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Application of Vacuum Salt Distillation Technology for the Removal of Fluoride

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EXECUTIVE SUMMARY

Vacuum distillation of chloride salts from plutonium oxide (PuO_2) and simulant PuO_2 has been demonstrated and deployed at the Savannah River Site (SRS) for the removal of sodium chloride (NaCl) and potassium chloride (KCl). The application of vacuum salt distillation (VSD) is of continued interest to the HB-Line Facility and the Mixed Oxide Fuel Fabrication Facility (MFFF) at SRS for the disposition of excess fissile materials. Many of these materials contain chloride and fluoride salt concentrations which make them unsuitable for dissolution at MFFF without prior removal of the chloride and fluoride salts.

Chloride and fluoride salts of interest – plutonium trifluoride (PuF_3), calcium fluoride (CaF_2), and calcium chloride (CaCl_2) — are less-volatile than NaCl and KCl . However, without increasing the operating temperature, the VSD technology has been successfully adapted for the handling of less-volatile halide salts. Experiments at the Savannah River National Laboratory (SRNL) demonstrated the chemistry for the removal of less-volatile halides and addressed the primary engineering questions associated with the change in the process chemistry.

SRNL has successfully demonstrated the removal of halide from CaCl_2 , CaF_2 and PuF_3 below 1000 °C using VSD technology. The level of halide removal has been more than adequate to meet the MOX fuel specification (7500 mg/kg) for fluoride. The removal of halide is facilitated by first reacting potassium hydroxide (KOH) with CaCl_2 , CaF_2 , and PuF_3 to form potassium fluoride (KF) or potassium chloride (KCl), water vapor, and an oxide; KF , KCl , and excess KOH can be removed by VSD.

Small-scale process demonstrations (25-30 g bulk feed) showed the removal of 45,000 mg/kg fluoride from CaF_2 and 84,000 mg/kg chloride from CaCl_2 to less than 4000 mg/kg using 40-60% molar excess of KOH . 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) mixed with cerium oxide (CeO_2) – a surrogate for PuO_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) mixed with CeO_2 was reduced from 45,000 mg/kg to <465 mg/kg.

The introduction of KOH and its reaction byproducts requires some changes to the way the salts are deposited and removed. A removable liner with a system of multiple reusable baffles may be sufficient to accommodate most of the process changes. The reaction of KOH with halide salts also produces water vapor as a byproduct. Although this water vapor could cause issues with the existing dry vacuum pump used by HB-Line, the installation of a low-cost, disposable, in-line moisture absorbent should be sufficient to protect the pump.

SRNL proposes an ongoing development program using available equipment that has the same internal dimensions as the VSD unit deployed in HB-Line. The program will define physical and chemical parameters needed for scale-up and deployment of a system for fluoride removal. The majority of the work will be with non-radioactive materials. Small-scale tests with PuO_2 and PuF_3 will supplement the non-radioactive experiments.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	de-ionized
DOE	Department of Energy
IC	ion chromatography
ID	inside diameter
MFFF	MOX Fuel Fabrication Facility
MOX	mixed oxide
NM	not measured
OD	outside diameter
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
VSD	vacuum salt distillation
XRD	X-ray diffraction

1.0 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 (SRS). Both facilities are involved in efforts to disposition excess 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.^[3] 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. Consequently, an alternate approach is required for the removal of fluoride without significantly increasing the operating temperature.

HB-Line Engineering requested SRNL to evaluate and demonstrate the feasibility of an alternate approach using both non-radioactive simulants and plutonium-bearing materials.^[4-5] Whereas the earlier developments targeted the removal of sodium chloride (NaCl) and potassium chloride (KCl), the current activities are concerned with the removal of the halide ions associated with plutonium trifluoride (PuF_3), plutonium tetrafluoride (PuF_4), calcium fluoride (CaF_2), and calcium chloride (CaCl_2).

This report discusses non-radioactive testing of small-scale and pilot-scale systems and radioactive testing of a small-scale system. Experiments focused on demonstrating the chemistry for halide removal and addressing the primary engineering questions associated with a change in the process chemistry.

2.0 Background

VSD technology takes advantage of the large difference in volatility between alkali halide salts and PuO_2 . As has been demonstrated, NaCl and KCl are sufficiently volatile that they can be distilled from PuO_2 at a satisfactory rate under vacuum above 900 °C.^[6] 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 2-1.^[7]

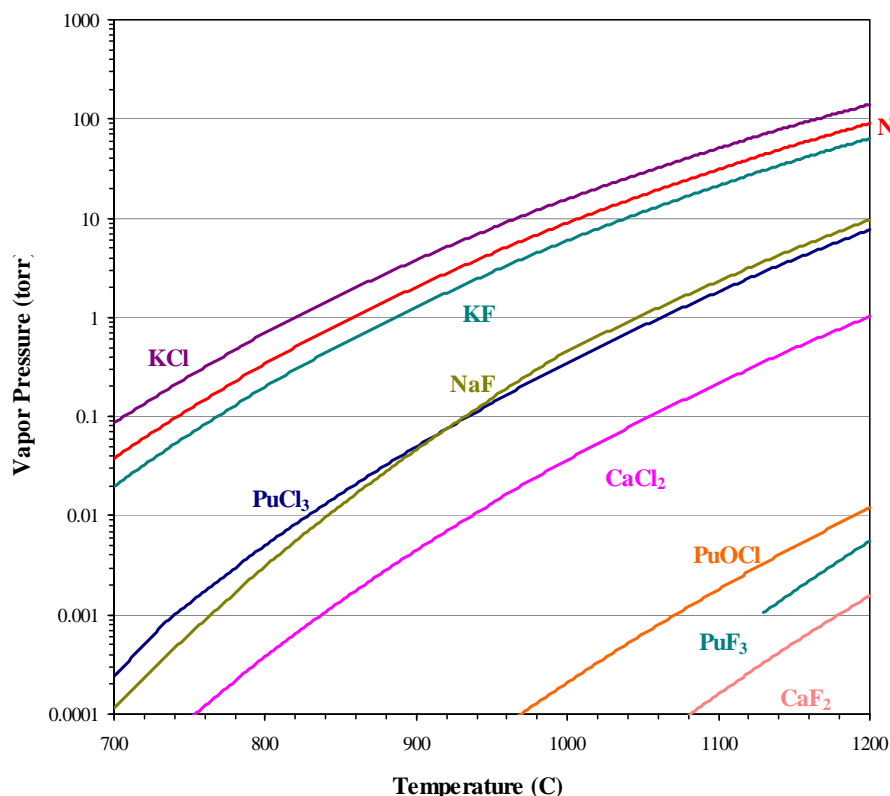
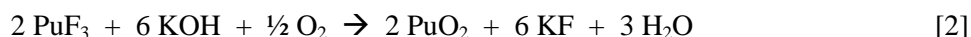


Figure 2-1. Comparison of Chloride and Fluoride Salt Volatility

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.^[8] 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.



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 2-2 shows the relative volatility of KOH and the relevant halide salts from Figure 2-1.^[7] 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 2-1 because the volatility of PuO_2 is about seven orders of magnitude lower than CaF_2 (to the right of CaF_2 in Figure 2-1); for comparison, the volatility of CaF_2 is about seven orders of magnitude lower than KCl and NaCl .

The literature indicates that PuF_4 will not be present in materials subjected to the 3013 process because it decomposes to PuO_2 at the temperatures used ($>750^\circ\text{C}$ for two hours) in the 3013 stabilization process.^[9] If it were, it is fully expected that any PuF_4 present would react similar to reaction 1.

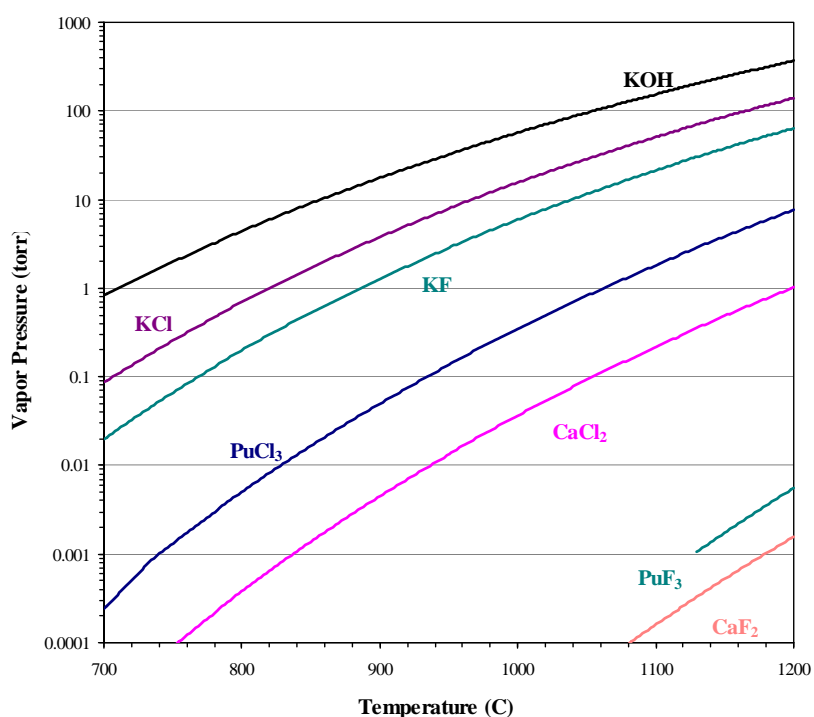


Figure 2-2. Salt Volatility Comparisons for Fluoride Removal by VSD

3.0 Experimental Procedure

3.1 Test Equipment

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 HB-Line, 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 PyrexTM end-flange and VitonTM 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. A photograph of the VSD setup is shown in Figure 3-1.



Figure 3-1. Small-Scale VSD System

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 vacuum chamber is shown in Figure 3-2, and a picture of the VSD apparatus in the furnace is provided in Figure 3-3. 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.

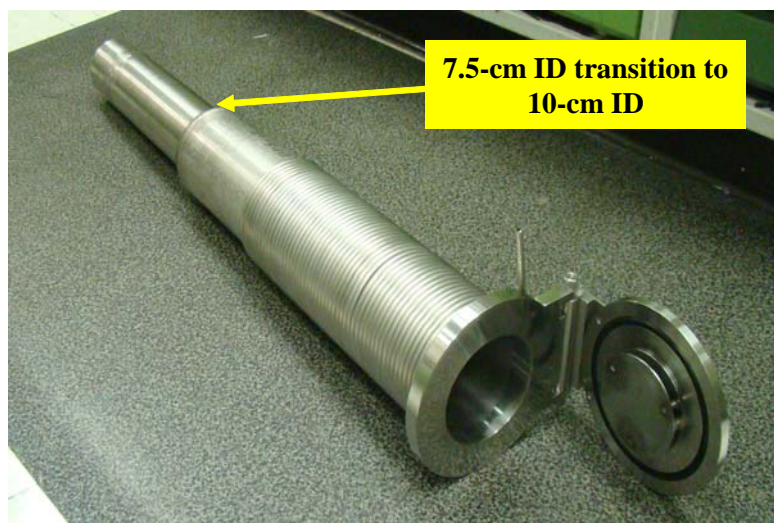


Figure 3-2. Intermediate-Scale Vacuum Chamber

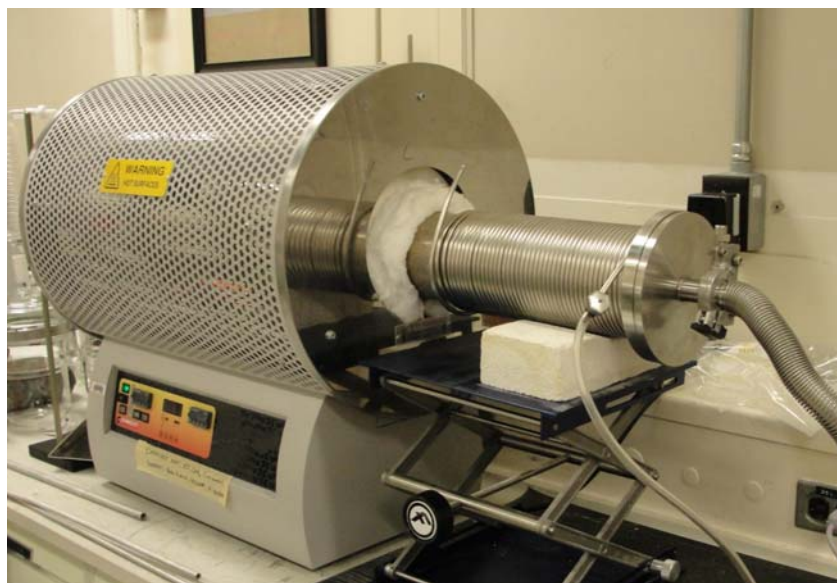


Figure 3-3. Intermediate-Scale System

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. Pictures and a discussion of the details of the unit are provided elsewhere.^[10]

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 3-4. 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 [Figure 3-5]. A modified baffle, shown in Figure 3-5, was also tested.

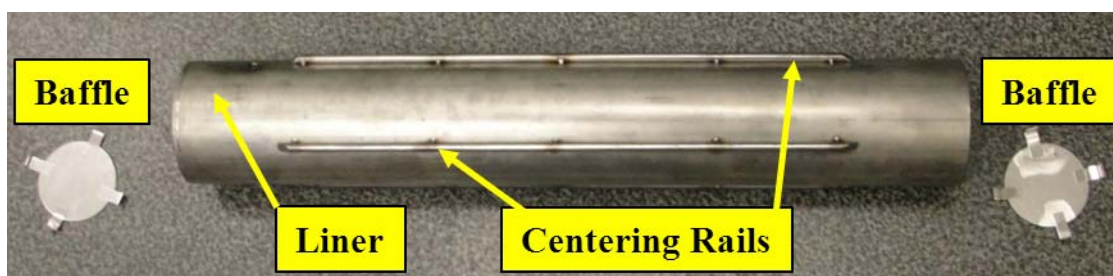


Figure 3-4. Removable Liner with Simple Baffle Plates



Figure 3-5. Removable Liner with Simple Baffle Plate (installed) / Modified Baffle Plate

Small-scale tests used either quartz or alumina boats with a quartz cover. The small-scale boats were nominally 12 cm long, 2.5 cm wide, and 2 cm deep. Pilot-scale tests used two similar boat designs during testing (Figure 3-6). The pilot-scale boats employed a two-piece lid design to create a tortuous path for any entrained oxide in 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.



Figure 3-6. Pilot-Scale Boats

The second pilot-scale boat is a 15-cm long, 6.5-cm wide boat fabricated from Alloy 600 by the SRNL Machine Shop (Figure 3-6). The boat has a semi-octagonal cross section to provide a stable base. The boat is a shortened version of the design used in HB-Line.

3.2 Test Methods

3.2.1 *Distillation of Alkali Hydroxides and Alkali Fluorides*

The relative distillation rates of KF and NaF were measured at 850-1000 °C. Similarly, the relative distillation rates of KOH and NaOH from CeO₂, a surrogate for PuO₂, were measured at 700-900 °C. Comparison of the distillation rates enables a decision regarding a preference for the use of KOH or NaOH as the reactant.

Distillation experiments with KF and NaF were completed in the small-scale VSD unit. For KF or NaF distillation, 5-13 g of alkali halide was placed in a weighed alumina boat. The boat was placed in the VSD vacuum chamber and the door closed. The chamber was heated to the test temperature. Once at temperature, the vacuum pump was turned on and the salt was distilled for 20 min. After 20 min, the vacuum was released and the furnace turned off to allow the boat to cool. The final weight of the boat and salt were recorded and the distillation rate calculated.

Distillation experiments with KOH and NaOH in a CeO₂ matrix were completed in the pilot-scale VSD unit. For each test, 6-15 g of hydroxide salt were mixed with 10-15 g of CeO₂ in an alumina

boat. The boat was placed in the VSD vacuum chamber and the door closed. The chamber was heated to the test temperature. Once at temperature, the vacuum was turned on and the salt was distilled for 20-45 min (20 min for tests with 10 g of CeO_2 and 45 min for tests with 15 g of CeO_2). After 20-45 min, the vacuum was released and the furnace turned off to allow the boat to cool. The final weight of the boat and salt were recorded and the distillation rate calculated.

3.2.2 Reaction of Halides with Alkali Hydroxide

The reaction of either NaOH or KOH with CaCl_2 , CaF_2 , and 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,^[8] 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.^[6] The quantities of reactants for each test are listed in Table 3-1.

Table 3-1. 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 3-2.

Table 3-2. Test Conditions for Reacting KOH with CaF₂ in a CeO₂ 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

3.2.3 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 CeO₂. The CeO₂ was then added and mixed with either 3.1-3.4 g of CaCl₂ or ~2.2 g of CaF₂. 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 CeO₂ mixture, other tests added it to the bottom of the crucible before the CeO₂ mixture was added, and most tests involved mixing the KOH into the CeO₂ mixture. The masses of reactants and locations of KOH are provided in Table 3-3. Table 3-3 also contains information on the heating cycles of each test.

Table 3-3. Small-Scale Demonstration Test Conditions

Test	CeO ₂ (g)	Halide Salt	Halide Salt (g)	KOH (g)	mol KOH per mol halide	KOH location	Heating Cycle
1	21.52	CaCl ₂	3.39	3.43	1.0	top	To 950 °C (vacuum)
2	21.51	CaCl ₂	3.42	3.46	1.0	bottom	To 950 °C (vacuum)
3	21.50	CaCl ₂	3.41	3.42	1.0	bottom	To 950 °C (vacuum)
4	21.51	CaCl ₂	3.41	3.46	1.0	mixed	To 950 °C (vacuum)
5	21.51	CaCl ₂	3.41	3.43	1.0	mixed	To 600 °C (vacuum) for 30 min; to 950 °C (vacuum)
6	21.50	CaCl ₂	3.41	3.43	1.0	mixed	To 450 °C (atm) for 30 min; to 950 °C (vacuum)
7	21.51	CaCl ₂	3.41	3.47	1.0	mixed	To 450 °C (atm) for 30 min; to 950 °C (vacuum)
8	21.51	CaCl ₂	3.14	5.18	1.6	mixed	To 950 °C (vacuum)
9	21.50	CaCl ₂	3.15	5.14	1.6	bottom	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
10	21.51	CaCl ₂	3.12	5.19	1.6	mixed	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
11	21.51	CaCl ₂	3.16	7.60	2.4	mixed	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
12	21.51	CaF ₂	2.19	3.14	1.0	mixed	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
13	21.50	CaF ₂	2.19	4.40	1.4	mixed	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
13b	Continuation of previous test						To 700 °C (atm) for 10 min; to 950 °C (vacuum)
14	21.51	CaF ₂	2.19	5.66	1.8	mixed	To 700 °C (atm) for 10 min; to 950 °C (vacuum)
14b	Continuation of previous test						To 700 °C (atm) for 10 min; to 950 °C (vacuum)

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 CeO₂ 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 [H₂SO₄] for 3 h at 115 °C), and the resulting solution analyzed by ion chromatography (IC).

3.2.4 Pilot-Scale Process Demonstration

Pilot-scale demonstrations were completed in the pilot-scale VSD unit using boats with a two-piece lid (see Figure 3-6). Each test started with a selected amount of CeO₂. We then added and mixed into the CeO₂ a pre-determined amount of either CaCl₂ or CaF₂. 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 CeO₂ mixture. The masses of reactants are provided in Table 3-4. 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 Section 3.2.3.

Table 3-4. 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						

3.2.5 Reactions with Plutonium Compounds

Two tests were performed separately to evaluate the reaction of alkali hydroxide with PuO₂ and with PuF₃. In the first test, NaOH reacted with PuO₂ that also contained about 3.3 wt % chlorides, including measurable amounts of CaCl₂. The PuO₂ sample (7.833 g) was mixed with NaOH (3.705 g) in a quartz crucible [2 moles of NaOH per mole of PuO₂ plus 60% molar excess]. 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 and the contents of the crucible sampled for XRD.

In the second test, PuF₃ was prepared by heating 5.72 g of PuO₂ with 7.03 g of ammonium bifluoride (NH₄F·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 PuF₃ (Figure 4-4), 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. Samples of the materials before and after VSD were submitted for XRD.

4.0 Results and Discussion

4.1 Distillation of Alkali Hydroxides and Alkali Fluorides

Evaporation rate data under VSD conditions were collected at 700-1000 °C for NaF, KF, NaOH in CeO₂, and KOH in CeO₂. The data are listed in Table 4-1. Although they do not directly indicate feasibility of the overall process, they do demonstrate that the evaporation rates of KF are roughly an order of magnitude greater than NaF, and that the evaporation rate of KOH from CeO₂ is measurably greater (1.5 to 3 times) than the evaporation rate of NaOH from CeO₂. During the development of the HB-Line system for chloride removal, a nominal evaporation target was arbitrarily set at ~1 g/min.^[6] Materials of construction limitations restrict the maximum operating temperature to ~982 °C.^[3] Consequently, the data in Table 4-1 suggest that NaOH and its reaction byproduct (NaF) are not sufficiently volatile to meet the targets used for chloride salt removal by VSD. The process can still work with NaOH and NaF, but the rates with KOH and KF are more in line with the processing rates desired for production-scale operations. Consequently, KOH is the preferred salt for converting fluoride salts with limited volatility to a more-volatile compound.

Table 4-1. Salt Evaporation Rates under VSD Conditions

Matrix	Distill Time (min)	Evaporation Rate (g/min)				
		850 °C	900 °C	950 °C	1000 °C	
NaF	20	0.024	0.044	0.086	0.214	
KF	20	0.164	0.517	0.896	NM	
Matrix	Distill Time (min)	Evaporation Rate (g/min)				
		700 °C	750 °C	800 °C	850 °C	900 °C
NaOH in CeO ₂	20	0.166	NM	0.223	NM	0.452
KOH in CeO ₂	20	0.250	0.400	0.644	NM	NM
KOH in CeO ₂	45	0.286	0.352	NM	NM	NM
NM = not measured						

4.2 Reaction of Halides with Alkali Hydroxide

The first tests to study the reaction chemistry used CaCl₂ instead of CaF₂ or CeF₃. 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 CaCl₂ could not be sufficiently distilled using the VSD flowsheet deployed in HB-Line, even above 1000 °C.^[11] When NaOH was reacted with CaCl₂ at 950 °C and then distilled, the residual chloride content in the product was <50 mg/kg. This test provided initial indication that the desired reactions occurred with CaCl₂.

Subsequent experiments reacted KOH with CaF₂ and CeF₃; 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 CaF₂ concentration was ~18 wt % and the starting CeF₃ concentration was ~25 wt % in KOH. The XRD spectra are provided in Figure 4-1 (for CeF₃) and Figure 4-2 (for CaF₂). For both products, XRD shows no presence of fluoride or residual KOH. Residual KOH would appear in the spectrum as KOH, KOH hydrate, or potassium carbon (K₂CO₃), depending on the extent of exposure to air and moisture. It is worth

noting that due to splattering during the evaporation of the KOH that some of the CeO_2 product ended up in the CaO. These results show that VSD can remove fluoride from CaF_2 and CeF_3 below 1000 °C, which is not practical without first reacting the salt with the alkali hydroxide.

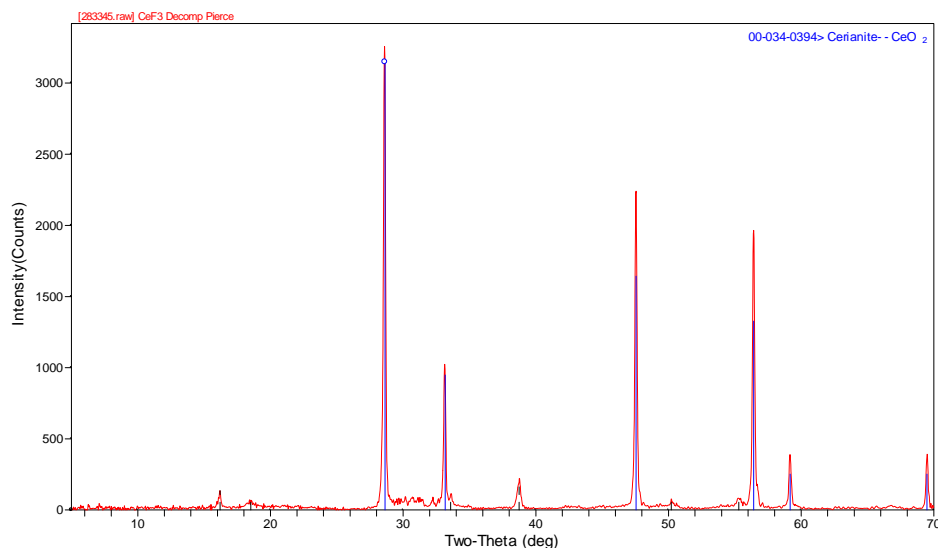


Figure 4-1. Product from Reaction of CeF_3 with KOH followed by VSD

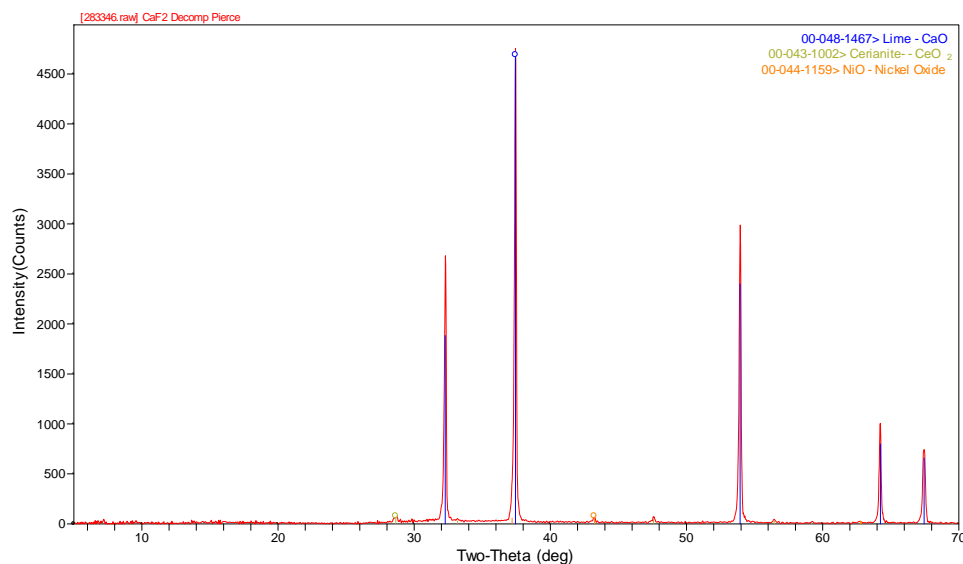


Figure 4-2. Product from Reaction of CaF_2 with KOH followed by VSD

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 , $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ (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 , $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$, 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.

4.3 Small-Scale Process Demonstration

The MOX feed specification for fluoride in PuO_2 is 7500 mg/kg. Of the impure PuO_2 materials in storage 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 and three experiments with ~4.5 wt % fluoride in CeO_2 were also conducted. The data are listed in Table 4-2. The data in Table 4-2 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 4-2. 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							
- Red-shaded cells indicate failure to meet MOX fluoride specification within 10% uncertainty; green-shaded cells meets the specification.							

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 4-2 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. Consequently, the current recommendation involves mixing the KOH with the feed material prior to processing.

The data also show that even when the KOH is mixed into the material, some controls have to be placed on the heating rate under vacuum. The method successfully used for these tests was a rapid heating (~14 min) to 700 °C at atmospheric pressure, a brief dwell time (~10 min), evacuation, and rapid heating (~10 min) to 950 °C. A slower heating rate under vacuum may be sufficient to control the evaporation rate of KOH, but it was not evaluated.

At some point in the future, it may be possible to demonstrate that, with proper boat design, the KOH can be loaded directly into the bottom of the boat, the feed material laid over it, and the boat heated rapidly under vacuum to 950 °C. Such an approach would simplify operations, but was not the subject of a feasibility demonstration.

The data in Table 4-2 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 4-2 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 2-1), 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.

4.4 Pilot-Scale Process Demonstration

The small-scale data (Table 4-2) provided the conditions for pilot-scale testing (Table 4-3). 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. Figure 3-6 shows the two boats used for pilot-scale testing. The boat on the left was used for the 100-g CaCl_2 tests; the boat on the right was used for the 268.6-g CaCl_2 test and the pilot-scale test with CaF_2 (Test 20). The significance of the boat on the right (Figure 3-6) is that it is of the same general design as the boat used in HB-Line.^[12] 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 4-3 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 light, fluffy nature of the CaF_2 used, only 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. The potential exists to further reduce the amount of the KOH added for fluoride removal.

Table 4-3. 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 - Red-shaded cells indicate failure to meet MOX fluoride specification within 10% uncertainty; green-shaded cells meets the specification.							

One other important point can be drawn from a comparison of data in Table 4-2 with Table 4-3. 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 4-2 which showed that placing the KOH at the bottom of the boat yielded better results than mixing the KOH with feed material.

4.5 Reactions with Plutonium Compounds

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 PuO₂ react with KOH and form some other Pu compound? If so, a potential issue would exist. Second, does PuF₃ react with KOH to form PuO₂? If not, a different issue would exist.

In the first radioactive test, PuO₂ with some CaCl₂ present was reacted with NaOH and distilled. However, during the test, the quartz lid over the crucible fell into the crucible and created a situation where the PuO₂ and NaOH were trapped between two quartz layers with no direct path for materials to distill. Significant effort was required to remove the cover and obtain a sample. The XRD analysis of the sample is shown in Figure 4-3. The analysis shows that the PuO₂ did not form an alternate Pu compound, but rather remained PuO₂. Also, no NaOH remained in the system. Last, the data suggest that the CaCl₂ was converted to NaCl, but was unable to distill. This last point is speculation based on what was known about the sample. Regardless, the primary point is that the first question mentioned above was answered – PuO₂ did not react with NaOH to form a different Pu compound.

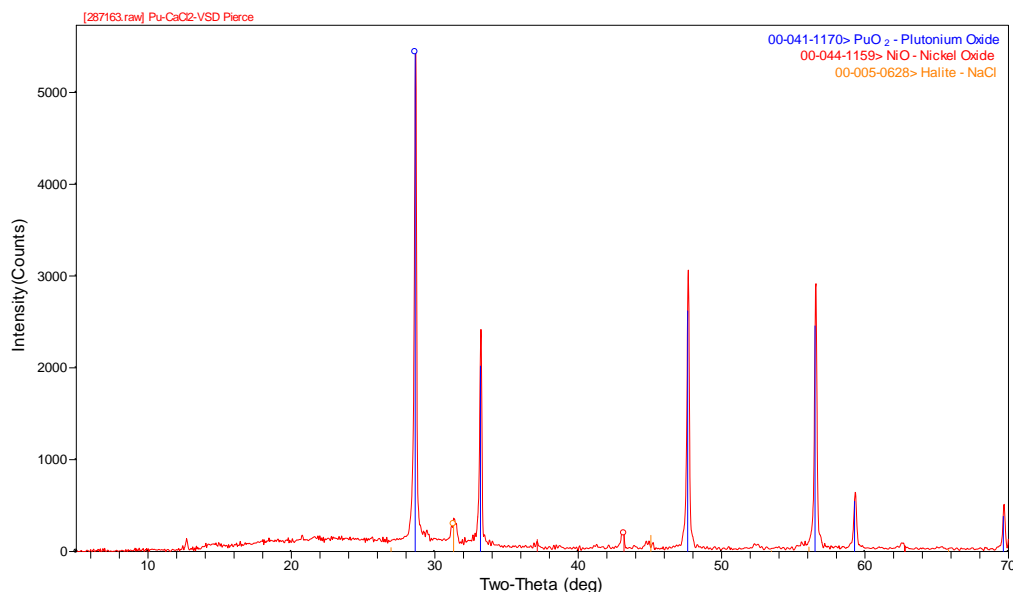


Figure 4-3. PuO₂ after Reaction with NaOH followed by VSD

In the second radioactive test, PuF₃ was reacted with KOH and distilled. XRD analyses of the initial and final compounds were obtained and are provided in Figure 4-4 (before) and Figure 4-5 (after). The data show that the PuF₃ was completely converted to PuO₂, and that no residual KOH was present in the product. This result addresses the second feasibility question mentioned above. It should be noted that the starting material was primarily PuF₃, but it did contain a minor amount of a Pu-ammonium-fluoride compound (analog to KU₆F₂₅ in Figure 4-4 data). The Pu ammonium fluoride was a byproduct of the method (ammonium bifluoride fusion) used to produce the PuF₃ sample. It is also worth noting that, similar to the previous test, KOH did not react with Pu to form a compound other than PuO₂.

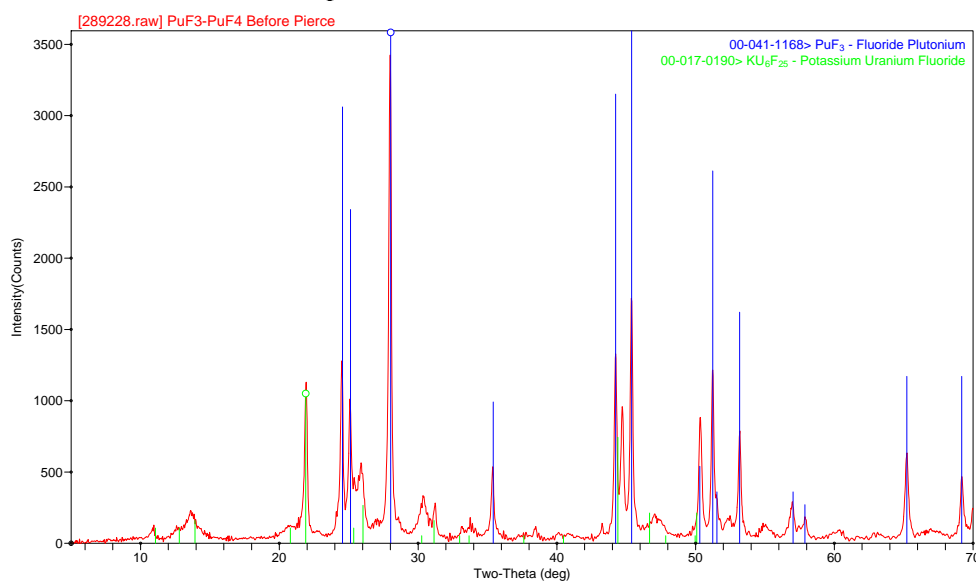


Figure 4-4. PuF₃ before Reaction with KOH

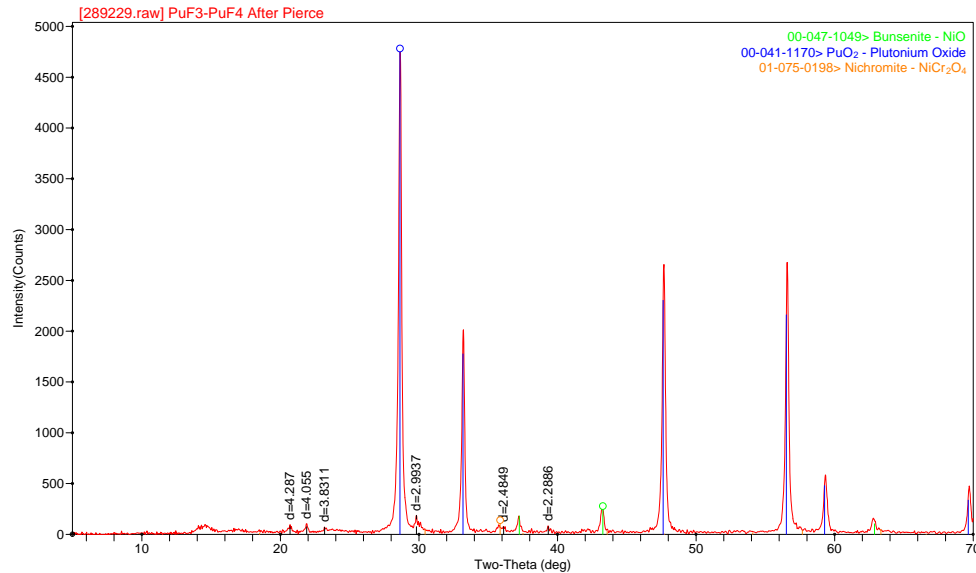


Figure 4-5. PuF₃ after Reaction with KOH followed by VSD

4.6 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.^[12] 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 complete 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 2-2). 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. 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 3-4). 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 3-5. 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 an issue.

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. During testing, different baffle configurations were tested. Although their location has not been optimized, a drawing of a successful configuration is shown in Figure 4-6. Figure 4-7 shows the salt deposition pattern inside of the liner from both the heated and cooled zones using the baffle configuration shown in Figure 4-6.



Figure 4-6. Successful Baffle Configuration inside Removable Liner

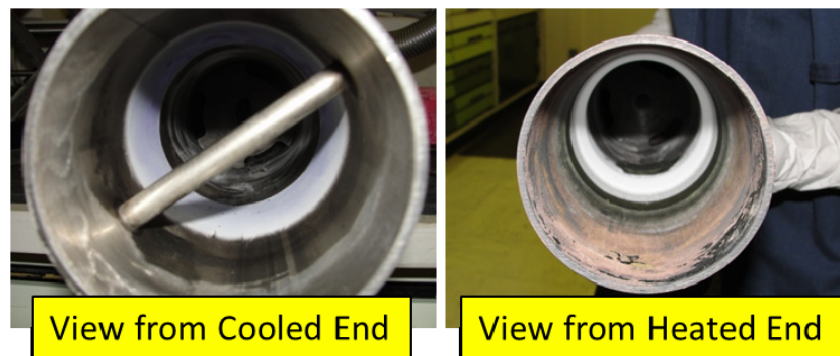


Figure 4-7. Salt Deposition Pattern inside Removable Liner

It should be noted that the removable liner, in its current design, cannot be used as a disposable liner. The liner is suitable for cleaning and multi-cycle use. Experiments have begun looking at a thin-walled collapsible liner that can be slid inside the current liner to provide the surface for salt deposition. After the distillation process, the collapsible liner can be slid from the thicker liner

and readily size-reduced along with the salt on its surfaces. Initial investigations of this salt collection and removal alternative have shown promise.

One final potential issue that has not been addressed is the removal of water vapor from the system. According to reaction 1, water vapor is a byproduct of the reaction between KOH and the halide salts. The current vacuum pump used to evacuate the HB-Line VSD unit is a two-stage dry pump. SRNL used a single-stage oil pump. The two-stage dry pump is more sensitive to the presence of water vapor, which can condense in the lines of the pump and impede achievement of the vacuum levels necessary for distillation. The oil pump used for SRNL testing is not as sensitive to water vapor and has not shown any adverse effects thus far. This issue can be overcome by installing a disposable in-line moisture absorbent in the vacuum line between the vacuum chamber and the pump.

5.0 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. The reaction of KOH with halide salts also produced water vapor as a byproduct. This water could cause issues with the existing two-stage dry pumps used by HB-Line. However, this issue can probably be overcome by installing a disposable in-line moisture absorbent in the vacuum line between the VSD chamber and the pump.

6.0 Future Work

SRNL proposes a development program using available equipment that has the same internal dimensions as the VSD unit deployed in HB-Line. The program will define physical and chemical parameters needed for subsequent scale-up and deployment. As before, the majority of

the work will be with non-radioactive materials. Testing for the development of VSD for NaCl and KCl demonstrated that non-radioactive simulants were appropriate.^[6,10,12] However, it is not known if the same will be true for CaCl₂, CaF₂, PuF₃, and PuF₄ processing.

The specific tasks follow.

- 1) Complete production-scale testing with CaF₂, CeF₃, and CaCl₂ mixed with CeO₂. Small-scale and pilot-scale testing are complete. The performance demonstrated in those tests will be proven at a 350-500-g scale.
- 2) Perform several tests with CaF₂ and CaCl₂ mixed in with PuO₂. The limited amount of data with PuO₂ and fluorides will be expanded to include the distillation of fluoride-bearing PuO₂ materials and testing with PuO₂ spiked with CaF₂, CaCl₂, and, if necessary, PuF₃.
- 3) Identify quantities of reactants and furnace cycles for varying concentrations of fluoride. Define the process conditions that will treat most of the high-fluoride concentrations (4.5 wt % is bounding for >98% of fluoride-bearing items) and then determine if the flowsheet should be constant or adjusted based on fluoride concentration.
- 4) Determine if NaCl and KCl have a negative effect on the quantity of KOH required. Tests to date have focused on one halide component (CaF₂, CaCl₂, or CeF₃) blended with CeO₂. Tests must be conducted to determine if NaCl and KCl will react with KOH and affect flowsheet inputs. Prior work with Na₂O₂ fusion suggests that NaCl and KCl will not negatively affect the reaction.^[8]
- 5) Identify necessary changes or appropriate improvements for the boat design (related to PuO₂ entrainment and materials), salt cleaning, and cooling. Assess whether a removable/reusable liner is a preferred alternative to current method of apparatus cleaning, especially in light of the hygroscopic nature of KOH. Demonstrate the design changes on a production scale.

7.0 References

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