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

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ABSTRACT

The River Protection Project – Hanford Tank Waste Treatment and Immobilization Plant (RPP-WTP) will use cesium ion exchange to remove ^{137}Cs from Low Activity Waste (LAW) down to 0.3 Ci/m^3 in the Immobilized LAW (ILAW) product. The 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 the Department of Energy (DOE) approved equivalent. SL-644 is solely available through IBC Advanced Technologies. To provide an alternative to this sole-source resin supply, the RPP-WTP initiated a three-stage process for selection and qualification of an alternative ion exchange resin for cesium removal in the RPP-WTP. It was recommended that resorcinol formaldehyde (RF) be pursued as a potential alternative to SL-644.

The first stage of the testing plan was completed using a spherical form of RF resin that provided the best combination of characteristics required for WTP operations. Testing of RF ground gel (GG) resin was included. Based on these results, the RPP-WTP initiated testing designed to qualify resorcinol-formaldehyde resin for cold commissioning in the WTP. The work includes batch testing to support determination of the isotherm of this resin, kinetics to address bead diameter and high sodium feed levels, multicycle column testing to determine temperature and chemical cycling effects, and spent resin analysis.

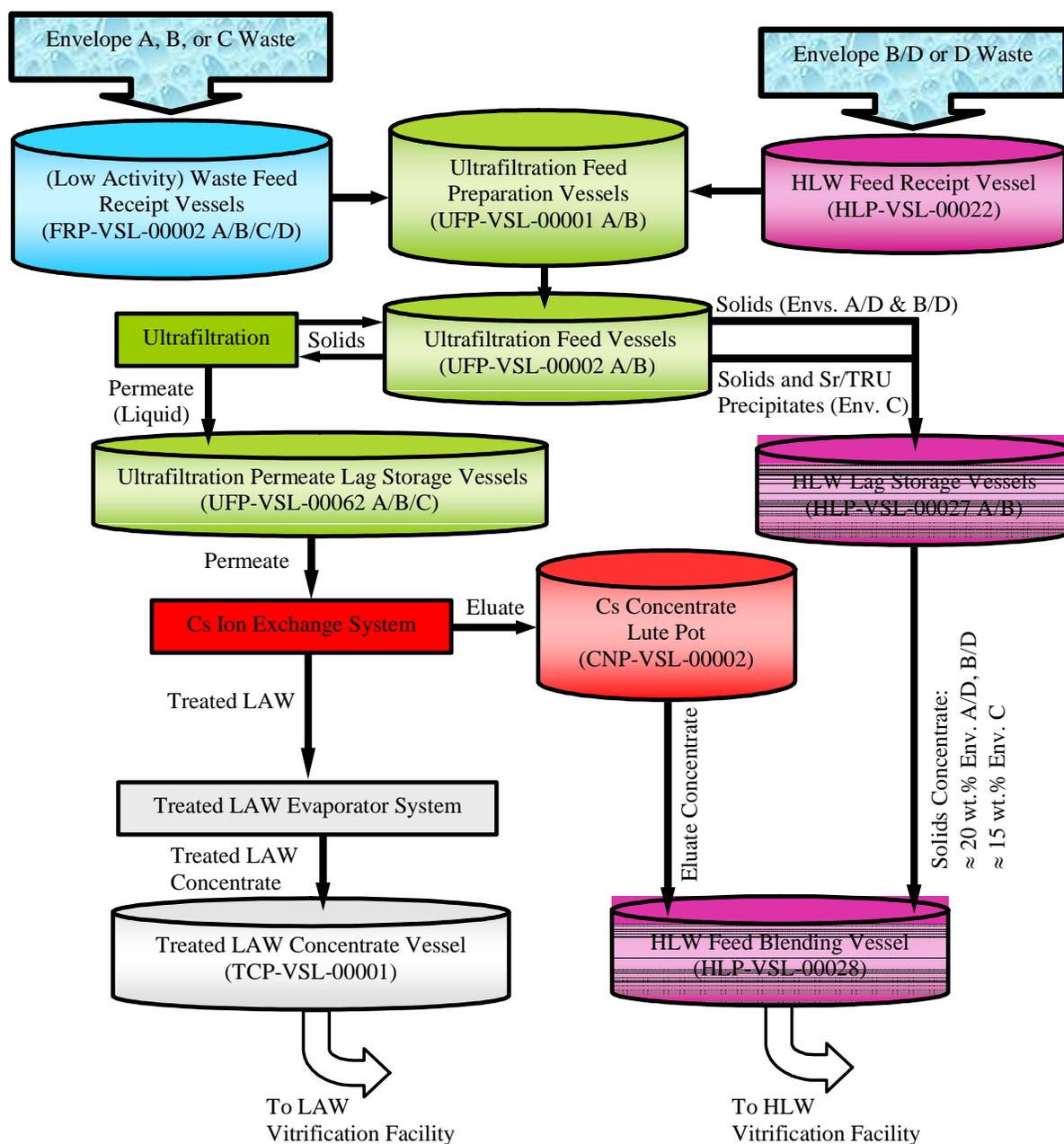
INTRODUCTION

The baseline cesium removal technology for the RPP-WTP is ion exchange 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 sodium form before the next loading cycle. The RPP project has completed a program to address the following issues with SL-644.

- Ability to meet design basis throughput and operating requirements for treatment of low activity waste (LAW) to remove ^{137}Cs .
- 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 ion exchange.
- Determine the effect of separable organics on process performance and fate of organics in system.

Figure 1. Flow Diagram for Hanford WTP Pretreatment Unit Operations



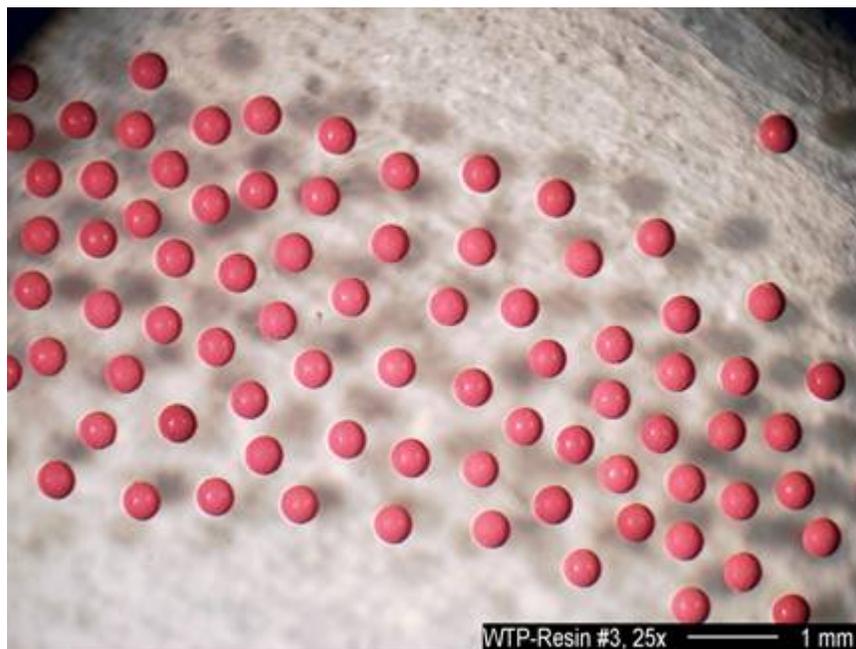
The RPP project is proceeding with a program to determine whether RF resin will meet WTP requirements. RF resin could cost less to procure than SL-644 in addition to providing a backup technology. The project is working on a spherical form of the RF resin.

Resorcinol-formaldehyde ion exchange resin was first developed at Savannah River National Laboratory (SRNL) in the 1980's for cesium removal from alkaline high-level waste [1,2]. It has been manufactured on the commercial scale and has been studied in many DOE programs since then [3]. Past forms of RF resin have always been ground gel (GG). Particles are irregular shards and are obtained from crushing and sieving larger pieces that are produced in the cure of the polymer. Figure 2 shows hydrogen-form resin. The sodium form has a much darker color.

Figure 2. Ground Gel Resorcinol-Formaldehyde Resin



A spherical-bead form [4] of the resin is now available 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 that tested in Phase I.

Figure 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 are known to shrink and swell significantly when cycled between acid and base conditions. SL-644 had been found to require a bed upflow strategy after elution to maintain good hydraulic performance [4]. Table I shows a resin comparison including data on RF forms obtained in Phase I [5,6]. 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 obtained in a 5-cm diameter column with a bed height to diameter ratio of $h/D = 2.7$. Fluid flow at 20 psi pressure drop was used to compress the bed. 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 determines if there is a problem with floating. Since feeds are not expected to exceed a specific gravity of 1.3 [7], RF resin floating is not expected to be a problem.

Table I. Comparison of Hydraulic Performance

	Spherical RF	GG RF	SL-644
Volume weighed 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 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 removal, negatively impacting resin selectivity and reducing the number of bed volumes to breakthrough.

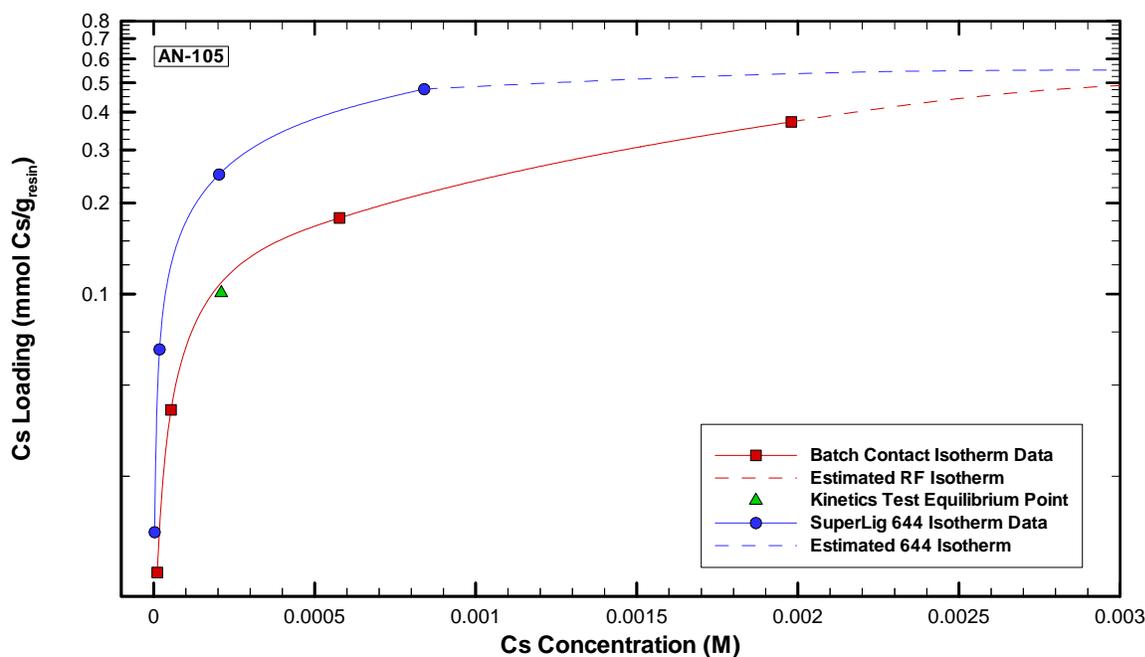
Table II. Cesium Removal and Resin Consumption

	Spherical RF	GG RF	SL644
Column distribution coef. AZ-102 / AW-101 / AP-101	130 BV in AZ-102	170 BV / ~210 BV @ 3BV/hr & 280/180 BV	185 BV / ~220BV @ 0.7 BV/hr & 275 / ~190BV
Relative Kinetics (% final in 1 hr, at given particle diameter)	62% (490 +/- 60 micron)	59% (620 +/- 180 micron)	52% (20 to 40 mesh)
K_d degradation	0 (+/-5)% in 4+ cycles		~40% in 25 cycles
Radiation stability		~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
Estimate gallons of resin 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.

Relative kinetics is the percent approach to cesium equilibrium in 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 the spherical form of RF resin has been determined and compared to the performance of the baseline SL-644 resin [8]. Both resins were tested under identical conditions using a 5 M sodium solution simulating the composition of Hanford Tank 241-AN-105. Cesium is typically 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 most problematic when processing waste supernates with high potassium concentrations.

Figure 4. Cesium Sorption Isotherms for Spherical RF and Granular Superlig® 644 Resins with Hanford Tank 241-AN-105 Simulant



CONCLUSIONS

Resorcinol-formaldehyde ion exchange resin appears to be a viable alternative technology to SL-644. Ground gel RF displays ion exchange column capacities for cesium that are comparable to those of SL-644. It is more stable in a radiation field relative to SL-644. Spherical RF is not as cesium-selective as ground gel RF or SL-644, but its kinetics and chemical degradation during cycling and storage are better. The greater in-column stability leads to longer bed life in terms of number of cycles before resin disposal. This provides operational as well as disposal savings. It is also attractive because bench hydraulic experiments indicate less fines generation and swelling, and less compression. The very monodisperse spherical shape of the particles should provide good hydraulic predictability over that of irregular ground particle resins. The RF program is planned to continue through 2005 so that a recommendation on WTP startup resin is to be made in 1Q 2006.

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