Application of Vacuum Salt Distillation Technology for the Removal of Fluoride and Chloride from Legacy Fissile Materials

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Abstract: Between September 2009 and January 2011, the Savannah River National Laboratory (SRNL) and the Savannah River Site (SRS) HB-Line Facility designed, developed, tested, and successfully deployed a production-scale system for the distillation of sodium chloride (NaCl) and potassium chloride (KCl) from plutonium oxide (PuO_2). Subsequent efforts adapted the vacuum salt distillation (VSD) technology for the removal of chloride and fluoride from less-volatile halide salts at the same process temperature and vacuum. Calcium chloride ($CaCl_2$), calcium fluoride (CaF_2), and plutonium fluoride (PuF_3) were of particular concern. To enable the use of the same operating conditions for the distillation process, SRNL employed *in situ* exchange reactions to convert the less-volatile halide salts to compounds that facilitated the distillation of halide without removal of plutonium. SRNL demonstrated the removal of halide from $CaCl_2$, CaF_2 and PuF_3 below 1000 °C using VSD technology.

Keywords: vacuum distillation, plutonium oxide, calcium fluoride, plutonium fluoride

INTRODUCTION

Vacuum distillation of chloride salts from plutonium oxide (PuO_2) and simulant PuO_2 has been previously demonstrated at Department of Energy (DOE) sites using kilogram quantities of chloride salt.[1-2] The apparatus for vacuum distillation contains a zone heated using a furnace and a zone actively cooled using either recirculated water or compressed air. During a vacuum distillation operation, a sample boat containing the feed material is placed into the apparatus while it is cool, and the system is sealed. The system is evacuated using a vacuum pump. Once a sufficient vacuum is attained, heating begins. Volatile salts distill from the heated zone to the cooled zone where they condense, leaving behind the non-volatile materials in the feed boat.

The application of vacuum salt distillation (VSD) is of interest to the HB-Line Facility and the MOX Fuel Fabrication Facility (MFFF) at the Savannah River Site. Both facilities are involved in efforts to disposition fissile materials. Many of these materials contain chloride and fluoride salt concentrations which make them unsuitable for dissolution without prior removal of the chloride and fluoride salts.

Between September 2009 and January 2011, the Savannah River National Laboratory (SRNL) and HB-Line designed, developed, tested, and successfully deployed a system for the distillation of chloride salts. Subsequent efforts are attempting to adapt the technology for the removal of fluoride. Fluoride salts of interest are less-volatile than the corresponding chloride salts, but the use of higher operating temperatures to facilitate distillation is problematic. Consequently, an
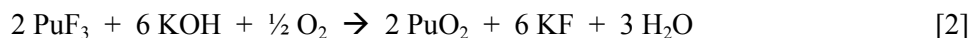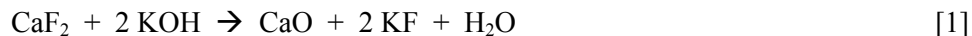
alternate approach is required for the removal of fluoride without significantly increasing the operating temperature.

Vacuum salt distillation takes advantage of the large difference in volatility between alkali halide salts and PuO_2. NaCl and KCl are sufficiently volatile that they can be distilled from PuO_2 at a satisfactory rate under vacuum above 900 °C.[3] Alkaline-earth halides and actinide halides also have a large enough difference in volatility from PuO_2 to enable distillation; however, they are not sufficiently volatile below 1000 °C to allow distillation at a rate sufficient for production-scale operations in HB-Line. A comparison of volatility of chloride and fluoride salts is shown in Figure 1.[4]
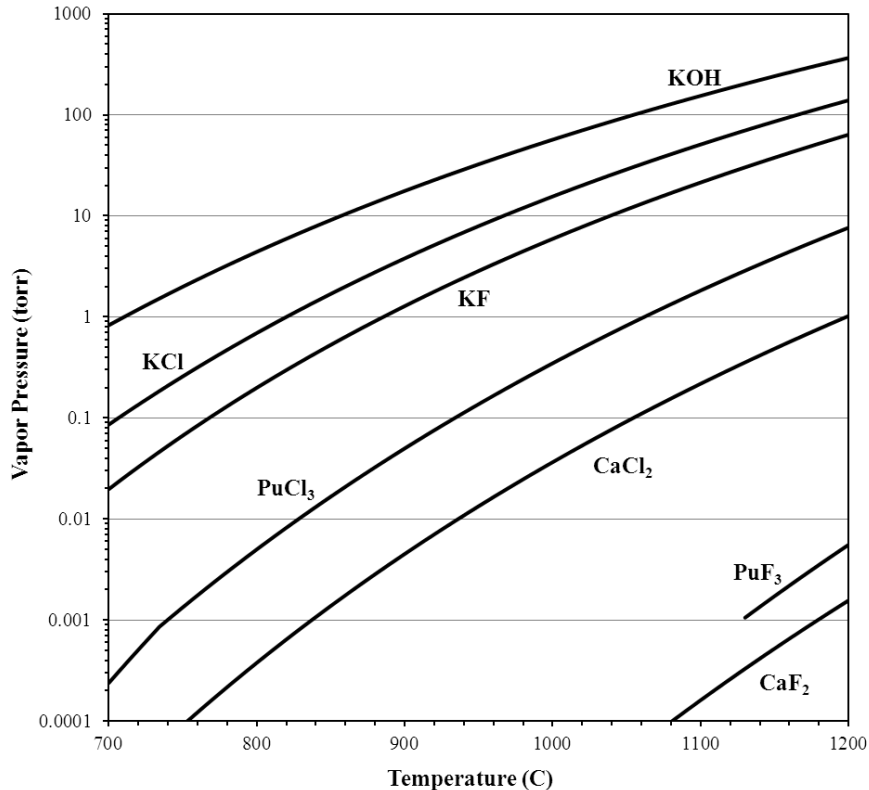
Figure 1. Comparison of chloride and fluoride salt volatility.

It was shown during the development of a sodium peroxide (Na_2O_2) fusion method for the dissolution of PuO_2 materials that alkaline earth and lanthanide halide salts would react with Na_2O_2 to form NaCl and the corresponding alkaline earth or actinide oxide.[5] It was speculated that sodium hydroxide (NaOH) or KOH might react in a similar manner with $CaCl_2$ and PuF_3 according to reactions 1 and 2.

$$CaF_2 \ + \ 2\,KOH \ \rightarrow \ CaO \ + \ 2\,KF \ + \ H_2O \qquad\qquad [1]$$

$$2\,PuF_3 \ + \ 6\,KOH \ + \ \tfrac{1}{2}\,O_2 \ \rightarrow \ 2\,PuO_2 \ + \ 6\,KF \ + \ 3\,H_2O \qquad\qquad [2]$$

If reaction 1 occurs, the less-volatile alkaline earth and actinide halide salts can be converted to oxides and the associated halide exchanged to form either KF or NaF, which may be sufficiently volatile below 1000 °C. Furthermore, KOH is more volatile than KF or NaF, which offers the potential for excess KOH to be distilled along with KF or NaF. Figure 1 shows the relative

2

volatility of KOH and the relevant halide salts from Figure 1.[4] The net result is that the distilled product shows a change from $CaCl_2$ and CaF_2 to CaO and from $PuCl_3$ and PuF_3 to PuO_2. PuO_2 is not shown in Figure 1 because the volatility of PuO_2 is about seven of orders of magnitude lower than CaF_2 (to the right of CaF_2 in Figure 1); for comparison, the volatility of CaF_2 is about seven orders of magnitude lower than KCl and NaCl.

**EXPERIMENTAL**

Apparatus

Three different test units were used: 1) a non-radioactive small-scale unit, 2) a non-radioactive pilot-scale unit of dimensions similar to the VSD unit deployed in the SRS HB-Line Facility, and 3) a radioactive small-scale unit. The non-radioactive small-scale distillation unit was fabricated from Alloy 600 by the SRNL Machine Shop and consisted of a 5-cm inside diameter (ID) heated zone (23 cm long) which opened up to a 8.5-cm ID cooled zone (21 cm long). The apparatus used a stainless-steel cooling coil wrapped around the outside of the 8.5-cm ID section and was cooled using 20 °C water. During testing, the system was closed and evacuated using a Pyrex™ end-flange and Viton™ o-ring. The end-flange was held in place only by the vacuum, negating the need for additional over-pressure protection measures. The end-flange was designed to enable the operator to view the interior of the VSD unit during testing. The radioactive small-scale unit has dimensions similar to that of the non-radioactive small scale unit with the exception of the cooled section being 38 cm long instead of 21 cm.

The non-radioactive pilot-scale system was fabricated from Alloys 600 and 690 by the SRNL Machine Shop. Its physical dimensions and features correspond to the vacuum chamber deployed in HB-Line. It consisted of a 28-cm long 7.5-cm ID heated zone which opened to a 53-cm long 10-cm ID cooled zone. The cooled zone contained 32 cm of 6.4-mm stainless-steel cooling coil wrapped around it. The VSD vacuum chamber was heated using a Carbolite GHC 12/450 three-zone tube furnace rated at 3120 W. It was cooled with either 20 °C water or compressed air. The system was evacuated using an Edwards RV5 oil vacuum pump. The vacuum pump was connected to the vacuum chamber using stainless-steel bellows hose. A picture of the VSD apparatus in the furnace is provided in Figure 2. The end cap was fabricated from 304L stainless steel with a groove for a Viton™ o-ring. Vacuum was measured adjacent to the flange with an Edwards Pirani™ gauge.
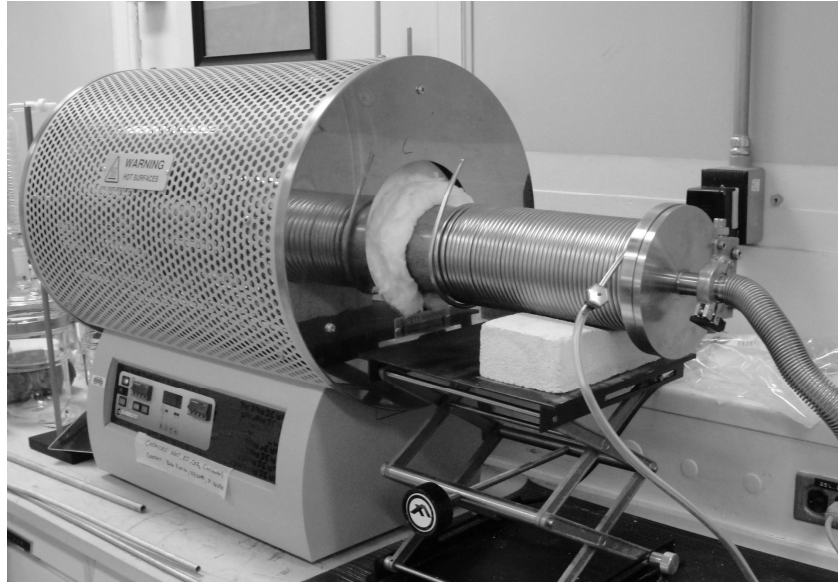
Figure 2. Non-radioactive pilot-scale VSD apparatus.

For pilot-scale testing, a removable liner was used for salt collection. The liner was fabricated from 304L stainless steel. Inside the liner were placed simple baffles also fabricated from 304L stainless steel. The liner and simple baffles are shown in Figure 3. The liner had a 9-cm outside diameter (OD) with rails on the outside to center the liner inside the 10-cm ID of the vacuum chamber (see Figure 4).
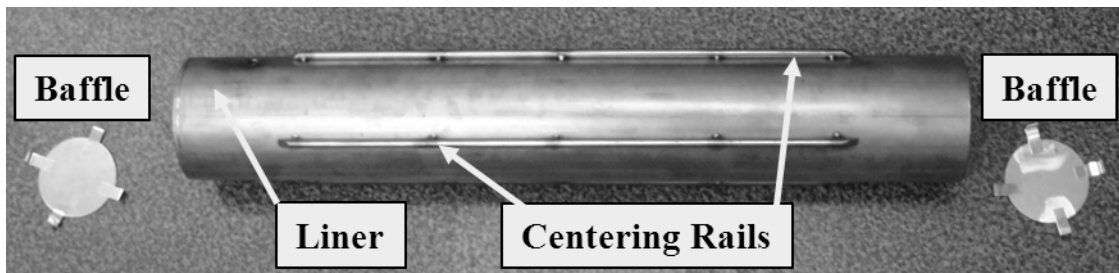
Figure 3. Removable liner with simple baffle plates.
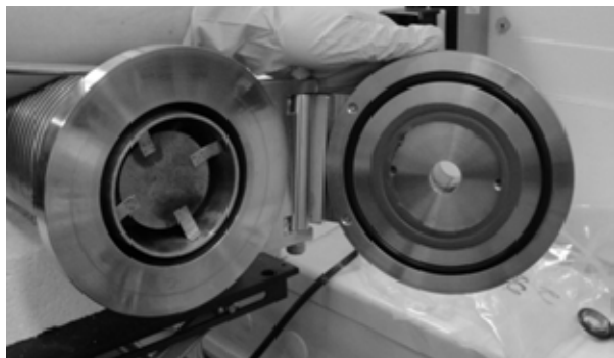
Figure 4. Removable liner installed in pilot-scale apparatus.

Small-scale tests used quartz boats with a quartz cover. The quartz boats were nominally 12 cm long, 2.5 cm wide, and 2 cm deep. Pilot-scale tests used two similar boat designs. The pilot-scale boats employed a two-piece lid design to create a tortuous path for any entrained oxide in

4

the halide vapor phase to leave the boat. The first boat was 15 cm long, 7 cm wide, and 2 cm deep alumina with Alloy 600 lids. The second pilot-scale boat was a 15-cm long, 6.5-cm wide boat fabricated from Alloy 600 by the SRNL Machine Shop. The boat has a semi-octagonal cross section and is a shortened version of the design used in HB-Line.

Test Methods

Reaction of Halides with Alkali Hydroxide

The reaction of either NaOH or KOH with $CaCl_2$, CaF_2, and cerium fluoride (CeF_3) – the latter a surrogate for PuF_3 – was studied. For these tests, known amounts of alkali hydroxide and halide salt were combined in a small alumina boat. They were placed into the pilot-scale vacuum chamber and the door closed. Based on previous work studying the reaction of sodium peroxide with halide salt,[5] the boat and contents were heated to 700 °C in air at atmospheric pressure. The boat was held at temperature for 30 min. Next, vacuum was applied and the boat heated to 980 °C for 30 min. The boat was then cooled under vacuum. The products remaining in the boat from the CaF_2 and CeF_3 tests were analyzed using X-ray diffraction (XRD).

The product remaining in the boat from the $CaCl_2$ test was analyzed for chloride concentration. The chloride content of the product was measured as follows. A sample of the oxide product was weighed into a plastic centrifuge tube with a screw-on cap. De-ionized (DI) water was added to the centrifuge tube and weighed. The screw cap was secured onto the tube and the tube was shaken vigorously for 3 min. Next, the chloride concentration of the water was tested using a Hach QuanTab® chloride test strip. The validity of this method was demonstrated during an earlier study.[3] The quantities of reactants for each test are listed in Table 1.

Table 1. Test conditions for reacting alkali hydroxide with halide salts.

Halide Salt	Halide Salt Mass (g)	Alkali Hydroxide	Alkali Hydroxide Mass (g)	Product Mass (g)
CaF_2	2.0159	KOH	9.1082	1.4359
CeF_3	3.0203	KOH	9.0688	3.8595
$CaCl_2$	2.9731	NaOH	8.8293	1.3333

Based on alkali halide distillation results (Section 3.2.1), the temperature of reaction for KOH with CaF_2 was studied to determine if the reaction would occur in the CeO_2 matrix before appreciable volatilization of KOH occurred under vacuum. Four parallel experiments were performed by combining KOH, CaF_2, and CeO_2 in a zirconium metal crucible, heating the crucible to a specified temperature in air using a muffle furnace, removing the crucible from the furnace, and analyzing the reaction products with XRD.

The contents of the four crucibles were weighed and the loaded crucible placed in the muffle furnace. The crucibles were heated in air to 400 °C and held at temperature for 20 min (KOH melts at 360 °C). After 20 min at temperature, one of the crucibles was removed from the furnace and placed in a desiccator to cool. Next, the furnace was heated to 475 °C and held for 20 min. After 20 min, a second crucible was removed and placed in the desiccator. The procedure was repeated at 550 °C and 625 °C. The crucibles and contents were all analyzed using XRD. The test conditions are listed in Table 2.

Table 2. Test conditions for reacting KOH with CaF_2 in a CeO_2 matrix.

Reaction Temp	400 °C	475 °C	550 °C	625 °C
CaF_2 (g)	0.2015	0.2035	0.2054	0.2003
CeO_2 (g)	2.0189	2.0086	2.0242	2.0038
KOH (g)	0.4460	0.4452	0.5345	0.5382

Small-Scale Process Demonstration

Small-scale demonstrations were completed in the small-scale VSD unit using small quartz crucibles. Each test started with ~21.5 g of CeO_2. The CeO_2 was then added and mixed with either 3.1-3.4 g of $CaCl_2$ or ~2.2 g of CaF_2. Last, KOH was added. The amount of KOH was calculated based on the mole ratios of reaction 1 plus varying amounts of excess KOH. The location of the KOH varied. Some tests added the KOH on top of the CeO_2 mixture, other tests added it to the bottom of the crucible before the CeO_2 mixture was added, and most tests involved mixing the KOH into the CeO_2 mixture. The masses of reactants and locations of KOH are provided in Table 3.

Table 3. Small-Scale Demonstration Test Conditions

Test	CeO_2 (g)	Halide Salt	Halide Salt (g)	KOH (g)	mol KOH per mol halide	KOH location
1	21.52	$CaCl_2$	3.39	3.43	1.0	top
2	21.51	$CaCl_2$	3.42	3.46	1.0	bottom
3	21.50	$CaCl_2$	3.41	3.42	1.0	bottom
4	21.51	$CaCl_2$	3.41	3.46	1.0	mixed
5	21.51	$CaCl_2$	3.41	3.43	1.0	mixed
6	21.50	$CaCl_2$	3.41	3.43	1.0	mixed
7	21.51	$CaCl_2$	3.41	3.47	1.0	mixed
8	21.51	$CaCl_2$	3.14	5.18	1.6	mixed
9	21.50	$CaCl_2$	3.15	5.14	1.6	bottom
10	21.51	$CaCl_2$	3.12	5.19	1.6	mixed
11	21.51	$CaCl_2$	3.16	7.60	2.4	mixed
12	21.51	CaF_2	2.19	3.14	1.0	mixed
13	21.50	CaF_2	2.19	4.40	1.4	mixed
13b	Continuation of previous test					
14	21.51	CaF_2	2.19	5.66	1.8	mixed
14b	Continuation of previous test					
Note: All tests at 950 °C for 60 min except Tests 13b and 14b which were at 950 °C for an additional 120 min						

Following the distillation experiment, the concentration of chloride or fluoride in the product boat was measured. The chloride content of the CeO_2 was measured as follows. A sample of the distilled oxide was weighed into a plastic centrifuge tube with a screw-on cap. De-ionized (DI) water was added to the centrifuge tube and weighed. The screw cap was secured onto the tube and the tube was shaken vigorously for 3 min. Next, the chloride concentration of the water was tested using a Hach QuanTab® chloride test strip. The fluoride concentration was analyzed by Analytical Development (AD). The sample was digested (~0.5 g in 10 mL of ~1 M sulfuric acid [H_2SO_4] for 3 h at 115 °C), and the resulting solution analyzed by ion chromatography (IC).

Pilot-Scale Process Demonstration

Pilot-scale demonstrations were completed in the pilot-scale VSD unit using boats described earlier. Each test started with a selected amount of CeO_2. We then added and mixed into the CeO_2 a pre-determined amount of either $CaCl_2$ or CaF_2. Last, KOH was added. The amount of KOH was calculated based on the mole ratios of reaction 1 plus a selected molar excess KOH. In all pilot-scale tests, the KOH was mixed into the CeO_2 mixture. The masses of reactants are provided in Table 4. For all pilot-scale tests, the boat was heated to 700 °C at atmospheric pressure, held for 10 min, evacuated, and then heated to 950 °C for a set amount of time. Following each distillation experiment, the concentration of chloride or fluoride in the product boat was measured using the methods discussed in the previous section.

Table 4. Pilot-Scale Demonstration Test Conditions

Test	CeO$_2$ (g)	Halide Salt	Halide Salt (g)	KOH (g)	mol KOH per mol halide	Time at 950 °C (min)
15	86.3	CaCl$_2$	13.6	22.1	1.6	60
16	86.3	CaCl$_2$	13.6	22.0	1.6	60
17	86.4	CaCl$_2$	13.6	22.0	1.6	60
18	86.3	CaCl$_2$	13.7	19.3	1.4	60
19	231.9	CaCl$_2$	36.7	51.6	1.4	60
19b	Continuation of previous test					180 (total)
20	200.1	CaF$_2$	20.4	40.9	1.4	180
Note: All tests heated to 700 °C at atm for 10 min and then to 950 °C under vacuum						

Reaction with Plutonium Fluoride

A sample of PuF_3 was prepared by heating 5.72 g of PuO_2 with 7.03 g of ammonium bifluoride (NH_4F-HF) in an alumina crucible under an argon gas purge for 30 min at 150 °C, 60 min at 300 °C, and 90 min at 450 °C. Next, 6.093 g of resulting material, predominantly PuF_3 (Figure 5), was mixed with 7.062 g of KOH and placed in a quartz crucible. A quartz cover was placed over the material. The crucible was placed in the glovebox VSD apparatus and heated under vacuum to 950 °C for 60 min. The crucible was cooled to room temperature under vacuum. A sample of the material after VSD was submitted for XRD.
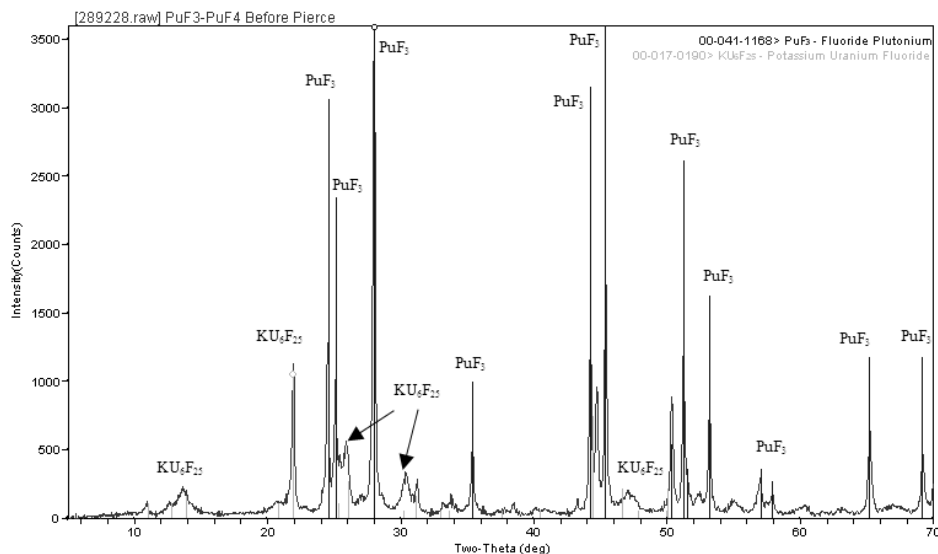
Figure 5. PuF$_3$ before reaction with KOH and distillation.

RESULTS AND DISCUSSION

Reaction of Halides with Alkali Hydroxide

The first tests to study the reaction chemistry used CaCl$_2$ instead of CaF$_2$ or CeF$_3$. There are two reasons. First, the presence of residual chloride can be determined immediately using chloride test strips. Second, previous VSD work had already shown that CaCl$_2$ could not be sufficiently distilled using the VSD flowsheet deployed in HB-Line, even above 1000 °C.[6] When NaOH was reacted with CaCl$_2$ at 950 °C and then distilled, the residual chloride content in the product was <50 mg/kg. This test provided an indication that the desired reactions occurred with CaCl$_2$.

Subsequent experiments reacted KOH with CaF$_2$ and CeF$_3$; the experiments were conducted side-by-side. The final product from each product crucible was analyzed using XRD, which has a nominal detection limit of 0.5 wt %. The starting CaF$_2$ concentration was ~18 wt % and the starting CeF$_3$ concentration was ~25 wt % in KOH. For both products, XRD showed no presence of fluoride or residual KOH. Residual KOH would appear in the spectrum as KOH, KOH hydrate, or potassium carbon (K$_2$CO$_3$), depending on the extent of exposure to air and moisture. These results show that VSD can remove fluoride from CaF$_2$ and CeF$_3$ below 1000 °C.

The presence of product splattering in the previous test raised a concern about whether conditions could be identified which would allow reaction of KOH with the halide salt at a temperature before significant KOH evaporation occurred. Experiments were completed that reacted CaF$_2$ with KOH in a CeO$_2$ matrix in air at 400 °C, 475 °C, 550 °C, and 625 °C. All four temperatures are above the melting point (~360 °C) for KOH. In all four tests, the KOH had already reacted with CaF$_2$ to produce either Ca(OH)$_2$ or CaO. XRD of the product from 400 °C test showed CeO$_2$, K$_2$CO$_3$-1.5 H$_2$O (reaction of KOH with air), and Ca(OH)$_2$. Analyses of products from tests at 475 °C, 550 °C, and 625 °C identified CeO$_2$, K$_2$CO$_3$-1.5 H$_2$O, and CaO. The four tests exhibit that KOH will begin reacting with CaF$_2$ (and presumably CaCl$_2$ and CeF$_3$) by the time the boat temperature reaches 400 °C. This result means that it is unlikely that a special heating cycle will be required to react KOH with the halide salts prior to the onset of significant KOH evaporation.

Small-Scale Process Demonstration

The MOX feed specification for fluoride in PuO_2 is 7500 mg/kg. Of the impure PuO_2 materials that do not meet the MOX specification because of fluoride contamination, all have fluoride concentrations below 4.5 wt % (or 45,000 mg/kg). Consequently, fluoride removal tests were run on CeO_2 combined with 4.5 wt % fluoride as CaF_2. When, as mentioned earlier, $CaCl_2$ was used instead of CaF_2 because of the ability to immediately analyze for chloride, tests were run at a nominal chloride concentration of 8.4 wt %. On a mole percent basis, 4.5 wt % fluoride and 8.4 wt % chloride yield the same molar concentration of halide.

Eleven experiments were completed with ~8.4 wt % chloride in CeO_2; three experiments with ~4.5 wt % fluoride in CeO_2 were also conducted. The data are listed in Table 5. The data in Table 5 address two process parameters, location of KOH and the amount of excess KOH needed to meet the MOX specification. Regarding the location of KOH, the easiest approach would be to place the KOH either above or below the oxide material in the boat. If placed above, it is hoped that the KOH will melt, diffuse through the product, and react with the halides. If placed below, the KOH can melt, diffuse through the product, and be forced to react with the halides as it is drawn through the product during evaporation.

Table 5. Small-Scale Demonstration Test Conditions

Test	CeO_2 (g)	Halide Content	% KOH Molar Excess	KOH location	Product Chloride (mg/kg)	Product Fluoride (mg/kg)	% Halide Removed
1	21.5	8.7 wt % Cl^-	0	top	25977	---	70.1
2	21.5	8.7 wt % Cl^-	0	bottom	4171	---	95.2
3	21.5	8.7 wt % Cl^-	0	bottom	6328	---	92.8
4	21.5	8.7 wt % Cl^-	0	mixed	6825	---	92.2
5	21.5	8.7 wt % Cl^-	0	mixed	11468	---	86.9
6	21.5	8.7 wt % Cl^-	0	mixed	8927	---	89.8
7	21.5	8.7 wt % Cl^-	0	mixed	11086	---	87.3
8	21.5	8.1 wt % Cl^-	60	mixed	1318	---	98.4
9	21.5	8.1 wt % Cl^-	60	bottom	1739	---	97.9
10	21.5	8.1 wt % Cl^-	60	mixed	2168	---	97.3
11	21.5	8.1 wt % Cl^-	140	mixed	457	---	99.4
12	21.5	4.5 wt % F^-	0	mixed	---	17582	60.9
13	21.5	4.5 wt % F^-	40	mixed	---	6608	85.3
13b	Continuation of previous test				---	3776	91.6
14	21.5	4.5 wt % F^-	80	mixed	---	2341	94.8
14b	Continuation of previous test				---	<494	>98.9

Note: All tests at 950 °C for 60 min except Tests 13b and 14b which were at 950 °C for 180 min total
- Shaded cells indicate ability to meet MOX fluoride specification within 10% uncertainty

A comparison of the data from Tests 1 and 2 show that placing the KOH on top of the material being processed is not a viable option. Although 70% of the halide is removed, it is apparent that the KOH did not diffuse far enough into the product. The halide-removal performance would likely be worse for deeper product beds. Comparison of Tests 2-3 with Tests 4-7 indicate that placing the KOH at the bottom of the boat performs better than mixing the KOH throughout the product. However, the data in Table 5 do not assess an important process impact of placing the KOH beneath the product. That is, in most cases, during the evaporation of KOH, entrainment of CeO_2 was a problem. The quantities of CeO_2 lost from the boat were not quantified because of

the difficulty of separating the CeO_2 from the distilled salt. The same issues were not prevalent when the KOH was mixed in the material.

The data in Table 5 also provide an estimate of the amount of excess KOH required to remove a particular amount of halide when the KOH is mixed into the feed material. Tests with $CaCl_2$ (Tests 1-11) show that using no excess KOH will likely result in a product that does not meet the MOX specification for fluoride (assuming fluoride and chloride behave the same). The data in Table 5 also show that 140% molar excess of KOH is an unnecessarily large amount. The use of 60% molar excess consistently meets the MOX specification with margin for error and uncertainty.

For the removal of CaF_2 (Tests 12-14), two observations were made. First, because KF is not as volatile as KCl (Figure 1), it takes longer for KF to distill. Comparison of the data from Tests 13 and 13b and Tests 14 and 14b depicts the impact of heating for three hours instead of one hour. A sizable decrease in residual fluoride in the product occurs. The second observation is that, similar to $CaCl_2$ removal, the use of 40-60% molar excess KOH is suitable for CaF_2 removal.

Pilot-Scale Process Demonstration

The small-scale data (Table 5) provided the conditions for pilot-scale testing (Table 6). Four tests with $CaCl_2$ were completed using 100 g of feed (not counting KOH) and one test (Test 19/19b) was performed with 268.6 g of feed. Two different boats used for pilot-scale testing, as described in the Experimental section. The more-shallow Al_2O_3 boat was used for the 100-g $CaCl_2$ tests; the Alloy 600 boat was used for the 268.6-g $CaCl_2$ test and the pilot-scale test with CaF_2 (Test 20). The significance of the Alloy 600 boat is that it is of the same general design as the boat used for HB-Line operations.[7] Consequently, Tests 19/19b and 20 give a strong indication of how effective fluoride removal can be in a VSD system similar in design to the system deployed in HB-Line.

At the 100-g scale, the data in Table 6 show that both 40% and 60% molar excess of KOH are sufficient to meet the MOX specification after 60 min at 950 °C. However, at the 268.6-g scale, because of the greater product depth, 180 min was needed to achieve excellent halide removal (>99.0%). Due to the bulk density of the CaF_2, 220.5 g of feed could be loaded into the boat for the pilot-scale removal of fluoride (versus 268.6 g for chloride removal). Only 40% molar excess of KOH was needed to remove greater than 99.0% of the fluoride after 180 min.

**Table 6.** Pilot-Scale Demonstration Test Conditions

Test	CeO_2 + Halide Salt (g)	Halide Content	% KOH Molar Excess	KOH location	Product Chloride (mg/kg)	Product Fluoride (mg/kg)	% Halide Removed
15	99.9	8.7 wt % Cl^-	60	mixed	1178	----	98.7
16	99.9	8.7 wt % Cl^-	60	mixed	3192	----	96.3
17	100.0	8.7 wt % Cl^-	60	mixed	925	----	98.9
18	100.0	8.7 wt % Cl^-	40	mixed	1307	----	98.5
19	268.6	8.7 wt % Cl^-	40	mixed	6516	----	92.5
19b	Continuation of previous test				516	----	99.4
20	220.5	4.5 wt % F^-	40	mixed	----	<465	>99.0
Note: All tests at 950 °C for 60 min except Tests 19b and 20 which were at 950 °C for 180 min total							
- Shaded cells indicate ability to meet MOX fluoride specification within 10% uncertainty							

One other important point can be drawn from a comparison of data in Table 5 with Table 6. Although the amount of data is limited, the same amount of KOH molar excess seems to yield better results as the bed depth increases (Tests 8-10, 16-18 vs. 19; Test 13/13b vs. 20). This result is consistent with the data in Table 5 which showed that placing the KOH at the bottom of the boat yielded better halide removal than mixing the KOH with feed material.

Reaction with Plutonium Fluoride

Although more data related to plutonium (Pu) will be required to fully demonstrate a VSD process for fluoride removal, proof of feasibility required two questions to be answered. First, does PuF_3 react with KOH to form PuO_2? Second, does KOH with Pu compounds to form some compound other than PuO_2?

In the radioactive test, PuF_3 was reacted with KOH and distilled. XRD analyses of the initial and final compounds were obtained and are provided in Figure 5 (before) and Figure 6 (after). The data show that the PuF_3 was completely converted to PuO_2, and that no residual KOH was present in the product; the detection limit for XRD is ~0.5 wt %. It should be noted that the starting material was primarily PuF_3, but it did contain a minor amount of a Pu-ammonium-fluoride compound (analog to KU_6F_{25} in Figure 6 data). The Pu ammonium fluoride was a byproduct of the method (ammonium bifluoride fusion) used to produce the PuF_3 sample. It is also worth noting that KOH did not react with Pu to form a compound other than PuO_2.
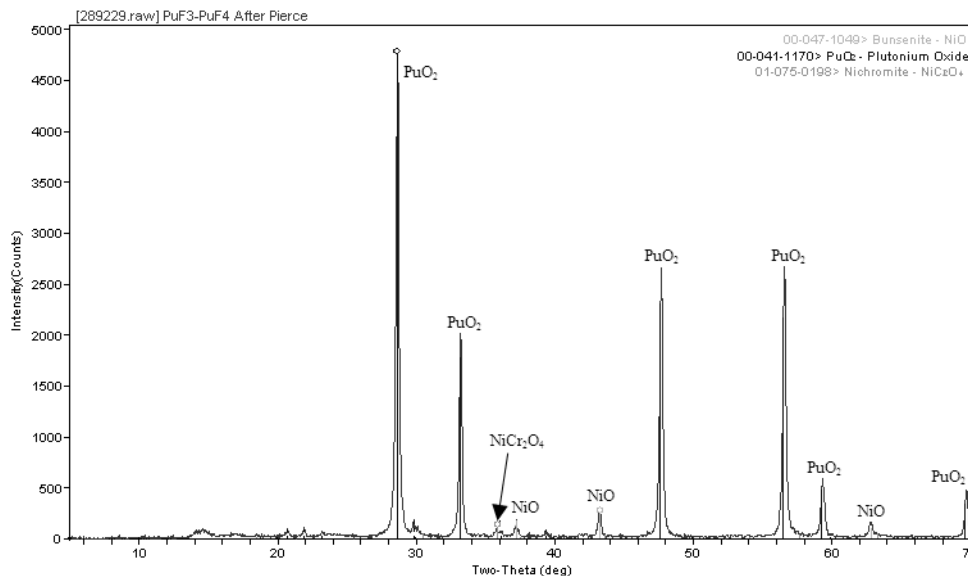
Figure 6. PuF3 after Reaction with KOH followed by VSD

Important Mechanical Design Considerations

During the deployment in HB-Line of a VSD system for NaCl/KCl removal, two minor system modifications were required for proper performance.[7] A baffle plate was installed on the VSD end cap to alter the flow pattern in the cooled zone which enabled salt deposition prior to it exiting the system. Also, a heat shield was attached to the feed boat to provide a thermal barrier between the cooled and heated zones which prevented the front of the feed boat from being too cold for adequate salt distillation.

The use of KOH as a reactant introduces two significant design considerations. First, allowances must be made for the increased volatility of KOH compared to NaCl/KCl (Figure 1). Can the KOH vapors be condensed before exiting the system? Early testing showed that the simple baffle on the vacuum chamber end cap would not be sufficient to promote KOH deposition. More importantly, a second impact was also observed. After initial VSD tests with KOH were performed, it was noted that KOH had deposited on the outside of the boat in the heated section. This behavior made it difficult to remove the boat from the vacuum chamber. Some design feature had to be identified to isolate the heated and cooled zones better to prevent back-evaporation and deposition of KOH in the heated zone as cooling occurred.

In addition to volatility issues associated with KOH, a second issue exists because KOH is extremely hygroscopic and readily absorbs moisture from the humid atmosphere of South Carolina. The absorption of moisture could complicate the cleaning of the vacuum chamber; the HB-Line deployed employed mechanical cleaning methods.[7] Also, any residual KOH in the vacuum chamber after cleaning could make subsequent system evacuation more difficult due to absorbed moisture.

The answer to both design considerations was realized through the use of a removable liner (Figure 3). The purpose of the removable liner is to provide a location for salt deposition that can be removed and either discarded or cleaned in an alternate location. The installed liner is shown in Figure 4. Although neither the VSD vacuum chamber nor the end of the liner was tapered to provide a tight fit between them, typical salt recovery in the liner was 98-99 wt %. It is expected that almost all of the salt can be collected in the liner by modifying the design of the VSD chamber and the liner to provide a tapered fit. The high salt recovery efficiencies also eliminated another concern associated with the use of a removable liner, which is having the liner get stuck in the chamber. For all liner trials, sticking of the liner was never observed.

The use of the removable liner also provided a means for resolving the issue associated with using baffles to adequately separate the heated and cooled zones. Without the presence of a removable liner, the use of a baffle in the heated zone that was separate from the feed boat seemed impossible. If a baffle was inserted into the vacuum chamber heated zone prior to distillation, the deposition of salt in the cooled zone during processing would make it impossible to remove the baffle without first disturbing the salt layer.

However, with the removable liner, a baffle can be placed into the heated end of the liner. With placement in the heated zone, no salts deposit on or around the baffle. Consequently, once the liner is removed from the chamber, the baffle in the heated end of the liner can be easily removed. When the liner with a baffle in the heated zone was deployed, no more issues were noted with the boat getting stuck in the heated zone. The baffle provided enough of a heat shield between the heated and cooled zones to prevent KOH deposition in the heated zone.

It should be noted that the baffles do more than act as heat shields. They also route the flow of gases in the liner to stay close to the liner walls for longer. Figure 7 shows the salt deposition pattern inside of the liner from both the heated and cooled zones.
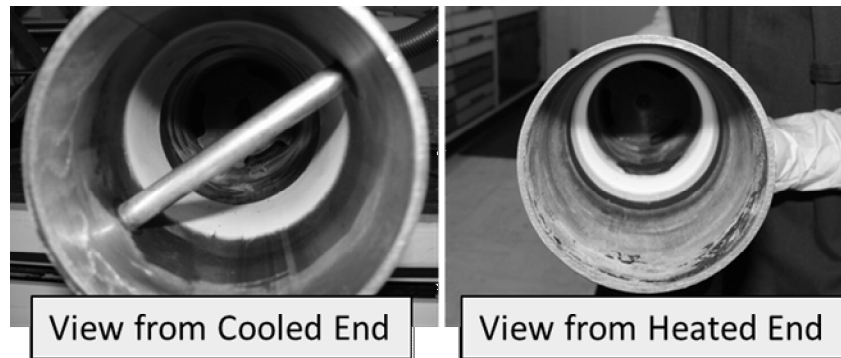
Figure 7. Salt Deposition Pattern inside Removable Liner

CONCLUSIONS

SRNL has successfully demonstrated the removal of halide from $CaCl_2$, CaF_2 and PuF_3 below 1000 °C using VSD technology. Although, NaCl, KCl, and KF are sufficiently volatile that they can be distilled from PuO_2 at a satisfactory rate under vacuum at 950 °C; other halide salts including $CaCl_2$, CaF_2, and PuF_3 are not. However, it has been shown that KOH reacts with $CaCl_2$, CaF_2, CeF_3, PuF_3 to form KF or KCl, water vapor, and an oxide (CaO, CeO_2, or PuO_2, respectively). The reaction of KOH with CaF_2 to form CaO begins below 400 °C and is complete by 475 °C. Once the reaction occurs, the products of KF, KCl, and excess KOH can be removed by VSD. Although NaOH can also be used to produce similar reactions, the NaF byproduct is not sufficiently volatile to meet the processing-rate targets used for chloride salt removal by VSD.

Small-scale process demonstrations (25-30 g feed) showed the removal of 45,000 mg/kg fluoride (as CaF_2) and 84,000 mg/kg chloride (as $CaCl_2$) to less than 4000 mg/kg using 40-60% molar excess of KOH. This level of halide removal is more than adequate to meet the MOX fuel specification for fluoride of 7500 mg/kg. The location of KOH in the feed boat is an important consideration. Placing the KOH at the bottom of the feed boat produces the best fluoride removal results but may lead to product loss from the boat. Mixing the KOH into the feed produces satisfactory fluoride removal without the loss of material from the feed boat.

Pilot-scale process demonstrations (100-270 g) using 40-60% molar excess of KOH yielded better results than the small-scale tests. In a 269-g test with 40% molar excess of KOH, chloride (as $CaCl_2$) in CeO_2 was reduced from 87,000 mg/kg to 516 mg/kg. In a 220-g test with 40% molar excess of KOH, fluoride (as CaF_2) in CeO_2 was reduced from 45,000 mg/kg to <465 mg/kg.

The introduction of KOH and its reaction byproducts into the process requires some changes to the way the salts are deposited and removed. To date, it appears that a removable liner with a system of multiple reusable baffles can compensate for the process changes.

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