WSRC-MS-2003-00110

Hanford Sr/TRU Decontamination Program: Research from Beaker to Pilot Scale

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Introduction

Plutonium and americium are present in the Hanford High Level Liquid Waste complexant concentrate (CC) waste due to the presence of complexing agents including di-(2-ethylhexyl) phosphoric acid (D_2EHPA), tributylphosphate (TBP), hydroxyethylene diamine triacetic acid (HEDTA), ethylene diamine tetraacetic acid (EDTA), citric acid, glycolic acid, and sodium gluconate.[1] The transuranic (TRU) concentrations approach 600 nCi/g and require processing prior to encapsulation into low activity glass. The Savannah River Technology Center (SRTC) has been actively participating in the development of a strontium/TRU decontamination process for the CC waste stored at Hanford in Tanks AN-107 and AN-102.[2,3,4,5] The current baseline flowsheet involves the addition of strontium nitrate to effectively remove radio-strontium through an isotopic dilution, followed by a sodium permanganate strike to co-precipitate the actinides in the *in-situ* produced manganese solid phases. Demonstration efforts to validate the Sr/TRU flowsheet have included beaker scale reagent optimization and reaction kinetics testing and engineering scale-up experiments at the multi-liter and 1/100th plant scale (200-gallon) using both simulated and actual waste samples. Several key process engineering and process chemistry needs were identified during a recent Hanford Waste Treatment Plant project risk review.[6]

Description

Testing on the laboratory scale (beaker scale) was performed by adding the precipitating agents to 50 mL of actinide-spiked simulant that had been adjusted to 6 M sodium ion concentration while being heated for 4 h at 50° C. The samples were allowed to cool and aliquots were filtered through a 0.45-micron filter. Samples were submitted for analysis following an additional filtration using a 0.1-micron filter. Simulant multi-liter scale tests (~50 gallons) were performed in 55-gallon drums and filtered using a cross-flow filter unit (the Cells Unit Filter or CUF). The CUF utilizes a 0.1 micron sintered metal filter with a 24-inch length and 3/8-inch diameter. The 1/100th scale facility included a 250-gallon reaction tank and a 150-gallon slurry hold tank. A mechanical agitator and four vertical baffles were used to ensure vigorous agitation for suspension of entrained solids in the sample and to provide thorough slurry mixing. Heating of the waste simulants was performed using a 208V electric heater in a re-circulating loop. Either a 40-inch by 0.5-inch or 90-inch by 0.5-inch seven element cross-flow filter bundle with a nominal porous rating of 0.1 microns was used to process the precipitated simulant batches. Particle size analysis was conducted using a Lasentec M400L chord length analyzer. The method is based on the detection of backscattered laser intensity (Focused Beam Reflectance Measurements - FBRM) from individual particles suspended in the process solution.

Results

Small-scale testing at SRTC centered focused on defining the minimum reagent additions required to meet process requirements for strontium, plutonium and americium using actual tank wastes and waste simulants. Americium-241 is the transuranic limiting isotope. Table 1 lists two flowsheet cases that have received extensive testing. The baseline flowsheet was demonstrated originally using actual radioactive waste from Tank AN-102 and the required Sr/TRU decontamination factors were met (see Table 1). Results with samples from Tank AN-107 revealed that americium and plutonium decontamination factors were far exceeded. Attempts to reduce reagent additions decontamination for Tank AN-107 waste simulant provided the optimal conditions (OC) for actinide removal with this sample. However, the optimized flowsheet failed when applied to an actual waste sample from Tank AN-102.

One interesting aspect of the work has been examining the kinetics of particle growth and strontium and actinide decontamination. Figure 1 shows the initial results for kinetics studies of the removal of radio-strontium and americium-241 from a Hanford CC waste simulant. The decontamination was accomplished well within the facility-imposed 4 hour duration. However, the particle growth kinetics (as indicated by total counts measured by FBRM), also shown in Figure 1, reveals that the formation of strontium particles upon addition of strontium nitrate solution and manganese oxide particles upon addition of sodium permanganate solution are complete in minutes. Unfortunately the time scale of the decontamination kinetics experiment was much longer. Most likely the decontamination occurs during the particle growth stages.

Following a disciplined approach, research into the decontamination of the Hanford CC waste focused next on the multi-liter (15 L to 200 L) scale. Program objectives were to establish the behavior of the surrogate slurry while measuring actinide decontamination through the use of lanthanide surrogates. Utilizing actual waste-generated correlation,[7] the decontamination factors obtained for the lanthanides indicated that, had americium and plutonium been present, both the baseline and optimized flowsheet would have produced decontaminated filtrate meeting the design requirements.

The slurry behavior with regards to cross-flow filtration is of utmost importance due to anticipated filter fluxes in the plant operation. Shown in Figure 2 are the crossflow filtration fluxes produced during various simulant and actual waste flowsheet tests. Three multi-liter lab-scale test results are shown where filtration was accomplished using the CUF filter. The results show very good agreement between the filtration run with waste simulant and actual CC tank waste. Filter fluxes rapidly decrease as the filter cake builds and the insoluble solids loading increases in the slurry. However, the time-averaged filter flux exceeded the design target of 0.01 gpm/ft^2. The third multi-liter filtration experiment utilized the reagent Optimized Conditions (OC). In general the filter fluxes agreed with the baseline results, although at higher solids loading the performance was lower compared to the baseline. These chemical and physical property results strongly suggested that either flowsheet would successfully remove the radio-strontium and actinide constituents of the Hanford CC waste.

Also included in Figure 2 are two sets of results from filtering the Sr/TRU precipitate slurry in the $1/100^{th}$ scale pilot facility. The conditions were the baseline and optimized conditions. A disappointing result was obtained at the pilot scale when the experiment was conducted under the reagent-optimized conditions (OC). In this experiment the filtration flux started at a very low value (0.055 gpm/ft^2) and rapidly dropped. Several studies examined the cause of the poor filtration performance. In hindsight, the multi-liter experiment under the same reaction conditions showed filtration results about 20 – 30% below the baseline flowsheet conditions. Previous beaker scale testing with actual tank waste from this particular tank had shown filtration rate dependence on the waste hydroxide level. This connection between beaker chemistry and pilot

scale demonstrations is very beneficial when designing full-scale facilities.

In the experiment conducted under the baseline flowsheet conditions, the slurry filtration behavior mirrored the actual and simulated waste testing at the multi-liter scale. Additionally, actinide suggorates were successfully decontaminated at all three experimental scales indicating a robust Sr/TRU decontamination flowsheet. Although further engineering is required to increase the scale to the plant environment, the strontium and actinide chemistry along with the slurry precipitate behavior strongly indicate that a successful treatment process has been developed.

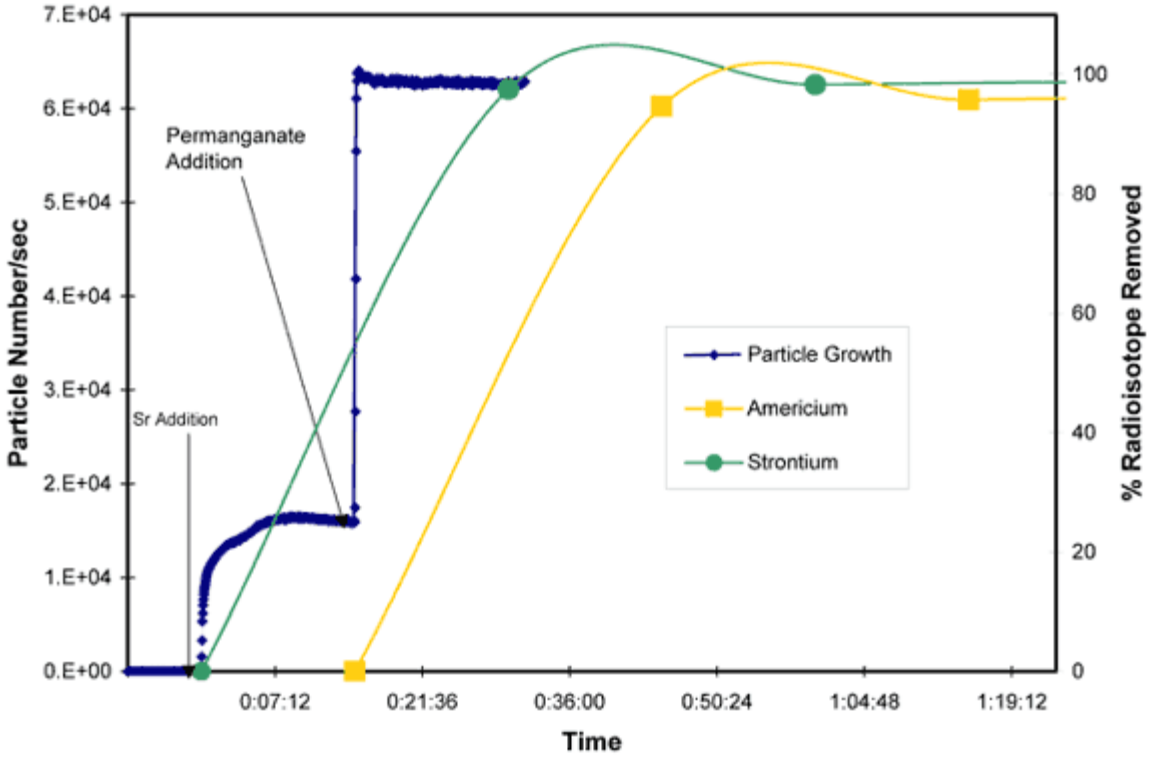

Figure 1. Particle Growth and Decontamination Kinetics

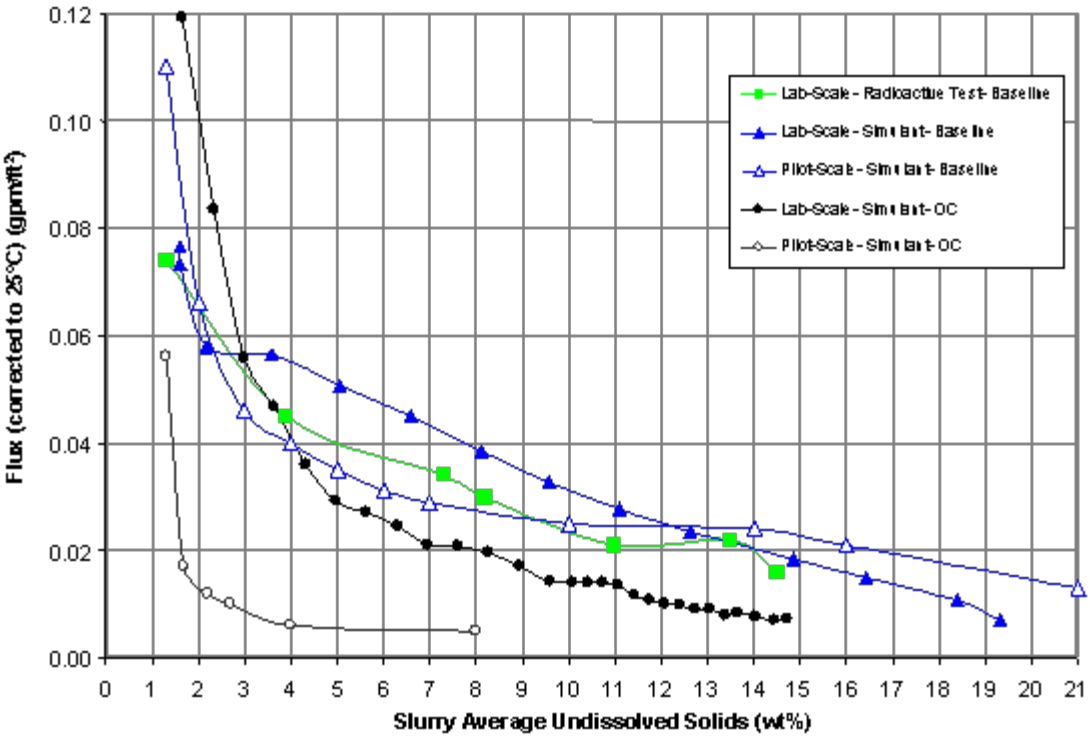

Figure 2. Crossflow Filtration Results from Various Sr/TRU Flowsheet Experiments

Table 1. Sr/TRU Decontamination Flowsheet Conditions and Decontamination Factors

Flowsheet Treatment Conditions				
	Temperature	Hydroxide	Strontium	Permanganate
Baseline	50° C	1 M	0.075 M	0.05 M
Optimized	25° C	No Added	0.03 M	0.03 M

Decontamination Factors			
	Strontium AN-107 (102)	Americium AN-107 (102)	Plutonium AN-107 (102)
Baseline	100 (65)	45 (5.9)	5 (2.1)
Optimized	7 (30)	3.1 (4.3)	3.4 (3.5)
Target	30	5	2

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