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Analyses of Surface and Variable Depth Samples from Tank 43H

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Summary

Researchers analyzed surface and variable depth samples from the feed tank, Tank 43H, for the 242-16H High Level Waste Evaporator. These analyses support the root cause analysis for the formation of solids in the 2H Evaporator Pot. Results of these analyses indicate the following:

- Silicon concentrations varied significantly over the depth of the tank reaching as high as 4 g/L near the sludge layer.
- Uranium concentrations measured near 15 mg/L in filtered and unfiltered supernate indicating the previous model of uranium solubility under predicted solubility for Tank 43H conditions.
- Modeling of solid formation reveals that the stratification of the silicon concentration in the settled tank will give rise to widely varying amounts of solids. The range of solid formation ranges from 0.03 g/L from the surface supernate to greater than 25 g/L from sludge slurry near the sludge layer assuming the silicon becomes soluble.

Introduction

The introduction of the Defense Waste Processing Facility's (DWPF) recycle water to the H-Tank Farm began in late 1996. Previous SRTC studies examined this stream for receipt with the focus on organic materials.[1] Subsequently, solids accumulated in the 242-16H Evaporator Gravity Drain Line.[2] These solids consisted of sodium aluminosilicate and sodium diuranate with the diuranate present as a minor constituent. Testing at SRTC indicated that the silicon, as frit, returning to the 242-16H Evaporator feed tank, Tank 43H, would dissolve and, under the expected high temperatures within the evaporator, convert the soluble aluminate ion to the insoluble aluminosilicate.[3]

In 1999, operational difficulties at the 242-16H Evaporator led to a video inspection of the evaporator pot during which personnel observed a large quantity of solid deposits. Sampling and chemical analysis of these deposits proved the solids as chemically identical to the solids from the Gravity Drain Line.[4] However, the amount of uranium inclusion in the aluminosilicate matrix had increased as well as the ^{235}U enrichment. This finding prompted the Concentrate, Storage, and Transfer Engineering to request that the Liquid Waste Processing group coordinate analysis of a number of surface and variable depth samples (VDS) from the 242-16H Evaporator feed tank, Tank 43H.[5]

Experimental

SRTC received the surface and variable depth (VDS) samples from the tank farms. The surface and VDS samples from the tanks entered B-block of the Shielded Cells upon receipt at SRTC. Personnel determined the density of the liquid samples by emptying the contents of the dip bottles into pre-weighed 100-mL graduated cylinders with the accuracy of the graduated cylinders verified to ± 1% at 100 mL prior to use. Personnel removed representative aliquots and diluted one-hundred fold into 0.2 M nitric acid.

Personnel placed the diluted samples in a sample bottle and removed from the shielded cell without filtering. Analytical Development Section performed the following analyses: Inductively Coupled Plasma – Mass Spectrometry,[6] Inductively Coupled Plasma – Emission Spectroscopy,[7] Gamma Spectroscopy,[8] and Alpha Pulse Height Analysis.[9]

Laboratory notebook WSRC-NB-97-64 contains data obtained during these tests and the procedures used.[10] Personnel used routine analytical protocol for the samples in this report.[11]

Results and Discussion

Sample Density and Observations

Table 1 contains the measured density and a brief description of the samples as received at SRTC. For Tank 43H, SRTC received three samples (1 surface and 2 VDS). The surface sample was taken 1/16/2000. The VDS samples were taken 2/2/2000. The density measured 1.19 g/mL for the surface sample and 1.31 and 1.39 g/mL for the VDS samples taken at 100 inches depth and at the 64 inches depth, respectively. The samples appeared clear with one very small solid particle in one of the VDS samples.

Table 1. Sample Information for Tank 43H

Tank	Sample Type	Density (g/mL)	Comments
43H	Surface	1.19	Clear
43H	VDS (100 inch) 201" from tank bottom	1.31	Clear, one piece of solid
43H	VDS (64 inches) Riser G, "3" above sludge	1.39	Thick, dark brown

Elemental Analysis

Table 2 contains the elemental analysis of the surface and variable depth samples from Tank 43H, the feed tank to the 242-16H Evaporator. The authors corrected the concentrations reported for the original 100-X dilution. Sodium ion concentration in Tank 43H measured 5.0 M for the surface samples, 8.7 M for the VDS sample at 100 inches, and 9.3 at the 64 inches height.

The aluminum and silicon concentrations indicate stratification occurs within the tank. Aluminum concentrations in the supernate samples (i.e., the surface and 100-inch depth samples) measured 3×10^3 mg/L (0.1 M) and 5×10^3 mg/L (0.2 M), respectively. The aluminum concentration in the 64 inches-level sample measured 1.35×10^4 mg/L (0.5 M). The 64-inch sample, as previously mentioned, appeared viscous and colored dark brown indicating significant sludge entrainment. The high iron content of 20 g/L substantiates this entrainment. The silicon measurements provide a better indicator of the stratification of the tank. Silicon concentrations increase from 87 mg/L (0.003 M) to 126 mg/L (0.005 M), and 4000 mg/L (0.14 M) at sample depth of surface, 100 inch and 64 inch, respectively. This sample was taken approximately 3 inches above the sludge level. Based on these measurements, one calculates K_{sp}'s (solubility product constant) for aluminosilicate formation of 3.11×10^{-4} M^2, 1×10^{-3} M^2, and 7×10^{-2} M^2 for the three sample depths in Tank 43H. Previous work for aluminum-silicon systems shows equilibrium K_{se}'s are on the order of 10^{-4} M^2; therefore, tank data indicates that equilibrium does not exist below 100 inches in Tank 43H.

Potential Solids Formation

Gasteiger et al.[12] indicated that solubility product for the aluminosilicate satisfies the following proportionality

$$K_{sp} \propto \frac{(OH^-)^3}{(I)^{1.666}}$$

with I representing the ionic strength.

They also indicated that the K_{sp} for a 1 M NaOH solution measured approximately 1.5×10^{-4} M^2. With this information, one may estimate the K_{sp} under a variety of tank conditions. Given the aluminum concentration in solution, one can estimate the soluble silicon concentration leaving the evaporator (assuming a 3-fold concentration across the evaporator). The difference between the soluble composition leaving the evaporator and the total quantity of soluble silicon present following evaporation represents the quantity of aluminosilicate that precipitates assuming no other silicon compounds form.

Assuming the solution phases exist at equilibrium entering the evaporator, one can calculate the effect of evaporating the liquid to a concentration three-fold the original by using the relations provided by Gasteiger, et al.[12] Table 3 contains an estimate of the amount of sodium aluminosilicate solids formed from each of the Tank 43H samples taken from the three depths in the tank (surface, 100 inches, and 64 inches). The starting silicon and aluminum concentrations in the historical Tank 43H sample come from composites of samples taken from 1991 through 1995.[2]

Table 2. Analytical Results from Tank 43H

Analyte	Units	Surface	Filtered Surface	VDS at 100 in.	Filtered VDS	VDS @ 64 in.
Ag	mg/L	< 8.2	< 0.6	< 7.5	< 0.6	
Al	mg/L	2.56E+03	2.89E+03	5.13E+03	5.1E+03	1.36E+04
B	mg/L	130.3	125.9	180.3	174.1	185.2
Ba	mg/L	< 2.7	< 0.2	< 2.6	< 0.2	34.8
Ca	mg/L	41.6	2.8	43.3	0.8	6.36E+03
Cd	mg/L	< 3.9	< 0.3	< 3.1	< 0.3	55.1
Co	mg/L	< 7.6	< 0.5	< 6.9	< 0.5	4.4
Cr	mg/L	67.9	60.7	133.0	120.6	134.02
Cu	mg/L	6.6	3.3	9.5	5.8	68.7
Fe	mg/L	11.7	7.5	27.2	18.7	2.00E+04
La	mg/L	< 14.9	< 1.1	< 18.2	< 1.1	9.6
Li	mg/L	12.6	9.4	22.8	19.8	157.1
Mg	mg/L	1.0	0.2	< 1.0	< 0.1	1078.4
Mn	mg/L	< 1.0	< 0.1	< 1.0	< 0.1	3037.7
Mo	mg/L	12.5	9.4	21.7	17.3	14.8
Na	mg/L	1.14E+05	1.11E+05	1.97E+05	1.99E+05	2.15E+05
Ni	mg/L	< 7.2	< 0.7	< 7.2	< 0.7	801.9
P	mg/L	183.0	175.8	369.5	339.3	1336.1
Pb	mg/L	29.6	3.8	28.8	4.3	45.5
Si	mg/L	95.5	95.7	126.1	105.0	403.8
Sn	mg/L	21.5	3.3	31.8	6.6	13.1
Sr	mg/L	< 1.3	< 0.1	< 1.2	< 0.1	19.1
Ti	mg/L	< 4.6	< 0.2	< 4.6	< 0.2	8.5
V	mg/L	7.8	0.5	7.7	0.7	2.6
Zn	mg/L	7.4	6.0	13.2	11.8	120.8
Zr	mg/L	8.4	0.9	9.2	0.9	3.5
Cs-137	dpm/mL	3.23E+03	2.00E+03	1.95E+03	3.55E+03	7.73E+03
Sr-90	dpm/mL	Not Measured	5.15E+05	Not Measured	5.17E+05	Not Measured
Pu-238/240	dpm/mL	< MDA	2.09E+04	< MDA	7.69E+03	6.44E+05
Pu-239	dpm/mL	2.77E+05	2.94E+05	2.78E+05	3.23E+05	7.58E+07
Z30	ppb					
Z31	ppb					
Z32	ppb					6.28E+04
Z33	ppb					1456
Z34	ppb					41583
Z35	ppb	641.6	256.7	481.0	472.5	71330
Z36	ppb	164.8		144.2	149.1	17430
Z37	ppb	174.5	118.9	189.5	223.2	10517.5
Z38	ppb	1.74E+04	1.21E+04	1.22E+04	1.61E+04	5.62E+05
Z39	ppb					7307.1
Z40	ppb					2777.3
Z41	ppb					1877.8
Z42	ppb					6214.3
Z43	ppb					738.5
Z44	ppb					449.8
Z45	ppb					58.6
Z46	ppb					45.4

Note: MDA indicates concentration below Minimum Detectable Amount.

Table 3. Estimated Aluminosilicate Solid Phase Formation

Tank	Evaporator	Timeframe	Solids (g/L)	Ref.
26F	2F	Historical	0.5	4
43H	2H	Historical	Minor	4
43H Surface	2H	Current	0.03	
43H-100 inch	2H	Current	0.5	
43H-64 inches	2H	Current	25	

Prior to sampling, Tank 43H had settled for about 6 weeks and thus the samples from the surface clarified to a large extent during this settling period. The amount of sodium aluminosilicate estimated to form during evaporation of the supernates are 0.03 g/L predicted to form from the surface material and 0.5 g/L from the material at a depth of 100 inches. These values agree with typical measurements of the F-Area Evaporator system (e.g., Tank 26F, the drop tank for the 2F Evaporator). However, the large amount of silicon present at the 64 inches level would generate significant amounts of sodium aluminosilicate solids according to this prediction. We doubt that all of the silicon from this sample represents soluble material because the implied K_{sp} for aluminum and silicon significantly exceeds experimentally measured equilibrium data. Likely, at this depth the supernant still contains suspended solids

potentially due to hindered settling or convective mixing. However, processing of this layer would likely allow the silicon – especially present as frit carryover from DWPF – to dissolve in the Evaporator pot resulting in formation of solids.

Radiochemical Analysis

Table 2 contains measured concentrations of a number of radionuclides. ^{137}Cs concentrations measured 3.2 x 10^8 dpm/mL, 1.95 x 10^8 dpm/mL, and 7.7 x 10^8 dpm/mL for Tank 43H at the surface, at 100 inches depth and at the 64 inches, respectively. Filtering the surface and 100 inch level samples, with a 0.45-micron syringe filter, resulted in slightly different ^{137}Cs values of 2 x 10^8 dpm/mL and 3.55 x 10^8 dpm/mL, respectively. These variances most probably reflect sampling and analytical error. Personnel measured ^{90}Sr concentrations for the filtered samples taken at the surface and at 100 inches. Both samples exhibited a ^{90}Sr concentration of 5 x 10^5 dpm/mL.

Personnel also measured the actinide concentrations for both of the unfiltered and filtered samples. We made these measurements because previous measurements performed by Analytical Laboratories showed greater than expected uranium concentrations. These concentrations measured greater than 10 mg/L with the expected concentrations much lower based on work by Hobbs, et al.[13]

We found negligible plutonium concentrations in the Tank 43H samples taken at the three depths. The combined ^{239}Pu and ^{240}Pu measurement in the supernate (surface and 100 in. samples) showed concentrations near 1 x 10^4 dpm/mL. Likewise ^{238}Pu concentration for the three samples measured approximately 3 x 10^5 dpm/mL. Filtering these samples (using a 0.45-micron syringe filter) showed no effect on the ^{238}Pu concentrations. Plutonium concentrations proved higher at the 64 inches height near the sludge layer. The ^{239}Pu-^{240}Pu and ^{238}Pu concentrations measured 6.4 x 10^5 dpm/mL and 7.6 x 10^7 dpm/mL, respectively. These higher concentrations -- roughly two orders of magnitude higher than the supernate concentrations – near the sludge further suggest the presence of suspended solids in that sample.

Personnel measured uranium concentrations in each of the as-received samples from the surface, from 100 inches deep and from 64 inches deep. Additionally, we filtered the surface and 100 inch variable depth samples using a 0.45-micron syringe filter. The unfiltered, uranium concentrations measured 18.2 mg/L, 12.8 mg/L and 575 mg/L, respectively. Clearly, the sample at the 64 inches contained significant concentrations of sludge since the sample appeared viscous and dark brown. The uranium concentrations in the supernate samples exceed model predictions but agree with measurements from Analytical Laboratories. Analysis of a second set of samples from the surface and 100 inch depth, filtered using a 0.45-micron syringe filter prior to dilution in nitric acid, indicated 12.4 mg/L and 16.7 mg/L total uranium. This data indicates that the uranium exists in a soluble form in the supernate. Therefore, additional solubility studies appear necessary at solution compositions more closely approximating those of Tank 43H.

Conclusions

Because of the aluminosilicate formation problems in the 242-16H Evaporator, SRTC characterized surface and variable depth samples from the feed tank (43H) after a six-week quiescent period. In particular, personnel measured the soluble aluminum, silicon and uranium concentrations. The results indicate silicon stratification with increased silicon concentrations near the sludge layer that suggests the presence of frit on or near the sludge surface. Uranium concentrations exceed 10 mg/L even after filtration through a 0.45-micron filter. This finding indicates previous modeling of uranium solubility under predicts dissolved uranium content in this solution matrix.

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