

Development and Deployment of Vacuum Salt Distillation at the Savannah River Site - 11178

Robert A. Pierce*, Dario C. Castiglione, ** Donald J. Pak,* and T. B. Edwards*

*Savannah River National Laboratory, Aiken, South Carolina 29808

**AWE, Reading, Berkshire, RG7 4PR United Kingdom

ABSTRACT

The Savannah River Site has a mission to dissolve fissile materials and disposition them. The primary fissile material is plutonium dioxide (PuO_2). To support dissolution of these materials, the Savannah River National Laboratory (SRNL) designed and demonstrated a vacuum salt distillation (VSD) apparatus using both representative radioactive samples and non-radioactive simulant materials. Vacuum salt distillation, through the removal of chloride salts, increases the quantity of materials suitable for processing in the site's HB-Line Facility.

Small-scale non-radioactive experiments at 900-950 °C show that >99.8 wt % of the initial charge of chloride salt distilled from the sample boat with recovery of >99.8 wt % of the ceric oxide (CeO_2) –the surrogate for PuO_2 – as a non-chloride bearing 'product'. Small-scale radioactive testing in a glovebox demonstrated the removal of sodium chloride (NaCl) and potassium chloride (KCl) from 13 PuO_2 samples. Chloride concentrations were distilled from a starting concentration of 1.8-10.8 wt % to a final concentration <500 mg/kg chloride.

Initial testing of a non-radioactive, full-scale production prototype is complete. A designed set of experiments evaluated the impact of distillation temperature, time at temperature, vacuum, product depth, and presence of a boat cover. Significant effort has been devoted to mechanical considerations to facilitate simplified operation in a glovebox.

INTRODUCTION

Vacuum distillation of chloride salts from 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 comprises a zone heated using a tube furnace and a zone actively cooled using either recirculated water or compressed air. 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 and, once a sufficient vacuum is attained, heating begins. Salt distills from the heated zone to the cooled zone where it condenses, leaving behind the non-volatile oxides in the feed boat as product.

The application of this technique is of particular interest to the Savannah River Site (SRS) HB-Line Facility. The HB-Line Facility has a mission to dissolve and disposition fissile materials. Many of these materials contain chloride salt concentrations which make them unsuitable for dissolution in the current HB-Line dissolvers due to the corrosion rate of the dissolver and downstream piping. The primary chloride salts present in the 3013 DE materials are NaCl and KCl; magnesium chloride (MgCl_2) originally present in the samples has been oxidized to magnesium oxide (MgO).

EXPERIMENTAL PROCEDURE

Test Equipment

The VSD apparatus was designed with simplicity and functionality as the two main objectives. Six separate VSD chambers were tested in the development; results from three of the chambers will be discussed. The quartz distillation unit was fabricated by the SRNL Glass Shop and consisted of a 5-cm inside diameter (ID) heated zone which opened up to a 7.5-cm ID cooled zone. The SRNL Machine Shop subsequently made a lab-scale unit of similar dimensions (25-cm long 5-cm ID to 38-cm long 8.5-cm ID) from Alloy 600. The SRNL Machine Shop also fabricated at production-scale prototype (31.5-cm long 10-cm ID to 51-cm long 15-cm ID) from Alloy 600.

The end cap of each unit is sealed to the vacuum chamber by a single elastomeric o-ring. The cooled zone of the quartz unit was jacketed and actively cooled using either recirculated chilled water or compressed air. The units fabricated from Alloy 600 unit used a cooling coil (6.4-mm OD stainless-steel tubing) wrapped around the outside of the larger-diameter ID section. Both Alloy 600 units were cooled using either recirculated chilled water or compressed air. All systems were evacuated using Edwards RV5 oil vacuum pumps attached to the system using a rubber vacuum hose. The end-flange is held in place only by the vacuum. Figure 1 provides a comparison of the three vacuum chambers. After initial check-out of the production-scale prototype, it was determined that a baffle plate was required adjacent to the flange to force the flow of gases to the outer walls of the vacuum chamber.

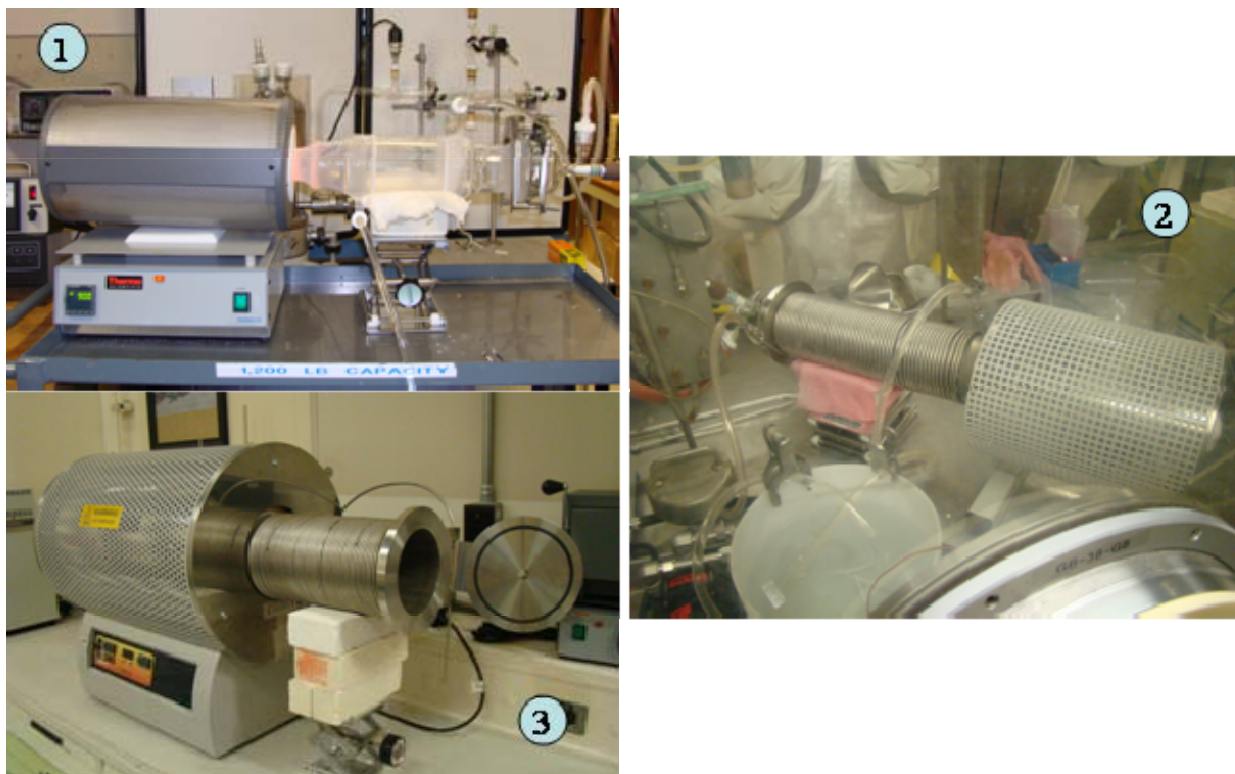


Fig. 1. Comparison of VSD furnaces and test chambers: 1) lab-scale quartz unit; 2) lab-scale Alloy 600 unit installed in radioactive glovebox; and 3) production-scale prototype.

Three different boat designs were used during testing. A simple, uncovered quartz boat (12.5-cm long, 3.4-cm diameter) was used for testing in the quartz and Alloy 600 lab-scale units. Two boats were used during prototype testing and are shown in Figure 2. The prototype-testing boats used a two-piece lid design to create a tortuous path for airborne oxide product to leave the boat. The first boat was a 14-cm long, 9-cm wide boat fabricated by the SRNL Glass Shop from a piece of quartz tubing. The boat was equipped with two side-by-side chambers to enable testing at two different powder depths at the same time. The two-piece cover was also fabricated from quartz. The second boat is 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 to provide a stable base. The boat is a shortened version of the design that will be used in HB-Line.

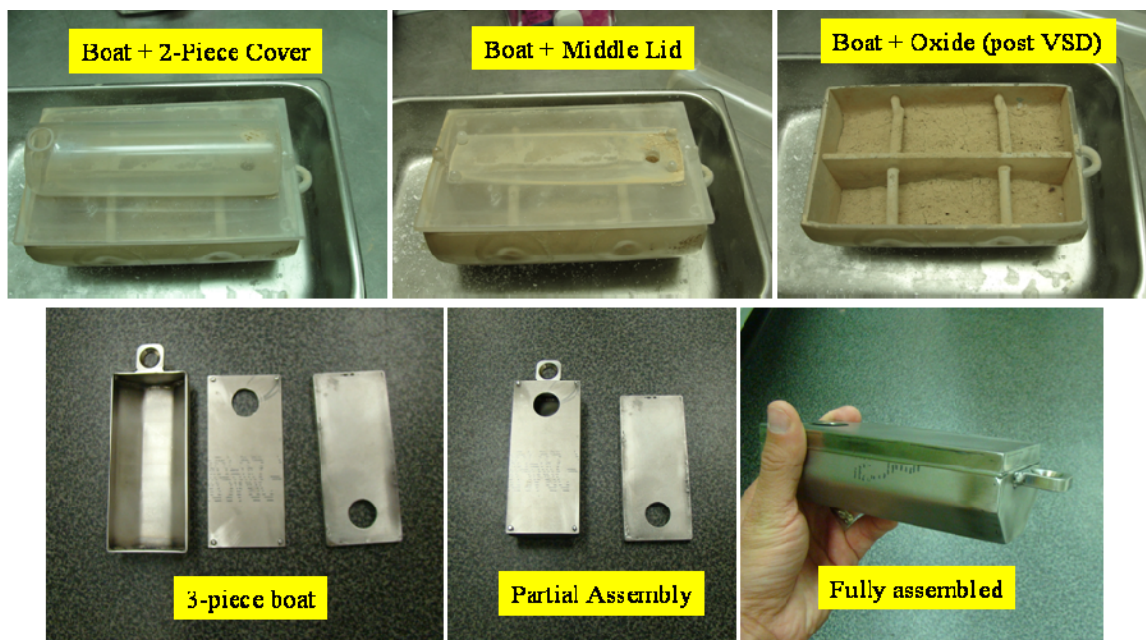


Fig. 2. Three-piece prototype testing boats: (top) two-chamber quartz and (bottom) single chamber Alloy 600

Test Methods

Distillation of chloride salts from the feed boat in the heated zone was performed following the standard experimental procedure outlined below. The chloride salts used in non-radioactive simulant studies were a 50:50 mol % mixture of NaCl and KCl; four tests used a 47.5:47.5:5 mol % mixture of NaCl, KCl and $MgCl_2$. For prototype testing, the 50:50 salt was used, and the feed material was nominally 80 wt % CeO_2 and 20 wt % NaCl-KCl. Testing evaluated the distillation characteristics the chloride salts. Table I contains a list of the non-radioactive lab-scale test conditions. Table II lists radioactive sample test parameters.

The chloride salt and oxide were weighed out separately to prepare specified ratios. The balance for non-radioactive testing was accurate to ± 0.0002 g and the balance for radioactive testing was accurate to ± 0.001 g. The feed materials were then combined and mixed thoroughly. For tests with Pu-bearing samples, the salt and oxide were already combined. The salt/oxide mixture was transferred to the sample boat and loaded into the VSD apparatus. The VSD apparatus was closed and evacuated to approximately 4-11 Pa or 0.01-0.04 Pa (as measured at the vacuum pump). The coolant flow (water or air) was initiated during the evacuation of the system and, once sufficient vacuum was attained, heating of the system began.

Table I. Non-Radioactive Lab-Scale Distillation Test Parameters

Test ID	Apparatus	Temp (°C)	Feed (g)	Salt (g)	CeO ₂ (g)	Coolant
VSD01	Quartz	900	63.719	12.749 ^a	50.970	20 °C water
VSD02 ^c	Quartz	900	63.653	63.653 ^a	0.000	18 °C Air
VSD03	Quartz	900	26.195	26.195 ^a	0.000	20 °C water
VSD04	Quartz	900	50.155	10.006 ^a	40.150	20 °C water
VSD05	Quartz	900	64.724	14.722 ^b	50.002	20 °C water
VSD06	Quartz	950	65.008	15.005 ^b	50.003	20 °C water
VSD07	Quartz	950	63.473	63.473 ^a	0.000	20 °C water
VSD08 ^c	Quartz	950	55.110	55.110 ^a	0.000	20 °C water
VSD09 ^c	Quartz	950	91.240	91.240 ^a	0.000	20 °C water
VSD10	Quartz	900	40.363	40.363 ^a	0.000	20 °C water
VSD11	Quartz	900	41.004	41.004 ^a	0.000	20 °C water
VSD12	Quartz	900	40.610	40.610 ^a	0.000	20 °C water
VSD13	Quartz	900	80.068	20.067 ^a	60.001	20 °C water
VSD14 ^c	Quartz	900	122.688	122.688 ^a	0.000	20 °C water
VSD15	Alloy 600	900	19.997	19.997 ^a	0.000	18 °C Air
VSD16	Alloy 600	950	20.067	20.067 ^a	0.000	18 °C Air
VSD17	Alloy 600	900-950	20.545	20.545 ^a	0.000	18 °C Air
VSD18	Alloy 600	900	20.779	20.779 ^a	0.000	18 °C Air
VSD19	Alloy 600	900	20.308	20.308 ^a	0.000	20 °C water
VSD20	Alloy 600	900	20.003	20.003 ^a	0.000	20-50 °C water
VSD21	Alloy 600	900	50.044	21.883 ^a	28.160	20-50 °C water
VSD22	Alloy 600	900	50.016	10.016 ^b	40.000	3-41 °C water
VSD23	Alloy 600	950	50.316	10.046 ^b	40.270	3-41 °C water

^a 50:50 mol % NaCl:KCl^b 47.5:47.5:5.0 mol % NaCl:KCl:MgCl₂^c Test intentionally discontinued to measure salt-distillation rates

Table II. Radioactive Sample Distillation Test Parameters

Sample Material	Feed (g)	Initial Cl ⁻ (mg/kg)	Temp (°C)	Time at Temp (min)
B196	9.89	59400*	900	60
B184	10.69	77400*	900	60
B202	9.82	83100*	900	60
B203	9.90	83100*	900	60
B239	10.44	77200*	925	45
B281/282	20.26	86400*	950	60
B293/294	20.70	17900*	950	60
Blend 1	118.46	107000 [#]	950	60
Blend 2	114.52	100000 [#]	950	60
Blend 3	76.54	97600 [#]	950	60
Blend 4	67.41	34500 [#]	950	60
Blend 5	45.79	13200 [#]	950	60
Blend 6	64.21	35600 [#]	950	60

* Reported by 3013 DE Surveillance Program

[#] Calculated from salt masses removed

Table III contains a list of the test conditions in chronological order for the parametric studies in the full-scale prototype vacuum chamber. For all tests of the parametric study, the 15-cm ID section of the vacuum chamber was inserted ~10 cm into the heated section of the furnace. The boat was placed at the back of the 10-cm ID section of the vacuum chamber, or as far into the furnace as possible. For the quartz boat, the chamber at a depth of 18 mm contained 96-97 g of feed; the chamber at a depth of 26 mm contained 185-189 g of feed. For the 15-cm long Alloy 600 boat, the chamber contained 360-362 g of feed.

Table III. Parametric Study Test Conditions in Production-Scale Prototype

Temp-Time – Vacuum-Cover	Boat	Temp (°C)	Time at Temp (min)	Vacuum at Pump (torr)	Powder Depth (mm)	Time to 900°C (min)	Time to Set Pt (min)	Cover
900-60-Hi-None	QTZ	900	60	2.5E-04	18 - 26	115	115	No
950-20-Hi-None	QTZ	950	20	2.5E-04	18 - 26	113	143	No
950-0-Hi-None	QTZ	950	0	2.5E-04	18 - 26	111	139	No
950-60-Lo-None	QTZ	950	60	1.2E-02	18 - 26	113	141	No
900-60-Hi-Cvr	QTZ	900	60	2.5E-04	18 - 26	114	114	Yes
900-0-Lo-None	QTZ	900	0	1.2E-02	18 - 26	115	115	No
950-60-Lo-Cvr	QTZ	950	60	1.2E-02	18 - 26	116	150	Yes
925-20-Hi-None	QTZ	925	20	2.5E-04	18 - 26	112	125	No
900-20-Lo-None	QTZ	900	20	1.2E-02	18 - 26	114	114	No
925-20-Hi-Cvr	QTZ	925	20	2.5E-04	18 - 26	117	131	Yes
950-60-Hi-Cvr	QTZ	950	60	2.5E-04	18 - 26	117	151	Yes
925-20-Lo-None	QTZ	925	20	1.2E-02	18 - 26	118	133	No
950-20-Hi-Cvr	QTZ	950	20	2.5E-04	18 - 26	121	160	Yes
950-60-Hi-Cvr-2	A600	950	60	2.5E-04	32	115	149	Yes
950-80-Hi-Cvr	A600	950	80	2.5E-04	32	114	150	Yes
900-115-Lo-Cvr	A600	900	115	1.2E-02	32	113	113	Yes
950-80-Hi-Cvr	A600	950	80	2.5E-04	32	116	148	Yes
950-95-Hi-Cvr	A600	950	95	2.5E-04	32	112	144	Yes

QTZ = quartz

A600 = 15-cm long Alloy 600

VSD was typically performed with the furnace set to 900-950 °C, although other temperatures were initially tested. The experiment typically held the material at temperature for a specified time after the furnace reached the target temperature. At the end of the experiment, heating was stopped and the VSD apparatus was allowed to cool. Once the system cooled below 600 °C, the apparatus was slowly vented to atmosphere to prevent dislodging any of the distilled chloride salts. The boat containing the oxide 'product' was removed from the VSD apparatus and weighed. The inside of the apparatus was then brushed or scraped clean. The distilled chloride salts were collected and weighed. For some of the tests, samples of the distilled product were analyzed for chloride concentration.

For lab-scale radioactive experiments, the chloride content of the PuO₂ product was measured as follows for most of the samples. A sample of the distilled oxide was weighed into a plastic centrifuge tube with 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 at least 3 min. Next, the chloride concentration of the water was tested using a Hach QuanTab[®] chloride test strip. For some tests, a sample of the liquid was submitted for analysis using ion

chromatography (IC) to verify the QuanTab[®] readings. Prototype testing analyzed the chloride content of the CeO₂ “product” using Hach QuanTab[®] chloride test strips and the method discussed above.

RESULTS AND DISCUSSION

Lab-Scale Distillation of Pure Salts

The first tests were performed in the lab-scale quartz and Alloy 600 vacuum chambers. The mixture of NaCl:KCl melted when the furnace temperature reached ~825 °C and initial salt condensation was observed at the transition zone between the heated and cooled zones when the furnace temperature reached ~895 °C. Except when the test was stopped prematurely, >99.8% removal of salt from the boat occurred. Table IV summarizes the results. When measured, salt recoveries were 97.9 (1.8% std dev). The distillation efficiency for salt was virtually identical with the quartz and Alloy 600 units. The percent of salt distilled was determined by measuring the weight change of the feed boat contents due to the distillation process. Some of the unrecovered salt remains adhered to the unit while a small amount is lost to the cleaning tools.

Table IV. Summary of Results from Lab-Scale Distillation of Pure Salts

Test ID	Temp (°C)	Salt Type	Salt (g)	% Salt Distill	Salt (g) Recovered	% Salt Recovered
VSD02 ^a	900	NaCl:KCl	63.653	82.3*	NM	NM
VSD03	900	NaCl:KCl	26.195	>99.8	25.846	98.7
VSD07	950	NaCl:KCl	63.473	>99.8	62.309	98.1
VSD08 ^a	950	NaCl:KCl	55.110	57.3*	NM	NM
VSD09 ^a	950	NaCl:KCl	91.240	76.1*	NM	NM
VSD10	900	NaCl:KCl	40.363	>99.8	39.750	98.5
VSD11	900	NaCl:KCl	41.004	>99.8	40.446	98.6
VSD12	900	NaCl:KCl	40.610	>99.8	40.230	99.1
VSD14 ^a	900	NaCl:KCl	122.688	46.5*	NM	NM
VSD15	900	NaCl:KCl	19.997	>99.8	19.330	96.7
VSD16	950	NaCl:KCl	20.067	>99.8	19.796	98.6
VSD17	900-950	NaCl:KCl	20.545	>99.8	19.772	96.2
VSD18	900	NaCl:KCl	20.779	>99.8	19.3	92.9
VSD19	900	NaCl:KCl	20.308	>99.8	20.278	99.8
VSD20	900	NaCl:KCl	20.003	>99.8	19.435	97.2

NM = not measured

^a Test intentionally discontinued to measure salt distillation rates

The bulk salt distillation rates were measured at 900 °C and 950 °C. This measurement was accomplished by measuring the mass of salt distilled during heating and cooling and comparing that with the mass of salt distilled during heating, cooling, and a specific amount of time at temperature. Calculations are also being performed to correlate the salt distillation rates with the Knudsen-Hertz equation for volatility in a vacuum [3]. These calculations will be documented elsewhere.

The amount of salt that distilled as part of the heating to, and cooling from, the furnace set temperature was measured as ~32 g at 900 °C (VSD-08) and ~69 g at 950°C (VSD-09). With the quantity of distillation associated with heating and cooling measured, it was possible to estimate the salt distillation rates at temperature. The distillation rate was estimated to be ~1 g/min at 900 °C (VSD-02) and 5 g/min at 950°C (VSD-14). Operating at 950 °C yields much higher distillation rates, but no appreciable benefit on the deposition location. Typical recovery of

distilled salt was at 98-99%. A concerted effort to carefully recover the distilled salt would have yielded in excess of 99% recovery, but this was not judged necessary for these initial experiments.

Lab-Scale Distillation of Salts Mixed with Ceric Oxide

Salts distilled readily from a mixture of salts and CeO₂ at 900-950 °C in either the quartz or the lab-scale Alloy 600 unit without displacing the CeO₂ from the feed boat (i.e., no “boiling over”, foaming, or eruption of salts from water evaporation observed). Whenever the objective of the test was to distill 100% of the salt from the feed boat, ~100% removal of the salt occurred and greater than 99.8% of the CeO₂ was retained. Table V summarizes the results. Recovery of salt varied in efficiency but was typically greater than 97.6% (1.5% std dev). These data were calculated using the pre-experiment and post-experiment weights of materials.

Table V. Summary of Results from Lab-Scale Distillation of Salts from CeO₂ at 900 °C

Test #	Feed Mass (g)	Salt Mass (g)	CeO ₂ Mass (g)	Salt Distill (%)	Salt Recovered (g)	Salt Recovered (%)	CeO ₂ Recovered (%)	Product [Cl] (mg/kg)
VSD01 [#]	63.72	12.75	50.97	>99.8	12.44	97.6	99.8	NM
VSD04 [#]	50.16	10.01	40.15	>99.8	9.69	96.8	>99.8	NM
VSD05 [†]	64.72	14.72	50.00	>99.8	14.33	97.4	>99.8	359 [‡]
VSD06 ^{†*}	65.00	15.00	50.00	>99.8	15.00	>99.8	>99.8	349 [‡]
VSD13 [#]	80.07	20.07	60.00	>99.8	19.79	98.6	>99.8	NM
VSD21 [#]	50.04	21.88	28.16	>99.8	20.61	94.2	>99.8	NM
VSD22 [†]	50.02	10.02	40.00	>99.8	9.80	97.8	>99.8	357 [‡]
VSD23 ^{†*}	50.32	10.05	40.27	>99.8	8.79	87.4	>99.8	262 [‡]

* Test at 950 °C

50:50 mol % NaCl-KCl

† 47.5:47.5:5.0 mol % NaCl-KCl-MgCl₂

[‡] Measurement uncertainty = 10%

NM = not measured

For further analysis of the products from VSD05 (900 °C) and VSD06 (950 °C), tests using 65 g of feed with ~23 wt % salt in the quartz apparatus, samples of the CeO₂ ‘product’ were submitted for NAA and X-ray diffraction (XRD) analyses to observe the species present and chloride content in the cerium oxide after VSD at 900 °C and 950 °C. Analyses of the chloride concentration of the 900 °C (VSD05) and 950 °C (VSD06) products from two tests using NAA showed that the chloride levels in the CeO₂ could be reduced to below 400 mg/kg using VSD. When the starting ratio of CeO₂ to salt was ~20 wt % salt in a 50 g total batch in the Alloy 600 VSD unit, the chloride content of the CeO₂ product after distillation was measured at 357 mg/kg at 900 °C (VSD-22) and 262 mg/kg at 950 °C (VSD-23).

When VSD was performed at 950 °C with 47.5:47.5:5 mol % NaCl-KCl-MgCl₂ (VSD06), the predominant compound observed in the XRD studies was CeO₂, as expected. Magnesium oxide was also identified at trace levels. According to the material safety data sheet (MSDS), MgCl₂ decomposes to MgO and hydrochloric acid (HCl) upon heating above 300 °C. It is likely that decomposition led to the formation of very small quantities of MgO. No chloride-bearing or other species were detected. The presence of MgO was not detected in the CeO₂ product from a similar experiment at 900 °C (VSD05).

Lab-Scale Distillation of Salts from Plutonium-Bearing Samples

Data from the analyses of oxide materials after salt distillation are tabulated in Table VI. The data show that the chloride concentration of the final oxide product was <500 mg/kg for all materials. Based on comparison with the IC data, the QuanTab[®] readings are most likely biased high. The bias can be attributed to the way the QuanTab[®] was read. The guidance from the manufacturer is to read the tab at the top of the chromatograph. However, the reading is subjective, so the approach employed for this program has been to read the tabs at the most-conservative (i.e., highest) value. A difference of one marking on the tab represents a bias of 10-20% for readings less than 100 mg/L.

Data from the two large-scale tests exhibit performance consistent with those of the much smaller samples. The data also indicate that the material depth in the boat can affect distillation. For both large-scale tests, the oxide product at the bottom of the boat analyzed at a higher chloride concentration than the oxide product at the top of the boat. The result is an indication that for production-scale operations it may be necessary to 1) limit the depth of the oxide in the feed boat, 2) increase the distillation temperature, or 3) increase the dwell time. However, it is important to note that in both tests the oxides at the top and bottom of the feed boat were well below the 500 mg/kg chloride concentration target. The average chloride concentration for Blend 1 was 201 mg/kg and the average for Blend 2 was 98 mg/kg.

Table VI. Chloride Concentrations of Distilled Plutonium-Bearing Samples

3013 DE Sample ID	Distill Temp (°C)	Agitation QuanTab [®] Cl ⁻ (mg/L)	IC Cl ⁻ (mg/L)	Oxide Product Cl ⁻ (mg/kg) by IC	Initial Cl ⁻ (mg/kg)
B196	900	55	47	123	59400 ^φ
B184	900	63	60	136	77400 ^φ
B202	900	33	NM	83*	83100 ^φ
B203	900	55	44	107	83100 ^φ
B239	925	80	80	206	77200 ^φ
B281/282	950	37	29	72	86400 ^φ
B293/294	950	<<27	10	25	17900 ^φ
Blend 1 (top)	950	27	22	140	107000 [#]
Blend 1 (bottom)		47	43	262	107000 [#]
Blend 2 (top)	950	40	34	88	100000 [#]
Blend 2 (bottom)		47	42	108	100000 [#]
Blend 3	950	55	NM	228*	97600 [†]
Blend 4	950	99	NM	479*	34500 [†]
Blend 5	950	<33	NM	<157*	13200 [†]
Blend 6	950	<33	NM	<182*	35600 [†]

* Oxide Product Cl⁻ calculated from QuanTab[®] data

^φ Reported by the 3013 DE Surveillance Program

[#] Calculated from mass of chloride salt added to previously-distilled materials

[†] Calculated from mass of chloride salt distilled from sample

IC uncertainty is 10%

NM = not measured

Production-Scale Prototype Distillation of Salts Mixed with Ceric Oxide

The test matrix for the parametric study was statistically-designed. The set of experimental trials was generated using the Custom Design feature available in JMP Version 7.0.2 [4]. The 12 tests of the statistical design were performed with two separate powder depths (18 mm and 26 mm) for each test. After the initial 12 tests were complete, the data was analyzed with JMP. Based on the analysis, five tests were conducted in an iterative fashion with the powder depth at 32 mm to further understand the key process parameters. The test results were compared with the model after each test. A powder depth of 26 mm approximates to the expected HB-Line operating depth; 32 mm is near the maximum allowable powder depth. The test data for all 17 tests are listed in Table VII. After the 17 tests were complete, all of the data were analyzed with JMP.

Statistical modeling of the data of Table VII was conducted to investigate for the effects of the factors of interest (temperature, time at temperature, vacuum at pump, and presence of a cover for each of the two powder depths studied, 18 mm and 26 mm). The chloride concentration data was fit to a linear model in the factors of interest for the 18 mm powder and 26 mm powder tests. The analysis showed that the level of vacuum at the pump did not have a statistically significant effect on the Cl⁻ response over the range of conditions tested in this study. When the vacuum at the pump is removed as a factor of the data analysis, the presence of a cover becomes insignificant for both the 18 and 26 mm trials. This result makes sense since both the vacuum generated by the pump and the pressure drop created by the cover are related. Consequently, the data were modeled only as linear functions of temperature and time at temperature.

Because of the long heating times for the furnace (~115 min to 900 °C and ~150 min to 950 °C), a modified time factor was applied. Instead of time at temperature, the model was adjusted to use data for total time above 900 °C. Also, the model was fit to the natural log of the chloride concentration in the distilled product. When this was done, the temperature effect became statistically insignificant and the only factor that mattered was time above 900 °C. Although surprising, this result may be the result of testing over a narrow temperature range.

Table VII. Parametric Study Results in Production-Scale Prototype

Temp-Time-Vacuum-Cover	Temp (°C)	Vacuum at Pump	Cover	Time at Temp (min)	Time > 900 °C (min)	Powder Depth (mm)	Powder [Cl] (mg/kg)
900-60-Hi-None	900	High	No	60	60	18	<50
						26	3180
950-20-Hi-None	950	High	No	20	50	18	134
						26	15100
950-0-Hi-None	950	High	No	0	28	18	159
						26	16000
950-60-Lo-None	950	Low	No	60	88	18	<50
						26	1050
900-60-Hi-Cvr	900	High	Yes	60	60	18	248
						26	16600
900-0-Lo-None	900	Low	No	0	0	18	10900
						26	21200
950-60-Lo-Cvr	950	Low	Yes	60	94	18	64
						26	84
925-20-Hi-None	925	High	No	20	33	18	627
						26	20600
900-20-Lo-None	900	Low	No	20	20	18	10500
						26	20800
925-20-Hi-Cvr	925	High	Yes	20	34	18	6200
						26	23400
950-60-Hi-Cvr	950	High	Yes	60	94	18	<50
						26	<50
950-20-Hi-Cvr	950	High	Yes	20	59	18	213
						26	3770
925-20-Lo-None	925	Low	No	20	35	18	203
						26	15000
950-60-Hi-Cvr-2	950	High	Yes	60	94	32	1890
950-80-Hi-Cvr	950	High	Yes	80	116	32	197
900-115-Lo-Cvr	900	Low	Yes	115	115	32	6900
950-80-Hi-Cvr	950	High	Yes	80	112	32	283
950-95-Hi-Cvr	950	High	Yes	95	127	32	63

Note: Low vacuum ~4-11 Pa and high vacuum ~0.01-0.04 Pa

The linear models predict that at a powder depth of 18 mm, the $\ln(\text{Cl}^-)$ concentration decreased 0.0527 for every minute above 900 °C; at 26 mm, the $\ln(\text{Cl}^-)$ decreased 0.0602 each minute above 900 °C. Based on these model fits, the system behavior was predicted for a powder depth of 32 mm. Using a linear extrapolation, the $\ln(\text{Cl}^-)$ rate of change for a powder depth of 32 mm was predicted to be 0.0658 for each minute above 900 °C. The linear models for all three powder depths (18 mm, 26 mm, and 32 mm) are shown along with the data from 32-mm test data in Figure 3. The open symbol is the 900 °C test and the closed symbols are the 950 °C tests. The oval around the three points represent three tests operated for the same amount of time above 900 °C. If temperature were not a factor, the three values would be much closer together. Consequently, temperature does matter (at least at 950 °C), and 950 °C is preferred to 900 °C.

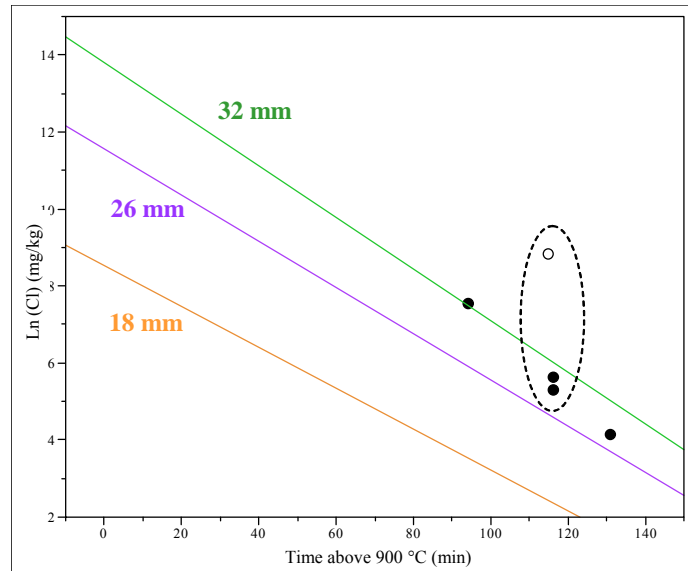


Fig. 3. Model fit of production-scale prototype data as a function of powder depth and process time for all data.

With the selection of 950 °C as the preferred data, the model fit was completed for only the data at 950 °C (Figure 4). The slopes of the lines for 26 mm and 32 mm are similar with the model predicting that $\ln(\text{Cl})$ decreases 0.0797/min at 26 mm and 0.0921/min at 32 mm. The data fit to the lines are good at both 26 mm ($R^2 = 0.83$) and 32 mm ($R^2 = 0.99$), with the 26-mm data accounting for more variables (vacuum and presence of cover) than the 32-mm data. The data for a powder depth of 18 mm yields a more-shallow line ($\ln(\text{Cl}) = 0.0156/\text{min}$). The significant change in slope is not surprising because for a shallow product bed, by the time the furnace reaches 950 °C, most of the chloride has distilled. The linearity of the fit for the 18-mm data is poor ($R^2=0.50$). However, it is worth noting that all of the data at 18 mm meet the product quality target of 500 mg/kg (black horizontal line in Figure 4).

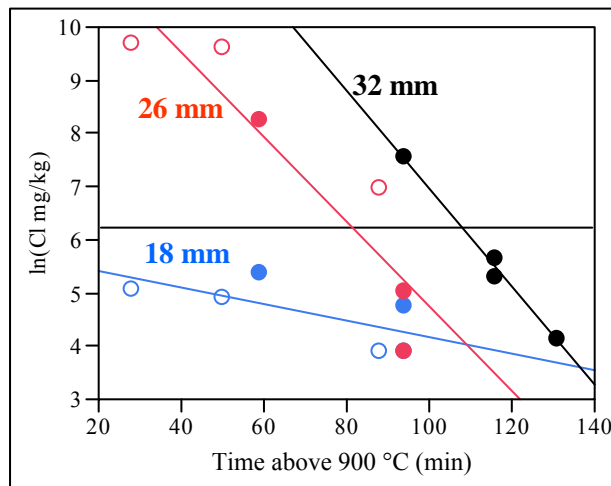


Fig. 4. Model fit of production-scale prototype data as a function of powder depth and process time for tests at 950 °C.

After one of the parametric tests (950-60-Hi-Cvr-2), the oxide product was measured in three ways. One sample was taken from near the surface of the product, a second sample was from the

bottom of the boat, and the third was an average of the remaining product. The chloride concentration of each sample was analyzed in the manner discussed above. The top sample measured 417 mg/kg Cl⁻, the bottom sample measured 871 mg/kg Cl⁻, and the average sample contained 1880 mg/kg Cl⁻. The oxide at the center of the product, which will be the last part of the product to reach temperature, has a higher Cl⁻ concentration than the material above and beneath it. The results further indicate that the overall rate of salt removal is controlled by the conduction of heat through the oxide product.

CONCLUSIONS

Vacuum salt distillation was demonstrated in both non-radioactive and radioactive environments for the removal of chloride salts from PuO₂ and CeO₂; CeO₂ is a simulant for PuO₂. Testing has been completed at both the lab scale and production-scale. Chloride salts distilled from the feed material and subsequently deposited towards the cooled end of the VSD unit. Analyses of the 900 °C and 950 °C CeO₂ and PuO₂ products showed that the chloride salt levels could be routinely reduced from 20 wt % to below 500 mg/kg by VSD within one hour. The salts distill at nominal rates of ~1 g/min at 900 °C and ~5 g/min at 950 °C.

Thirteen PuO₂-bearing samples ranging from 10-120 g were distilled from initial chloride concentrations of 18,000-108,000 mg/kg to final concentrations of <500 mg/kg chloride. The maximum feed material depth was about 20 mm. A non-radioactive production-scale prototype distilled 20 wt % salt from 280-360 g of CeO₂. Feed material depths in the product boat ranged from 18 to 32 mm.

A statistically-designed parametric study identified the statistically-significant and insignificant process variables. Two related variables, vacuum level at the pump and presence of a lid, were found to be statistically-insignificant. Heating time, powder depth, and process temperature were statistically-significant. At the conclusion of testing and data analysis, the preferred operating temperature was set at 950 °C.

With the selection of 950 °C as the preferred operating temperature, a model fit for the data at 950 °C yielded lines for ln(Cl) versus time. The slopes of the lines for feed depths of 26 mm and 32 mm are similar to each other with the model predicting that ln(Cl) decreases 0.0797/min at 26 mm and 0.0921/min at 32 mm. The data for a powder depth of 18 mm yields a more-shallow line where ln(Cl) decreases at 0.0156/min. The significant change in slope for an 18-mm feed material depth is not surprising for a shallow product bed because of the long time required for the furnace to reach 950 °C.

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