

Key Words:

**Chloride
Washing
Salt
Plutonium**

**Retention:
Permanent**

Tracking No. 10560

CHLORIDE REMOVAL FROM SIMULATED 3013 SOLIDS

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AUGUST 2006

Washington Savannah River Company

Prepared for the U. S. Department of Energy Under Contract Number DE-AC09-96SR18500

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Printed in the United States of America

**Prepared For
U.S. Department of Energy**

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Introduction

HB-Line is evaluating methods for removal of chloride from chloride-bearing plutonium (Pu) residues to permit processing of the Pu in HB-Line. Most of the Pu considered for these studies is stored as plutonium dioxide (PuO_2). Some of the PuO_2 contains varying amounts of chloride salt, typically less than 25 wt%. Several methods for washing similar materials have been evaluated at Pacific Northwest National Laboratory (PNNL) and shown to be effective. (Gerber and Sevigny, 2002) Comparable demonstrations have also been conducted at Lawrence Livermore National Laboratory (LLNL). (Dodson, et al., 2006) The methods all involve dissolving the chloride salts away from the PuO_2 using water. The Pu processing in HB-Line is part of the program to destructively evaluate 3013 storage containers in the K-Area Material Storage (KAMS) facility.

The Savannah River National Laboratory (SRNL) is participating in the evaluation of an alternate washing technique that contacts the contents of the 3013 containers with water. The solids are expected to contain sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2). The expected chloride salts are known to dissolve in water. It is important to minimize the amount of liquid waste generated because the liquid must be immobilized prior to disposal. The Actinide Technology Section (ATS) is defining the baseline washing performance for evaluating production-scale process options.

Experimental

Simulant development had several objectives: 1) simulate the PuO_2 , 2) simulate the major chloride-bearing materials, 3) provide worst-case conditions for chloride concentration, and 4) prepare the simulant in a manner that has significant potential for embedding chloride in the PuO_2 simulant. Ceric oxide (CeO_2) is a common simulant for PuO_2 and was selected for these tests. The primary chloride salt for the 3013 samples is a 50:50 mixture of NaCl and KCl ; other minor chloride compounds such as MgCl_2 and CaCl_2 were omitted because they are expected to dissolve in a manner similar to NaCl and KCl . Expectations are that 3013 samples will contain no more than 25 wt% chloride salt. Consequently, surrogates were made with 33% and 50% NaCl-KCl . A small amount of ferric oxide (Fe_2O_3) was added with the thought that it might interact with NaCl-KCl and simulate the presence of plutonium trichloride (PuCl_3).

The 50:50 NaCl-KCl mixture was prepared by weighing out equal amounts of NaCl and KCl in a quartz crucible, heating to 830 °C for 90 minutes, and then cooling to room temperature. Once cooled, the NaCl-KCl was ground into a powder using a mortar and pestle. To prepare a simulant that could entrap chloride in the CeO_2 matrix, low-fired CeO_2 was produced from cerium oxalate hydrate. Cerium oxalate hydrate was calcined at 450 °C for two hours to yield low-fired CeO_2 . Low-fired CeO_2 is more porous and has a higher surface than high-fired CeO_2 . When heated to a higher temperature, the crystal structure of the low-fired CeO_2 collapses and has the potential to embed chloride salt. Measurements of CeO_2 specific surface area at 450 °C, 600 °C, 700 °C and 900 °C have been reported as 70, 37, 4 and <1 m^2/g , respectively. (Altas and Tel, 2001) Analogous

data for PuO_2 has measured specific surface areas of 44.8, 3.3, and $0.09 \text{ m}^2/\text{g}$ for samples calcined at $500 \text{ }^\circ\text{C}$, $950 \text{ }^\circ\text{C}$, and $1700 \text{ }^\circ\text{C}$, respectively. (Bray, et al., 1986) Low-fired CeO_2 , Fe_2O_3 , and NaCl-KCl were blended in the appropriate amounts in a quartz crucible and heated to $850 \text{ }^\circ\text{C}$ for two hours. After heating, the mixture was cooled and ground into a powder for wash testing.

Two scoping tests were conducted. The first test was conducted with a surrogate made of 65 wt% CeO_2 , 33 wt% KCl/NaCl , and 2 wt% Fe_2O_3 . Tests started with three samples – one containing powder, another pellets, and a third chunks (see Figure 1) – containing 50 g of surrogate in 75 mL of deionized H_2O . All three were washed at ambient temperature in a shaker bath. The pellets and chunks disintegrated into a fine powder shortly after testing began. As a result, data was only collected for the washing of the chunks. Water samples (1 mL) were withdrawn at 15, 30, 45, 75 and 120 minutes for analysis of chloride content. After two hours, the water was decanted and a fresh batch of H_2O added. The protocol was repeated for a total of four washes. Samples were submitted for chloride analysis using ion chromatography (IC).



Figure 1. Test #1 Surrogate Samples

For the second test, one sample was prepared containing a mixture of powder, pellets and chunks. The second test was conducted with a surrogate made of 50 wt% CeO_2 , 48 wt% KCl/NaCl , and 2 wt% Fe_2O_3 . Deionized H_2O was added to 21.2 g of the surrogate and washed at ambient temperature in a shaker bath. A total of four washes lasting as long as 180 min each were conducted. The first two washes used 75 mL of H_2O and the last two used 50 mL of H_2O . After the first wash, the solids were allowed to settle briefly and the H_2O decanted; the solids were filtered through a 0.45-micron filter after the final three washes. Water samples (1 mL) were periodically withdrawn for analysis of chloride content using IC. The final filtered solids were rinsed with water and added to 150 mL of 8 M nitric acid with 0.1 M potassium fluoride at $95 \text{ }^\circ\text{C}$ for three hours. The resulting solution was cooled and analyzed for chloride using IC.

Results and Discussion

Test #1

The data for Test #1 are in Attachment 1. In Test #1, the first wash reached a maximum almost immediately. The last three washes, as evidenced by the chloride concentration at 15 minutes, show the effect of residual chloride from the previous wash due to decanting of the liquid. The first and second wash data show that the chloride concentration between the washes decreases by a factor of six. The last three washes decrease in chloride concentration by a factor of about three between washes. The last three washes also suggest that all of the chloride has not yet been washed from the solids because the chloride values gradually increase throughout the respective wash cycles. Even the fourth wash cycle shows a steady increase from 1090 mg/L to 1850 mg/L over a 120-minute period. The small increase in the fourth wash suggests that the undissolved chloride is small in comparison with the initial concentration. It also indicates that a longer cycle time for the second wash can be used to improve recovery in the second wash. Although there is enough error in the ion chromatography data, particularly with the magnitude and fluctuation of the chloride concentrations for the first wash cycle, the data indicate effective removal of chloride from the solid.

A calculation of a mass balance indicates that nearly all of the chloride (97.8%) has been recovered in the wash solution, but that there is still a small amount remaining in the solid or unaccounted for because of experimental error. The conclusion that a small amount of undissolved chloride remains in the undissolved solids is consistent with the data showing a gradual increase in chloride concentration with time as salts are washed in the last three wash steps. The mass balance calculation assumes that the chloride concentration for the first wash is 92,400 mg/L after 120 minutes. However, if one assumes the higher value measured at 75 minutes, the mass balance improves to 99.0%. The recovery percentages may be skewed high because any liquid not decanted will also be counted as part of the next wash. An evaluation of the data after 15 min for the last three washes indicates that as much as 50% of the chloride in the last three washes may be attributed to residual chloride not decanted from the first wash. If 50% of the chloride for the last three washes was attributable to the residual liquid, the total chloride recovered in the wash solutions drops to 87.7%.

Test #2

The data for Test #2 are in Attachment 2. For Test #2, the wash H₂O to chloride ratios were adjusted with more water being added to the first two washes (from 0.22 g of KCl/NaCl per mL of H₂O for Test #1 to 0.14 for Test #2). The wash cycle times were also increased. Another major difference involved liquid removal following the wash steps. After the first wash, the liquid was decanted more carefully than Test #1 to minimize residual liquid. After each of the last three washes, the solids were filtered.

The results for Test #2 are similar to those of Test #1. While the data show that Test #2 required only two washes to dissolve virtually all chloride compared to four washes for

Test #1, this is misleading. Comparing the volume of H₂O used for two washes in Test #2 with four washes in Test #1 reveals 0.030 g chloride/mL H₂O for Test #1 and 0.038 g chloride/mL H₂O for Test #2. Considering the test variations, the wash efficiency for the two tests is comparable.

A significant difference between the two tests relates to the difference between decanting and filtering. For Test #1, the difference in measured chloride concentration between washes ranged from a factor of three to six. For Test #2, the difference was about a factor of ten. The difference is the result of better liquid removal using filtration versus decanting.

A calculation of a mass balance suggests that not all the chloride has been removed (91.2%). As with Test #1, the recovery percentages may be skewed high because any liquid not decanted or filtered will also be counted as part of the next wash. This is evident by the fact that the third and fourth washes have chloride in the first sample, but show no increase thereafter. An evaluation of the data for the last three washes suggests that as much as 90% of the chloride in the last three washes may be attributed to residual chloride not decanted from the first wash. If 90% of the chloride for the last three washes is attributed to the residual liquid, the overall mass balance drops to 83.9%.

Any concern about undissolved chloride in the solid residue is eliminated by the analysis of chloride in the residual solids. The residual solids were dissolved in 150 mL of 8 M nitric acid (HNO₃) with 0.1 M potassium fluoride (KF) at 95 °C for three hours. Although only about 50% of the solids dissolved, the solution was a dark orange color, indicative of the dissolution of CeO₂. The aggressive dissolution step is expected to dissolve any residual chloride. The chloride concentration of the final dissolution liquid was below the IC detection limit of 20 mg/L. A worst-case calculation, using a solution concentration of 20 mg/L Cl⁻, yields a total chloride amount in solution of 0.003 g, which is 0.05% of the initial chloride. Assuming that none of the CeO₂ or Fe₂O₃ was dissolved during washes with H₂O, the final chloride concentration in the washed oxide would be 280 ppm (3000 µg Cl⁻/10.6 g undissolved oxide), or three orders of magnitude reduction in Cl⁻ concentration.

The result for the undissolved solids leads to questions about the mass balance. The discrepancy cannot be attributed to analytical uncertainty alone. One explanation may be tied to the preparation of the surrogate. It is known that the heating of NaCl/KCl to melting can cause volatilization of some of the salt. Also, if moisture is present while heating in air, some chloride salts such as magnesium chloride and calcium chloride can react and form oxides. The conversion of some of the salt to an oxide could lead to a low mass balance because the masses of simulant weighed into each sample assume that the NaCl/KCl salt exists only as chloride.

Conclusions

Testing at SRNL indicates that washing of chloride salts with water can effectively remove the salt from oxide materials used to simulate Pu oxide. An aggressive dissolution using a flowsheet comparable to the HB-Line PuO₂ dissolution flowsheet (8 M HNO₃/0.1 M KF at 95 °C for 3 hours) was conducted on the residual solids. The extra dissolution removed only 0.1% of the initial chloride in the test simulant, thus confirming the potential effectiveness of washing with water. Optimal loading for the first wash is between 0.14 and 0.22 g of chloride salt per mL of H₂O. It may be possible to dissolve all of the chloride with the first wash using a chloride loading between 0.14 and 0.22 g chloride salt/mL H₂O. Subsequent rinsing will be necessary to remove chloride-containing liquid from the interstitial spaces of the undissolved solid. Analysis of the chloride content of 3013 Pu materials can be performed in SRNL prior to processing them in HB-Line. Using filtration to separate the undissolved solids from the wash H₂O is about a factor of 2 better than decanting.

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ATTACHMENT 1 – Test #1 Data

ION CHROMATOGRAPHY DATA – CHLORIDE CONCENTRATION (mg/L)

Wash Time (min)	Wash Cycle			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
15	91500	12000	2770	1090
30	93400	13900	3590	1290
45	90200	14600	4490	1590
75	93900	15200	4870	1710
120	92400	16600	5830	1850
<i>g KCl-NaCl/mL H₂O*</i>	<i>0.22</i>	<i>0.22</i>	<i>0.22</i>	<i>0.22</i>

* based on initial solid added to the test

CHLORIDE IN LIQUID SAMPLES/ALIQUOTS (g)

Wash Time (min)	Wash Cycle			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
15 (1-mL sample)	0.092	0.012	0.003	0.001
30 (1-mL sample)	0.093	0.014	0.004	0.001
45 (1-mL sample)	0.090	0.015	0.004	0.002
75 (1-mL sample)	0.094	0.015	0.005	0.002
120 (71 mL left)	6.560	1.179	0.414	0.131
<i>Total Cl in wash (g)</i>	<i>6.929</i>	<i>1.235</i>	<i>0.430</i>	<i>0.137</i>

MASS BALANCE DATA

Simulant Weight (g)	50
Wt% NaCl/KCl	33
Wt (g) NaCl/KCl	16.50
Total Wt Cl(g)	8.93
Mass Balance %	97.8

ATTACHMENT 2 – Test #2 Data

ION CHROMATOGRAPHY DATA – CHLORIDE CONCENTRATION (mg/L)

Wash Time (min)	Wash Cycle			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
15	57000	5100	563	----
45	----	5370	551	57
75	60400	5460	598	----
120	61100	5560	566	60
180	----	5500	582	60
<i>g KCl-NaCl/mL H₂O*</i>	<i>0.14</i>	<i>0.14</i>	<i>0.21</i>	<i>0.21</i>

CHLORIDE IN LIQUID SAMPLES/ALIQUOTS (g)

Wash Time (min)	Wash Cycle			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
15 (1-mL sample)	0.057	0.005	0.001	----
30 (1-mL sample)	----	0.005	0.001	0.000
45 (1-mL sample)	0.060	0.005	0.001	----
75 (1-mL sample)	4.460	0.006	0.001	0.000
120 (residual wash)	----	0.391	0.027	0.003
<i>Total Cl in wash (g)</i>	<i>4.577</i>	<i>0.412</i>	<i>0.031</i>	<i>0.003</i>

MASS BALANCE DATA

Simulant Weight (g)	21.2
Wt% NaCl/KCl	48
Wt (g) NaCl/KCl	10.2
Total Wt Cl(g)	5.51
Mass Balance %	91.2