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Characterization of Post-Cleaning Solids Samples from the 2H Evaporator Pot

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SUMMARY

Samples retrieved from the 2H Evaporator Pot in October of 2003 were of a similar nature as previous materials. The bulk of the sample was comprised of a sodium aluminosilicate phase, cancrinite. The concentration of uranium in the evaporator solids, however, was very low: < 0.1 wt%. The uranium enrichment was depleted as expected and measured 0.6 %. These data agree with uranium contents generated during experimental testing. Additionally, the overall specific radionuclide content is lower for this sample than previous measured on samples from the Gravity Drain Line in 1997 and the cone and wall in 2000.

INTRODUCTION

Effective management of High Level Waste (HLW) products during hydrothermal processing in waste evaporators is crucial to the Savannah River Site (SRS) tank farm operations. The formation and accumulation of waste products comprising sodium aluminosilicate (NAS) solid polytypes (e.g. amorphous, zeolite, sodalite and cancrinite) and uranium-based solids (e.g. sodium diuranate) that are enriched in fissionable uranium lead to a serious fouling problem and criticality concern in the 242-16H (2H) Evaporator.[1,2] The control, handling and mitigation of aluminosilicate formation pose a challenge, that previously warranted systematic studies that provided a greater understanding and new knowledge of the mechanism of fouling, particularly uranium incorporation into NAS phases.[3,4,5]

The uranium in the 2H Evaporator system was rendered initially depleted by the addition of depleted uranyl carbonate.[6] This effectively made the formation of sodium aluminosilicates in the 2H system an operational issue rather than a nuclear safety issue. The system ahs remained depleted through control of waste additions to the 2H system. Operations performed routine video inspection of the evaporator pot following startup of the evaporator. The results of these inspections started to show some signs of solids during June of 2003. A later inspection in September of 2003 showed a buildup of solids in the Evaporator cone. Figure 1 shows pictures taken from the video recording of the June and September inspections. The picture showing the cone of the pot also shows a sampling tool that was used to obtain a solid sample that was sent to SRTC for analysis.

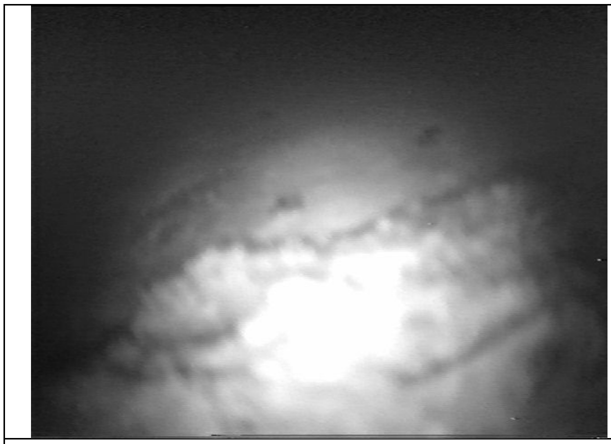
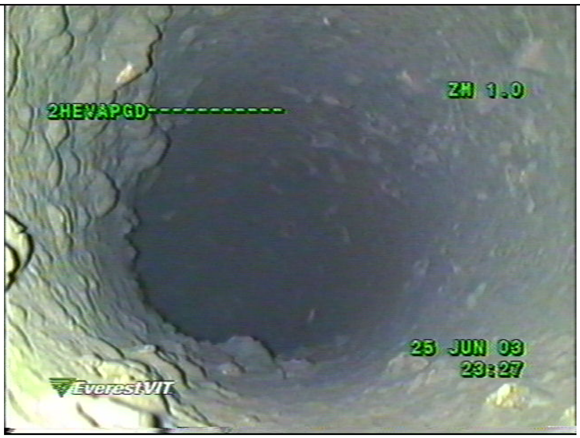
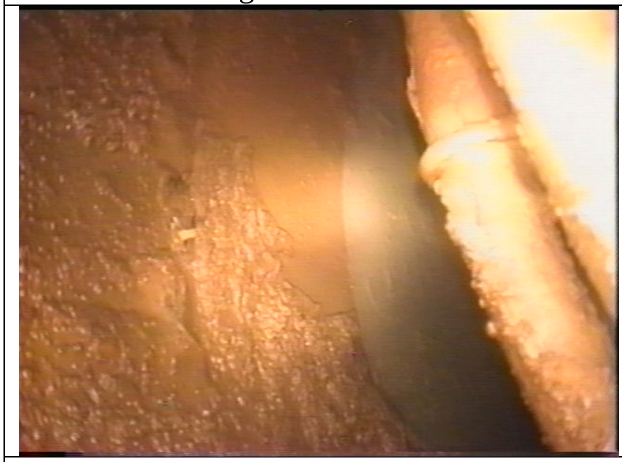
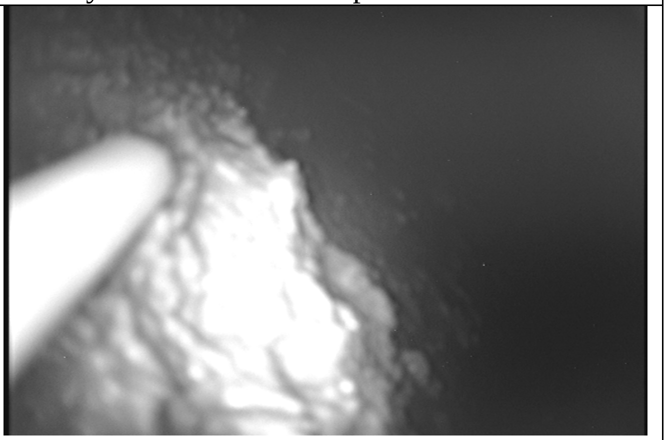
	
Wall near Cooling Coils on 6-25-03	Gravity Drain Line near Separator Pot on 6-25-03
	
Evaporator Wall in September 2003	Solids Buildup in Evaporator Cone in September 2003

Figure 1. Pictures from 2H Evaporator Pot

EXPERIMENTAL DETAILS

The sample was received at SRTC and placed into the Shielded Cells for examination and sampling. Figure 2 shows the contents of the sample. SRTC received approximately 40 – 50 mL of liquid with roughly 0.75 g of “wet” solids. Sub-samples were taken and submitted for X-ray diffraction analysis and microscopy by scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS). Additionally, a sample of the solids was sent for microwave dissolution in nitric acid. The acid was then analyzed for metals content by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) and actinide content by radiochemical counting and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

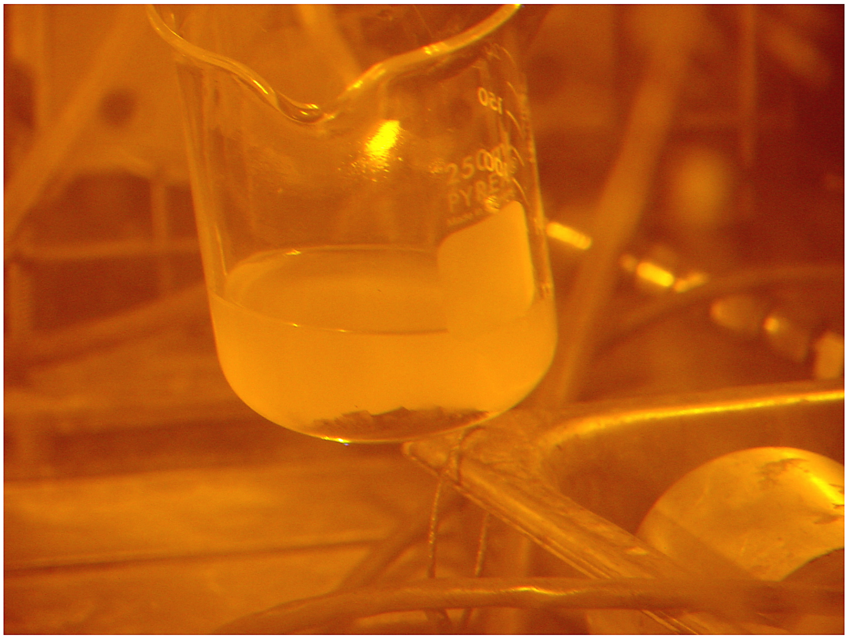


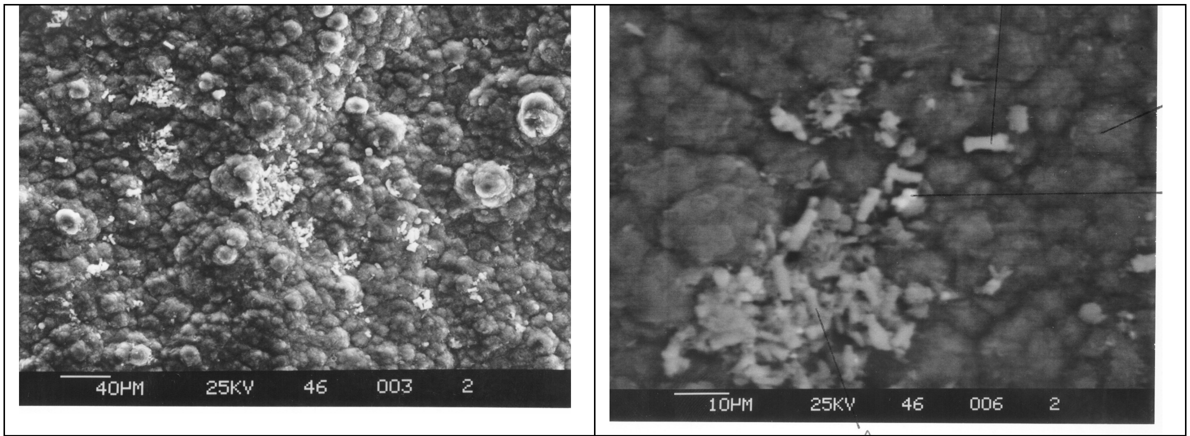
Figure 2. Picture of As-Received Sample

RESULTS and DISCUSSION

Solid State Characterization

As previously discussed, solids were found during inspections of the 2H Evaporator pot in September of 2003. Operations personnel were experiencing difficulty in lifting the pot contents to the concentrate tank. Siphon rates had dropped from 40 gallons per minute to 15 gallons per minute. As a result a sample of the solids was sent to SRTC for characterization. Solid state characterization of the sample was performed to determine the physical structure and morphology of the solids removed from the 2H Evaporator cone.

Figure 3 shows SEM back-scatter micrographs taken from two different sub-samples of the solids. The image (250x magnification) on the left of Figure 3 shows the typical "yarn ball" morphology of the aluminosilicates formed under the hydrothermal testing using simulants of the SRS waste.[7,8,9] This spherical morphology was later correlated to aluminosilicate phase cancrinite.[10]



250x Magnification

1000x Magnification

Figure 3. SEM Images of the 2H Solids

The image (1000x magnification) on the right in Figure 3 is a back-scatter micrograph showing a dark aluminosilicate background with a region of brighter (higher atomic number) material. An elemental mapping of this area using energy dispersive spectroscopy identified three types of material. The first material exhibited a EDS spectrum shown at left in Figure 4 that included peaks due to sodium, aluminum and silicon. This spectrum was taken from the dark background in the SEM micrograph (Figure 3, 1000x magnification, right side) and is typical of aluminosilicates. The gold and palladium peaks are due to coating placed on the sample prior to the analysis.

The spectrum in the center of Figure 4 is rich in calcium and phosphorous, perhaps a calcium phosphate since oxygen has an atomic mass that is too light to be detected in the radiologically contained instrument. Lastly, the spectrum on the right in Figure 4 is from the bright area in the 1000x magnification micrograph from Figure 3. The EDS spectrum exhibits a significant peak from iron. This could be a contaminant or a very small amount of sludge.

Figure 5 shows the a representative X-ray powder diffraction pattern obtained from sub-samples of solids from the 2H Evaporator cone. Duplicate results were obtained from two sub-samplings. The pattern was computer matched to the theoretical pattern for cancrinite ($Na_8Al_6Si_6O_{24}(NO_3)_2-4H_2O$). This material agrees with previous samples taken from the Gravity Drain Line[11] in 1997 and the 2H Evaporator cone[12] and wall[13] in 2000. The material possesses a hexagonal structure with a crystallographic space group designation of $P6_3$. The crystal density is 2.51 g/mL. Differing from the X-ray diffraction analysis of the previous solid samples, the X-ray powder pattern does not exhibit peaks due to the presence of sodium diuranate. Presumably, this indicates that the uranium content in the solids is well below the previous maximum of 8.8 wt %.[14]

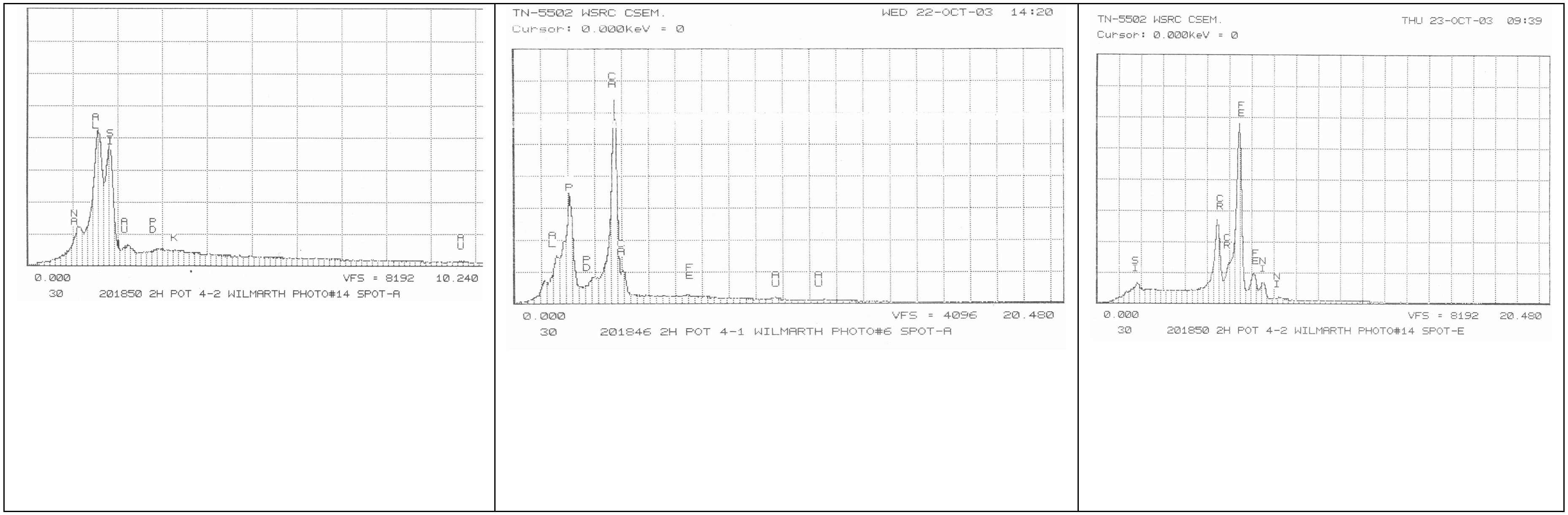


Figure 4. EDS Spectra of 2H Solids Material

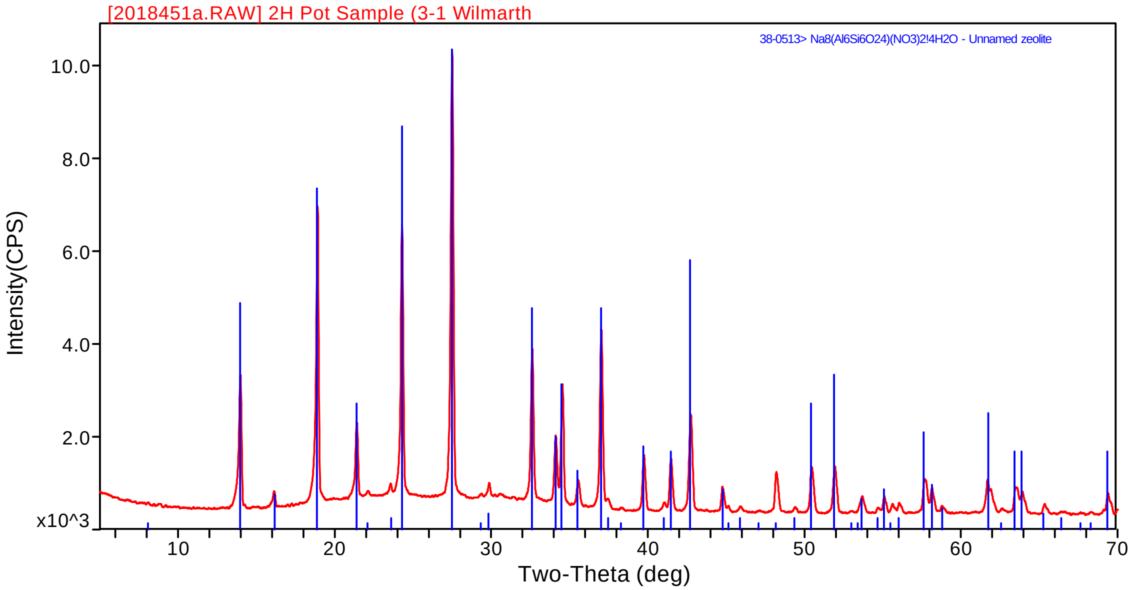


Figure 5. X-ray Powder Diffraction Pattern from 2H Solids

Red lines are the measured diffraction data and blue lines are the theoretical data.

Radiochemical Characterization

An abbreviated suite of analysis was performed on the solid samples due to the limited amount of material retrieved from the 2H Evaporator cone. Analysis focused on actinide content and some elemental analysis. A single sub-sample was taken and dissolved using a microwave, nitric acid process by personnel from the Analytical Development Section of SRTC. Each analyses was performed in duplicate on the single dissolution sample. Table 1 shows the results of these analyses.

The elemental data showed sodium, aluminum and silicon concentrations of 139, 117.5 and 1.98 mg/g, respectively. This is a ratio of 8 mmole/g of sodium, 5.8 mmole/g of aluminum and only 0.1 mmole/g of silicon. The molar ratio of sodium and aluminum agree well with the chemical formula for the sodium aluminosilicate ($Na_8Al_6Si_6O_{24}(NO_3)_2$-$4H_2O$). However, the silicon does not conform to the chemical stoichiometry. The microwave digestion process involves heating the sample to elevated temperatures in nitric acid. A very similar measurement phenomenon was observed during the actual acid cleaning to the 2H Evaporator.[1] In these analyses, silicon concentrations never exceeded the minimum detection limits. Silicon is not very soluble in nitric acid. The experimental testing[14] did show silicon concentrations in the nitric acid dissolution fluid at similar concentrations to sodium and aluminum. This behavior evidently represents a supersaturated solution. Conversely, the amount of silicon may be lower in the solid sample indicating the chemical species does not have a 1:1 silicon to aluminum ratio. This material would have to be amorphous as its not observed in the X-ray pattern.

As observed in the SEM-EDS analysis, the elemental analysis does show the presence of iron. The measured concentration was ~ 7 mg/g of iron in the solid sample. Previous analysis of the other solids taken from the evaporator had not shown this level of iron contamination or occlusion. Had the uranium been enriched, the presence of iron, a neutron poison, may have been advantageous.

Table 1. Elemental and Radiochemical Data

Analyte	Units	Concentration
Al	mg/g	117.5
Fe	mg/g	6.93
Na	mg/g	139
Si	mg/g	1.98
Mass No. 232	microg/g	0.55
Mass No. 234	microg/g	0.5
Mass No. 235	microg/g	4.9
Mass No. 236	microg/g	0.7
Mass No. 237	microg/g	0.4
Mass No. 238	microg/g	823
Mass No. 239	microg/g	1
Total U	mg/g	0.831
% Enrichment	%	0.59
Sr-90	dpm/g	< 4E+07
Pu-238	dpm/g	2.90E+07
Pu-239/240	dpm/g	3.76E+05
Cs-137	dpm/g	2.40E+05
Cs-134	dpm/g	1.01E+02

Note: Several other elements were measured but were below detection limits.

Also included in Table 1 is the mass spectrometry data from the dissolved 2H Evaporator solid. The total uranium measured 0.83 mg/g or 0.083 wt % for the total solid. This is significantly lower than the percentage found in the pot samples from 2000. Additionally, as expected, the uranium enrichment was depleted and measured 0.59 %. This is expected since a prohibition of enriched uranium transfers to the 2H system was established after the addition of depleted uranyl carbonate.[6]

The measured uranium inclusion in the sodium aluminosilicate solids agrees with past work by personnel from SRTC and the Oak Ridge National Laboratory. Several experiments have been performed that examined the inclusion of uranium into sodium aluminosilicate phases. The first attempt[15] studied the reaction under batch conditions and found the task on including uranium was not successful. The uranium formed stable supersaturated solutions. These authors followed the batch tests with a continuously fed experiment[16] and found uranium could be occluded into the aluminosilicate matrix. Their results, however, only showed about 0.25 wt% uranium. Others have attempted to further the knowledge of uranium entrapment. Hu, et al.,[17] studied the various aluminosilicate phases to ascertain if a certain phase had a higher affinity for uranium. They concluded that minute quantities of uranium (as measured by scanning electron microscopy) could be occluded during precipitation and precipitation of diuranate on the amorphous gel and cancrinite occurred. Lastly, Oji and Williams[18] attempted to overlap the precipitation of aluminosilicate and diuranate. Their results showed uranium loadings of 0.02, 0.004, 0.005 and 0.063 wt% U in the amorphous gel, Zeolite A, Zeolite A 6012 and sodalite, respectively. Taken collectively, these experiments indicate the difficulty in incorporating large amounts of uranium in sodium aluminosilicate scale.

The remaining radiochemical data for the sample in Table 1 gives plutonium isotopic concentrations and radio-cesium concentrations. By and large, the radioactivity content of this solid sample is well below the data from samples of the 2H pot in 2000. The Pu-239/240 and Pu-238 concentrations were 3.76×10^5 dpm/g and 2.9×10^7 dpm/g, respectively. This is compared to the cone sample[19] that had a Pu-238 specific activity of ~4×10^8 dpm/g. Similarly, the Cs-137 activity in the 2000 sample was 3×10^8 dpm/g while the current sample measures 2.4×10^5 dpm/g. these lower activities reflect the processing of predominantly DWPF recycle which is a low specific activity feed.

CONCLUSIONS

The Savannah River Technology Center received a sample of solids from the cone of the 2H Evaporator pot and performed initial characterization. The analysis shows that the solid is comprised of a previously identified sodium aluminosilicate phase, cancrinite. Since this is the highest temperature phase of the Zeolite family having the general formula of $Na_6Al_6Si_6O_{24}$-2NaX-nH_2O where X is a singly charged ion such as nitrate or nitrite and n is the number of waters of hydration, the solids were probably produced at the surface of the tube bundle, the hottest surface in the 2H pot. As the tube bundle is shocked to remove salt/scale, the solids accumulated in the cone.

Differing from previous analysis of samples from the Gravity Drain Line in 1997 and from the 2H cone and wall in 2000, this sample had a very low uranium content (< 0.1 wt

%). This uranium concentration agreed with laboratory testing that was performed previously. Additionally, the overall radioactivity of this sample was very low reflecting the shift in evaporator operation to processing the low activity DWPF recycle stored in the Tanks 20H, 21H, and 24H.

APPROVALS

Authors

W. R. Wilmarth, Waste Processing Technology Date

J. T. Mills, Waste Processing Technology Date

V. H. Dukes, Waste Processing Technology Date

P. U. Burkhalter, Shielded Cells Operations Date

Design Check

C. J. Martino, Waste Processing Technology Date

Management

W. R. Wilmarth, Waste Processing Technology Date

E. J. Freed, Closure Business Unit Date

J. C. Griffin, Waste Processing Technology Date

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