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CESIUM ION EXCHANGE PROGRAM AT THE HANFORD RIVER PROTECTION PROJECT WASTE TREATMENT PLANT

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ABSTRACT

The Hanford Waste Treatment and Immobilization Plant (WTP) will use cesium ion exchange to remove Cs-137 from Low Activity Waste (LAW) down to a maximum activity of 0.3 Ci/m^3 in the Immobilized LAW (ILAW) product. The WTP Project baseline for cesium ion exchange is the elutable SuperLig® 644 (SL-644) resin (registered trademark of IBC Advanced Technologies, Inc., American Fork, UT) or a U. S. Department of Energy (DOE) approved equivalent. SL-644 is solely available through IBC Advanced Technologies. The WTP Project is conducting a three-stage process for selecting and qualifying an alternative ion exchange resin. Resorcinol formaldehyde (RF) is being pursued as a potential alternative to SL-644, to provide a backup resin supply. Resin cost relative to SL-644 is a primary driver.

Phase I of the testing plan examined the viability of RF resin and recommended that a spherical form of RF resin be examined further. Phases II and III, now underway, include batch testing to determine the isotherm of this resin, kinetics to address the impacts of bead diameter and high sodium feed levels on processing Hanford waste with the resin, and multicycle column testing to determine how temperature and chemical cycling affects waste processing. Phases II and III also examine resin performance against simulated WTP feeds, radiolytic and thermal stability, and scale-up to pilot scale performance. We will discuss early results obtained from Phase II testing here.

INTRODUCTION

The baseline cesium removal technology for the RPP-WTP is ion exchange (IX) using SuperLig® 644 (SL-644) resin. Figure 1 shows a summary flowsheet for the plant. The cesium ion exchange unit is designed to remove trace cesium from 5 M sodium caustic salt solution feed. After each cycle the resin is washed with dilute caustic and water, and then eluted with 0.5 M nitric acid. After acid is displaced with water the resin is regenerated to the sodium form before the next loading cycle.

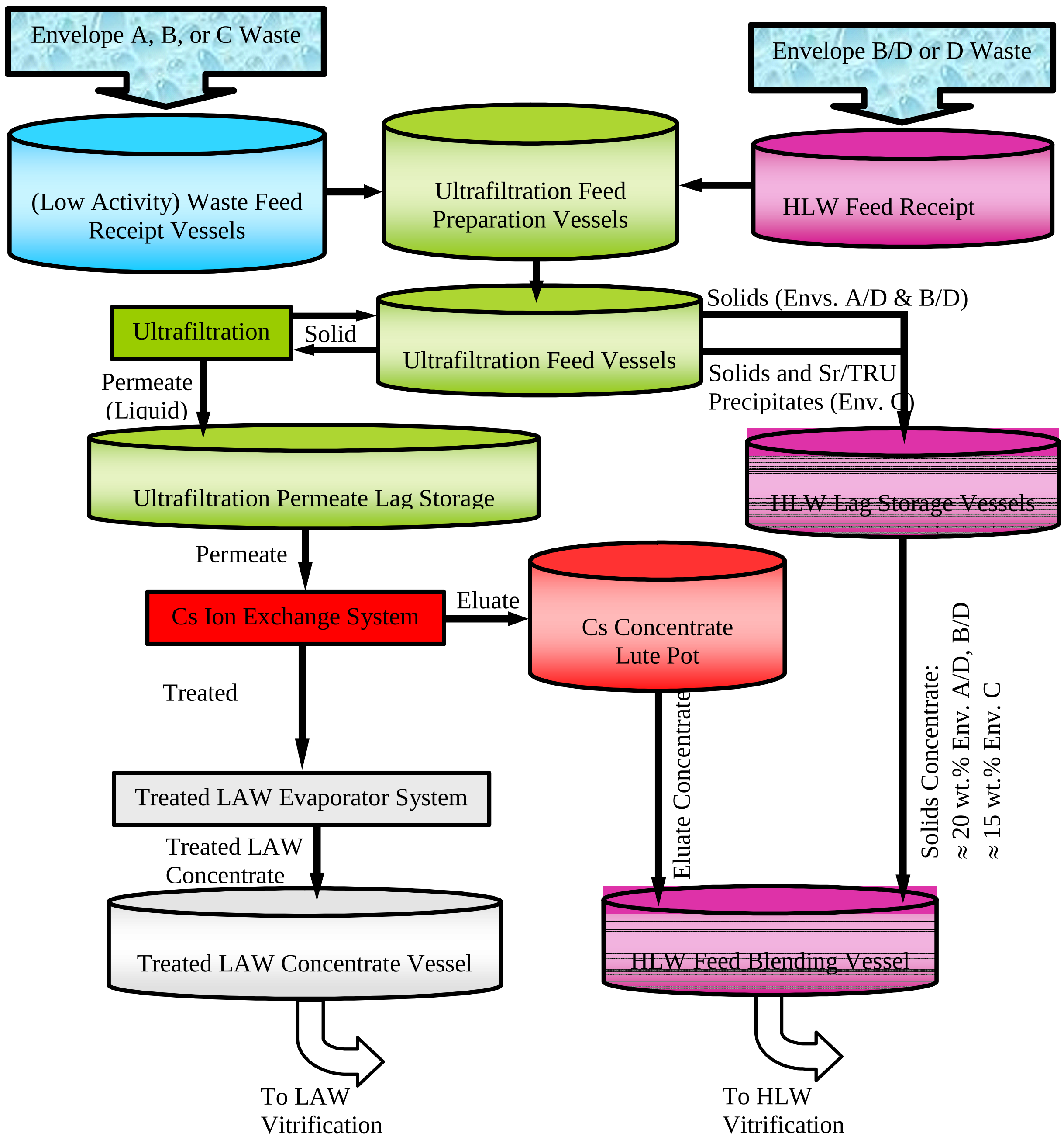

Fig. 1. Flow diagram for Hanford WTP pretreatment unit operations

RPP-WTP has completed a program that addressed the following issues with SL-644.

- Ability to meet design basis throughput and operating requirements for treatment of low activity waste (LAW) to remove Cs-137.
- Demonstrate scale-up of the ion exchange process for treatment of LAW.
- Demonstration of ion exchange resin chemical and radiological durabilities and gas generation rate.

- Demonstrate scale-up of the resin manufacturing process and determine batch-to-batch consistency requirements.
- Ability to handle secondary waste streams.
- Ability to meet design basis operability requirements for treatment of LAW using IX.
- Determine the effect of separable organics on process performance and fate of organics in the system.

The WTP Project is proceeding with a program to determine whether RF resin will meet WTP requirements. RF resin could cost less to procure than SL-644 in addition to providing a backup technology. The project is pursuing a spherical form of the RF resin.

The resorcinol-formaldehyde ion exchange resin was first developed at Savannah River National Laboratory (SRNL) in the 1980’s to remove cesium from alkaline high-level radioactive liquid waste [1,2]. It has been manufactured commercially and also studied by many DOE programs since then [3]. Past forms of RF cesium IX resin have always been alkaline polymerized ground gel (GG); particles are irregular shards obtained from crushing and sieving larger pieces produced after the polymer is cured. Figure 2 shows the hydrogen form of the resin. The sodium form is much darker in color relative to hydrogen form.

Fig. 2. Ground gel resorcinol-formaldehyde resin

An acid polymerized spherical-bead form of RF resin is now available [4] and is being evaluated because of its good kinetics and because its uniform, spherical particle size improves hydraulic performance. Figure 3 shows the spherical RF product typical of the patented process [4] and typical of resin tested in Phase I.

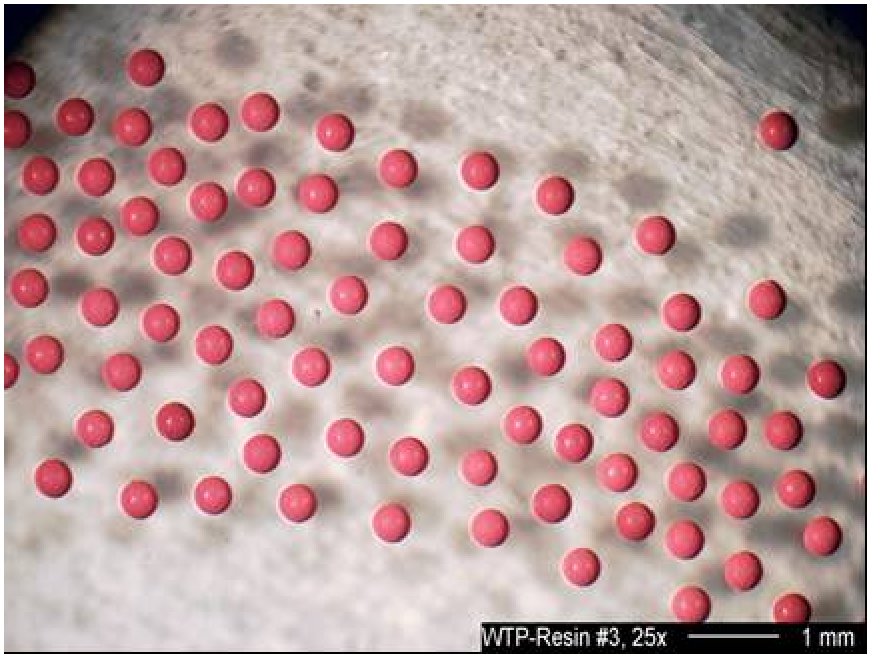

Fig. 3. Spherical resorcinol-formaldehyde resin

RESIN PROPERTIES

Operability and scale-up of the ion exchange process require consideration of the resin hydraulic behavior. Both SL-644 and RF resins shrink and swell significantly when cycled between the acidic and basic conditions used to operate an ion exchange column. We have found that with a SL-644 resin bed upflow after elution is required to maintain hydraulic performance [5]. Table I compares some hydraulic properties for the three resins [6,7]. Size reduction is affected by fines generation when the resin shrinks (from 0.5 M nitric acid exposure) and swells (from unconstrained swelling caused by 1 M NaOH). The spherical form of RF generates the least fines.

Bed compression was measured in a 5-cm diameter column with a bed height to diameter ratio of *h/D* = 2.7. The bed was compressed to 20 psig under static conditions and the bed height was measured. Spherical resin compressed the least of the three resins tested and also showed the least volume change between the acid (shrunken) and sodium (swollen) states.

Skeletal density is the effective density of the resin solids and indicates whether the bed will float. Since waste feeds with specific gravity larger than 1.3 are not expected [8], floating is not expected to be a problem for RF resin beds. Floating was never found to be a problem with SL-644.

Table I. Comparison of Hydraulic Performance

	Spherical RF	GG RF	SL-644
Volume weighted size reduction in 4 cycles	499 to 491 micron (2%) (2% to 5% broken spheres)	670 to 600 micron (**10%**)	770 to 620 micron (**20%**)
Bed Compression at 20 psi	0.5%	3%	**15%** (20 to 70 mesh)
% Swell (acidic to basic)	~33% swell	~41% swell	~53% swell
Skeletal Density, g/ml	1.58 to 1.63		1.4 to 1.5

Various measures of cesium removal performance are shown in Table II. The column distribution coefficient is the number of column bed volumes (BV) to 50% cesium breakthrough. All waste feeds were caustic, 5 M sodium solutions simulating supernates from Hanford waste tanks. The supernate from Tank 241-AZ-102 has a relatively low potassium concentration (0.15 M), while wastes from Tanks 241-AW-101 and 241-AP-101 have concentrations of 0.46 and 0.71 M, respectively. Potassium is a competitor for cesium exchange in the resin, negatively impacting cesium removal and resin selectivity and reducing the number of bed volumes to breakthrough.

Table II. Cesium Removal and Resin Consumption

	Spherical RF	GG RF	SL644
Column distribution coef. AZ-102 / AW-101 / AP-101	130 BV in AZ-102/na/na	170 BV / ~210 BV @ 3BV/hr & 280/ 180 BV	185 BV / ~220BV @ 0.7 BV/hr & 275 / ~190BV
Relative Kinetics (% of equilibrium concentration reached in 1 hr, at given particle diameter)	62% (490 +/- 60 micron)	59% (620 +/- 180 micron)	52% (840 to 420 micron)
K_d degradation **	0 (+/-5)% in 4+ cycles	na	~40% in 25 cycles
Radiation stability	na	~10% capacity reduction at 10^8 rad	~60% capacity reduction at 10^8 rad
Estimate of # cycles to disposal	25	6 to 15 attrition limits	5 to 10 attrition limits

Table II continued

	Spherical RF	GG RF	SL644
Estimate of gallons of resin used for Phase I tank processing	10,000	20,000	20,000
Degradation in storage	4 (+/-4)% in ~3 months in use	<50% in ~10 years stored in dry Na-form	Best submerged in Na-form ~15% in 6 mo.

“na” entries in Table II indicate data not available
* Extensive testing with AP-101 simulating solution is planned in Phase II
** A 25-cycle column test in Phase II is planned for mid-2005 and is not complete

Relative kinetics is the percent approach to cesium equilibrium after one hour. While the spherical resin had the least capacity in the AZ-102 column comparison it had faster kinetics than the other resins.

The cesium isotherm for spherical RF resin was determined and compared with the baseline SL-644 resin [9]. Both resins were tested under identical conditions using a 5 M sodium solution simulating the composition of Hanford Tank 241-AN-105. Cesium is present at concentrations which are several orders of magnitude lower than sodium. Since sodium and potassium ions compete with cesium for sorption sites on the resin, cesium removal requires very high selectivity. The cesium sorption isotherms are provided in Figure 4. It is apparent from the maximum loading values that the total cesium capacities of the two resins are similar (0.49 and 0.54 mmol Cs^+/g dry resin for RF and SL-644, respectively). However, the selectivity of the SL-644 resin for cesium over sodium and potassium is considerably better than spherical RF, as indicated by the shapes of the two loading curves. This selectivity difference is detrimental when processing waste supernates with high potassium concentrations.

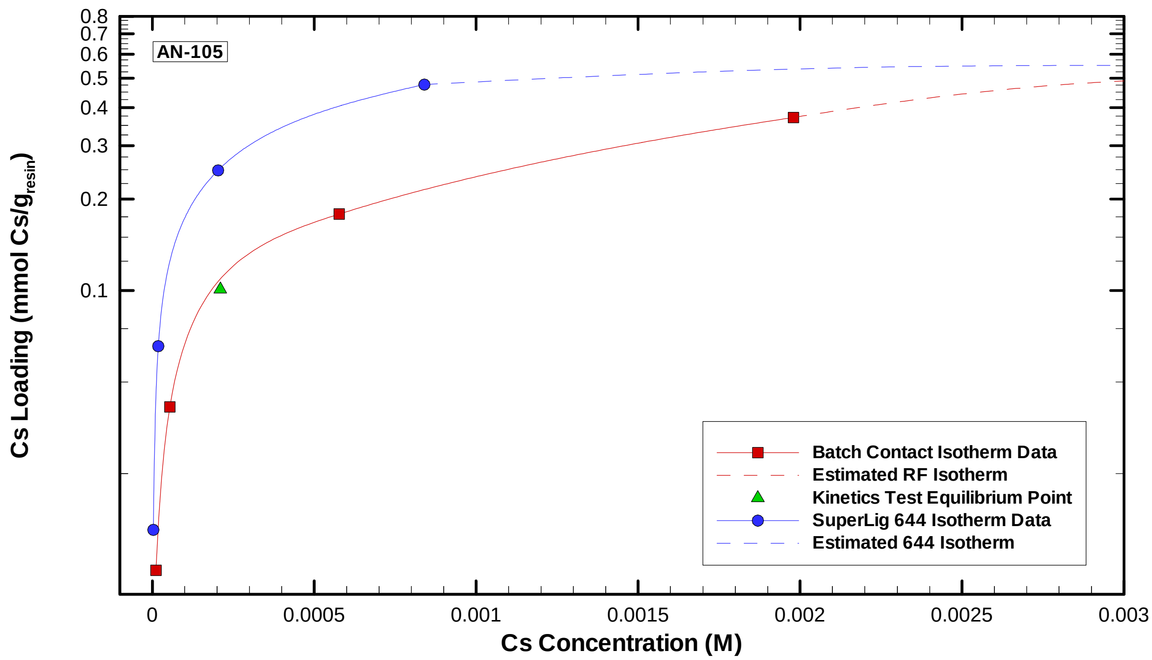

Fig. 4. Cesium sorption isotherms for spherical RF and granular Superlig® 644 resins with Hanford Tank 241-AN-105 simulant

CONCLUSIONS

RF ion exchange resin appears to be a viable alternative to SL-644. The cesium ion exchange column capacity displayed by ground gel RF is comparable to that of SL-644. And it is more stable in a radiation field than SL-644. Spherical RF resin is not as cesium-selective as ground gel RF or SL-644, but its kinetics and chemical degradation during cycling and storage are better. Increased resin stability leads to longer bed life (number of cycles) so less resin must be disposed of, saving operational as well as disposal costs. The spherical RF is also attractive because bench hydraulic experiments indicate lower generation of fines, less resin swelling, and lower bed compression. The behavior of monodisperse spherical particles should have more predictable hydraulic properties than the irregular shaped ground particle resins.

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