Characterization of the Tank 41H Saltcake Insoluble Solids

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SUMMARY
The particle sizes of the insoluble solids from two of the Tank 41H saltcake samples have been determined by scanning electron microscopy. Settling velocities of the solids have been calculated using Stokes' Law. Based on these settling velocities, it is concluded that uranium cannot be segregated from the bulk of the insoluble solids during salt dissolution operations by gravity settling. Selective dissolution of uranium and neutron absorbers (e.g., Cr, Fe, Mn, and Zn) was not observed upon contacting the insoluble solids briefly with 0.015M NaOH solution and for six days with deionized, distilled water. Thus, it is concluded that the formation of a solid phase consisting of uranium without significant amounts of Cr, Fe, Mn, and Zn is not possible during the dissolution of saltcake.

INTRODUCTION
Dissolution of saltcake stored in Tank 41H is scheduled to be initiated during FY95. The resulting salt solution will be transferred to In-Tank Precipitation (ITP) for waste processing. A total of four saltcake samples have been taken from the top of the tank and analyzed for chemical and radiochemical content. Approximately 1 wt % of the samples were determined to be comprised of solids that do not readily dissolve in inhibited water (0.015M NaOH) [1,2]. Although the solids contain fissile isotopes of uranium and plutonium, the concentration of fissile material is well below that to be of concern for nuclear criticality safety. However, during a safety review of salt dissolution, questions arose concerning the possibility of the fissile material separating from the bulk of the insoluble solids and accumulating in a separate layer in the tank. Therefore, samples of the insoluble solids from the saltcake samples were isolated and characterized by Scanning Electron Microscopy (SEM) to determine the particle sizes and distribution of uranium. Settling velocities were then calculated based on the measured particle sizes. The insoluble solids were also contacted for 3-6 days with deionized, distilled water to determine if significant changes in the particle size, uranium and other neutron absorbers content would occur upon prolonged contact with unsaturated aqueous solution.

EXPERIMENTAL

Sufficient material from Tank 41H saltcake samples #2-1 and #2-3 were available for characterization. A measured quantity of saltcake from each sample was placed in a glass centrifuge tube in the Shielded Cells of 773-A. Twenty-five milliliters of 0.015M sodium hydroxide solution (inhibited water) was added to each sample to dissolve the water-soluble solids. After dissolution was judged to be complete by visual observation that no further dissolution of solids was occurring, the tubes were centrifuged for 30 minutes. The clear solution was decanted from the undissolved solids and placed in a clean polyethylene bottle. The solids were rinsed with three 10 mL portions of inhibited water. After each rinse, the tubes were centrifuged for 30 minutes, and the rinse water decanted from the undissolved solids. A fourth rinse was performed on the #2-1 sample because of the larger solids content. The final rinse solution from each sample was submitted for uranium and elemental analyses.

The undissolved solids were transferred to a radiohood in laboratory module B-126/130. Each sample was suspended in 2 mL of deionized, distilled water (pH=5.6). Small portions of the suspended solids were placed on lens paper and allowed to air dry. SEM mounts containing double-sided tape were contacted with the dry solids to transfer solids onto the mount. The mounts were transferred to the SEM laboratory and analyzed. Two mounts were prepared for each sample. After three days, a second set of mounts were prepared as described above. The objective of preparing the second set of mounts was to determine if soaking the solids in deionized, distilled water would result in significant changes to the particle size and distribution of uranium. After 6 days, the deionized, distilled water was decanted from the undissolved solids and submitted for uranium analysis by kinetic phosphorescence spectroscopy and elemental analysis by inductively-coupled plasma emission spectroscopy.

RESULTS AND DISCUSSION

SEM Results

1. General Particle Morphology, Elemental Composition, and Size Characteristics

The bulk of the insoluble solids were observed to be comprised of irregular-shaped solids from 1 to 10 μm in diameter. A small fraction of particles having spherical, rectangular, and hexagonal shapes were also observed. The larger rectangular particles, 15-200 μm in diameter, were thin.

Elements identified in the solids included: Cr, Fe, Al, Si, Na, Ca, Zn, P, and U. These elements are consistent with previous results from inductively-coupled plasma emission spectroscopy and inductively-coupled plasma mass spectrometry [1,2]. Micrographs of the solids after soaking in the deionized, distilled water for three days did not indicate any significant changes in the particle size, morphology or elemental composition.

2. Particle Size Measurements

Particle diameters were measured from the micrographs obtained for each of the samples. Table I gives the average particle diameter as well as the smallest and largest diameters for each sample. The majority of the solids particles are comprised of particles ranging in diameter from about 1 μm to 10 μm. Both samples contained a small number of larger particles ranging in diameter from 14 μm to 91 μm (number average of 43 μm) for sample #2-1 and 18 μm to 190 μm (number average of 96 μm) for sample #2-3. A small number of particles containing uranium were also detected. The number average particle diameter of these particles was determined to be 6.6 μm for sample #2-1 and 4.9 μm for #2-3. The uranium-rich particles ranged in diameter from 1.4 to 12 μm.

Table I. Average Particle Sizes for the Tank 41H Saltcake Insoluble Solids

		Particle Diameter (μm)		
Sample ID	ADS #	Average[a]	Minimum	Maximum
#2-1	3-38820	2.9	1.2	8.5
#2-1 After Soaking	3-38821	3.6	1.5	7.9
#2-3	3-38822	2.8	0.9	9.5
#2-3 After Soaking	3-38823	2.7	0.9	9.3

[a]number average

Settling Velocities

Settling velocities in solutions of varying density and viscosity were calculated using Stokes' Law

$$V = 2g(d_s - d_l)r^2/9n$$

where V is the settling velocity in cm/sec, g is the gravitational constant (980 cm/sec^2), d_s is the particle density in g/cm^3, d_l is the solution density in g/cm^3, r is the radius of the particle in cm, and n is the viscosity of the solution in poises.

Based on the dissolution of Tank 19F salt, salt solution densities would be expected to range between 1.2 and 1.4 g/cm during the dissolution of saltcake in Tank 41H [3]. As salt dissolves, the density of the salt solution increases as does the viscosity. Karraker previously measured the viscosities (3.5-12.5 cP) of salt solutions over similar density ranges (1.28-1.42 g/cm^3), as well as the particle density for $Na_2U_2O_7$[4]. The crystalline densities of solid phases identified in the Tank 41H insoluble solids range from 1.75 to 5.7 g/cm^3[2]. Using the crystalline densities to bound the range of of particle densities for the bulk insoluble solids, a particle density of 3.93 for the uranium solids [4], the previously reported salt solution viscosities and densities [4], and the measured particle diameters from the SEM results, the settling velocities for the insoluble solids were calculated. The minimum and maximum settling velocities for the uranium-rich particles and the bulk insoluble solids in the Tank 41H saltcake samples are given in Table II.

Table II. Settling Velocities for Uranium and Bulk Solid Particles in Tank 41H Saltcake

	Settling Velocity (in/day)	
Particle Description	Minimum	Maximum
Uranium particle of average diameter	8.9	34
Uranium particle of smallest diameter	0.73	2.8
Uranium particle of largest diameter	54	200
Bulk particle of average diameter	0.38	20
Bulk particle of smallest diameter	0.040	1.9
Bulk particle of largest diameter	450	21000

For the range of uranium-rich particle diameters observed in the Tank 41H insoluble solids, the settling velocities range from 0.73 in/day to 200 in/day. For the bulk of the insoluble solids the settling velocities are calculated to range from 0.040 to 21000 in/day. The wide range is a result of primarily the wide range in particle sizes (0.9-96 μm), and to a lesser degree, the range in the particle densities (1.75-5.7 g/cm^3) and the variation in solution density (1.28-1.42 g/cm^3) and viscosity (3.5-13.3 cP). Based on the calculated settling velocities, it is concluded that segregation of the uranium-rich particles from the bulk solids is not possible by gravity settling since the settling velocities of the bulk insoluble solids bound those of the uranium particles.

Analytical Results for Rinse and Soak Solutions

The final inhibited water rinse solution and the deionized, distilled water soak solution were submitted for measurement of uranium and elemental composition. The uranium, chromium, iron, manganese, and zinc concentrations for each solution are provided in Table III.

Table III. Uranium and Neutron Absorber Concentrations in Final Rinse and Soak Solutions

	Concentration (mg/L)			
	#2-1		#2-3	
Element	Final Rinse	Soak Solution	Final Rinse	Soak Solution
U	0.082	0.18	0.038	0.18
Cr	9.87	30.4	7.95	8.84
Fe	0.82	3.38	1.07	1.88
Mn	0.038	<0.091	0.032	<0.091
Zn	0.26	1.04	3.07	3.16

The percent of total dissolved was calculated for U, Cr, Fe, Mn, and Zn in each solution along with the mole ratio of each element to that of uranium for the insoluble solids and each of the solutions. The results are provided in Table IV.

For both samples, the percent of uranium and the other elements removed in the soak solution is less than that found in the final rinse solution. This indicates that the removal of uranium and the other elements from the solids is not significantly increased although the initial pH of the solution is much lower (initial pH of soak solution is 5.6 versus a calculated pH for the rinse solution of 12.2) and the contact time increased from approximately 90 minutes to six days. The final pH of the soak solution was not measured, but would be higher than 5.6 due to the presence of residual rinse solution.

The mole ratio of the various elements to uranium are similar for both the final rinse and soak solutions. This indicates that there is not significant preferential dissolution of any of the elements over the wide range in pH. For sample #2-1, the mole ratios in the rinse and soak solutions are all higher than that determined in the insoluble solids with the exception of Mn. This indicates that these elements are removed in concentration relative to that of U in the insoluble solids. However, the extent of removal is not sufficient to significantly change the mole ratios after rinsing and soaking. For sample #2-3, the mole ratios in the rinse and soak solutions are all lower than that determined in the insoluble

solids. Thus, it is concluded that the formation of a solid phase consisting of uranium without significant amounts of Cr, Fe, Mn, and Zn is not possible during the dissolution of saltcake.

Table IV. Percent of Total Dissolved and Mole Ratio of Absorbers to Uranium

Sample #2-1

Element	Solids mol/mol U	Final Rinse Solution mol/mol U	Final Rinse Solution % Removed	Soak Solution mol/mol U	Soak Solution % Removed
Cr	420	550	1.9	770	1.1
Fe	160	430	0.38	80	0.32
Mn	2.3	2	1.22	<2.2	<0.58
Zn	71	120	0.23	210	0.19
U	1	1	1.4	1	0.62

Sample #2-3

Element	Solids mol/mol U	Final Rinse Solution mol/mol U	Final Rinse Solution % Removed	Soak Solution mol/mol U	Soak Solution % Removed
Cr	1800	960	9.9	220	2.2
Fe	3000	120	0.75	44	0.26
Mn	17	3.6	4.1	<2.2	<2.3
Zn	1200	290	4.7	64	0.97
U	1	1	19	1	18

QUALITY ASSURANCE

The handling and analysis of the samples were performed in accordance with the requirements specified in the Task and Quality Assurance Plan[5]. Due to the limited quantity of saltcake, only a single subsample of samples #2-1 and #2-3 could be analyzed. All laboratory data are recorded in laboratory notebook, WSRC-NB-93-151, maintained by D. T. Hobbs.

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