiring further decontamination before discharge from the plant.

As originally conceived, the HWVP process liquid waste handling system was to have decontaminated all intermediate waste streams by means of reevaporation, with the evaporator bottoms recycled to the feed preparation equipment. Although this technique can effectively decontaminate process liquids, it does not permit the aqueous purge of potentially undesirable chemical species from the process recycle loop. These chemicals could leave the plant only by incorporation into the product glass. However, the high melter volatility of species such as fluoride and chloride, and their ease of solubility in the SBS scrub solution, meant that they could build up to potentially high concentrations in aqueous recycle streams before steady-state removal from the system in the glass. Such a buildup could accelerate process equipment corrosion rates and cause other processing problems.

It was therefore determined that the HWVP process design should be modified to permit the recovery of dissolved and particulate radionuclides from the SBS liquid effluent without also recycling dissolved cold chemicals. Achieving this goal will facilitate control of the product glass chemical composition and minimize the corrosiveness of the aqueous process recycle streams.

This capability also will be needed on those occasions, notably plant shutdowns, when large volumes of spent equipment cleaning solutions

will be generated by plant maintenance activities. These streams will contain dissolved chemical species such as sodium, nitrates, phosphates, and organic carbon, which should be purged from the plant rather than recycled to vitrification. Unlike the SBS liquid effluent, which contains significant levels of dissolved cesium and strontium, the spent equipment cleaning solutions will contain predominantly particulate contamination, especially after neutralization of excess acids.

The process liquid waste discharged from HWVP must have a TRU concentration less than 100 nano Ci/g of waste. It must also satisfy the limit on dissolved cesium and strontium, as shown in Eq. 1:

$$(^{137}Cs/0.33) + (^{90}Sr/0.3) < 1.0 \text{ Ci/L.} \qquad (1)$$

To the extent practical, it is desirable to reduce the residual levels of contamination to well below these limits.

Finally, a review of the overall HWVP process design indicated that reevaporation followed by bottoms recycle remained the appropriate decontamination technique for most of the intermediate process liquid waste, which consists of condensates low in dissolved and suspended solids.

REMOVAL OF DISSOLVED FISSION PRODUCTS

Available technical literature indicated that zeolite adsorption was the best method for removing dissolved cesium and strontium from aqueous streams. A report describing decontamination work performed at Three Mile Island identified UOP's Ionsiv™ IE-96, which is a chabazite type of zeolite in the sodium form, as the best sorbent for both cesium and strontium.[1] Similarly, IE-96 has been used for treatment of supernatant at the West Valley Demonstration

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™Ionsiv is a registered trademark of UOP.

Project (WVDP) where cesium removal was the primary consideration.[2] The selection of IE-96 was based on its "... high sorption rate, high decontamination factor, ion exchange capacity, and compatibility with the glass formers for borosilicate glass in direct melter feed."[2] Process conditions found to promote the removal of cesium from the liquid phase included low temperatures, low concentrations of dissolved salt, pH levels below 13, and lower sodium to cesium mole ratios. Both Three Mile Island and WVDP used zeolite-filled contacting columns to treat their contaminated process streams.

The equilibrium loading of a given dissolved contaminant on a solid adsorbent can be quantified by Eq. 2:[3]

$$R_d = \frac{Cs}{Cl} \quad (2)$$

where

R_d = Radionuclide distribution ratio (mL or cm^3 of solution per gram of anhydrous adsorbent)

Cs = Concentration of the radionuclide exchanged on the solid phase (Ci or grams of radionuclide per gram of anhydrous adsorbent)

Cl = Concentration of the radionuclide remaining dissolved in the coexisting liquid phase at equilibrium (Ci or grams of radionuclide per mL or cm^3).

The distribution ratio (R_d) for cesium adsorption by zeolite was expected to vary roughly inversely with the concentration of dissolved sodium, assuming all other process parameters remain unchanged. This relationship can be expressed as

shown in Eq. 3:

$$R_d = \frac{Constant}{[Na^+]}. \quad (3)$$

The measured distribution ratios reported by Three Mile Island[1] and WVDP,[3] which were based on the adsorption of cesium at 25 °C by IE-96, suggested the following, as shown in Eq. 4:

$$R_d (cm^3/g) = \frac{294}{[Na^+] \text{ g-mol/L}}. \quad (4)$$

Following development of this theoretical framework, laboratory-scale tests were performed by Pacific Northwest Laboratory (PNL)* to confirm the feasibility of zeolite adsorption under the predicted HWVP process conditions. These tests utilized a batch-contacting mode, which allowed the test solution and the zeolite adsorbent to remain in contact for a finite period of time inside an agitated container. This technique was preferred to column contacting because it simplifies both the required process equipment as well as the handling of fresh and spent zeolite, particularly when the operation must be conducted inside a remote cell as will be the case at HWVP.

In summary, the results of these tests were as follows:

(a) Of the adsorbents tested (IE-96, IE-95, and A-50), Ionsiv IE-96 was best for the removal of cesium, which is by far the most abundant fission product contaminant for the projected application at HWVP.

(b) Of the adsorbents tested, Ionsiv A-50 was best for strontium removal.

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*Operated for the U.S. Department of Energy by Battelle Memorial Institute.

(c) The IE-96 and A-50 were both found to be chemically stable during prolonged contact at 75 °C with solutions containing levels of chloride and fluoride close to those expected at HWVP.

(d) Maintaining the solution pH above 7 will reduce the combined solubilities of plutonium and americium to below 2 nano Ci/g of solution. These TRU contaminants then may be removed from the process liquid as solid particles rather than by means of adsorption from the liquid phase. Maintaining the solution pH below 10 will prevent caustic attack on the alumino-silicate structure of the IE-96 zeolite.

(e) The distribution ratio for cesium adsorption by IE-96 was found to decrease by about 35 percent as the solution temperature was increased from 25 °C to 43.3 °C. The currently anticipated contact temperature will be near the upper end of this range.

(f) A 99.7 percent approach to equilibrium was achieved after a 100-min contact time at 25 °C, using IE-96 to remove cesium.

(g) The cesium R_d for IE-96 did not vary greatly with solution pH. For this adsorbent, the cesium R_d value decreased from 10,000 to 7,000, and the strontium R_d value increased from 600 to 2,000 as the pH increased from 5 to 11. The amount of cesium removal will not vary significantly with these high R_d values.

(h) The experimentally measured distribution ratios for cesium adsorption were in all cases higher than the values predicted by Eq. 4, based on the measured concentration of

dissolved sodium in the test solutions. The variability of the data also shows that there is not an exact inverse relationship between R_d and [Na$^+$]. Averaging the test data suggested that R_d for cesium removal could be estimated as 462/[Na$^+$] g-mol/L, based on the use of IE-96 at 25 °C. For purposes of the HWVP process design calculation, R_d was more conservatively estimated as 380/[Na$^+$] under these conditions and 247/[Na$^+$] at the 100 °F projected contact temperature.

The PNL test data were used to support the HWVP process design calculations dealing with the adsorption of fission products from the SBS liquid effluent. Starting with a defined stream composition and batch volume, acid-base stoichiometry was used to determine the sodium hydroxide addition needed for pH neutralization. The resulting dissolved sodium concentration was used to predict cesium and strontium distribution ratios for the selected adsorbent, IE-96. These R_d values were inserted into the expanded version of Eq. 2, as shown in Eq. 5.

$$R_d = \frac{\frac{Adsorbed\ Cs\ (g)}{Zeolite\ (g)}}{\frac{Residual\ Dissolved\ Cs\ (g)}{Solution\ Volume\ (mL)}} . \quad (5)$$

Next, numerical values for "Adsorbed" and "Residual Dissolved" cesium were generated from the known mass of cesium in the feed stream and a target adsorption efficiency. The required mass of zeolite was then found by solving Eq. 5. Finally, the strontium removal expected from this same charge of zeolite was calculated using Eq. 5 and the separate distribution ratio for strontium.

Table 2, which is based on one HWVP plant batch or operating cycle, summarizes the composition and volume of incoming SBS effluent and shows the projected results of neutralization and fission product adsorption.

As indicated by the Table 2 data, the sodium concentration after neutralization is 0.151 g-mol/L. The residual levels of dissolved ^{137}Cs and

Table 2. Submerged Bed Scrubber Liquid Effluent - Before and After Zeolite Contacting.

Constituent	Untreated SBS liquid (g)	Neutralized SBS liquid with zeolite (g)
Suspended solids:		
TRU	4.5	4.5
IE-96	--	82,606
Adsorbed Cs	-- 646.3	
Adsorbed Sr	-- 16.0	
Other	19,132	19,132
Total	19,136	102,405
Dissolved solids:		
Cs+	694.9	48.6
Sr++	19.1	3.1
Na+	2,625	35,262
HNO_3	59,778	--
NO_3^-	--	58,809
H_2SO_4	23,105	--
$SO_4^=$	--	22,626
Other	12,974	12,974
Total	99,196	129,720
Water	7.822 E+06	1.016 E+07
Total mass	7.941 E+06	1.039 E+07
Liquid phase,		
Volume	7,840 L	10,180 L
Cs-137	10,620 Ci	743.4 Ci
Sr-90	402.6 Ci	65.6 Ci

^{90}Sr are 0.073 Ci/L and 0.006 Ci/L, respectively. Substituting these values into Eq. 1 yields a composite of 0.241 Ci/L, which is well below the prescribed limit of 1.0 Ci/L.

The process liquid waste stream discharged from the plant will consist of treated SBS liquid effluent plus a much greater volume of liquids decontaminated by reevaporation. The composite ^{137}Cs/^{90}Sr concentration in this total stream, as defined by Eq. 1, will be well under 0.05 Ci/L.

REMOVAL OF SUSPENDED SOLIDS

Following zeolite contacting, high-efficiency filtration of the SBS liquid effluent (or spent equipment cleaning solution) will produce a treated waste stream containing minimal TRU and other particulates, acceptable levels of dissolved ^{137}Cs and ^{90}Sr, and soluble chemical species deemed to be undesirable for recycle to the melter feed. This stream will be combined with other decontaminated liquids to form the HWVP process liquid waste, which will be pumped to other Hanford Site facilities for further treatment and final disposal. The filtered solids will include TRU and other particulates originally captured from the melter offgas by the SBS, spent zeolite laden with adsorbed cesium and strontium, and diatomaceous earth (DE) filter aid. By using a cleanable filter, these solids can be recycled periodically to the HWVP feed preparation area and then on to the melter for incorporation into the product glass.

Based on development experience at the Hanford Site, it was determined that a pneumatic hydropulse filter would be appropriate for the remote cell application at HWVP. The specific filter configuration tested, Hypulse LSM, is a registered trademark of Mott Metallurgical Corp. As shown by Figure 1, the unit is very similar to a vertically mounted, single pass shell-and-tube heat exchanger, with the straight exchanger tubes replaced by sintered metal filter elements. These elements may be constructed of stainless steel or other corrosion-resistant materials and typically have a nominal pore size of 2 µm.

The filter operating cycle consists of precoat, filtration, and backflush steps. At the start of precoat, an aqueous slurry containing 0.3 to 0.6 wt% DE will be introduced to the bottom head of the empty filter housing. Displaced air will be vented from the top head until the filter housing is filled. Closure of the vent valve will force the incoming liquid to pass radially outward throught the porous elements. The liquid flux will be 1 gal/min-ft^2 of element area. Precoating will continue until the insides of the elements have accumulated a loading of 0.1 lb of DE (Manville Standard Super-Cel™ or equivalent) per ft^2.

™Super-Cel is a registered trademark of Manville Corporation.

Figure 1. Pilot-Scale Filtration Test Unit.

VENT

PROCESS SLURRY
INLET

BACKFLUSH
GAS INLET

FILTRATE OUTLET

PRECOAT SLURRY
INLET

BACKFLUSH
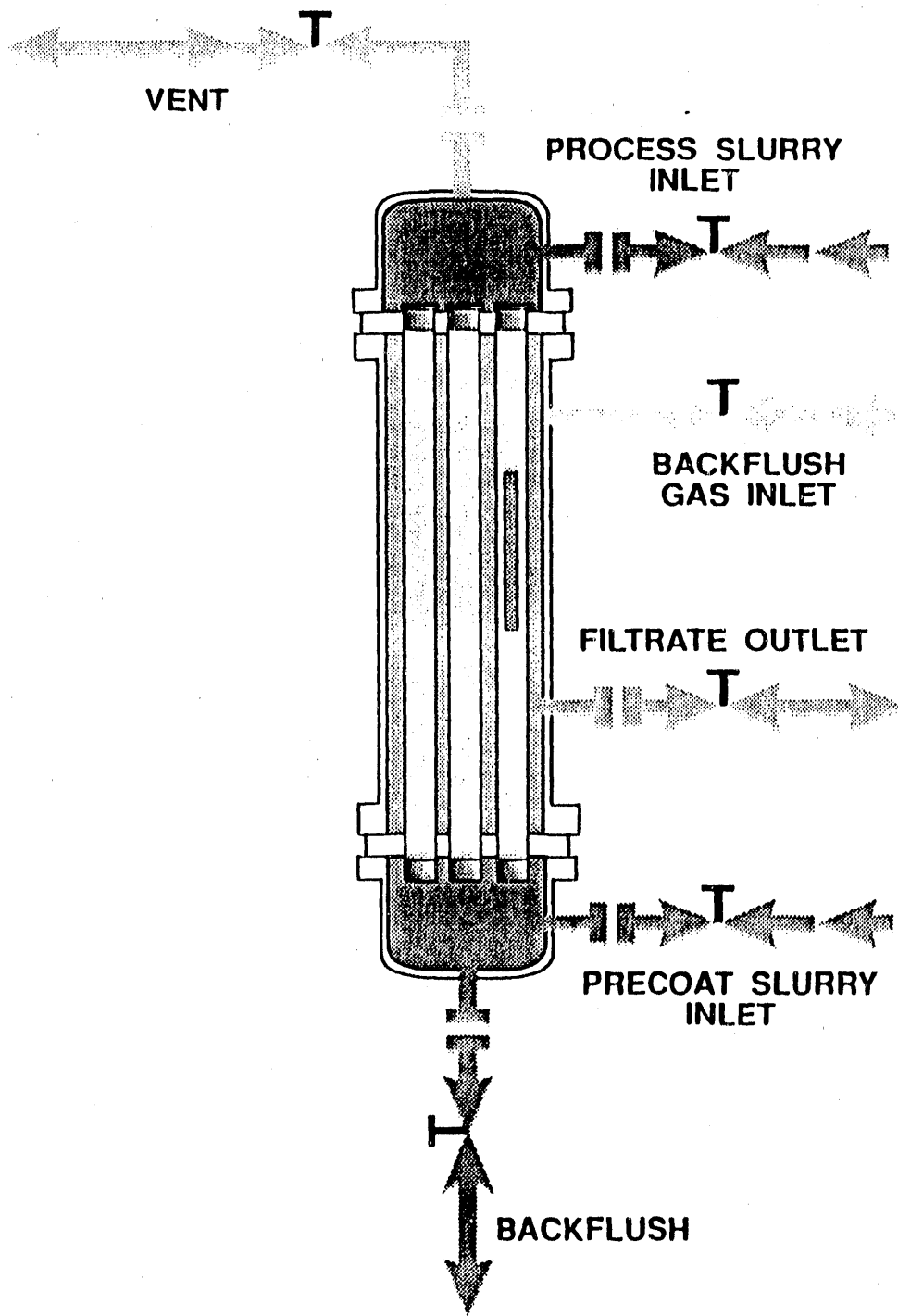
HYPULSE™ LSM FILTER
Patent pending

MOTT METALLURGICAL CORPORATION
FARMINGTON INDUSTRIAL PARK
FARMINGTON, CONNECTICUT

The precoat layer will prevent plugging of the porous media during the subsequent filtration of process slurry. The precoat filtrate from the shellside will be returned to the precoat slurry supply tank for reuse, thereby reducing the total volume of liquid waste discharged from the plant.

Upon completion of precoat, there should be a smooth transition to the filtration mode to prevent the precoat layer from sloughing off. The incoming feed slurry, containing 2 to 10 μm process solids, zeolite, and DE body feed, will enter the top head at a rate of 0.2 gal/min-ft^2 of element area. The liquid will flow downward into the elements then radially outward through the sintered metal media. Leaving the shellside of the unit as clean filtrate, this liquid will accumulate in the plant process liquid waste tanks. Meanwhile, the suspended solids will form a filter cake on top of the precoat layer. These solids may continue to accumulate until the pressure drop across the elements rises to 40 lbf/in^2. In some cases, heavy solids may settle out from the flowing liquid and collect in the bottom head, from which they will later be purged during backflush.

The appropriate concentration of DE body feed in the filter feed slurry was determined by pilot-scale tests. These tests used slurries containing 30 to 50 μm zeolite particles and 180 ppm of suspended Fe(OH)$_3$. Laboratory-scale filtration tests had previously shown that this level of Fe(OH)$_3$ provides a good simulation of the filtration behavior of the projected 1,000 ppm process solids in the actual SBS liquid. The pilot tests demonstrated that DE concentrations as low as 500 ppm yielded filtration efficiencies of 99 percent or better at low pressure drops. Without the use of DE body feed, the zeolite particles alone were not sufficient to prevent the terminal pressure drop from exceeding the desired 40 lbf/in^2 limit at the test volume throughput. Terminal solids

loadings are usually limited by the allowable differential pressure across the elements. The tests showed that the correct use of body feed permitted the projected loadings of 250 g (zeolite plus process solids)/ft^2 element area at pressure drops of only 10 lbf/in^2 or less.

When the filter pressure drop rises to its allowable maximum, the backflush step will be initiated. After making the appropriate valving changes around the filter, a pulse of high-pressure air will be admitted to the shellside of the housing. This will cause the clean filtrate to reverse flow back through the elements, thereby dislodging the precoat layer and filter cake. These solids, along with all liquid contained in the housing, will be purged from the bottom head and ultimately recycled to the melter feed.

The HWVP process design calculations predict that the plant consumption of zeolite adsorbent and DE filter aid will be respectively 1 percent and 0.35 percent of the previously determined demand for glass-forming frit. As shown by Table 3, the chemical compositions of Ionsiv IE-96 and Manville Standard Super-Cel are very close to that of frit. This will permit the recycle of spent zeolite and DE to reduce glass frit consumption by a corresponding amount. Thus, the radionuclides recovered by means of adsorption and filtration can be incorporated into the plant product glass without altering its chemical composition or total volume.

CONCLUSION

Laboratory- and pilot-scale tests using simulated HWVP process streams have confirmed that fission product adsorption followed by high-efficiency filtration will achieve a more than adequate degree of liquid waste decontamination. This technique can be used in place of reevaporation in situations requiring

Table 3. Chemical Compositions of Glass Frit, Zeolite, and Diatomaceous Earth.

Component	HWVP glass frit (wt%)	Zeolite Ionsiv IE-96 (wt%)	Manville Standard Super-Cel (wt%)
SiO_2	70.0	<65	91.1
B_2O_3	14.0	--	--
Na_2O	9.0	<10	1.1*
Li_2O	5.0	--	--
CaO	1.0	<5	0.5
MgO	1.0	<5	0.6
Al_2O_3	--	<20	4.0
Fe_2O_3	--	<5	1.3
K_2O	--	<5	--
TiO_2	--	--	0.2
P_2O_5	--	--	0.2
Quartz	--	<4	--

*$Na_2O + K_2O$

the purge of water-soluble chemical species from a process recycle loop. The spent adsorbent and powdered filter aid are suitable for incorporation into a borosilicate glass matrix, substituting for a small portion of the glass-forming frit.

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