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Pacific Northwest
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Furnace System Testing to Support Lower-Temperature Stabilization of High Chloride Plutonium Oxide Items at the Hanford Plutonium Finishing Plant

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Prepared for the U.S. Department of Energy
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Managed for DOE by Fluor Hanford

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

Thermal stabilization of high chloride content plutonium (HCP) items at 750°C (without water washing) is being investigated as an alternative method for meeting the intent of DOE STD 3013-2000. Four furnace tests were conducted at 750°C to develop material balance and system operability data for supporting the evaluation of lower-temperature thermal stabilization. For each test, a process boat was loaded with simulant (CeO_2 for PuO_2) that represented a 2000-g HCP charge containing 20 wt% chloride salt (i.e., 1600 g PuO_2 + 400 g chloride salt). The loaded boat was placed in an RMC-line prototypical furnace system, and the charged furnace was ramped to and held at 750°C for 2 hr. Air flow through the furnace (room air at 20% to 40% relative humidity) was maintained at 1 SCFM. Results from the 750°C testing were compared with previous results from furnace testing using the same test apparatus but conducted at 1000°C with simulant that contained 16 to 20 g of chloride salt per charge (i.e., simulant represented washed HCP items containing 1 wt% residual chlorides salts).

The chlorides present in the HCP items pose considerable challenges to stabilization, because volatile chloride salts and decomposition products (e.g., HCl) can corrode furnace heating elements and downstream ventilation components. In the cooler zones of the ventilation system, the chloride salts can condense and blind filters or plug the offgas lines. Chloride salt vapor pressures are about 25 times higher at 1000°C than at 750°C, and pyrohydrolysis reactions (reaction of water vapor with chloride salt to produce HCl) occur more readily at higher temperature. Therefore, processing at lower temperature potentially can decrease the deleterious effects of the chloride salts.

The following conclusions, derived by comparing results from the 750°C/20 wt% salt (unwashed) and 1000°C/1 wt% salt (washed) tests, show the operational benefits in the lower-temperature processing without washing:

- Less than 0.9 g (0.5 wt%) of the chloride was volatilized into process equipment by 750°C processing of a simulant containing 400 g of NaCl and KCl. In contrast, 6.9 to 8.5 g (65% to 99%) of the chloride was volatilized in 1000°C processing of a nominal washed simulant containing 16 to 20 g of NaCl and KCl.

- For the same experiments, less HCl (generated by pyrohydrolysis of the NaCl/KCl by the humid purge air) was produced from 400 g of salt at 750°C than from 16 to 20 g of salt at 1000°C.

- Less corrosion and salt deposition in offgas lines occurred in the four tests with 20 wt% chloride salt at 750°C (i.e., 1600 g chloride salt in the four tests) than in a single test with 1 wt% chloride salt at 1000°C (i.e., 16 to 20 g chloride salt).

- At 750°C, severe corrosion was confined to the materials in direct contact with the high salt content simulant (boat, metal coupon, and thermocouples); at 1000°C, severe corrosion was noted in offgas lines as well.

In summary, the low chloride removal and subsequent reduced corrosion to the offgas lines at 750°C can largely be attributed to the significantly lower vapor pressure of the chloride salts and the reduced pyrohydrolysis reactions at 750°C vs. 1000°C.

Summary and Conclusions

Approximately 1.1 metric tons of impure plutonium oxide scrap items (939 items) that were generated at the Rocky Flats Environmental Technology Site (formerly the Rocky Flats Plant) from pyrochemical operations (electro refining, molten salt extraction, and direct oxide reduction) are being stored at the Hanford Plutonium Finishing Plant (PFP). A significant fraction of these items, referred to as high chloride content plutonium (HCP) oxides, contain NaCl, KCl, $MgCl_2$ and/or $CaCl_2$ salts. While these items were previously stabilized at 450°C, they must now be stabilized in accordance with the U.S. Department of Energy (DOE) Standard, *Stabilization, Packaging, and Storage of Plutonium-bearing Materials* (DOE-STD-3013-2000), which specifies 950°C as the stabilization temperature. The chlorides present in the HCP items pose considerable challenges to stabilization, because volatile chloride salts and decomposition products (e.g., HCl) can corrode furnace heating elements and downstream ventilation components. In the cooler zones of the ventilation system, the chloride salts can condense and blind filters or plug the offgas lines. Also, some of the chloride salt impurities are hygroscopic, and those remaining in the calcined solids can make it more difficult to meet the DOE standard for moisture content prior to sealing the stabilized product in 3013 canisters.

The present plan for processing the HCP oxides includes water washing to remove chloride to <1 wt% total salt, before thermal stabilization in the RMC line furnaces, to mitigate moisture re-absorption and corrosion problems. Fifty cycles of furnace tests (discussed in a separate report[(a)]) were conducted by Pacific Northwest National Laboratory (PNNL), using simulated HCP oxides, to examine system vulnerabilities in the RMC line furnaces under baseline thermal stabilization conditions (2 hr at 1000°C), and to develop and validate system improvements. These tests showed that, at a 1 wt% chloride salt loading, most of chloride salt was removed during thermal processing and, consequently, resulted in corrosion to offgas lines and deposition/plugging in cooler downstream offgas lines and offgas filters. However, with process improvements, three to five cycles could be completed during testing before the system had to be shut down for line cleaning and/or filter replacement.

To improve furnace system operability, reduce process and waste disposal costs, and decrease the potential dose to workers involved in the washing process, lower-temperature stabilization of HCP items at 750°C (without water washing) is being investigated as an alternative approach for meeting the intent of DOE-STD-3013-2000. A series of four furnace tests were conducted by PNNL to develop material balance and system operability data to support the evaluation of lower-temperature thermal stabilization. Furnace tests were conducted in a system that included a prototype RMC line furnace, a prototype offgas system (offgas lines and a 5-µm filter), a wet scrubber, a chilled condenser, and an offgas blower. For each test, a Hastelloy X process boat was loaded with simulant that represented a 2000-g HCP charge containing 20 wt% chloride salt (i.e., 1600 g PuO_2 + 400 g chloride salt). CeO_2 was used as a surrogate for PuO_2, and two chloride salt compositions were tested: NaCl and KCl added at a 50:50 mole ratio; and NaCl, KCl, and $MgCl_2$ added at a 45:45:10 mole ratio. Thermocouples and metal coupons were placed in the process boat, and the charged furnace was ramped to and held at 750°C for 2 hr. Air flow through the furnace (room air at 20% to 40% relative humidity) was maintained at 1 SCFM.

[(a)] Fischer, C. M., M. R. Elmore, A. J. Schmidt, M. A. Gerber, D. S. Muzatko, S. R. Gano, and B. M. Thornton. 2002. *Evaluation of PFP Furnace Systems for Thermal Stabilization of Washed High Chloride Plutonium Oxide Items.* PNNL-14260, Pacific Northwest National Laboratory, Richland, WA.

Because the HCP items stored at PFP were previously thermally processed at or above 450°C at the Rocky Flats Plant (many items were thermally processed twice), it is unlikely that significant quantities of $MgCl_2$ are still present. Consequently, the results and observations from the testing conducted with the $MgCl_2$-containing simulant are expected to be more severe than those anticipated from actual thermal stabilization operations, since the simulant was not preconditioned at 450°C before the 750°C furnace testing.

The furnace testing showed that, at 750°C, severe corrosion was confined to the materials in direct contact with the high salt content simulant. Test results indicate that the quantity of HCl generated at 750°C from pyrohydrolysis of NaCl and KCl in HCP items (without washing) would be less than that generated from washed HCP items processed at 1000°C. Thermal stabilization of HCP items (without washing) at 750°C reduces the technical challenges to the furnace system operations compared with processing washed HCP items at 1000°C. However, removal and size-reduction of the calcined material from the boats processed at 750°C were found to be labor-intensive. In addition, if HCP items contain appreciable quantities of $MgCl_2$ or other hygroscopic species (e.g., $CaCl_2$), actions will need to be taken to minimize exposure of the calcined product to humid air before the material is packaged.

Specific key findings from the furnace testing at 750°C are summarized below:

Material Balance

- Less than 0.5 wt% of the chloride and less than 0.1 wt% of the initial simulant mass (~1.4 g) was removed while processing the NaCl/KCl simulant at 750°C. Of the chloride recovered in the offgas system, about 75% to 80% was captured in the wet scrubber and the condenser, both located downstream of a 5-µm filter. Approximately 80% of the chloride in the wet scrubber was derived from HCl generated from the simulant in the furnace, presumably due to a reaction (pyrohydrolysis) between the alkali chloride salts and the moisture in the furnace sweep gas.

- About 7% to 13% of the chloride in the charge was removed while processing the NaCl/KCl/$MgCl_2$ simulant at 750°C. Most of the chloride removal was from the decomposition of $MgCl_2$ in moist air, resulting in the release of HCl. Based on mass balance data, approximately 40% of the $MgCl_2$ in the feed simulant decomposed to produce HCl, which was removed from the simulant in the boat, and MgO, which was retained in the boat. $MgCl_2$ decomposition continued during furnace cooldown. About one-third of the HCl in the scrubber was captured while the furnace cooled from 750ºC to 400ºC. Results from X-ray diffraction (XRD) analyses support the conclusion that some $MgCl_2$ remained in the simulant after processing at 750ºC.

- The effects of the presence of $CaCl_2$ in HCP oxides were not evaluated as part of the current furnace testing. However, previous work included limited furnace testing with a simulant containing 34.5 wt% $CaCl_2$ in CeO_2 that was calcined at 750°C for 2 hr before using the material in washing tests.(a) Based on chemical analyses and evaluation of the data, it was estimated that between 2 and 6 wt% of the $CaCl_2$ was pyrohydrolyzed to CaO and HCl during the calcining at 750°C for 2 hr. This finding suggests that the extent of pyrohydrolysis of $CaCl_2$ will be between that of NaCl/KCl and $MgCl_2$.

(a) PNNL Letter Report 41291-RPT02, "Evaluation of Solids Rinsing to Treat PFP High Chloride Plutonium Solids," transmitted to P. Sato, Fluor Hanford, by K. L. Silvers, PNNL, December 20, 2002.

- XRD analysis of the calcined material identified significant quantities of binary sodium/potassium chloride salts.

- In the tests with the NaCl/KCl/$MgCl_2$ simulant, significant quantities (5 to 10 g per test) of hydrated iron and nickel chloride compounds accumulated in the filter housing and on the filter. As there was no evidence of corrosion to the filter housing or filter, the iron chloride compounds most likely originated in the furnace (generated from reactions between simulant, moisture, and boat/metal coupons) and were transported to the filter as vapor. In these tests, very little iron was collected in the wet scrubber.

- The mass of material removed from the boat while processing 20 wt% NaCl/KCl/$MgCl_2$ simulant at 750ºC was comparable to the mass lost when processing 1 wt% chloride salt at 1000ºC under otherwise similar conditions.

Operability

- During the 2-hr hold time, the temperature of the material in the boat was 50ºC to 120ºC higher than the furnace control thermocouple (750ºC). Thus, little incentive or justification exists to control the furnace at a temperature higher than 750ºC.

- While processing 20 wt% NaCl/KCl simulant at 750°C, corrosion and plugging of offgas lines were minimal, and very little material was collected on the filter. It is estimated that more than 10 batches of such material could be charged to the furnace before shut down is required to clean or replace offgas lines or filters. The extent of corrosion to the Hastelloy X boat was similar to that experienced while processing 1 wt% chloride salt at 1000°C.

- The Hastelloy X boat and the metal coupons (RA602CA and Inconel 690) experienced severe weight loss due to corrosion while processing the 20 wt% NaCl/KCl/$MgCl_2$ simulant at 750°C. However, the severe corrosive attack was confined to materials in direct contact with the simulant (e.g., boat, thermocouples, and metal coupons). Significant quantities of material (alkali chlorides and hydrated nickel and iron chlorides) did accumulate in the filter element. It is estimated that three to five batches of composition like the NaCl/KCl/$MgCl_2$ simulant could be completed before blinding the filter element.

- The cumulative extent of corrosion and salt deposition within the offgas lines during the four tests conducted with 20 wt% chloride salt at 750ºC was less than that experienced in a single test with 1 wt% chloride salt at 1000ºC.

- The high salt loading resulted in the creation of brick-like calcined products. A hammer and a screwdriver were needed to chip the calcined material out of the boat after processing the NaCl/KCl simulant. The thermally processed NaCl/KCl/$MgCl_2$ simulant was more friable and was removed by inverting the boat, then dropping the boat down several inches onto a hard surface.

- In the test system used, HCl was largely removed from the offgas stream in the wet scrubber and chilled condenser. Post-test rinsing of offgas lines downstream of the scrubber was performed to remove any HCl. At the PFP, engineering and operational controls will likely be required to minimize the potential for HCl condensation and subsequent chloride-induced pitting and stress corrosion cracking in the offgas line components.

- Intake air flow (at ambient humidity in the RMC) should be maintained at the minimum rate to guarantee oxidizing conditions required by the 3013 standard while minimizing water vapor and the resulting pyrohydrolysis reactions that form HCl.

Post-Calcination Moisture Uptake Testing

Moisture uptake testing was conducted by re-heating (to 250°C and 500°C) the feed and calcined samples from the 750°C furnace tests and then placing the samples in a controlled humidity chamber (51% relative humidity).

- In general, samples from the NaCl/KCl simulant only gained about 0.1 wt% after 24 hr in the controlled humidity chamber. Samples from the NaCl/KCl/$MgCl_2$ simulant that were crushed and screened to less than 1/4 in. (6.35 mm) gained ~0.5 wt% after 8 to 10 hr, while a sample that was screened to less than 16 mesh (1 mm) gained ~0.5 wt% after only 2 hr. The CeO_2 used in the simulants exhibited a very low moisture uptake capacity. Moisture uptake rates for actual HCP items (containing the same chloride salts) would likely be slightly higher given the moisture uptake behavior of PuO_2 calcined at 750°C.

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We thank Todd Hart, who performed inductively coupled plasma (ICP) analyses, and David McCready, who performed X-ray diffraction (XRD) analyses. The ICP and XRD analyses were performed at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research. EMSL is located at the Pacific Northwest National Laboratory, which is operated for DOE by Battelle.

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1.0 Introduction

Approximately 1.1 metric tons of impure plutonium oxide scrap items (939 items) that were generated at the Rocky Flats Environmental Technology Site (formerly the Rocky Flats Plant) from pyrochemical operations (electro refining, molten salt extraction, and direct oxide reduction) are being stored at the Hanford Plutonium Finishing Plant (PFP). A significant fraction of these items, referred to as high chloride content plutonium (HCP) oxides, contain NaCl, KCl, $MgCl_2$ and/or $CaCl_2$ salts. While these items were previously stabilized at 450°C, they must now be stabilized in accordance with the U.S. Department of Energy (DOE) Standard, *Stabilization, Packaging, and Storage of Plutonium-bearing Materials* (DOE-STD-3013-2000), which specifies 950°C as the stabilization temperature. The chlorides present in the HCP items pose considerable challenges to stabilization, because volatile chloride salts and decomposition products (e.g., HCl) can corrode furnace heating elements and downstream ventilation components. In the cooler zones of the ventilation system, the chloride salts can condense and blind filters or plug the offgas lines. Also, some of the chloride salt impurities are hygroscopic, and those remaining in the calcined solids can make it more difficult to meet the DOE standard for moisture content prior to sealing the stabilized product in 3013 canisters.

In an evaluation conducted for PFP, Pacific Northwest National Laboratory (PNNL) recommended converting PFP's existing solutions precipitation equipment to a washing process as the preferred option for treating the HCP oxides [PNNL Letter Report 43925-L01, "Technical Evaluation of Candidate Alternatives for Treating High Chloride Content Plutonium Oxides at the Plutonium Finishing Plant" transmitted to D. R. Speer, Fluor Hanford (FH), by K. L. Silvers, PNNL, April 15, 2002]. A target salt concentration of ~0.25 wt% or less was proposed to ensure that most washed batches of HCP solids would meet the 0.5 wt% moisture limit established by the DOE 3013 Standard, and to minimize corrosion to furnace components during thermal stabilization. The evaluation also recommended that the existing RMC line furnaces(a) be used to thermally stabilize the washed material. The PFP SPE line furnaces(b) were not recommended for processing the HCP items, because the wall in those furnaces (constructed of alloy RA602CA) constitutes a primary glovebox containment barrier, and undue corrosion and penetration of this wall would cause Pu particles to escape into the manned process areas.

PFP contracted with PNNL to conduct testing to validate the use of existing furnaces in the RMC for thermal stabilization of the washed material. A high-temperature furnace (same make and model as used at the RMC line at PFP) and the associated offgas system were set up at PNNL to identify system vulnerabilities and to investigate alternative materials and operating conditions that would reduce any corrosion and plugging of furnace and offgas components. The key areas of interest for this testing were the furnace heating elements; the offgas line located inside the furnace; the offgas line between the furnace and the filter/knockout pot; the filter/knockout pot itself; the sample boat; and corrosion coupons (to evaluate alternative materials of construction). The testing was conducted by charging the furnace with CeO_2, a PuO_2 surrogate, that had been impregnated with a mixture of chloride salts (selected to

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(a) The RMC line furnaces are muffle furnaces that draw ambient air through the furnace chamber during operation. The relative humidity (RH) of the ambient air at PFP and in the RMC line can reach 60% or more, because swamp coolers are used to cool the building. This humidity can affect the calcination chemistry in the furnace and can create a challenge to meeting the 0.5 wt% moisture limit when samples are cooled and removed from the oven. Thermal stabilization operations are administratively controlled so as not to occur when RH is greater than 60%.

(b) The humidity is controlled in the SPE line furnaces and glovebox, with the moisture content maintained to less than 300 to 600 ppm.

represent the expected residual chloride salt level in washed HCP items) and heated to 1000°C in the furnace in accordance with the temperature ramp rates and hold times used at PFP. [Note: a hold temperature of 1000°C is used in the RMC line furnaces at PFP to guarantee the material in the boat is stabilized at 950°C in accordance with the DOE 3013 Standard]. The simulant charge loaded into the furnace for each cycle represented 1600 or 2000 g of PuO_2 containing 1 wt% chloride salt. The chloride salt mixture consisted of 45 mole% NaCl, 45 mole% KCl, and 10 mole% $MgCl_2$. Fifty furnace test cycles (Cycles 1 through 50) were completed with the furnace test system (Fischer et al. 2002). These tests showed that, at a 1 wt% chloride salt loading, the chloride salts evaporate (and decompose) from the process boats and corrode offgas lines, and deposit and plug the cooler downstream offgas lines and the offgas particulate filters. However, with process improvements, three to five cycles could be completed during the testing before the system had to be shut down for line cleaning and/or filter replacement.

The work discussed here is a follow-on to the previous tests at 1000°C (Cycles 1 through 50) to evaluate thermal stabilization of the HCP items at 750°C. Chloride salt vapor pressures are about 25 times higher at 1000°C than at 750°C, and pyrohydrolysis reactions (reaction of water vapor with chloride salt to produce HCl) occur more readily at higher temperature. Therefore, processing at lower temperature potentially can decrease the deleterious effects of the chloride salts. Reducing the thermal stabilization temperature is expected to provide a number of benefits:

- improve the efficiency of PFP operations
- decrease (perhaps eliminate) the complex and dose-intensive washing operation
- decrease liquid waste generation from the water wash steps
- avoid radiological worker exposure associated with equipment repair due to corrosion
- free personnel resources for other stabilization and Decontamination and Decommissioning activities.

As part of the lower-temperature thermal stabilization investigation, a case is being developed to demonstrate that technical equivalency with DOE 3013 Standard goals can be maintained at the lower temperature. This report was prepared for the Plateau Transition Division of DOE's Richland Operations Office, and was funded under a technical assistance program through the DOE-Environmental Management (EM) Office of Science and Technology.

A series of four furnace tests (Cycles 51 through 54) were conducted by PNNL to develop material balance and system operability data in support of the technical equivalency demonstration for thermal stabilization of HCP items at 750°C. Section 2.0 of this report describes the test approach, as well as the furnace system equipment, test materials, and testing methods. To the extent practicable, the furnace system equipment used in the testing at 1000ºC was also used in the 750ºC testing.

Section 3.0 presents the test results and includes detailed material balances, analytical results, equipment and materials performance data, component operability information, and moisture uptake testing performed on HCP simulant material calcined at 750°C. Where appropriate, comparisons with results of prior furnace testing at 1000°C were made.

Appendix A summarizes the procedures used to conduct each furnace test cycle. Appendix B provides X-ray patterns from X-ray diffraction (XRD) analyses performed on select samples. Plots of the furnace and boat temperature profiles from each test are provided in Appendix C.

2.0 Test Approach, Equipment, and Methods

This section describes the test approach, as well as the furnace system equipment (furnace, offgas lines, filter, scrubber, and condenser), test materials, and testing methods.

2.1 Approach

A series of furnace tests were conducted to develop material balance and system operability data for supporting the evaluation of lower-temperature thermal stabilization. Four furnace tests (Cycles 51 through 54) were conducted in a system that included a prototype RMC line furnace, a prototype offgas system (offgas lines and a 5-µm filter), a wet scrubber, a chilled condenser, and an offgas blower. For each test, a Hastelloy X process boat was loaded with simulant that represented a 2000-g HCP charge containing 20 wt% chloride salt (i.e., 1600 g PuO_2 + 400 g chloride salt). CeO_2 was used as a surrogate for PuO_2.[a] Two chloride salt compositions were tested: 1) NaCl and KCl added at a 50:50 mole ratio and 2) NaCl, KCl, and $MgCl_2$ added at a 45:45:10 mole ratio. A crucible loaded with simulant, thermocouples, and metal coupons was placed in the process boat, and the charged furnace was ramped to and held at 750°C for 2 hr. Air flow through the furnace (room air at 20% to 40% relative humidity) was maintained at 1 SCFM. The temperature ramp profile and air flow rates were prototypical of, but did not constrain, expected PFP operations.

The furnace performance was evaluated by monitoring the current and voltage to the heating elements and monitoring the temperature in the furnace chamber. The offgas system performance was monitored by measuring temperature, pressure drop, and flow rate. Between cycles, furnace and offgas system components and metal coupons were examined, photographed, and weighed to obtain material balance information and to evaluate corrosion. Samples were collected from the feed simulant, calcined simulant, filter, filter housing, scrubber, and condenser, and were subjected to chemical analyses to determine the distribution of chloride and chloride salt throughout the test system.

2.2 Equipment

The test stand used for the furnace system evaluation is illustrated in Figure 2.1, which shows the major components of the test system (prototype RMC line furnace, prototype offgas system, wet scrubber, chilled condenser, and offgas blower). Figure 2.2 is a detailed schematic of the furnace, 3/4-in. offgas lines, and the particulate filter. Figures 2.1 and 2.2 also show the location of thermocouples, pressure gauges, and the offgas flow meter.

(a) The suitability of CeO_2 as a surrogate for PuO_2 in chloride salt melts was examined. While CeO_2 is a more powerful oxidant than PuO_2 and thus potentially able to oxidize chloride to chlorine gas, the potential reactions of CeO_2 with melts of NaCl, KCl, and eutectic NaCl/KCl to form chlorine

$$CeO_2 + Cl^- \rightarrow Ce^{3+} + 2\ O^{2-} + Cl$$

have been considered in past studies to determine the solubility of CeO_2 (and Ce_2O_3) in these media from just above their respective melting points (i.e., 800°C, 770°C, and 700°C) to 1000°C (Reinhard and Naumann 1968). However, in their carefully designed studies, the researchers observed no evidence of free chlorine. Their investigations instead showed that, at given temperature, cerium concentrations in the melts with CeO_2 (e.g., for the NaCl/KCl eutectic at 700-1000°C, 6.5×10^{-6} -5.4×10^{-5} moles/kg salt) were ~5 to 10 times higher than those found for similar experiments using Ce_2O_3 (5.7×10^{-7} -1.2×10^{-5} moles/kg salt). The higher solubility of CeO_2 was attributed to the higher charge density of the Ce^{4+} ion compared with the Ce^{3+} ion. No solid phases in the tests, other than CeO_2, were observed.

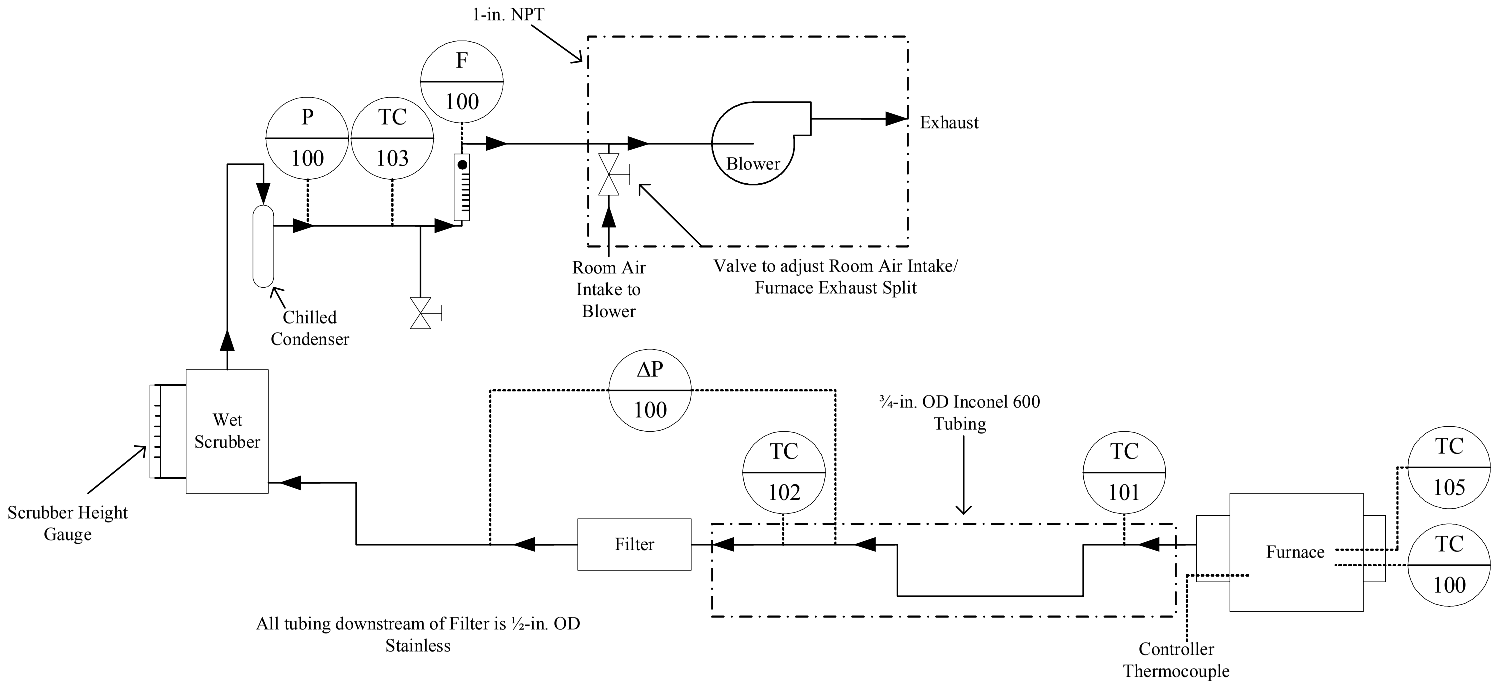

Figure 2.1. Diagram of Furnace and Offgas System Used for Testing

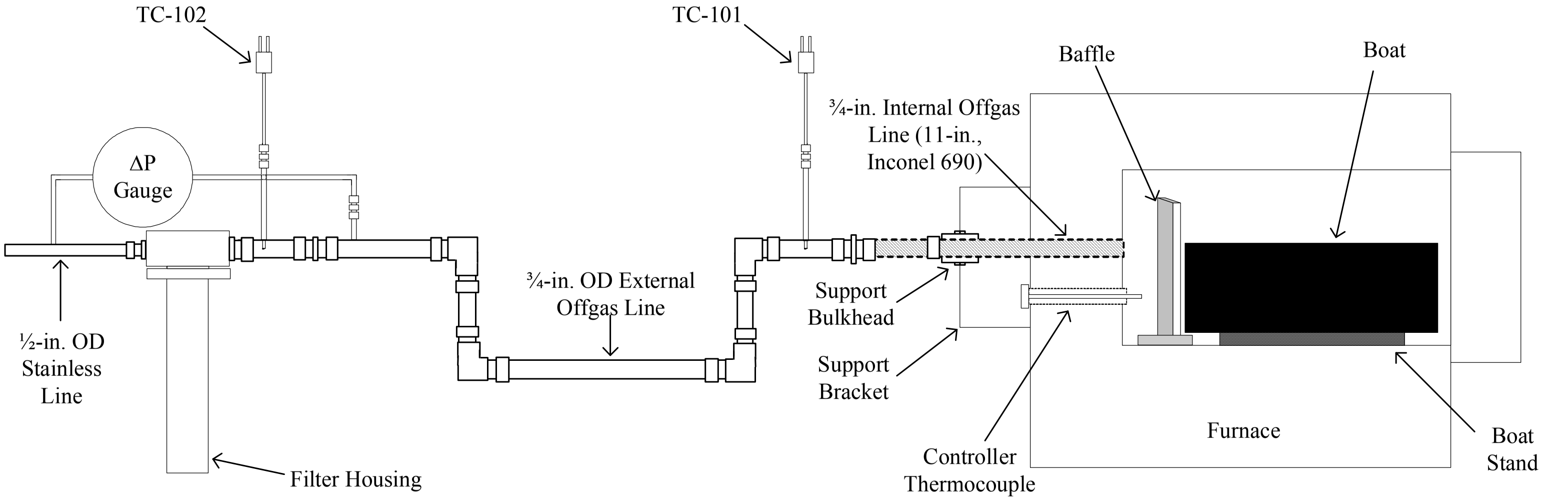

Figure 2.2. Furnace, ¾-in. Offgas Lines, and Filter Configuration

2.2.1 Furnace

A Thermolyne Model FA-1630-1 muffle furnace was used, (i.e., the same furnace model that is used in the PFP RMC line for materials stabilization). Four 240 VAC, 17.0 A heating elements, wired in series, lined the top, bottom, and side walls of the furnace. Actual dimensions of the furnace chamber with heating elements installed were 5.5 in. wide x 5 in. high x 13 in. deep (total chamber volume: 357.5 in.^{3}). Maximum short-term and continuous operating temperatures recommended by the manufacturer were 1177°C and 1066°C, respectively. A ceramic stand was placed inside the furnace directly on the bottom heating element to support a Hastelloy X boat, which was 11 in. long x 5 in. wide x 2.5 in. high. The boat was used to hold simulant, a crucible, and the metal coupons used for corrosion evaluation. A baffle constructed of Haynes HR-160 alloy was located at the back wall of the furnace chamber behind the boat, directly in front of where the gases exited the furnace. The arrangement of the baffle, support stand, and sample boat in the furnace is shown in Figure 2.3.

The furnace temperature was controlled with a proportional-integral-derivative (PID) controller coupled with a silicon-controlled rectifier (SCR). The PID controller was a Eurotherm Model 818 process controller capable of running temperature ramp/dwell sequences. The SCR was a Control Concepts, Inc., Model 1039 power controller rated for 30 A at 208 VAC (P/N 1039-V-208V-30A-F30-4/20MA). Both the process controller and the SCR were properly fused and grounded. Temperature input to the controller was provided by an Omega 1/4-in.-outer diameter (OD), 7-in.-long type K thermocouple (I-600 sheathed, P/N TJ48-CAIN-14U-7-SB-OSTW-M). Figures 2.2 and 2.4 show the location of the controller thermocouple. Two Omega 1/8-in.-OD, 24-in.-long type K thermocouples (I-600 sheathed, P/N KQIN-18U-24) were inserted through the front of the furnace between the door and the furnace housing with the tips submerged into the simulant. A Kaowool pad (i.e., refractory ceramic fiber) was inserted between the furnace housing and the furnace door to provide a reasonable seal around the thermocouples.

The available power supply in the lab was 208 VAC, not 240 VAC as rated by the heating elements. This did not appear to affect the furnace element operation.

2.2.2 Offgas Line, 3/4 in.

The 3/4-in.-OD offgas line between the furnace and the filter housing was divided into an internal and external section, as shown in Figure 2.2. The internal offgas line began inside the furnace with the inlet mounted flush with the back wall of the furnace (Figure 2.4). It extended out the back wall of the furnace and was supported by a bracket/bulkhead assembly mounted to the back of the furnace. The internal offgas line used in these tests was an 11-in.-long section of 1/2-in. Schedule 80 Inconel 690 pipe (0.840-in. OD), turned to 3/4-in.-OD, 6-in.-long, 0.102-in. wall thickness (i.e., same material and configuration being installed at PFP in the RMC line for processing the HCP items). The internal offgas line was inserted completely through a bored-out bulkhead fitting (Figure 2.5).

The external offgas line was connected directly to the internal offgas line with a union. The 38-in.-long external line was 3/4-in.-OD Inconel 600 tubing, 0.028-in. wall thickness. There were four 90-degree bends to better represent the current system used by PFP (Figure 2.2). The four bends used 90-degree elbows constructed of 316L stainless steel. Two Omega 1/8-in.-OD, 12-in.-long type K thermocouples (I-600 sheathed, P/N KQIN-18U-12) were inserted into the offgas line. See Figure 2.2 for locations.

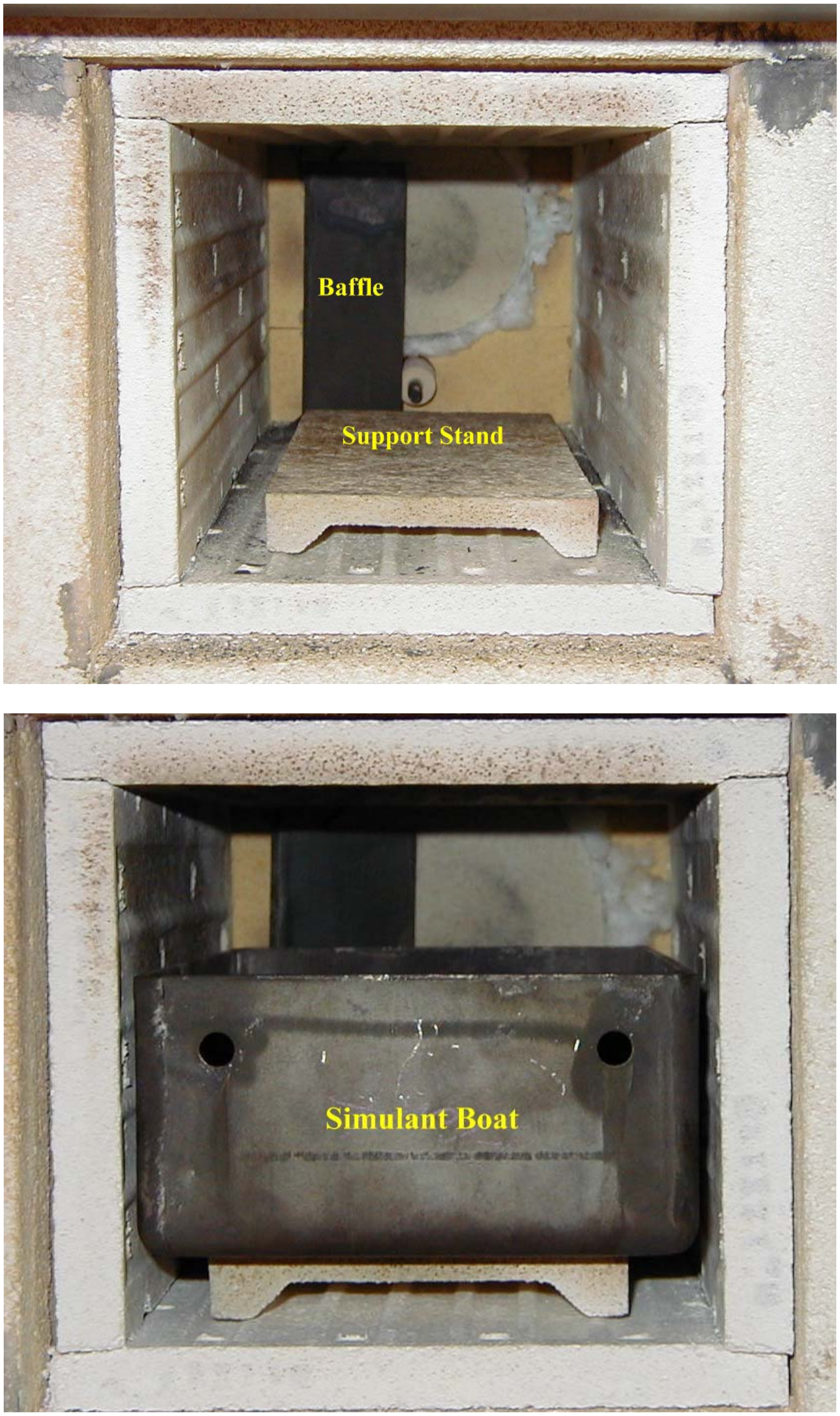

Figure 2.3. Front View of the Furnace Chamber to Show the Arrangement of the Baffle and Support Stand (above) and the Boat (below). Note that the furnace chamber was just wide enough for the boat to fit.

Figure 2.4. Internal Offgas Line Inlet and Controller Thermocouple as Installed in the Furnace (baffle removed)

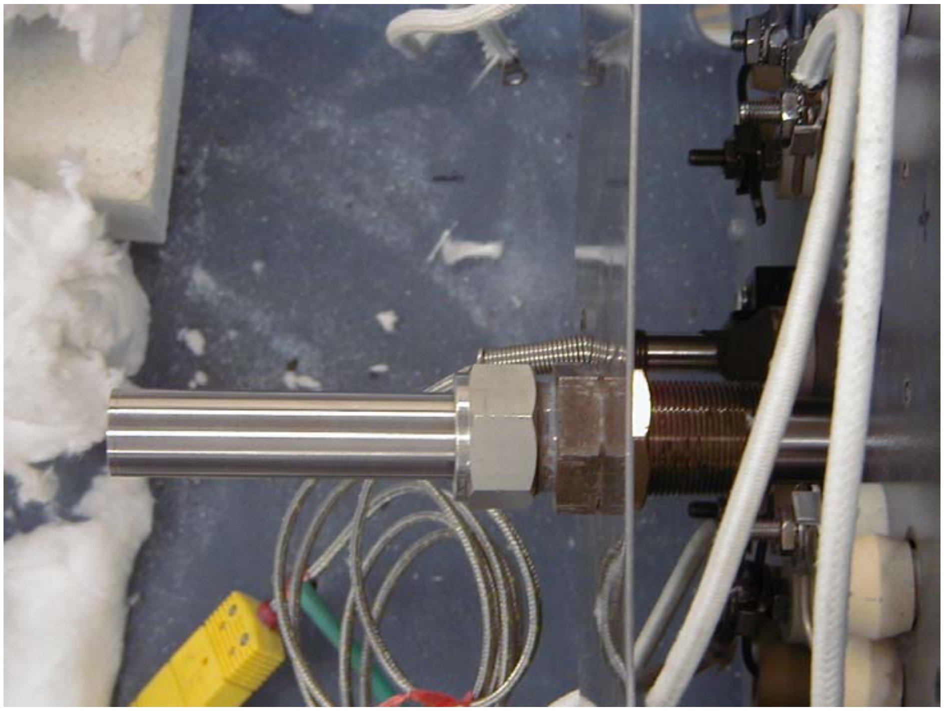

Figure 2.5. Bored-out Bulkhead for Supporting 11-in.-long Internal Offgas Lines

2.2.3 Filter and Housing

A filter was connected downstream of the external offgas line for particulate removal (Figure 2.1). The filtration system evaluated is comparable to the system being installed at PFP downstream of the RMC line furnaces.

The installation schematics and photos of the filter and housing used in the testing are shown in Figures 2.6 and 2.7. Both the filter element and the filter housing were supplied by Rosedale Products of California, Inc. (Coarsegold, California), and are described below.

Housing:

- P/N 4-1-20-3/4P-2-50-S-(SP)-N-NPT (NPT = National Pipe Taper Thread), Model 4, 304 stainless steel, 4.5-in. OD (body), 10-in. OD (flange), 30-in. overall length (including flange thickness and outlet port), 91 lb shipping weight.
- Holds one 20-in.-long filter cartridge.
- 593°C maximum temperature (at 50 psi max).

Filter:

- 5-µm (P/N 20-5-P-S-1NPTF-SP), 304 stainless steel pleated element.
- 20-in.-long, 2.6-in. OD (per cartridge).
- 593°C maximum temperature.
- Filter surface area (for one cartridge): 500 in.^2

The pressure drop across the filter was measured with a Dwyer 0-15 in.-H_2O 2000 Series Magnehelic ΔP gauge (Model 2015).

2.2.4 Gas Scrubbing System

The layout of the scrubbing system is shown in Figure 2.1. All tubing downstream of the filter housing was 1/2-in.-OD 304 stainless steel. The offgas exiting the filter was directed through a sparge tube located inside a 12 5/8-in.-OD x 24 5/8-in.-high 304 stainless steel tank. The sparge tube was ~10 in. long with ten 1/8-in. holes and submerged in 8 to 11 in. of water. A sight glass was installed onto the side of the tank to monitor water level.

The offgas exited the top of the scrubber tank and entered a 1-L condenser pot (304L stainless steel) to remove water from the saturated offgas stream. The condenser pot was submerged in a 5-gal bucket filled with ice and water during each run. After passing through the condenser, the offgas was re-heated to ~30°C with a heat tape, and then passed through a Dwyer Model RMA-10-TMV 0-200 SCFH flow meter. (the offgas was heated to raise its temperature to the flow meter calibration temperature and to prevent condensation within the flow meter.) An Omega 1/8-in.-OD, 12-in.-long type K thermocouple (I-600 sheathed, P/N KQIN-18U-12) and a Dwyer 0-30 in.-H_2O 2000 Series Magnehelic ΔP gauge (Model 2030) were located on the 1/2-in. stainless steel line between the heat tape and the flow meter. Directly below the flow meter was a section of 1/2-in.-OD tubing that served as a drop leg to catch any remaining condensate.

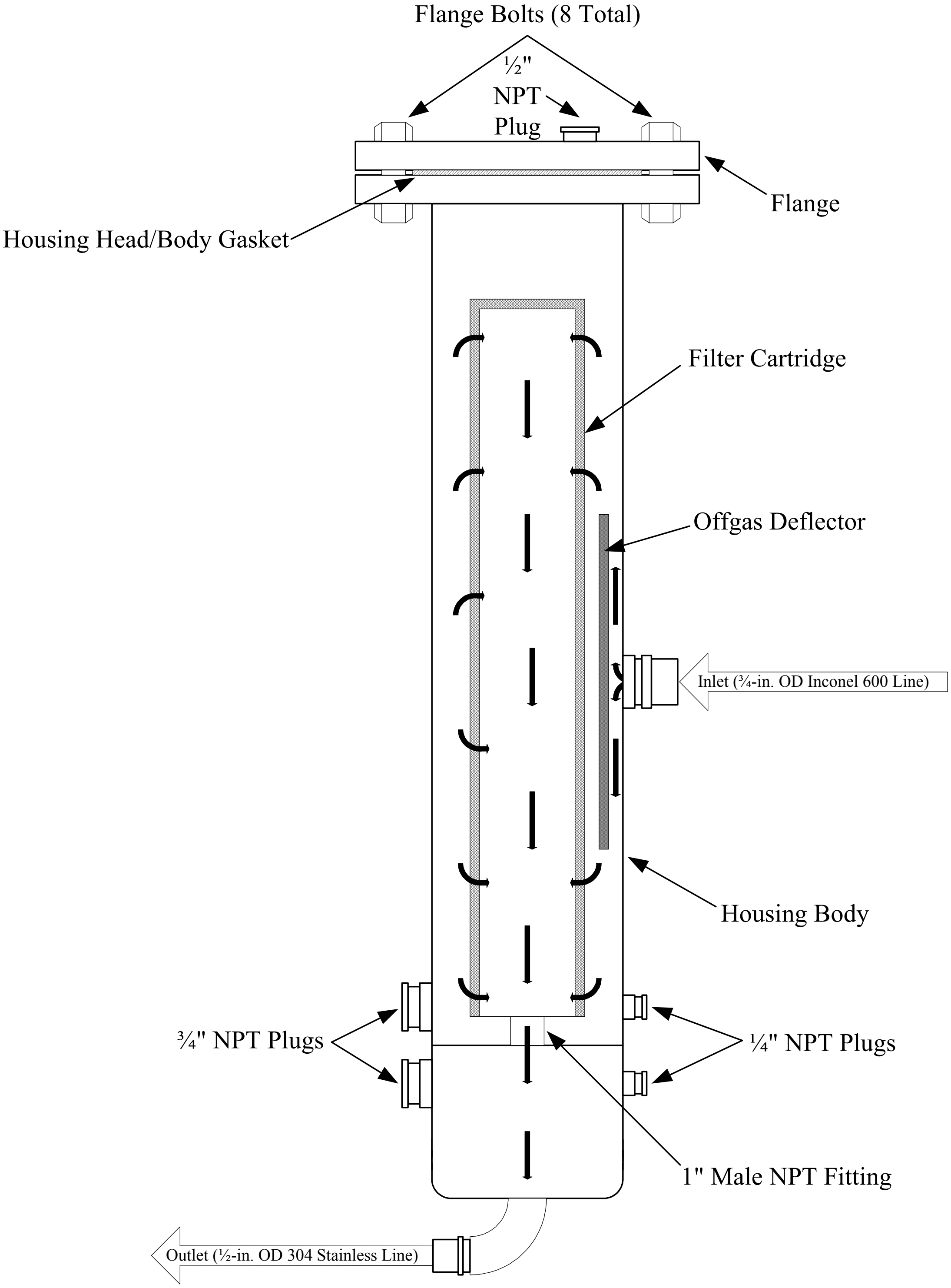

Figure 2.6. Schematic of the Rosedale Filtration System Implementing Pleated Metal Filter Cartridges

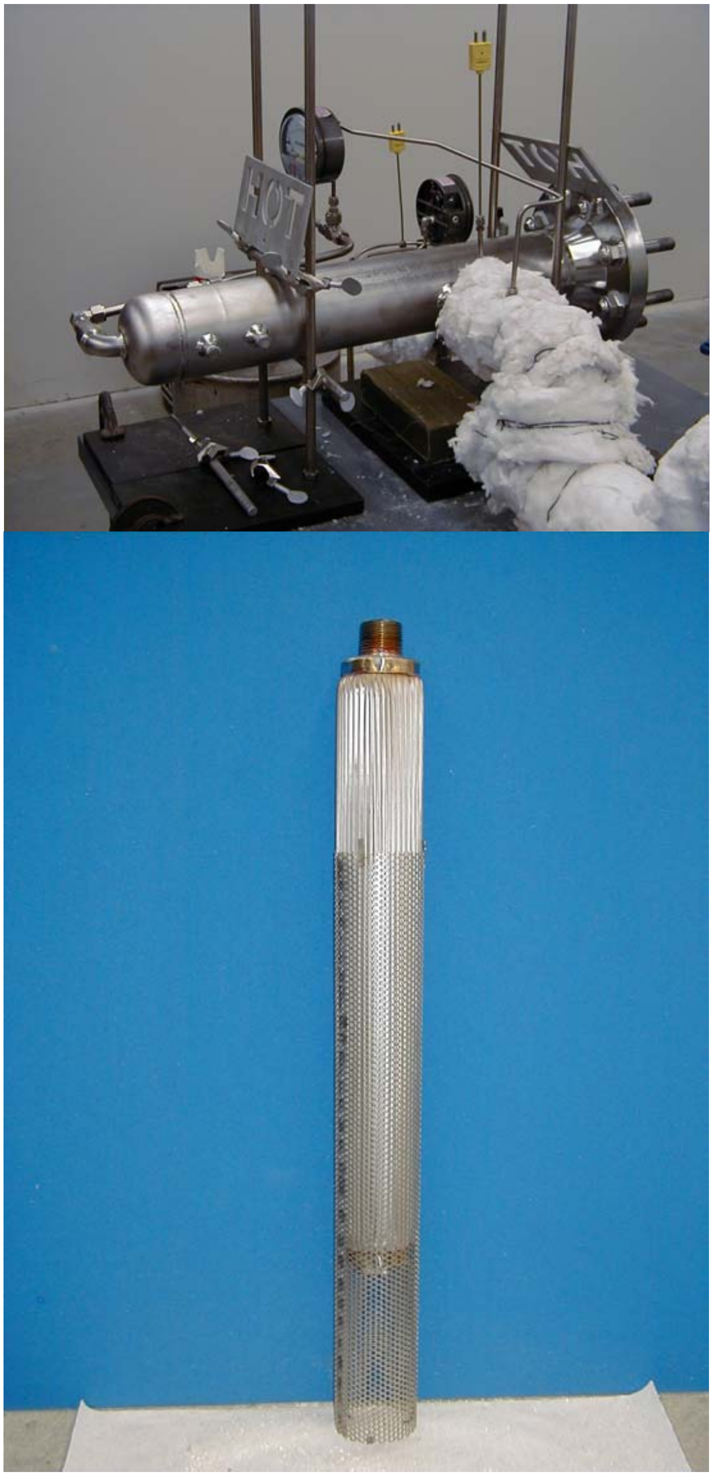

Figure 2.7. Rosedale Filter Housing and Element Before Installation. Housing outer diameter was 4.5 in. and shipped at 91 lb. Filter element was 2.6-in. OD and 20-in. long, and is shown with the pleat protector partially removed.

2.2.5 Offgas Blower

The offgas flow was provided by a Model R2103 Gast Regenair blower (P/N LTD139) capable of 42 CFM free air flow (20°C, 14.7 PSIA) or 35 in.-H_2O vacuum. Due to the high capacity of the blower, the majority of air flow was pulled directly from the room, while the target 1.0 SCFM offgas flow from the furnace was maintained with a valve located on the room air inlet (Figure 2.1). The room air inlet and the blower exhaust lines were 1-in. NPT.

2.2.6 Data Logging System

An Iotech Personal Daq/56 data logging system was used to record process data. Temperatures were recorded from the process controller thermocouple and others located in the simulant boat, Inconel 600 offgas line, and just upstream of the flow meter. Furnace voltage and current data from the SCR were also recorded. At the end of a furnace test cycle, the data were downloaded to an Excel worksheet for analysis.

2.3 Methods

The methods used to conduct the furnace system testing and to obtain test data are described.

2.3.1 Material Balance

Material balances were performed for each run (cycle) conducted at 750°C. The mass of simulant in the boat was measured before and after each test. A mass balance was also performed around the offgas lines, the filter element, and the scrubber and condensate water. As expected, a direct material balance around the boat was found to be inconclusive. Corrosion products from the boat and metal coupons commingled with the calcined material in the boat. Consequently, to develop a more precise material balance, a cylindrical crucible was placed in the center of the boat in each run and was filled with simulant to the same level as that in the boat. The walls of the crucible thus minimized the amount of corrosion products mixing with the contents.

Chemical analyses [inductively coupled plasma spectrometry (ICP) for cations and ion selective electrode (ISE) for chloride] were performed on simulant (fresh and calcined), on material collected on the filter, and on scrubber and condensate water samples. Select samples were also analyzed via XRD for phase identification.

2.3.2 Simulant Composition

Each furnace charge was formulated to represent a 2000-g charge containing 20 wt% chloride salt (i.e., 1600 g PuO_2 + 400 g chloride salt). On a mole basis, 1016 g CeO_2 is equivalent to 1600 g PuO_2; therefore, ~1016 g CeO_2 was used in each test. Two compositions of chloride salt were tested. The first composition was a mixture of NaCl and KCl at mole ratio of 50:50. The second composition was a mixture of NaCl, KCl, and $MgCl_2$(a) at a mole ratio of 45:45:10, respectively. The $MgCl_2$ used for preparing the simulant was hydrated ($MgCl_2 \cdot 6H_2O$). For both simulant compositions, the chloride salt was first ground to a fine powder then mixed with CeO_2 using a large mortar and pestle. To carefully control the simulant composition heterogeneity, simulant charges were prepared individually for each test. Fresh reagent-grade chemicals (CeO_2, NaCl, KCl, $MgCl_2 \cdot 6H_2O$) were used in all tests The simulant compositions are given in Table 2.1.

Table 2.1. Simulant Composition for Cycles 51 Through 54

Component	Molecular Weight	Mole Fraction	Weight Fraction	Mass Per Charge, g	
				Target	Simulant
Plutonium Oxide Fraction					
PuO_2	271.1	1.0	1.0	1600	--
CeO_2	172	1.0	1.0	--	1016.02
Chloride Salt Fraction					
Simulant 1 - Cycles 51 and 52					
NaCl (Used in simulant)	58.44	0.50	0.439	175.76	175.76
KCl (Used in simulant)	74.56	0.50	0.561	224.24	224.24
Simulant 2 - Cycles 53 and 54					
NaCl (Used in simulant)	58.44	0.45	0.379	151.64	151.64
KCl (Used in simulant)	74.56	0.45	0.483	193.46	193.46
$MgCl_2$ (Target)	95.220	0.1	0.137	54.90	
$MgCl_2 \cdot 6H_2O$ (Used for $MgCl_2$ in simulant)	203.31	--			117.23

2.3.3 Corrosion Testing

A combination of standard coupon corrosion tests and in-service testing of system components (e.g., heaters, boats, baffles, offgas tubing, etc.) was used for the corrosion and materials evaluations. Coupon corrosion tests utilized rectangular specimens of candidate metal alloy materials. Initial specimens were prepared from standard mill-finish plate. Tests consisted of initially characterizing all specimens, followed by exposing the specimens to furnace/offgas conditions during the test cycles. The corrosion specimens were first characterized by carefully weighing (nearest 0.0001 g) and measuring dimensions (nearest 0.01 in.). Coupons were placed in the boats (~1/2 submerged in the simulant). After exposure, the coupons were evaluated for corrosion types and penetration rates. The evaluation included observations of the condition "as is" upon removal and cleaning to remove corrosion products, followed by weighing and visual examination. Similar post-test examinations were conducted for the furnace and offgas system components to evaluate the nature and degree of chloride attack during operation.

(a) Because the HCP items stored at PFP were previously thermally processed at or above 450°C at the Rocky Flats Plant (many items were thermally processed twice), it is unlikely that significant quantities of $MgCl_2$ are still present. Additionally, the Rocky Flats Plant processes from which the HCP items were generated should have resulted in the decomposition of most of the $MgCl_2$. Consequently, the results and observations from the testing conducted with the $MgCl_2$-containing simulant are expected to be more severe than those anticipated from actual thermal stabilization operations, since the simulant was not preconditioned at 450°C before the 750°C furnace testing.

The following alloys were used for corrosion specimen materials during Cycles 51 through 54:

- RA602CA (mill-finish plate)
- Inconel 690 (mill-finish plate)

RA602CA, the material of construction of the retort system in the SPE furnaces, was evaluated to explore the potential processing of HCP items in the SPE line. Inconel 690 coupons were also examined. Inconel 690 coupons were previously evaluated in the furnace system testing conducted with 1 wt% chloride salt at 1000°C (Fischer et al. 2002). The results from both sets of data were compared.

Cycle 54 included two additional RA602CA coupons, provided by PFP. These coupons, which included several welds, were heat treated at 1000°C for 3.75 hr to form a protective oxide coating.

2.3.4 Offgas Line Materials

A new internal offgas line was initially cleaned, photographed, weighed, and measured in the same manner as the corrosion specimens. The external offgas line was thoroughly cleaned and weighed before Cycle 51. To duplicate the RMC line furnace system operations, the offgas line between the furnace and filter housing was insulated with Kaowool. At PFP, the offgas line is insulated to minimize the heat load to the glovebox.

2.3.5 Filter

A new filter element was installed before Cycle 51. In previous testing, filter elements were considered blinded and replaced after the pressure drop increased significantly (approximately 6 to 8 in.-H_2O). In the current testing, the same filter element was used for all test cycles. The performance of the filter was tracked during the testing by monitoring pressure drop. After each test, the filter element and housing were inspected and photographed as appropriate. The filter element was also removed and weighed to quantify particulate collection.

2.3.6 Scrubber and Condenser Operation

The offgas scrubber and condenser were cleaned, and a measured quantity of deionized water was added to the scrubber before the first test. Scrubber water samples were collected before and after each test. After Cycle 51 (simulant containing NaCl and KCl), a relatively small drop in the pH of the scrubber water was measured. Therefore, the scrubber water was not replaced for Cycle 52. However, the scrubber water was replaced before Cycles 53 and 54 (simulant containing NaCl, KCl, and $MgCl_2$). Also, during Cycles 53 and 54, scrubber water samples were collected immediately after completion of the 2-hr hold time at 750°C and after the furnace had cooled to about 400°C. Offgas flow was continued during the cooldown from 750°C to 400°C.

Condensate was removed from the condenser after each test. The condensate (~130 ml) was combined with the liquid captured in the drop leg (0.3 to 2 ml) to form the "condensate sample" for each test. After each test, the condenser, the flow meter, and the offgas lines between the scrubber and the blower were cleaned.

2.3.7 System Leak Check and Offgas Flow Rate Control

Before each test cycle, a leak check was performed on the offgas system. First, a high flow rate was established through the offgas system. Next, the internal offgas line was blocked, and the flow meter and pressure gauge were observed. If a high vacuum and zero flow through the flow meter were observed, the offgas system was considered leak tight.

The offgas flow rate was maintained at 1 SCFM during furnace operations. In general, once the flow rate was set at the beginning of the run, no adjustments were necessary. The temperature of the offgas passing through the rotameter was maintained at approximately 30°C with heat tape located between the chilled condenser and the flow meter. Before any testing, the calibration of the flow meter was verified at 30°C.

2.3.8 Furnace Operation/Process Variables

For each cycle, a CeO_2 simulant containing chloride salt was loaded into a boat; the boat was placed in the furnace chamber; and the furnace was heated in accordance with the proposed low-temperature PFP thermal stabilization protocol:

1. Room temperature to 500°C @ 300°C/hr
2. 500°C to 700°C @ 200°C/hr
3. 700°C to 750°C @ 125°C/hr
4. Hold at 750°C for 2 hr, then shut off furnace power and cool.

The furnace operation procedure and a list of the measured process variables with sampling frequencies can be found in Appendix A.

3.0 Results and Discussion

A total of four furnace cycles (Cycles 51 through 54) were completed, with approximately 400 g of chloride salt (i.e., 20 wt% chloride salt) charged to the furnace in each cycle. For Cycles 51 through 54, the temperature was ramped to and held at 750°C for 2 hr. Cycles 51 and 52 were conducted with NaCl and KCl added at a 50:50 mole ratio. Cycles 53 and 54 were conducted with NaCl, KCl, and $MgCl_2$ added at a 45:45:10 mole ratio. The results of the four test cycles are discussed here. In previous furnace testing (Fischer et al. 2002), Cycles 2 through 7 and 9 were conducted with 16 g of chloride salt (NaCl, KCl, and $MgCl_2$ added at a 45:45:10 ratio); and Cycles 34 through 36 were conducted with 20 g of chloride salt (NaCl, KCl, and $MgCl_2$ added at a 45:45:10 mole ratio). Results from those tests, conducted with a 1 wt% chloride salt loading at 1000°C, are also discussed.

3.1 Material Balance

Material balances were performed for each run (cycle) conducted at 750°C, as discussed in Section 2.3.1. Cycles 51 and 52 used simulants containing CeO_2 with NaCl/KCl; Cycles 53 and 54 used simulants containing CeO_2 and NaCl/KCl/$MgCl_2$. The mass of simulant in the boat was measured before and after each test. Figure 3.1 shows a loaded boat, with crucible and metal coupons, before and after calcination during Cycle 51. A mass balance was also performed around the offgas lines, the filter element, and the scrubber and condensate water. As expected, a direct material balance around the boat was found to be inconclusive. Corrosion products from the boat and metal coupons commingled with the calcined material in the boat. Consequently, to develop a more precise material balance, a cylindrical crucible was placed in the center of the boat in each run and was filled with simulant to the same level as that in the boat. The walls of the crucible thus minimized the amount of corrosion products mixing with the contents. Based on analyses of the material balance data, it was found that most of the mass lost from the simulants during calcination was removed from the boat in the form of acid chloride (e.g., HCl and iron/nickel chlorides), as compared to volatilization of intact chloride salts from the feed simulant (discussed below in greater detail).

Table 3.1 presents the material balances for Cycles 51 through 54. The first section of the Table 3.1, "Crucible Sample Mass Balance," provides the basis for calculating the quantity of chloride and chloride salt removed from the total simulant charged to the furnace. For the crucible mass balance analysis, the mass of the simulant in the crucible was accurately weighed before and after the furnace cycle, and the mass loss was determined by difference. The mass loss was then apportioned to three sources: 1) removal of moisture in the initial simulant; 2) removal of waters of hydration associated with $MgCl_2 \cdot 6H_2O$; and 3) removal of chloride and chloride salt. The initial moisture content of the simulant was determined by heating samples of the NaCl/KCl simulant to 500°C and measuring the weight loss. The initial moisture content (0.0500 wt%) was used for both simulants, since $MgCl_2$ is a relatively small fraction of the NaCl/KCl/$MgCl_2$ simulant and heating the NaCl/KCl/$MgCl_2$ simulant to 500°C would have resulted in loss of waters of hydration. All waters of hydration associated with the $MgCl_2 \cdot 6H_2O$ in Cycles 53 and 54 were assumed to be removed during the furnace cycle (i.e., 4.22 wt% of the NaCl/KCl/$MgCl_2$ salt consisted of waters of hydration; the source of $MgCl_2$ used for preparing the simulant was $MgCl_2 \cdot 6H_2O$. After accounting for the removal of initial moisture and waters of hydration, the remaining crucible sample mass loss was attributed to the removal of chloride and chloride salt.

Figure 3.1. Cycle 51, Boat, Simulant, Coupons and Crucible, Before (top) and After (bottom) Calcination

Table 3.1. Mass Balance for Cycles 51 Through 54

	NaCl/KCl		NaCl/KCl/$MgCl_2$	
Crucible Sample Mass Balance	**Cycle 51**	**Cycle 52**	**Cycle 53**	**Cycle 54**
Initial (fresh) simulant in crucible, g	40.9637	39.6011	30.3204	31.5848
Calcined simulant in crucible, g	40.9074	39.5429	28.7248	29.9054
Moisture in fresh simulant,(a) wt%	0.0500	0.0500	0.0500	0.0500
Crucible simulant weight loss due to moisture removal, g	0.0205	0.0198	0.0151	0.0158
Crucible simulant weight loss due to removal of waters of hydration associated with $MgCl_2 \cdot 6H_2O$,(b) g	0.0000	0.0000	1.2782	1.3315
Crucible simulant weight loss due to removal of chloride and chloride salt, g	0.0358	0.0384	0.3022	0.3321
Crucible simulant weight loss due to removal of chloride and chloride salt, wt%	0.0875	0.0970	0.9968	1.0514
Simulant in Boat	**Cycle 51**	**Cycle 52**	**Cycle 53**	**Cycle 54**
Simulant charge to boat, g	1398.6	1399.4	1466.3	1464.7
Chloride salt in charge, g	395.2	395.3	396.7	396.317
Chloride in charge, g	210.7	210.7	223	222.8
Calculated weight loss from boat,(c) based on crucible wt% loss, due to chloride and chloride salt removal, g	1.22	1.36	14.62	15.40
Recovered Salt Mass(d)	**Cycle 51**	**Cycle 52**	**Cycle 53**	**Cycle 54**
Chloride recovered from filter housing, g	0	0	1.29	1.29
Chloride recovered from filter, g	0.1720	0.1720	2.0571	2.4699
Chloride recovered from scrubber, g	0.5203	0.7059	12.0660	12.2915
Chloride recovered from condenser, g	0.0144	0.0018	0.1377	0.1107
Total chloride recovery, g	0.7067	0.8797	15.5509	16.1621
Na+K+Mg(e) recovered from filter housing, g	0	0	0.4890	0.4890
Na+K+Mg(e) recovered from filter, g	0.1876	0.1876	0.2506	0.3008
Na+K+Mg(e) recovered from scrubber, g	0.0698	-0.0348	0.0334	0.0037
Na+K+Mg(e) recovered from condenser, g	0.0036	0.0009	0.0025	0.0017
Total Na + K + Mg recovery, g	0.2610	0.1536	0.7755	0.7952
Total chloride + Na + K + Mg recovery, g	0.9677	1.0333	16.3263	16.9573
Total chloride + Na + K + Mg recovery,(f) %	79.1	76.1	111.7(g)	110.1(g)

(a) The initial moisture content of the simulant determined by heating samples of the NaCl/KCl simulant to 500°C and measuring the weight loss.

(b) 4.216 wt% of NaCl/KCl/$MgCl_2$ simulant mass consisted of waters of hydration associated with the $MgCl_2 \cdot 6H_2O$ used for the simulant makeup.

(c) Based on extrapolation of the results from the crucible sample mass balance.

(d) Chloride, Na, K, and Mg quantities determined from ICP and ISE analysis of scrubber and condenser solutions and from solutions generated by dissolving/leaching solids recovered from the filter and filter housing.

(e) Although Mg was present in NaCl/KCl/$MgCl_2$ simulant, Mg was not detected in samples from offgas components.

(f) *Total chloride + Na + K + Mg recove*ry divided by *Calculated weight loss from boat* x 100%.

(g) This value would be reduced to 89% to 91% if the mass of O_2 to form MgO (during the decomposition of $MgCl_2$, assuming 36% to 39% decomposition) was accounted for in the *Calculated weight loss due to removal of chloride and chloride salt.*

The second section of Table 3.1, "Simulant in Boat," presents information on the mass and makeup of the total simulant charged to the boat. This portion of the table also provides the projected mass of chloride and chloride salt removed from the total charge, based on extrapolation of the results from the crucible sample mass balance. For Cycles 51 and 52, only 1.22 g and 1.36 g, respectively, of chloride and chloride salt were removed from the boat. For Cycles 53 and 54, 14.62 g and 15.40 g, respectively, of chloride and chloride salt were removed.

The third section of Table 3.1, "Recovered Salt Mass," accounts for the chloride and Na+K+Mg recovered in the offgas system components (filter housing, filter, scrubber, and condenser). It was found that Mg was below analytical detection limits in all samples collected from offgas components. Very small weight changes were observed in the offgas lines, with most of the changes likely the result of corrosion. However, routine cleaning/sampling of the offgas lines was not performed between cycles to allow for a multi-cycle assessment of the operability of the offgas lines. Consequently, Table 3.1 does not include recoveries from the offgas lines. For Cycles 51 and 52, Table 3.1 shows that between 0.70 and 0.88 g of chloride was recovered in the offgas system, with 75% to 80% of the chloride recovered in the scrubber water and condensate. Based on the chloride and Na+K+Mg recovery measurements, during Cycles 51 and 52, 79.1% and 76.1%, respectively, of the chloride and chloride salt removed from the charges were recovered in the offgas system. For Cycles 53 and 54, about 112% and 110%, respectively, of the chloride and chloride salt removed from the simulant were recovered in the offgas system. Part of the over-recovery of chloride and chloride salt in Cycles 53 and 54 can be attributed to underestimating the quantity of chloride and chloride salt removed from the charge. Oxygen, which is not accounted for in Table 3.1, is added to the charge mass as a result of the formation of MgO during the decomposition of $MgCl_2$. The weight gain associated with the oxygen offsets and masks some of the weight loss associated with the removal of chloride and chloride salt. Assuming that 36% to 39% of the $MgCl_2$ decomposed (as shown below), and accounting for the oxygen added to the simulant, the recoveries for Cycles 53 and 54 would be 89% to 91%.

Table 3.2 shows the relative mole fractions of Na, K, and Mg (derived from ICP data) in samples of feed and calcined samples. The mole fraction data on the feed simulants are in excellent agreement with the target mole ratios established for the simulant makeup (i.e., NaCl and KCl added at a 50:50 mole ratio for Cycles 51 and 52; and NaCl, KCl, and $MgCl_2$ added at a 45:45:10 mole ratio for Cycles 53 and 54, see Table 2.1). Both the feed and calcined simulants from Cycles 51 and 53 contained essentially equimolar concentrations of Na and K (i.e., no selective depletion of either Na or K occurred during calcination). This behavior is expected since only a very small portion of the salts in the simulant was volatilized during calcinations.

The Mg concentration in the calcined simulant from Cycle 53 is significantly lower than that in the feed simulant. This suggests that either $MgCl_2$ preferentially volatilized during calcining or it decomposed to form HCl and MgO/$Mg(OH)_2$. In the latter case, the MgO/$Mg(OH)_2$ that formed from the decomposition of $MgCl_2$ would not leach(a) to any significant degree (supported by the leachate pH of 9.41). The magnitude of the Mg depletion indicates that about 36% to 39% of the $MgCl_2$ may have decomposed to form MgO. This level of decomposition corresponds to the removal of 14.7 to 16.0 g of chloride

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(a) Leaching was performed to prepare samples for chemical analyses. Feed simulant samples (uncalcined) were prepared for analyses of chloride by ISE and Na/K/Mg by ICP by grinding a nominal 15-g sample in a mortar and pestle to homogenize the samples, and then taking a nominal 1.00-g subsample for leaching in 100 ml of deionized water. Calcined simulant recovered from the crucibles (entire sample) were dissolved in 500 ml of deionized water. The slurries were filtered to remove the suspended solids, and the pHs of resulting leachates were measured.

Table 3.2. Relative Mole Fractions of Na, K, and Mg in Feed and Calcined Simulants

Analyte	Cycle 51 Simulant		Cycle 53 Simulant		Cycle 54 Simulant
	Feed	**Calcined**	**Feed**	**Calcined**	**Feed**
	Mole Fraction				
Na	0.499	0.494	0.448	0.462	0.448
K	0.501	0.506	0.444	0.472	0.449
Mg	0.00	0.00	0.108	0.0664	0.104
Total	1.00	1.00	1.00	1.00	1.00

(chloride in $MgCl_2$ within the feed simulant = 40.9 g), assuming the chloride in the decomposed $MgCl_2$ left the boat in the form of HCl. Further, this level of chloride removal is consistent with the quantity of chloride recovered (15.5 g) in the offgas system during Cycle 53 (Table 3.1). Also, a 36% to 39% $MgCl_2$ decomposition in Cycle 53 would correspond to 3.3 to 3.6 g of oxygen being added to the charge mass. The test conditions and overall chloride removal results from Cycles 51 through 54 are summarized in Table 3.3. For comparison, some results from the previous furnace testing at 1000°C with 1 wt% chloride salt as $NaCl/KCl/MgCl_2$ (Fischer et al. 2002) are also provided.

Table 3.3. Test Conditions and Chloride Removal

		Chloride Salt in Simulant		**Mass of Chloride and Chloride Salt Lost from Simulant in Boat**		**% of Chloride Removed from Boat**	
Cycle No.	**Furnace Hold Temp., °C**	**Mass in Charge, g**	**Mole ratio, $NaCl:KCl:MgCl_2$**	**Gram per Charge(a)**	**As % of Chloride Salt in Charge(b)**	**Chloride Chemical Analysis(c)**	**Based on Chloride Recovered(d)**
51	750	395.2	50:50:0	1.22	0.309	[Note e]	0.34
52	750	395.3	50:50:0	1.36	0.344		0.42
53	750	396.7	45:45:10	14.62	3.69	13.2	6.97
54	750	396.3	45:45:10	15.40	3.89		7.25
2-7	1000	16	45:45:10	15.6*	No data	97.5	No data
9 (front)	1000	16	45:45:10	15.7*	No data	98.4	No data
9 (back)	1000	16	45:45:10	15.6*	No data	97.6	No data
34	1000	20	45:45:10	16.6	83	No data	No data
35	1000	20.1	45:45:10	16.5	82	66.3	No data
36	1000	20.1	45:45:10	20.0	99.7	72.4	No data

(a) Values from Cycles 51 through 54 taken from Table 1. Values marked with * were determined based on chloride analyses and by assuming chloride and chloride salt losses are proportional.

(b) = 100% x *Mass of Chloride and Chloride Salt Lost from Simulant in Boat (g/charge)* divided by *Chloride Salt in Simulant*.

(c) Values based on measured chloride (ISE) content in feed simulant and calcined simulant.

(d) Values based on recovery of chloride from materials collected in the filter, filter housing, scrubber water, and condensate (see Table 1).

(e) Due to analytical uncertainty introduced in sample preparation and ISE analyses, and the very small difference between the feed and calcined sample, no measurable difference in chloride content was found between the feed and calcined material.

Table 3.3 compares values for the masses of chloride and chloride salt removed from the charge during the present and prior calcination testing (for Cycles 51 through 54, these values were taken from Table 3.1). To compare the furnace cycles, the mass losses of chloride and chloride salt are also presented as percent of the initial chloride salts in the feed charge.

Table 3.3 also presents the results of two techniques used to estimate the amount of chloride removed from the charge during calcination. In the first technique, chloride removal was estimated by leaching the feed simulant and the calcined simulant taken from the crucible, and measuring the chloride content in the leachate with an ISE. This technique provides a reasonably accurate estimate of chloride removal when a significant quantity of chloride has been removed.

For the second technique, chloride removal was estimated by knowing the chloride content in the feed simulant and measuring the chloride captured in the various components of the offgas system. Assuming all chloride removed from the simulant in the charge was captured, this technique provides a reasonably accurate estimate of chloride removal.

For Cycles 51 and 52, both the feed and the calcined simulant contained high concentrations of chloride, and very little chloride removal occurred. Consequently, use of the first technique did not provide a reliable chloride removal estimate for these two tests. During Cycles 51 and 52, the observed carry-over of salts and liquid beyond the condenser was minimal; therefore, most of the chloride removed from the charges was captured. Good recoveries were also demonstrated by the mass balance (Table 3.1). Consequently, the second technique, based on chloride recovery measurements, should have provided reasonably accurate estimates for percent chloride removal for Cycles 51 and 52, found to be 0.34 and 0.42 wt%, respectively.

Based on the feed makeup, the simulant charged to the boat in Cycles 53 and 54 should have contained 223 g of chloride. ISE results indicated that the feed simulant and calcined product material contained 229 g and 199 g chloride, respectively (i.e., ~30 g, or 13%, of chloride was removed, based on the first technique). During Cycles 53 and 54, a small amount (several ml) of liquid carry-over into the flow meter was noted while the furnace was being ramped to 750°C, but acid was not detected when litmus paper was placed in the offgas blower exhaust. Chloride recovery measurements indicate that 6.97 to 7.25 wt% of the chloride was removed from the charge during Cycles 53 and 54. Considering the errors associated with the ISE measurements of chloride in the feed and calcined product (measurement of relatively small differences between large values), the chloride removal estimates based on the chloride recovery measurements are probably more accurate for Cycles 53 and 54.

For Cycles 2 through 7, 9, 35, and 36, conducted at 1000°C with $NaCl/KCl/MgCl_2$, use of the first technique to estimate chloride removal provides reasonably accurate values (i.e., measurement of relatively large differences between chloride content in feed and calcined material).

Table 3.3 shows that very small quantities of chloride and chloride salt were removed during Cycles 51 and 52 (NaCl/KCl at 750°C). In contrast, the masses of chloride and chloride salt removed during Cycles 53 and 54 ($NaCl/KCl/MgCl_2$ simulant at 750°C) are comparable to the masses removed when the furnace was charged with 16 to 20 g of the same chloride salt mix and operated at 1000°C in the previous testing.

During Cycles 51 through 54, only a small fraction of the chloride in the charge was removed at 750°C. In Cycles 2 through 7 and 9 (1000°C), which included 16 g of chloride salt in the charge, essentially all of the chloride was removed. However, in Cycles 35 and 36 (also at 1000°C), which included 20 g of chloride salt in the charge, only ~70% of the chloride was removed.

3.2 Scrubber/Condenser Water Analysis

3.2.1 Cycles 51 and 52 (NaCl and KCl Simulant)

Before Cycle 51, the offgas scrubber was cleaned, then loaded with 22.72 kg deionized water. A sample of the fresh scrubber water was collected. Scrubber water and condensate samples were also collected after Cycles 51 and 52. The scrubber water was not replaced or neutralized between Cycles 51 and 52. The results of the ICP and ISE analyses of scrubber and condenser water samples are given in Table 3.4. The measured pH values for these samples and the chloride concentrations that would be associated with HCl based on these pH values are also provided. With the exception of chloride, the concentrations of the analytes measured in the scrubber water were very low. The data indicate that small quantities of Na and K were captured in the scrubber during Cycle 51. However, the concentration of Na and K decreased slightly during Cycle 52. As noted in past observations, small quantities of salts initially pass through new stainless steel pleated filters, but after a coating/cake of salts is laid down on the filter, no further salt penetration occurs.

Assuming all measured Na and K in Cycle 51 scrubber water (in excess of that measured in the fresh scrubber water) entered the scrubber as salts, then 123 mg and 41 mg of NaCl and KCl, respectively, were captured in the scrubber. The total chloride in the scrubber associated with the projected NaCl and KCl is ~94 mg. In comparison, based on the chloride data (ISE), the scrubber contained a total of 540 mg chloride (with ~390 mg associated with HCl). These data suggest that ~0.2% of the chloride in the feed simulant (224 g) was converted to HCl (via pyrohydrolysis).

Table 3.4. Analyte Concentrations in Scrubber and Condenser Water - Cycles 51 and 52 (NaCl/KCl Simulant)

Analyte	Scrubber Water			Condenser Water	
	Pre Cycle 51 Fresh	Post Cycle 51 Spent	Post Cycle 52 Spent	Post Cycle 51	Post Cycle 52
	Concentration, mg/L				
B	2.028	3.502	3.807	3.675	4.272
Ca	<det	<det	1.474	1.500	<det
Cr	<det	0.248	<det	<det	<det
Cu	<det	<det	<det	1.285	<det
Fe	<det	<det	2.257	29.266	0.251
K	0.457	1.409	0.565	16.148	0.958
Mn	<det	<det	<det	3.440	<det
Na	3.975	6.094	5.411	11.520	5.578
Ni	<det	<det	<det	24.108	3.100
Si	6.346	1.792	2.041	3.005	2.473
Chloride (ISE)	NA	23.8	55.3	111.3	14.0
pH	6.8	3.31	2.98	3.64	4.05
Acid Derived Chloride	NA	17	37	8	3

Approximately 720 mg of chloride were collected in the scrubber water during Cycle 52. The chloride content predicted to be associated with HCl based on the pH of the scrubber water was 450 mg. Considering that little or no Na, K, Fe, or Cr accumulated in the scrubber water during Cycle 52, HCl, generated from pyrohydrolysis of NaCl and KCl, is the probable source for most of the 720 mg of chloride.

During Cycles 51 and 52, 131 g and 132 g of condensate, respectively, were collected. There is a small but significant concentration of Fe, Ni, and chloride in the Cycle 51 condensate water. The relatively low pH of the condensate solution could have resulted in some minor corrosion of the stainless steel condenser (i.e., potential source of Fe and Ni). Minor concentrations of Mn and Cu are also probably corrosion products. The presence of Na and K in the condenser water is attributed to aerosols containing these analytes passing uncaptured through the scrubber or accompanying aerosols generated by the scrubber.

3.2.2 Cycles 53 and 54 (NaCl, KCl, and $MgCl_2$ Simulant)

Before Cycles 53 and 54, the offgas scrubber was cleaned and then filled with 20.01 and 20.15 kg of deionized water, respectively. Samples of the fresh scrubber water were collected. Two spent scrubber water samples were collected during each cycle. The first sample was collected immediately after completing the 2-hr hold time at 750°C. The second sample was collected after the furnace had cooled to about 400°C. During the cooling period, offgas flow through the furnace was continued. Condenser water was also collected after each cycle. The results of the ICP and ISE analyses of scrubber and condenser water samples are given in Table 3.5. The measured pH values for these samples and the

Table 3.5. Analyte Concentrations in Scrubber and Condenser Water - Cycles 53 and 54 (NaCl/KCl/$MgCl_2$ Simulant)

Analyte	**Cycle 53 Scrubber Water**			**Cycle 54 Scrubber Water**			**Condenser Water**	
	Concentration, mg/L							
	Fresh	**Spent (at 750°C)**	**Spent (final)**	**Fresh**	**Spent (at 750°C)**	**Spent (final)**	**Cycle 53**	**Cycle 54**
B	2.370	2.877	2.148	2.184	1.292	<det	1.429	1.521
Ca	<det	<det	<det	<det	<det	<det	1.738	1.021
Cr	<det	1.300	2.176	<det	1.757	3.222	8.503	22.032
Cu	<det	<det	<det	<det	<det	<det	2.234	1.171
Fe	<det	4.655	7.963	<det	6.916	12.511	91.211	113.220
K	0.095	1.154	1.745	<det	<det	<det	9.977	6.277
Mg	<det	<det	<det	<det	<det	<det	<det	<det
Mn	<det	<det	<det	<det	<det	<det	2.608	1.718
Mo	<det	<det	<det	<det	<det	<det	<det	2.657
Na	3.660	5.822	5.331	3.309	3.959	3.491	8.524	6.622
Ni	<det	<det	1.201	<det	1.004	1.835	11.453	9.488
Si	6.169	2.433	2.085	6.261	1.310	1.229	2.500	2.522
Chloride (ISE)		415	603		393	610	1021	858
pH	7.49	1.92	1.77	6.5	2.08	1.93	1.57	1.98
Acid Derived Chloride	NA	426	602	NA	295	417	954	371

chloride concentrations that would be associated with HCl based on these pH values are also provided. With the exception of chloride, the concentrations of the other analytes measured in the scrubber water were very low. The data indicate that small quantities of Na and K were captured in the scrubber during Cycle 53, but essentially no Na, K, or Mg was captured in the scrubber water during Cycle 54. The chloride captured in the scrubber during Cycle 53 is two orders of magnitude greater than that of the Na and K. The data are consistent with HCl as the source of essentially all of the chloride in the scrubber.

Low concentrations of Fe, Cr, and Ni were observed in the scrubber, and it is possible that some of these entered the scrubber as chloride salt. However, these analytes could also be attributable to minor corrosion of the stainless steel scrubber vessel.

There is very good agreement between the ISE chloride concentrations and the chloride associated with HCl based on the pH measurements for Cycle 53 scrubber and condenser water, supporting that HCl is the source for most of the chloride in these samples. The pH-based HCl concentrations do not compare as well with the ISE measurements for Cycle 54 scrubber and condenser water, but still suggest that HCl is the predominant chloride source.

In Cycles 53 and 54, the chloride concentration in the second scrubber sample was about 50% greater than the concentration in the first sample. This strongly supports that significant amounts of HCl were evolved from the simulant during cooldown.

During Cycles 53 and 54, 135 g and 129 g, respectively, of condensate were collected. Small but significant concentrations of Fe, Cr, and Ni present in the condenser water can likely be attributed to corrosion of the condenser vessel. The trace accumulations of Ca, Cu, Mn, and Co shown in Table 3.5 were not measurable in the scrubber water. The presence of Na and K in the condenser water is attributed to aerosols containing these analytes passing through or generated in the scrubber.

3.2.3 Cycle 13 Previous Furnace Testing at 1000°C (NaCl, KCl, and $MgCl_2$ Simulant)

During the previous furnace testing, chemical analyses were performed on scrubber water before and after Cycle 13 but were not reported in Fischer et al. (2002). For Cycle 13, the furnace was charged with 1016 g of simulant that included 16 g of chloride salt (NaCl, KCl, and $MgCl_2$ added at a mole ratio of 45:45:10). The masses of the individual chloride salts in the charge were: NaCl, 6.08 g; KCl, 7.76 g; and $MgCl_2$, 2.20 g. For Cycle 13, the furnace was ramped to and held at 1000°C for 2 hr. Based on analyses of the calcined product from similar runs (Cycles 2 through 7 and 9, Table 3.3), nearly all of the chloride in Cycle 13 should have been removed from the charge during the processing. Unlike the filter used in Cycles 51 through 54, a packed knockout pot was used in Cycle 13 to remove particulate from the offgas stream. The particle removal efficiency of the knockout pot was much lower than that of the 5-μm filter, allowing more chloride salt into the scrubber.

Before Cycle 13, the scrubber was cleaned and then filled with 23.4 kg of tap water. Samples of the fresh scrubber water were collected and analyzed (Table 3.6). The measured pH values for these samples and the chloride concentrations that would be associated with HCl based on these pH values are also provided. As expected, due to the use of the knockout pot and the higher furnace temperature, the concentrations of Na and K in the spent Cycle 13 scrubber water are significantly higher than those measured in the spent scrubber water from Cycles 51 through 54.

Table 3.6. Analyte Concentrations in Scrubber Water - Cycle 13 (Previous Furnace Testing; NaCl/KCl/$MgCl_2$ Simulant, 1 wt% Chloride Salt, 1000°C)

	Cycle 13 Scrubber Water	
Analyte	**Pre Cycle 13 Fresh, mg/L**	**Post Cycle 13 Spent, mg/L**
Al	<det	0.240
B	2.676	5.214
Ca	17.482	20.587
Ce	<det	<det
Cr	<det	0.803
Cu	<det	0.506
Fe	0.585	3.183
K	2.872	13.291
Mg	4.040	4.212
Mn	<det	<det
Mo	0.270	1.349
Na	5.712	14.169
Ni	<det	0.514
S	2.224	2.254
Si	6.241	5.297
Zn	<det	0.410
Chloride (ISE)	18.58	153.14
pH	7.55	2.59
Acid Derived Chloride	--	91

Table 3.7 shows a chloride mass balance performed around the scrubber water, which was based on the composition of the Cycle 13 simulant charge, the mass of scrubber water, and the data in Table 3.6. For analysis of the sources of chloride in the scrubber, it was assumed that 100% of the chloride in the $MgCl_2$ (from the simulant charge) was captured in the scrubber as HCl (i.e., $MgCl_2$ underwent pyrohydrolysis in the furnace). It was also assumed that all measured Na, K, Fe, and Cr in the scrubber water (in excess of that measured in the fresh scrubber water) entered the scrubber as chloride salt. The mass of chloride in the scrubber water measured by ISE (3.15 g) exceeded the mass of chloride that could be attributed to the sources listed in Table 3.7 (2.33 g). The only other possible source for the balance of chloride in the scrubber water (0.82 g) is HCl generated from the decomposition (pyrohydrolysis) of some of the NaCl and KCl. The sum of the chloride derived from $MgCl_2$ decomposition and the chloride derived from pyrohydrolysis of NaCl and KCl (1.64 g + 0.82 g = 2.46 g) is comparable to the acid-derived chloride value (2.13 g), which supports that most of this chloride entered the scrubber in the form of HCl. In comparing the scrubber water analysis results from Cycle 13 with those of Cycles 51 and 52, the estimated quantity of HCl generated from pyrohydrolysis of NaCl and KCl in Cycle 13 is greater than the amounts estimated in Cycles 51 and 52 (0.39 g and 0.72 g, respectively). This finding suggests that HCl generation from pyrohydrolysis of NaCl and KCl in unwashed HCP items (with nominal 20 wt% salt) processed at 750°C will be less than that of washed HCP items (nominal 1 wt% salt) processed at 1000°C.

Table 3.7. Cycle 13 Scrubber Water Chloride Balance

Source of Chloride	Chloride, g
Simulant Charge	9.02
Acid Derived Chloride in Scrubber	2.13
Total Measured in Scrubber (ISE)	3.15
Sources for Chloride in Scrubber	
Derived from $MgCl_2$ (assuming all 100% $MgCl_2$ decomposition to form HCl and MgO)	1.64
Derived from NaCl	0.31
Derived from KCl	0.22
Derived from $FeCl_3$	0.12
Derived from $CrCl_3$	0.04
Total from derived sources	2.33
Balance (Measured – Chloride derived from source)	0.82

3.3 Analysis of Filter and Filter Housing Solids

3.3.1 Filter Solids After Cycle 52

A total of 0.80 g of salt precipitate was collected on the 5-µm filter after Cycles 51 and 52. A 0.02-g sample of these solids was removed from the filter surface after Cycle 52 and dissolved and analyzed via ICP. Na and K account for 98.1% of all the cations measured (Table 3.8). A stoichiometric balance for chloride (assuming Na and K exist as chloride salt) accounts for 97.7% of the total sample mass, which suggests that NaCl and KCl are the predominant constituents in these filter solids. Consistent with the higher vapor pressure of KCl relative to NaCl, the mole ratio of K:Na was found to be 1.53:1.0.

Table 3.8. Composition of Filter Solids After Cycle 52

Analyte	Concentration, g/g
Cr	0.006
Cu	0.001
K	0.339
Na	0.130
Si	0.002
Zn	0.001
Total Cations	0.479
Stoichiometric Chloride (NaCl, KCl)	0.509

3.3.2 Material from Filter Housing After Cycle 53 and Leached Filter After Cycle 54

After Cycles 53 and 54, a green crystalline deposit was found at the bottom of the filter housing (Figure 3.2). The appearance of the deposit suggests that the material was in a molten state before system

Figure 3.2. Deposits Inside Filter Housing After Cycle 53

cooldown. The mass of the deposit (after each cycle) was estimated to be from 2 to 4 g. A 1.25-g sample was collected after Cycle 53 and leached and analyzed (Table 3.9). Na and K account for about 46% of the cations; Fe, Cr, and Ni account for another 51%. The total of the cations and chloride measured with the ISE probe accounts for 78% of the sample mass, and insoluble residues account for another 1%. Table 3.9 lists the mass of water, associated as waters of hydration, with $FeCl_2 \cdot 4H_2O$ and $NiCl_2 \cdot 6H_2O$. Adding the assumed mass of the waters of hydration to the total accounts for 98% of the sample mass. The chloride associated with HCl based on the pH of the sample is very small relative to the total chloride concentration. Before starting Cycle 54, the filter housing was cleaned. After Cycle 54, the green crystalline deposit was sampled and analyzed by XRD (Section 3.4). Most of the material was identified as iron chloride compounds. One minor phase containing K was identified, but no Na phases were found.

After Cycles 53 and 54, the filter element showed appreciable mass gain; however, solids deposits on the filter were not seen by visual inspection (Figure 3.3). The appearance of this filter differed greatly from that of loaded filters from the 1000°C testing (Figure 3.4). To locate the accumulated mass on the filter,

Table 3.9. Composition of Material from Filter Housing After Cycle 53 and Leached Filter After Cycle 54

	Material Collected from Filter Housing After Cycle 53		**Solids Leached from Filter Material After Cycle 54**	
Analyte	**Leachate Solution Concentration, mg/L**	**Solids Fraction, g/g**	**Leachate Solution Concentration, mg/L**	**Solids Fraction, g/g**
Al	3.449	0.0003	< det	<det
Bi	1.101	0.0001	<det	<det
Ca	1.650	0.0001	1.234	0.0003
Co	4.461	0.0004	3.042	0.0008
Cr	447.3	0.0356	168.2	0.0428
Cu	12.89	0.0010	7.358	0.0019
Eu	2.681	0.0002	1.257	0.0003
Fe	1605	0.1279	779.7	0.1982
K	1454	0.1159	118.1	0.0300
Mn	40.69	0.0032	13.55	0.0034
Mo	59.46	0.0047	18.62	0.0047
Na	591.3	0.0471	46.73	0.0119
Ni	192.1	0.0153	128.7	0.0327
Si	--	--	1.194	0.0003
Total Cations	4416	0.3519	--	0.3274
Chloride (ISE)	5388	0.4294	1354	0.3443
pH	2.25	--	3.14	--
Acid Derived Chloride	199.3	--	25.7	--
Insoluble Residue, g/g	--	0.0094	--	0.0102
Waters of Hydration ($FeCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$), g/g	--	0.1930	--	0.3157

Figure 3.3. Condition of 5-µm Rosedale Pleated Metal Filter Element After Cycle 54 (i.e., four test cycles)

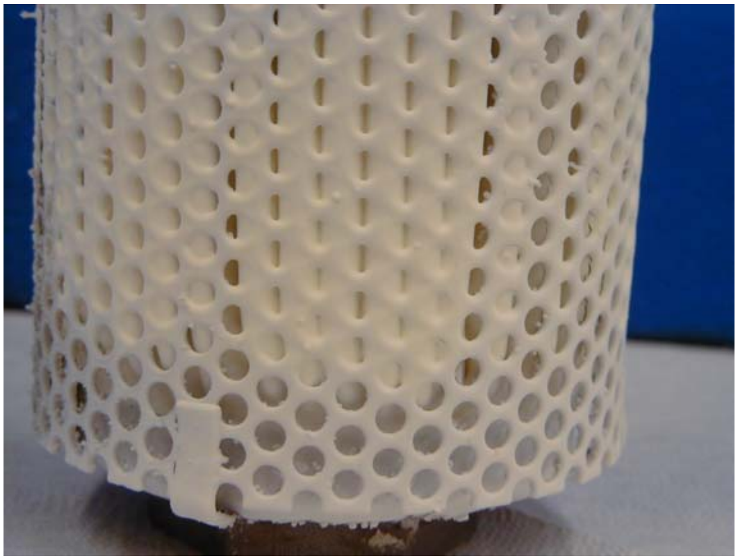

Figure 3.4. Salt Deposits on Outer Shell (pleated protector) of 20-µm Rosedale Pleated Metal Filter Cartridge After Five Test Cycles of Processing 1 wt% Chloride Salt at 1000°C (Fischer et al. 2002)

after Cycle 54, a 9-in.^{2} patch was removed from the filter and leached in water. Water leaching removed 0.4722 g of material from the 9-in.^{2} patch of the pleated stainless steel filter. The analytical results given in Table 3.9 show that Fe, Cr, and Ni account for nearly 84% of the cation analytes. Na and K account for another 13% of the cations leached from the sample. The total mass of cations and chloride measured using the ISE probe accounts for 67% of the sample weight, and the insoluble solids residue accounts for another 2%. The balance of the mass is attributed to waters of hydration associated with the leached Ni and Fe, which are presumed to be present as hydrated chloride compounds. This presumption is supported by XRD data (Section 3.1.4). The Fe and Ni present in the filter leachate most likely originated as corrosion products formed in the boat. Close inspection of the leached filter patch showed no indications of the filter media corroding.

Table 3.9 also provides the expected weight of water that would be included in the sample, based on the presence of $FeCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$. Adding this water mass to the total measured mass of individual analytes (using the ISE value for chloride) and the insoluble residue accounts for 100% of the sample mass. The pH of the leachate and the corresponding quantity of chloride that would be associated with HCl in the solution are also given in Table 3.9. It can be seen that HCl contributes very little to the chloride inventory of this sample.

3.4 Results from X-ray Diffraction (XRD) Analysis

Seven samples from Cycles 51 through 54 were submitted for phase identification analysis by XRD. The results are presented in Table 3.10. The X-ray patterns from these analyses are provided in Appendix B. In addition to phase identification, a semi-quantitative analysis on the relative abundance of the various phases is provided. The phases listed in Table 3.10 were positively identified, unless indicated otherwise. Potassium and sodium chloride binary salts were identified in many of samples, and the approximate sodium content was estimated. The only cerium phase found in the samples was CeO_2, suggesting the CeO_2 in the simulant did not react during the testing.

Samples from the crucible and boat (Tan Layer) from Cycle 52 were found to contain only CeO_2 and NaCl and KCl salts and binary salts. The various layers in the calcined simulant are shown in Figure 3.5. While this figure shows material from Cycle 51, both Cycles 51 and Cycle 52 were conducted under the same conditions, and the calcined materials appeared the same.

In addition to CeO_2, NaCl and KCl salts, and binary salts, the crucible sample from Cycle 54 contained MgO (probable) and $MgFe_2O_4$ (tentative). While no $MgCl_2$ was identified in this sample by XRD, chemical analysis of the crucible sample from Cycle 53 (Cycles 53 and 54 were duplicate runs) indicated that some $MgCl_2$ was still present in the crucible after calcination. The tentative identification of $MgFe_2O_4$ indicated that coupon and boat corrosion products migrated to the crucible.

$MgCl_2$ was tentatively identified in the Tan Layer (material in which corrosion products diffused into and discolored the simulant) from the boat after Cycle 54. In addition to the CeO_2 and NaCl and KCl salts, NiO was identified. The material collected immediately adjacent to the bottom and wall of the boat (Cycle 54, Dark Layer) contained an appreciable quantity of $MgCr_2O_4$ (15% relative abundance). The presence of this phase indicates $MgCl_2$ is interacting with the boat material (Hastelloy X). Other boat corrosion products were also observed (NiO and Cr_2O_3). Figure 3.6 shows the various layers in the calcined simulant after Cycle 53.

Table 3.10. Results from X-ray Diffraction Analyses

Sample	Phases	Relative Abundance, Weight %
Cycle 52 Crucible Sample	Cerianite, CeO_2	~80
	Sylvite, KCl	~10
	Sylvite [Solid Solution/Binary Salt, Na ~0.1]$^{(a)}$	<5
	Halite, NaCl	<5
	Halite [Solid Solution/Binary Salt, Na ~0.9]$^{(a)}$	<5
Cycle 52 Tan Layer (40% to 60% of boat contents)	Cerianite, CeO_2	~85
	Sylvite, KCl	~10
	Halite, NaCl	<5
	Halite [Solid Solution/Binary Salt, Na ~0.9]$^{(a)}$	<5
Cycle 54 Crucible Sample	Cerianite, CeO_2	~90
	Sylvite, KCl	<5
	Sylvite [Solid Solution/Binary Salt, Na ~0.1]$^{(a)}$	<5
	Halite [Solid Solution/Binary Salt, Na ~0.9]$^{(a)}$	<5
	Periclase, MgO (Probable ID)	<1
	Magnesioferrite, $MgFe_2O_4$ (Tentative ID)	<1
Cycle 54 Tan Layer (40% to 60% of boat contents)	Cerianite, CeO_2	~90
	Sylvite, KCl	<5
	Halite [Solid Solution/Binary Salt, Na ~0.9]$^{(a)}$	<5
	Bunsenite, NiO (Probable ID)	<5
	Magnesiochromite, $MgCr_2O_4$ (Tentative ID)	<1
	Chloromagnesite, $MgCl_2$ (Tentative ID)	<1
Cycle 54 Bottom Layer (5% to 10% of boat contents)	Cerianite, CeO_2	~60
	Sylvite, KCl	<10
	Halite [Solid Solution/Binary Salt, Na ~0.9]$^{(a)}$	<5
	Bunsenite, NiO	<10
	Magnesiochromite, $MgCr_2O_4$	~15
	Eskolaite, Cr_2O_3	<5
	Two weak peaks could not be identified	
Cycle 54 Scrapings from Filter Element	Sylvite, KCl	~60
	Halite, NaCl	~40
	Erythrosiderite, $K_2FeCl_5 \cdot H_2O$ (Tentative ID)	
	Rinneite, $K_3NaFeCl_6$ (Tentative ID)	
	Hydromolisite, $FeCl_3 \cdot H_2O$ (Tentative ID)	
	Bischofite, $MgCl_2(H_2O)_6$ (Tentative ID)	
	Several weak peaks could not be identified	
Material from Filter Housing, Cycle 54	$FeCl_2 \cdot 4H_2O$	~85
	Erythrosiderite, $K_2FeCl_5 \cdot H_2O$	~10
	Hydromolisite, $FeCl_3 \cdot H_2O$	~5
(a) Sodium content in binary salts is approximate.		

Figure 3.5. Crumbled Calcined Material from Cycle 51

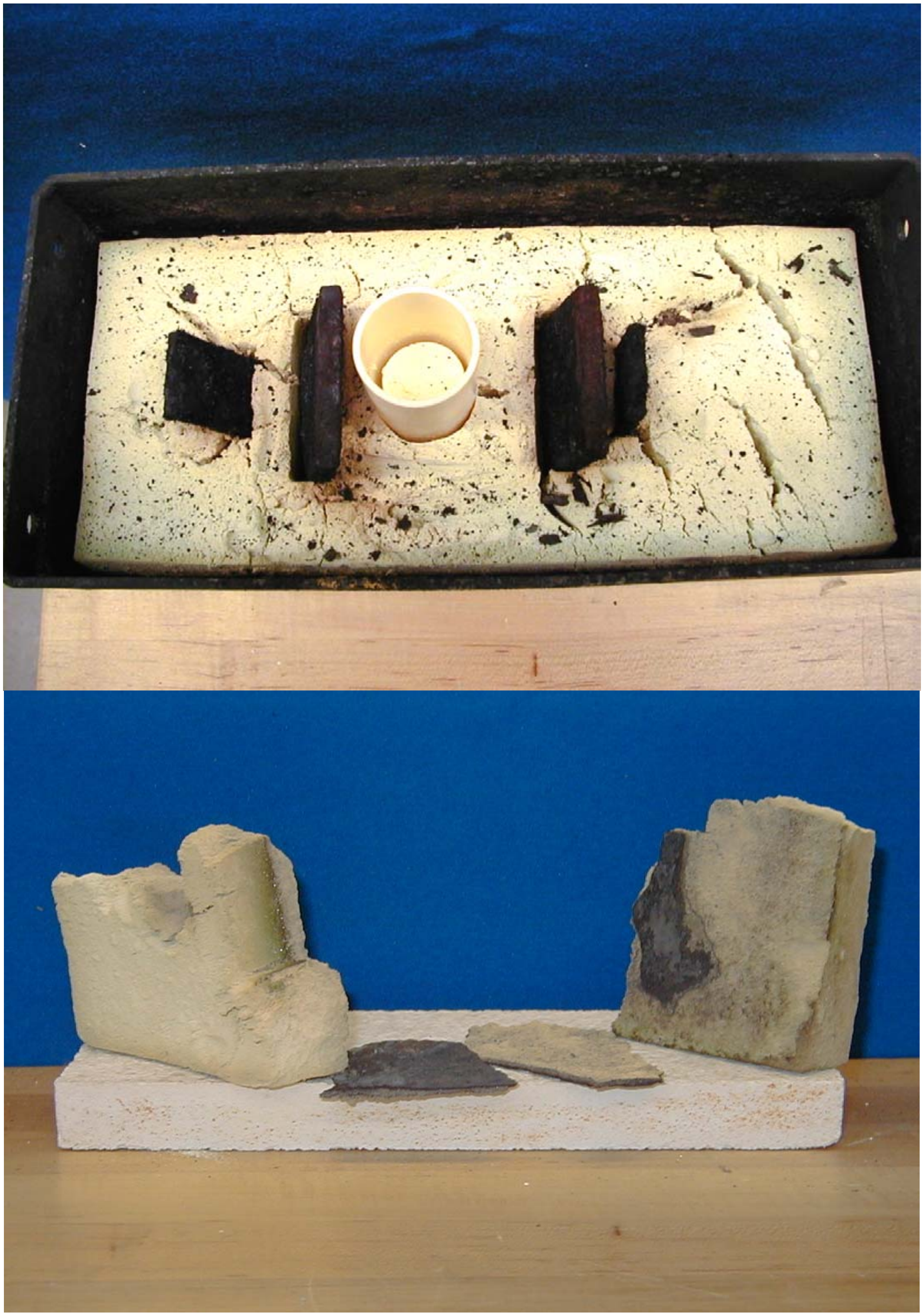

Figure 3.6. Calcined Material After Cycle 53 (Cycles 53 and 54 were run under duplicate conditions.)

The material scraped from the filter element surface after Cycle 54 was composed primarily of KCl and NaCl. These salts may have been deposited from Cycles 51 and 52, since the same filter was used for all runs. The minor phases tentatively identified in this sample are consistent with the composition of the material collected from the filter housing.

The material collected from the filter housing after Cycle 54 (a green crystalline deposit, Figure 3.2) was found to consist of various iron chloride compounds ($FeCl_2{\cdot}4H_2O$, $K_2FeCl_5{\cdot}H_2O$, and $FeCl_3{\cdot}H_2O$). After Cycle 54, the filter housing was thoroughly cleaned and inspected, and the electro-polished surface showed no evidence of corrosive attack. Based on this observation, the iron chloride compounds most likely originated within the simulant and boat.

3.5 Material Performance Testing

Material performance testing was conducted by observing the appearance and weight change of system components (boat, air baffle, offgas lines, filter element) and metal coupons. After each cycle, the boat, air baffle, and coupons were cleaned (nylon brush and water washing) and weighed.

3.5.1 System Components

Weight change data on system components are provided in Table 3.11. During Cycles 51 and 52, the loaded boat (Boat + Simulant + Coupons + Crucible) gained 6 to 7 g [see Figure 3.1, which shows the loaded boat (simulant, coupons and crucible) before and after Cycle 51]. For these tests, the weight gain associated with oxidation of the boat and coupons more than offset the weight loss resulting from chloride salt volatilization/decomposition. In Cycles 53 and 54, the loaded boat (Boat + Simulant + Coupons + Crucible) lost 38 to 42 g. Most of this weight loss can be attributed to the removal of the waters of hydration associated with the $MgCl_2{\cdot}6H_2O$ (~62 g).

Table 3.11. System Component Weight Data

System Component	Weight Change, g			
	NaCl/KCl Simulant		NaCl/KCl/$MgCl_2$ Simulant	
	Cycle 51	Cycle 52	Cycle 53	Cycle 54
Boat + Simulant + Coupons + Crucible, g	+6	+7	-42	-38
Hastelloy X Boat, g	-27	-11	-112	-85
HR-160, Air Baffle, g	0.0	+0.05	-0.42	-0.10
Internal Offgas Line, g [Corrosion products removed,[a] g]	+0.15 [0]	+0.24 [0]	+0.55 [0.44]	+0.39 [0.79]
External Offgas Line, g	0.0	+0.26	+0.24	+0.15
Filter Element, g	+0.4	+0.4	+5.98	+7.18
Waters of hydration in simulant feed, g	0	0	61.8	61.8

(a) After the internal offgas line was weighed, the line was tapped, and loose corrosion products were removed and weighed.

The mass losses to the Hastelloy X boat during Cycles 51 and 52 (27 g and 11 g, respectively) are similar to the 12 to 25 g/cycle weight losses observed in the testing conducted with 16 to 20 g chloride salt at 1000°C. However, with the addition of $MgCl_2$ in Cycles 53 and 54, the Hastelloy X boat experienced very severe corrosive attack, with weight losses to the boat of 112 g and 85 g, respectively.

Corrosion to the Haynes HR-160 air baffle, the Inconel 690 internal offgas line, the Inconel 600 external offgas line, the filter, and the filter housing was minimal during Cycles 51 through 54. After Cycles 53 and 54, small quantities of loose corrosion products were removed from the internal offgas line and weighed. Weight gains measured on the filter element were the result of particulate material that collected on the filter.

3.5.2 Metal Coupons

The performance of RA602CA and Inconel 690 (mill finish plate) was examined by placing metal coupons in the boat, half submerged in the simulant. RA602CA is the material of construction of the retort system in the PFP SPE furnaces. Inconel 690 was found to be one of the better performing materials during the testing conducted with 1 wt% chloride salt at 1000°C. Therefore, it was included in this testing to provide an indication of the relative severity of the corrosion environments. Figures 3.7 through 3.10 show the initial and corroded conditions of the metal coupons.

For Cycle 54, two additional RA602CA coupons, provided by PFP, were included in the test (Figure 3.9). These coupons, which included several welds, were heat treated at 1000°C for 3.75 hr to form a protective oxide coating before Cycle 54 was run.

The corrosion rates, expressed as mg-loss/cm^2 initial surface area, per cycle are provided in Table 3.12. During Cycles 51 and 52 (20 wt% NaCl/KCl at 750°C), the corrosion rates were similar to those measured during the tests with 1 wt% salt at 1000°C. With 16 g chloride salt per charge and a 2-hr hold at 1000°C, two Inconel 690 coupons exhibited corrosion rates of 20.8 and 26.5 mg/cm^2 per cycle (average rates from 19 cycles). During Cycles 53 and 54 (20 wt% NaCl/KCl/and $MgCl_2$ at 750°C), significantly higher corrosion rates were observed. This trend is consistent with the boat weight loss data given in Table 3.11. The presence of the $MgCl_2$, some fraction of which likely decomposes to MgO and HCl, greatly increases the severity of the corrosion. From the data in Table 3.12, it is unclear whether the heat treatment improved the corrosion resistance of coupons RA602CA-E and RA602CA-A. While the corrosion rates are lower for the heat-treated coupons, the actual surface areas of coupons RA602CA-1 and -2 were likely much greater as the result of the corrosion experienced during Cycles 51 through 53 (visually, the surfaces of RA602CA-1 and -2 were rough after Cycle 53).

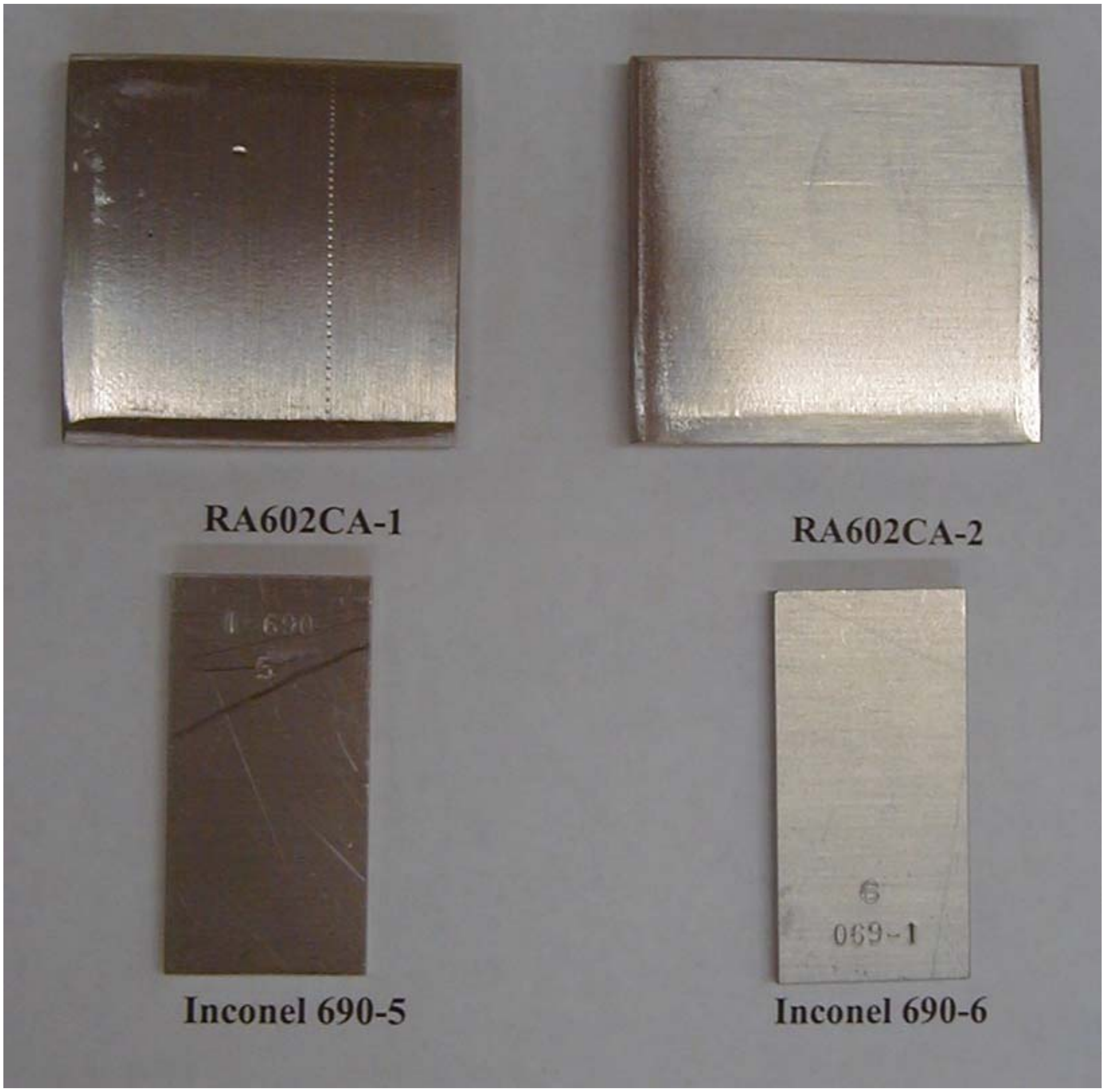

Figure 3.7. Initial Condition of RA602CA and Inconel 690 Metal Coupons

Figure 3.8. RA602CA and Inconel 690 Metal Coupons After Cycles 51 and 52. Coupons were partially submerged in simulants.

Figure 3.9. Initial Condition of Heat-Treated RA602CA Coupons

RA602CA-1

RA602CA-2

RA602CA-E

RA602CA-A

Inconel 690-5

Inconel 690-6

Figure 3.10. RA602CA and Inconel 690 Metal Coupons After Cycle 54 Coupons Were Partially Submerged in Simulant

Table 3.12. Coupon Corrosion Rates During Cycles 51 Through 54

Coupon ID	Corrosion rate, mg/cm^2 per cycle			
	NaCl/KCl Simulant		NaCl/KCl/MgCl$_2$ Simulant	
	Cycle 51	Cycle 52	Cycle 53	Cycle 54
RA602CA-1	14.0	33.7	83.8	91.5
RA602CA-2	10.0	35.3	74.8	92.3
RA602CA-E(a)	Not tested			54.5
RA602CA-A(a)	Not tested			40.9
Inconel 690-5	32.6	33.0	128	149
Inconel 690-6	38.0	42.8	126	143

(a) RA602CA-E and RA602CA-A heat treated at 1000°C for 3.75 hr before Cycle 54.

3.6 System Operability Observations

3.6.1 Furnace Temperature Profile

Temperatures were monitored during Cycles 51 through 54 in the furnace chamber (control thermocouple) and in the boat. The control thermocouple protrudes several inches through the back wall of the furnace chamber and is located about 1 in. above the floor at the middle of the back wall (Figure 2.4). The offgas exit port is approximately 2.5 in. from the control thermocouple. To monitor the simulant temperature, two thermocouples were placed in the Hastelloy X boat (11 in. long, 5 in. wide, and 2.5 in. tall), with the tips of the thermocouples submerged in the simulant. One thermocouple was placed about 2 to 3 in. from the front of the boat (end closest to the furnace door), and the second was placed near the center of the boat. A Kaowool pad was used to provide a reasonable seal between the furnace housing, boat thermocouples, and the furnace door. Furnace sweep gas enters the furnace through this Kaowool pad (i.e., front of the boat is slightly cooler than the back of the boat). For all testing, the sweep air flow rate was maintained at 1.0 SCFM.

Table 3.13 provides a summary of the offgas profiles in the furnace and boat during Cycles 51 through 54. Appendix C provides plots of the furnace and boat temperature profiles. The cross-over temperature

Table 3.13. Temperature Profile in Boat and Furnace During Cycles 51 Through 54

Cycle No.	Cross-Over Temperature, °C		Temperature When Furnace Control First at 750°C		Boat Temperature Range While Furnace at 750°C Hold			
					Front of Boat		Center of Boat	
	Front	Center	Front	Center	High	Low	High	Low
51	417	154	803	846	820	803	849	836
52	181	174	848	861	857	847	869	855
53	360	296	842	854	851	842	857	842
54	366	384	841	852	845	837	862	853

is defined as the point at which the boat temperature exceeds that of the furnace temperature (as measured by the furnace control thermocouple). As shown in Table 3.13, cross-over temperatures at the front and center of the boat are well below 750°C. When the furnace initially reaches the 750°C hold temperature, the temperature of the material in the boat is 50°C to 110°C warmer. The results in Table 3.13 and Appendix C strongly support that the temperature in the material in the boat will exceed 750°C for the entire 2-hr hold time, and that there is little incentive or justification to control the furnace at a higher temperature.

3.6.2 Operability of Furnace System Components

3.6.2.1 Furnace Elements

No degradation was observed in the physical condition or performance of the furnace elements during Cycles 51 through 54. The current and voltage profiles for all runs were essentially the same. The performance and physical condition of the furnace control thermocouple did not change during the tests.

3.6.2.2 Boat

Even though the Hastelloy X boat lost significant mass during Cycles 53 and 54 (Table 3.11), no deep pits were observed, nor was there any indication of localized corrosion attack to the welds. The boat was still in serviceable condition after Cycles 51 through 54. During the testing at 1000°C with 1 wt% chloride salt, the width of the boat would increase by 1/32 in. to 3/32 in. each cycle. During Cycles 51 through 54, conducted at 750°C, the boat width remained constant.

3.6.2.3 Removal of Calcined Material from Boat

A hammer and a screwdriver were needed to remove the calcined material from the boat after Cycles 51 and 52. The calcined material was tenaciously bound to the walls of the boat, and significant physical effort was required to thoroughly clean the boat. Figure 3.5 shows the recovered calcined material from Cycle 51.

The calcined material in Cycles 53 and 54 apparently contracted during cooldown and pulled away from the boat walls. The material was removed by inverting the boat, then dropping the boat to a hard surface from a height of several inches. A residual layer was left at the bottom of the boat that required moderate effort to remove.

Calcined material was crushed and sieved to minus 1/4 in. to prepare samples for moisture uptake testing. This size reduction was performed with moderate effort using a mortar and pestle.

3.6.2.4 Internal and External Offgas Lines

During Cycles 51 and 54, only minimal corrosion and salt deposition occurred in the offgas lines. After Cycles 53 and 54, small quantities of loose corrosion products were removed from the internal offgas line and weighed (Table 3.11). The cumulative extent of corrosion and salt deposition in the offgas lines during Cycles 51 through 54 was less than that experienced during a single cycle with 20 g of salt at 1000°C. Figure 3.11 shows the minimal salt deposits on the internal offgas line after Cycle 54 (this line was not cleaned during Cycles 51 through 54). In comparison, Figure 3.12 shows a plug that formed in the external offgas line from salt deposition after three cycles of processing 1 wt% chloride salt (20 g) at 1000°C.

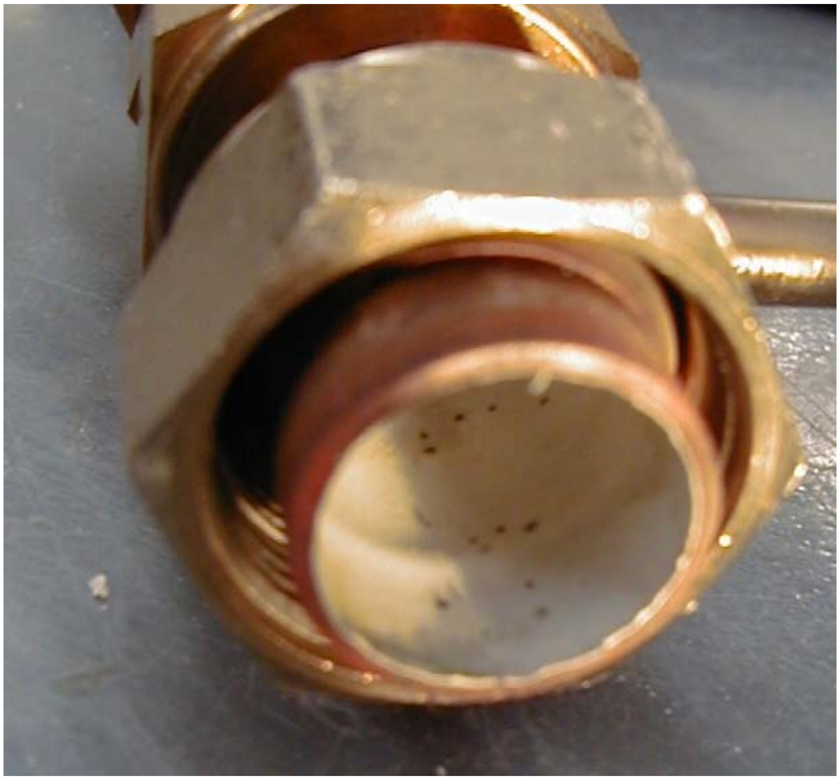

Figure 3.11. Minimal Salt Deposits on Inconel 600 Internal Offgas Line After Cycle 54

Figure 3.12. Final Bend on Inconel 600 External Offgas Line Plugged with Salt Deposits After Three Cycles of Processing 1 wt% Chloride Salt at 1000°C (Fischer et al. 2002)

3.6.2.5 Filter Element

Only a small quantity of material was collected on the 5-µm filter (~0.4 g in each cycle) during Cycles 51 and 52, resulting in very little permanent pressure drop across the filter (~0.1 in.-H_2O). The material deposited on the filter during Cycles 51 and 52 was a fine, low-density powder that from visual observation appeared identical to the material collected on filters and knockout pots in the previous testing at 1000°C.

During Cycles 53 and 54, 5.98 g and 7.18 g of material, respectively, were collected on the filter. With this material collection, the pressure drop across the filter element increased from about 0.55 to 2.9 in.-H_2O. It is estimated that three to five cycles (similar to Cycles 53 and 54) could be completed before blinding the filter element. During the testing with 1 wt% chloride salt at 1000°C, it was found that five furnace cycles could be completed before blinding the pleated stainless steel filters.

3.6.2.6 Disposition of HCl

The wet scrubber and chilled condenser effectively captured the HCl generated in the furnace. Immediately after each test, the offgas lines downstream of the scrubber were disassembled and rinsed to remove any HCl. As a result, no pitting was observed or revealed during leak testing of the offgas system.

3.7 Post-Calcination Moisture Uptake Testing

Moisture uptake testing was conducted on fresh and calcined samples from Cycles 51, 52, and 54. Also, a sample of the CeO_2 used for preparing the simulants was included in the testing. Calcined simulant from Cycles 52 and 54 were crushed and sieved to prepare size-classified samples (nominally 5 g each). [At PFP, calcined PuO_2 material is passed through a 1/4-in. screen before being loaded into convenience cans for sealing into 3013 containers.] Next, the samples were placed in a preheated oven (250°C or 500°C) for 30 min to remove moisture that may have been absorbed between the time the furnace tests were completed and when the moisture uptake testing was initiated. After heating, the samples were cooled (in a desiccator), and then placed into a controlled humidity chamber (51% relative humidity). Sample weight gain (moisture uptake) was monitored as a function of time.

The samples used for the moisture uptake testing, the initial drying temperature, and the weight loss results from the initial 30-min drying are shown in Table 3.14. All of the Cycle 51 and 52 samples (NaCl/KCl simulant) were dried at 500°C, since decomposition of the salts was expected to be negligible. The percent weight loss of the fresh and calcined simulants is only slightly greater than the percent weight loss of CeO_2, which is consistent with NaCl and KCl not forming hydrated species.

The weight loss of the Fresh Cycle 54 sample (NaCl/KCl/$MgCl_2$ simulant, with $MgCl_2{\cdot}6H_2O$ as the source of $MgCl_2$), calcined at 250°C, is 4.29 wt%. In comparison, if all waters of hydration from the $MgCl_2{\cdot}6H_2O$ were removed, the theoretical weight loss would be 4.22 wt%. In addition to the removal of waters of hydration, weight loss from the CeO_2, which comprises 71.8 wt% of the Fresh Cycle 54 sample, also contributed to the weight loss of the sample. The weight loss exhibited by the Fresh Cycle 54 sample, dried at 250°C, suggests very little, if any, of the $MgCl_2$ decomposed. This finding is consistent with Smith et al. (2000), who list the minimum temperature for $MgCl_2$ decomposition at 350°C. This finding also suggests that a low-temperature hold (e.g., at 250°C) during thermal processing could be used to drive off hydrate water without incurring pyrohydrolytic HCl formation.

Table 3.14. Sample Descriptions and Initial Drying Results

Sample	Drying Temperature, °C	Initial Weight, g	Dry Weight, g	% Weight Loss
CeO_2 (Used for simulant makeup)	500	5.0070	5.0049	0.042
NaCl/KCl Simulant Samples				
Fresh Cycle 51 (Non-calcined feed, fine powder)	500	5.0041	5.0016	0.050
Post Cycle 52 (-1/4-in. mesh)[(a)] 500°C (Collected from boat, sample was previously calcined at 750°C;	500	5.0053	5.0025	0.054
Post Cycle 52 Crucible (-16 mesh) 500°C (Collected from crucible; previously calcined at 750°C)	500	5.0026	4.999	0.054
NaCl/KCl/$MgCl_2$ Simulant Samples				
Fresh Cycle 54 (Non-calcined feed, fine powder)	250	5.0035	4.7890	4.29
Fresh Cycle 54 (Non-calcined feed, fine powder)	500	4.5871	4.3632	4.88
Post Cycle 54 (-1/4-in. mesh)[(a)] 250°C (Collected from boat, sample was previously calcined at 750°C)	250	5.0021	4.9973	0.10
Post Cycle 54 (-1/4-in. mesh)[(a)] 500°C (Collected from boat, sample was previously calcined at 750°C)	500	5.007	4.9898	0.34
Post Cycle 54 Crucible (-16 mesh) 500°C (Collected from crucible, sample was previously calcined at 750°C)	500	5.0023	4.9675	0.70

(a) Approximately 65 wt% of sample made up of particles between 1/4 in. (6.35 mm) and 16 mesh (1 mm). The remaining ~35 wt% of sample is made up of particles less than 16 mesh.

The percent weight loss of the Fresh Cycle 54 sample dried at 500°C (4.88 wt%) compared to the Fresh Cycle 54 sample dried at 250°C (4.29 wt%) suggests that a fraction of the $MgCl_2$ decomposed to MgO and HCl, the latter of which would have evolved from the sample. Smith et al. (2000) report that when $MgCl_2$ is calcined at between 350°C and 500°C in the presence of moisture, decomposition occurs according to the following reaction:

$$MgCl_2 + H_2O \rightarrow Mg(OH)Cl + HCl$$

For the Fresh Cycle 54 sample to experience a net 1 wt% weight loss due to this reaction, the sample would have to evolve 1.92 wt% of the initial sample mass as HCl (or 1.86 wt% as evolved chloride), as a result of the offsetting weight gained when the (OH) group was added to the sample. Therefore, the 0.59 wt% additional weight loss (4.88 to 4.29 wt%) that was measured when drying the sample at 500°C corresponds to an evolution of 1.10 wt% of the initial sample mass weight as chloride in HCl, which is equivalent to 40 wt% of the chloride associated with the initial $MgCl_2$.

The much lower percent weight losses of the Post Cycle 54 samples indicates that much of the $MgCl_2$ was decomposed when the material was processed in the furnace at 750°C. The relatively low weight losses could also be partially attributed to the materials being stored in closed jars. The materials may not have reached equilibrium moisture content before being dried for these tests. A comparison of the two Post Cycle 54 (-1/4 in. mesh) samples shows that the sampled dried at 500°C exhibited a weight loss about 0.24 wt% greater than the sample dried at 250°C. This observation is consistent with the behavior of the Fresh Cycle 54 samples, and indicates additional $MgCl_2$ decomposition occurred in the Post Cycle 54 (-1/4-in. mesh) sample during the drying at 500°C.

After the samples were dried and weighed, they were placed into a controlled humidity chamber (51% relative humidity), and weight gain (moisture uptake) was monitored as a function of time. Figure 3.13 shows the moisture uptake data from the CeO_2 sample and the samples from Cycles 51 and 52. Fresh Cycle 51 and Post Cycle 52 samples exhibited moisture uptake behavior that is only slightly greater than that exhibited by the CeO_2 sample. The results in Figure 3.13 also show that the particle size of the Post Cycle 52 samples had no apparent effect on the moisture uptake behavior.

Figure 3.14 shows the moisture uptake data of the Cycle 54 samples during 48 hr of testing. Figure 3.15 is an expanded view of the first 12 hr of moisture uptake testing. The lower moisture uptake of the Fresh Cycle 54 sample dried at 500°C compared with the sample dried at 250°C is consistent with the apparent loss of $MgCl_2$ during drying at the higher temperature. A similar trend occurs between the Post Cycle 54 (-1/4-in. mesh) samples dried at the two temperatures. The Post Cycle 54 Crucible sample exhibited higher initial moisture uptake than the Post Cycle 54 (-1/4 in. mesh) samples, which is attributed to the smaller average particle size of the crucible sample. However, the Post Cycle 54 sample has a slightly different composition than that of the Post Cycle 54 (-1/4-in. mesh) samples, which contain metal corrosion products (i.e., -1/4-in. mesh samples were collected from the boat); therefore, rigorous comparisons cannot be made.

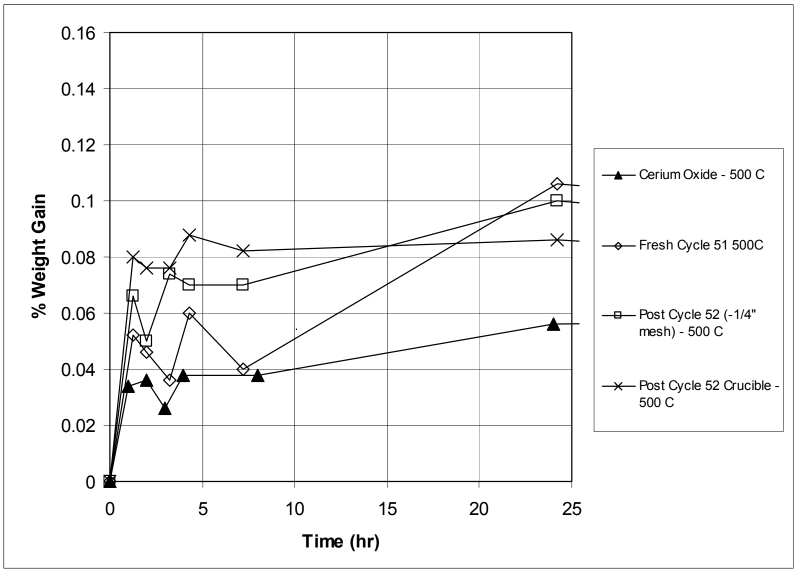

Figure 3.13. Percent Weight Gain of CeO_2 and Cycle 51 and 52 Samples (NaCl/KCl simulant). Samples were dried at 500°C for 30 min and then placed in a nominal 51% relative humidity environment.

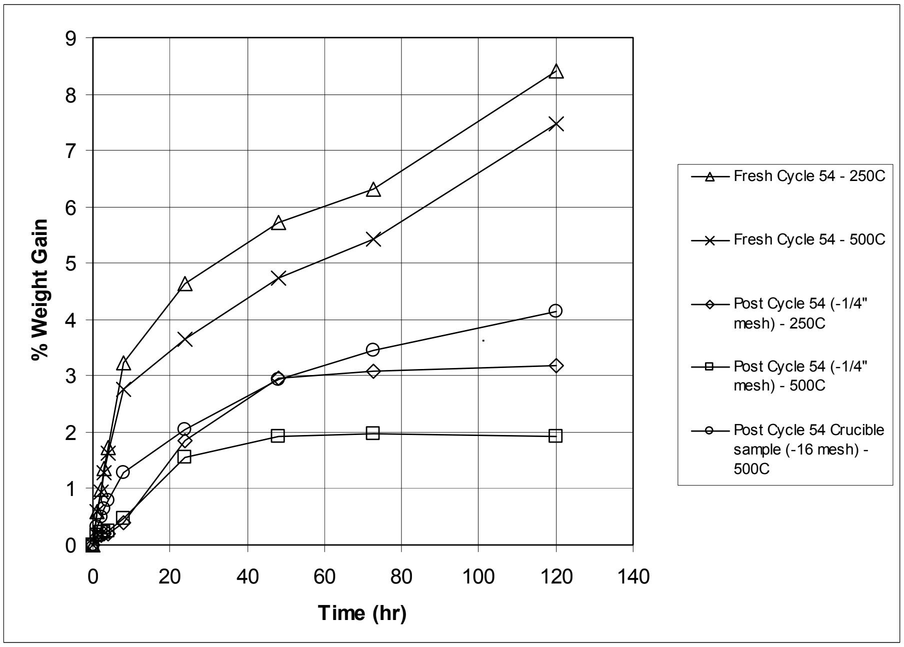

Figure 3.14. Percent Weight Gain of Cycle 54 Samples (NaCl/KCl/$MgCl_2$ simulant). Samples were dried at 250°C or 500°C and then placed in a nominal 51% relative humidity environment.

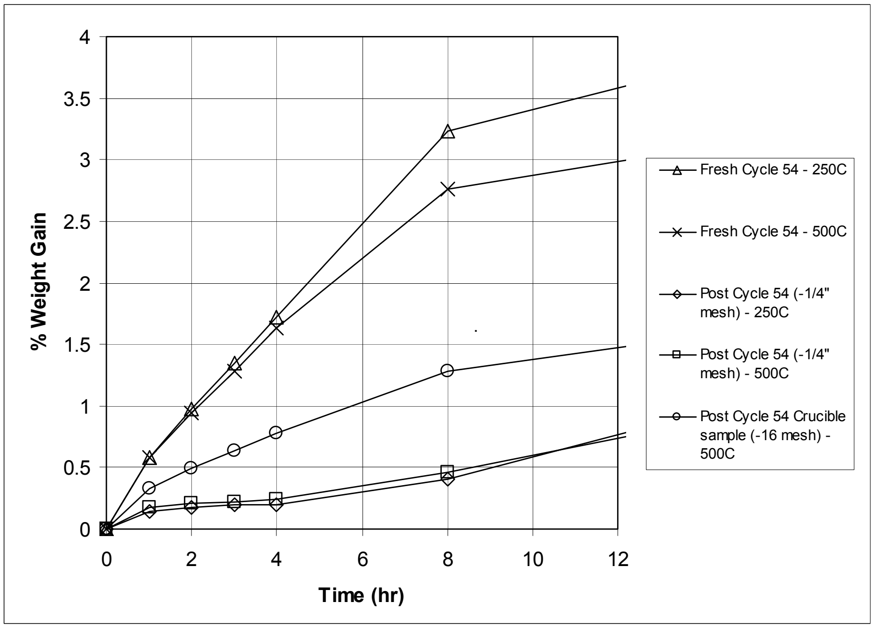

Figure 3.15. Expanded View of Percent Weight Gain of Cycle 54 Samples (NaCl/KCl/$MgCl_2$ simulant). Samples were dried at 250°C or 500°C and then placed in a nominal 51% relative humidity environment.

In summary, samples from the NaCl/KCl simulant (Cycles 51 and 52) only gained about 0.1 wt% after 24 hr in the controlled humidity chamber. Samples from the NaCl/KCl/$MgCl_2$ simulant (Cycle 54) that were crushed and screened to less than 1/4 in. (6.35 mm) exhibited a weight gain of ~0.5 wt% after 8 to 10 hr, while a sample that was screened to less than 16 mesh (1 mm) exhibited a weight gain of ~0.5 wt% after only 2 hr. These results show that meeting the 0.5 wt% moisture limit established by the DOE 3013 Standard will be challenging if HCP items are encountered that contain appreciable quantities of $MgCl_2$ and if thermal stabilization is performed at 750°C in the RMC line (relative humidity in the RMC line can reach 60%).

NOTES:

A number of factors should be considered when interpreting the results of moisture uptake testing to predict the behavior of actual HCP items (containing the same chloride salts) after thermal stabilization at 750°C. The CeO_2 used in these tests exhibited a significantly lower moisture uptake than CeO_2 used in earlier tests (PNNL Letter Report 41291-RPT02, "Evaluation of Solids Rinsing to Treat PFP High Chloride Plutonium Solids," transmitted to P. Sato, FH, by K. L. Silvers, PNNL, December 20, 2002). Comparison of the test data suggests that the CeO_2 used in the earlier tests had a very low surface area. The moisture uptake of the samples in the current tests would be 0.3% to 0.5% higher if a higher surface area CeO_2 had been used in preparing the fresh simulant.

The size of the samples used in current moisture uptake tests was nominally 5 g, while the samples used in the earlier tests were nominally 10 g. Also, all of the samples in the earlier tests were finely divided powders. The finely divided powders would promote higher initial moisture uptake rates, which would counteract, to some extent, the effect of the larger sample size.

Partial decomposition of $MgCl_2$ likely occurred when the samples in the current testing were dried at 500°C. As a result, the weight gains shown in Figure 3.14 for the Post Cycle 54 crucible and (-1/4-in. mesh) sample dried at 500°C are probably lower than would have occurred if the samples had been dried at 250°C.

Finally, the results are based on weight gains in a humidifier, where the air was stagnant and mass transfer limitations existed between the sulfuric acid solution used to control humidity and the solids (relative humidity as low as 40% for the first several hours of moisture uptake). It is anticipated that the initial moisture uptake rates would be greater in a glovebox with well-mixed humid air flow, as would be experienced in the RMC line at PFP.

4.0 References

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Smith, D. M., M. P. Neu, E. Garcia, and L. A. Morales. 2000. "Hydration of Plutonium Oxide and Process Salts, NaCl, KCl, $CaCl_2$, $MgCl_2$: Effect of Calcination on Residual Water and Rehydration." *Waste Management* 20:479-490.

Appendix A

Furnace Operation for HCP Oxide Testing with 750°C Hold Temperature

Appendix A

Furnace Operation for HCP Oxide Testing with 750°C Hold Temperature

1. Clean furnace and/or replace heating elements and any other corroded or otherwise damaged components, including the offgas system.
2. Document condition of the test apparatus by photographing the inside of the furnace and (as possible) the insides of the offgas system components. Weigh the boat, crucible, baffle, the Inconel-690 offgas internal offgas line, the Inconel 600 offgas line, and the filter element.
3. Add fresh water to the scrubber tank.
4. Mix water in scrubber tank and collect sample.
5. Collect a sample of CeO_2/Cl simulant.
6. Load ceramic crucible with simulant, and place in center of boat.
7. Load a boat with CeO_2/Cl simulant.
8. Place corrosion coupons into the boat half immersed in powder.
9. Weigh boat+coupons+crucible, and record weight on Data Sheet.
10. Position two Type K thermocouples into the CeO_2 powder in the boat (one in front, one in back), and plug thermocouples into reader/datalogger.
11. Place the loaded boat into furnace, close the door and turn on controller.
12. Start offgas blower and set offgas flow rate at 1 SCFM.
13. Heat from room temp to 500°C @ 300°C/hr
14. Heat from 500°C to 700°C @ 200°C/hr
15. Heat from 700°C to 750°C @ 125°C/hr
16. Hold temperature @ 750°C for 2 hr.
17. Turn off controller and allow to cool to below 200°C before removing boat.
18. Remove boat and set aside to cool.
19. Weigh boat+coupons+crucible and record on Data Sheet.

20. Before emptying the boat removed from the furnace, photograph the boat with simulant and the corrosion coupon set.
21. Weigh crucible+CeO_2/Cl, and record on Data Sheet. Place material in crucible in a sample vial. Label the vial with cycle number, and store the vial in archive sample storage for later analysis.
22. Empty the boat when cool enough, and collect calcined material in a jar labeled with the cycle number.
23. Clean out boat by dry brushing with nonmetallic brush to remove residue but without significantly affecting corrosion products if any.
24. Carefully dry brush the corrosion coupons with same or similar brush.
25. Photograph the empty boat (as necessary), thermocouple, and coupons.
26. Weigh the boat and coupons, and record on Data Sheet.
27. Check boat dimensions, and resize if significant bowing is observed.
28. Photograph the air baffle (if any changes in appearance noted).
29. Brush off the air baffle, reweigh, and record on Data Sheet.
30. Photograph the inside of the furnace (as necessary) when cool enough, and clean out any residue inside the furnace cavity.
31. Remove the internal offgas line from the back of the furnace when cool.
32. Weigh the internal offgas line, and record on Data Sheet.
33. Inspect the inside, and photograph if possible.
34. If significant plugging is noted, brush out the tube with a nonmetallic brush, weigh, and record data and observations.
35. Remove the external offgas line when cool.
36. Weigh the external offgas line, and record on Data Sheet.
37. Inspect the inside, and photograph if possible.
38. If significant plugging is noted, brush out the tube with a nonmetallic brush, weigh, and record data and observations.
39. Remove the filter element when cool.
40. Weigh the filter element, and record on Data Sheet.
41. Collect sample from scrubber. Label sample with cycle number.

42. Drain scrubber and collect scrubber water. Weigh scrubber water, and record on Data Sheet.
43. Wash scrubber.
44. Neutralize spent scrubber water.
45. Reassemble the furnace/offgas system to prepare for the next cycle.
46. Repeat steps 1 – 45 for next cycle.

Table A.1. Matrix of Parameters to be Measured During Testing

Parameter	Frequency[a]	Method
Furnace Temperature	Continuously	Furnace controller
Boat/Simulant Temperature	Once per 10 sec	Thermocouple readout/datalogger
Offgas Line Temperature near Furnace Exit	Once per 10 sec	Thermocouple readout/datalogger
Offgas Flow Rate	Once per hour	Visual/Manual – Data Sheet
Condition of Boat w/Coupons	Once per cycle	Photograph/written observations[b]
Condition of Cleaned Boat	Once per cycle	Photograph/written observations
Condition of Cleaned Coupons	Once per cycle	Photograph/written observations
Weight of Boat	Once per cycle	Data sheet
Weight of Coupons	Once per cycle	Data sheet
Weight of Crucible	Once per cycle	Data sheet
Condition of Furnace Interior (includes heating elements)	Once per cycle	Photograph/written observations
Heater Element Performance	Once per 10 sec	Voltage/Current – Datalogger
Condition of Offgas Line (Section exiting furnace)	Once per cycle	Photograph/written observations
Weight of Internal Offgas Line	Once per cycle	Photograph/written observations
Weight of External Offgas Line	Once per cycle	Photograph/written observations
Condition of Filter Element and Filter Holder	Once per cycle[c]	Photograph/written observations
Weights of Filter Element	Once per cycle	Data sheet
Mass of Spent Scrubber Water	Once per cycle	Data sheet
As testing progresses, the monitoring frequency of any parameter may be adjusted up or down as determined necessary by the principal investigator. Photographs, observations and other recorded data shall clearly identify the cycle number and other pertinent information. The filter element may need to be monitored more frequently (e.g., a DP cell to measure pressure drop from plugging). This will be determined from initial testing, and additional monitoring added at that time if necessary.		

Appendix B

X-ray Patterns from XRD Analysis

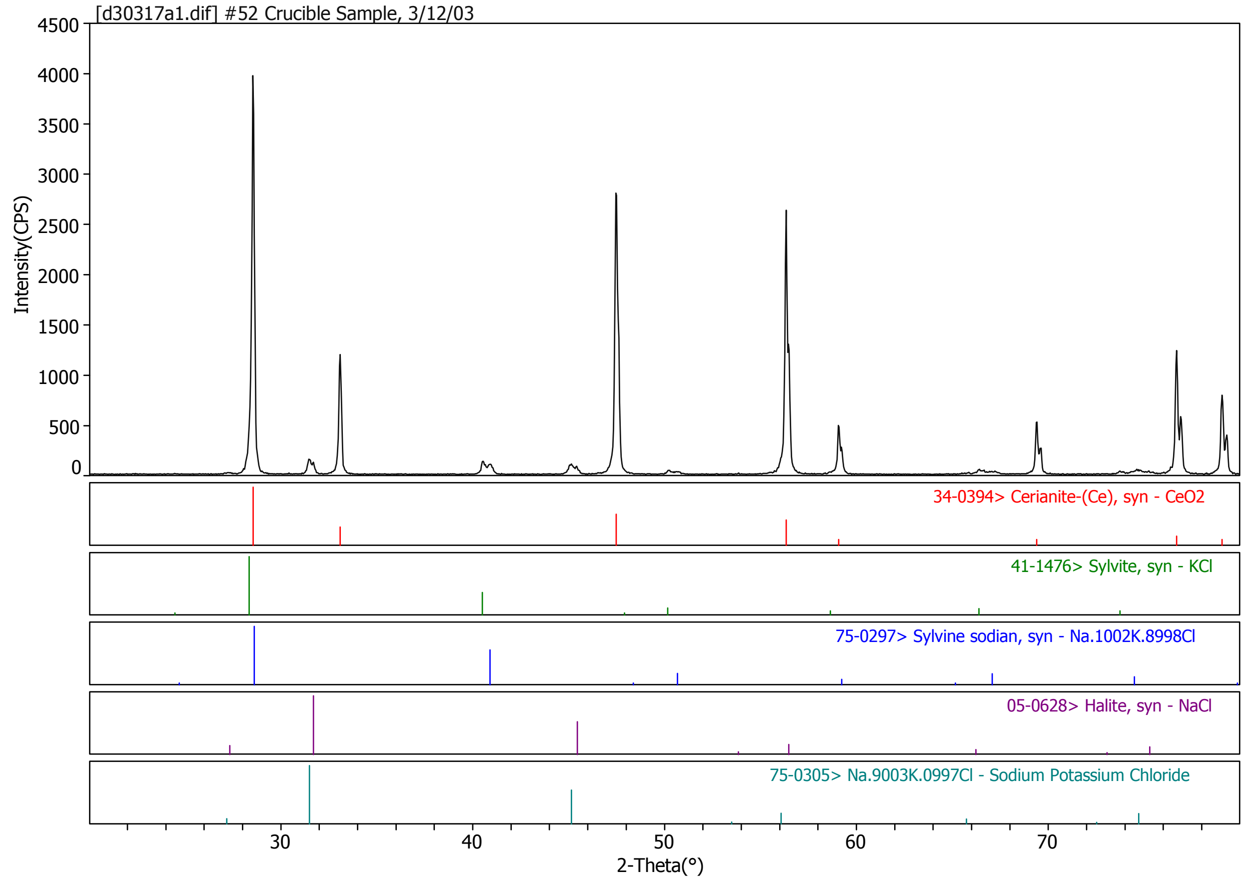

Figure B.1. Full-scale XRD Pattern for Cycle 52 Crucible Sample

Sample: #52 Crucible Sample, 3/12/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30317A

<u>Phase/Qualification/Semi Quant</u>

Cerianite, CeO_2, PDF 34-0394/Positive ID/~80 wt%
Sylvite, KCl, PDF 41-1476/Positive ID/<10 wt%
Sylvite [Solid-Solution/Binary Salt, Na ~0.1], PDF 75-0297/Positive ID/<5 wt%
Halite, NaCl, PDF 05-0628/Positive ID/<5 wt%
Halite [Solid-Solution/Binary Salt, Na ~0.9], PDF 75-0305/Positive ID/<5 wt%

<u>Notes</u>

[1] Sodium content in binary salt was <u>approximate</u>.

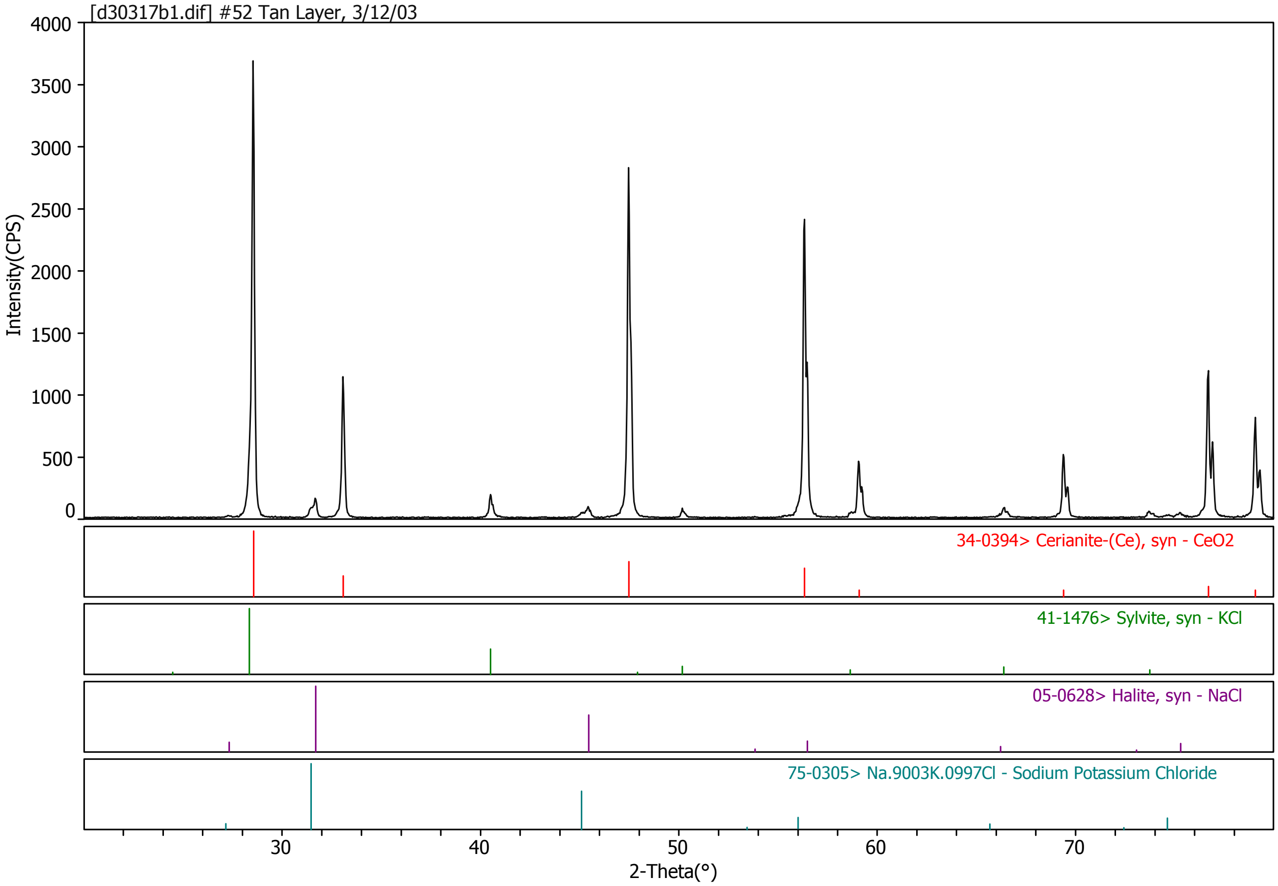

Figure B.2. Full-scale XRD Pattern for Cycle 52 Tan Layer Sample

Sample: #52 Tan Layer, 3/12/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30317B

<u>Phase/Qualification/Semi Quant</u>
Cerianite, CeO_2, PDF 34-0394/Positive ID/~85 wt%
Sylvite, KCl, PDF 41-1476/Positive ID/~10 wt%
Halite, NaCl, PDF 05-0628/Positive ID/<5 wt%
Halite [Solid-Solution/Binary Salt, Na ~0.9], PDF 75-0305/Positive ID/<5 wt%

<u>Notes</u>
[1] Sodium content in binary salt was <u>approximate</u>.

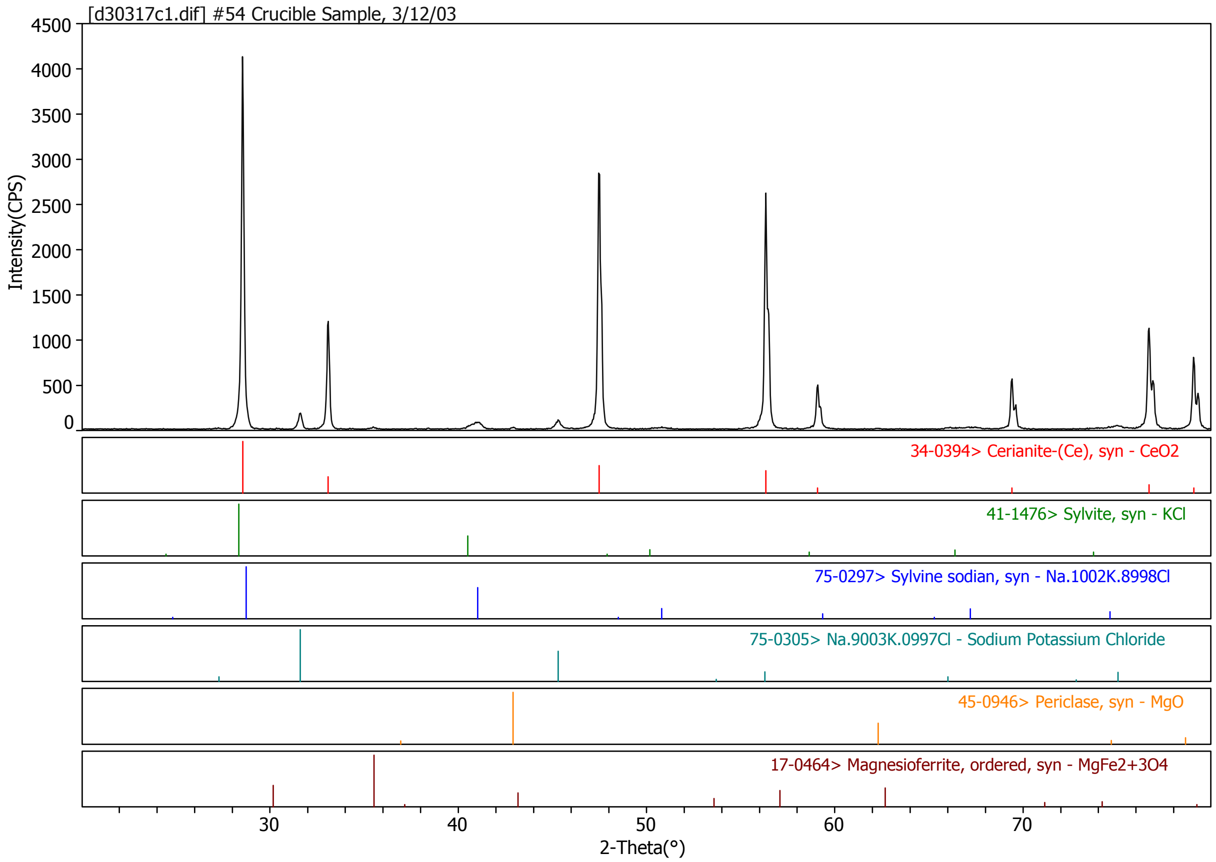

Figure B.3. Full-scale XRD Pattern for Cycle 54 Crucible Sample

Sample: #54 Crucible Sample, 3/12/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30317C

Phase/Qualification/Semi Quant

Cerianite, CeO_2, PDF 34-0394/Positive ID/~90 wt%
Sylvite, KCl, PDF 41-1476/Positive ID/<5 wt%
Sylvite [Solid-Solution/Binary Salt, Na ~0.1], PDF 75-0297/Positive ID/<5 wt%
Halite [Solid-Solution/Binary Salt, Na ~0.9], PDF 75-0305/Positive ID/<5 wt%
Periclase, MgO, PDF 45-0946/Probable ID/<1 wt%
Magnesioferrite*, $MgFe_2O_4$, PDF 17-0464/Tentative ID/<1 wt%

Notes

[1] Sodium content in binary salt was approximate.
[2] Presence of Magnesioferrite* (spinel-type) was indicated by only one peak:
(311)/100% @ ~35.5° 2Theta.
[3] Another spinel-type (and/or another phase/structure) may have accounted for this peak.

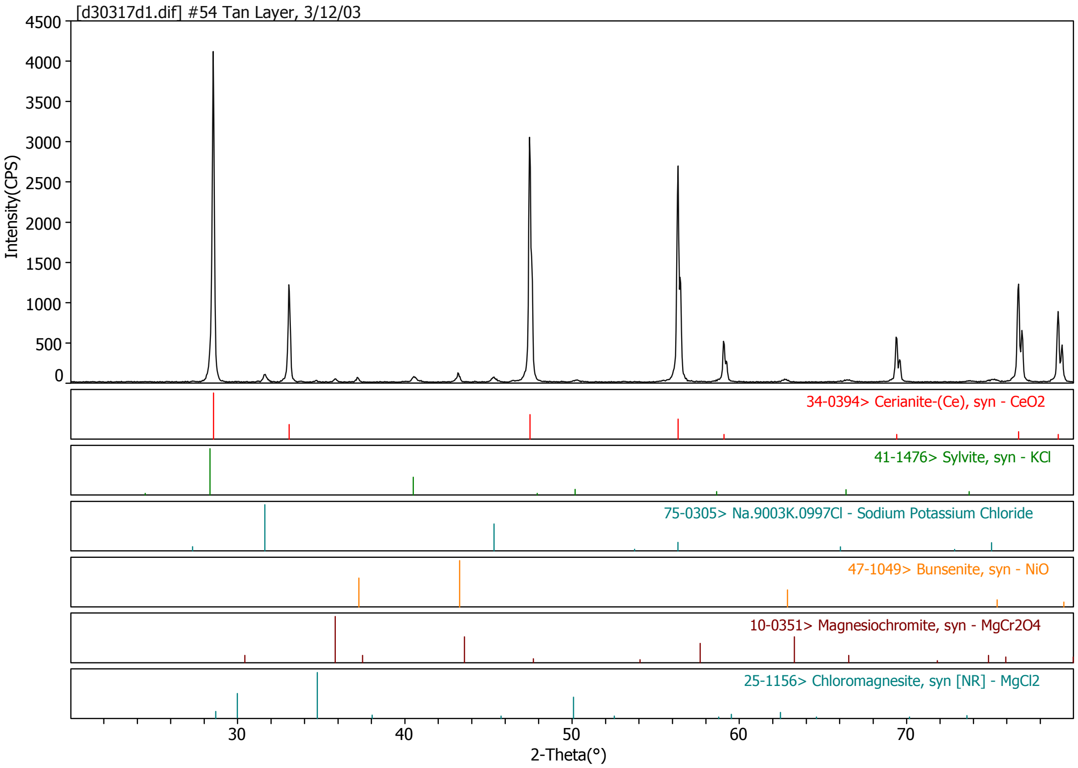

Figure B.4. Full-scale XRD Pattern for Cycle 54 Tan Layer Sample

Sample: #54 Tan Layer, 3/12/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30317D

<u>Phase/Qualification/Semi Quant</u>
Cerianite, CeO_2, PDF 34-0394/Positive ID/~90 wt%
Sylvite, KCl, PDF 41-1476/Positive ID/<5 wt%
Halite [Solid-Solution/Binary Salt, Na ~0.9], PDF 75-0305/Positive ID/<5 wt%
Bunsenite, NiO, PDF 47-1049/Probable ID/<5 wt%
Magnesiochromite*, $MgCr_2O_4$, PDF 10-0351/Tentative ID/<1 wt%
Chloromagnesite**, $MgCl_2$, PDF 25-1156/Tentative ID/<1 wt%

<u>Notes</u>
[1] Sodium content in binary salt was <u>approximate</u>.
[2] Presence of Magnesiochromite* (spinel-type) was indicated by only one peak: (311)/100% @ ~35.8° 2Theta.
[3] Another spinel-type* (and/or another phase/structure) may have accounted for this peak.
[4] Presence of Chloromagnesite** was indicated by only one peak: (104)/100% @ ~34.5° 2Theta.
[5] Another phase/structure** may have accounted for this peak.

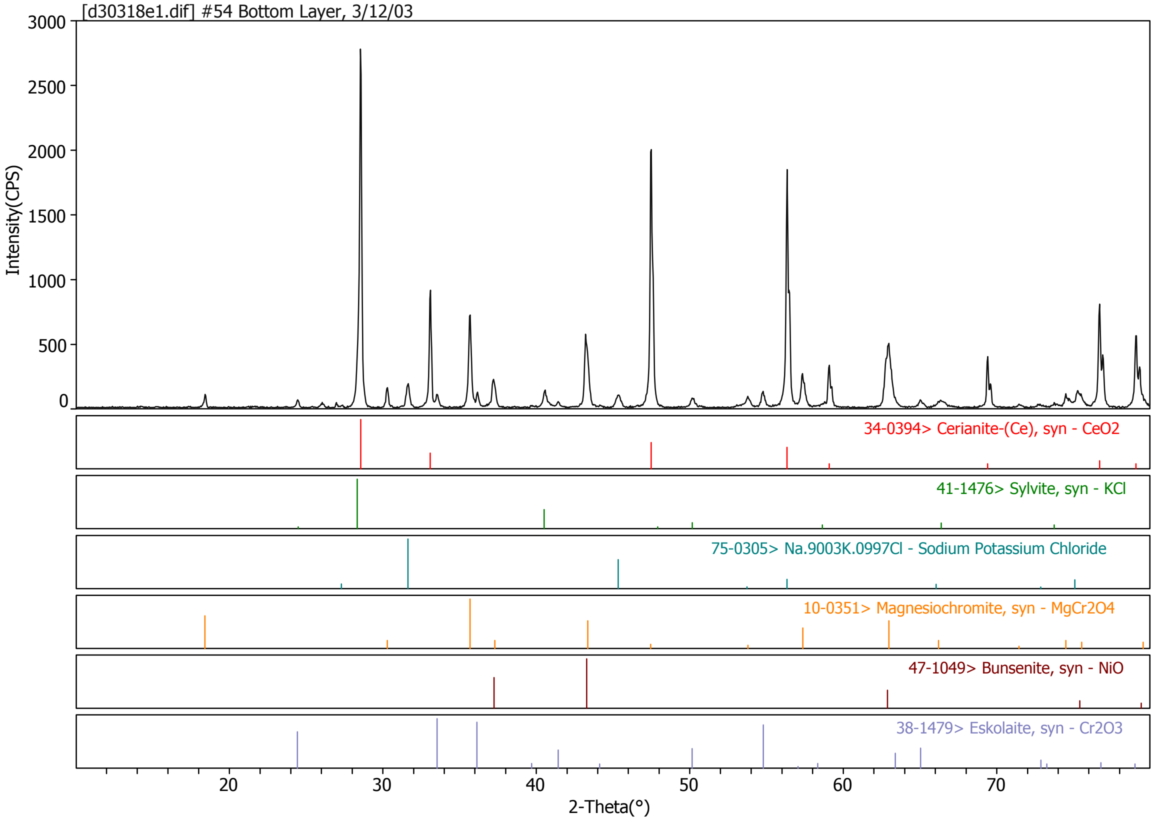

Figure B.5. Full-scale XRD Pattern for Cycle 54 Bottom Layer Sample (Unidentified Peaks Not Illustrated)

Sample: #54 Bottom Layer, 3/12/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30318E

<u>Phase/Qualification/Semi Quant</u>
Cerianite, CeO2, PDF 34-0394/Positive ID/~60 wt%
Sylvite, KCl, PDF 41-1476/Positive ID/<10 wt%
Halite [Solid-Solution/Binary Salt, Na ~0.9], PDF 75-0305/Positive ID/<5 wt%
Bunsenite, NiO, PDF 47-1049/Positive ID/<10 wt%
Magnesiochromite*, MgCr2O4, PDF 10-0351/Positive ID/~15 wt%
Eskolaite, Cr2O3, PDF 38-1479/Positive ID/<5 wt%

<u>Notes</u>
[1] Sodium content in binary salt was <u>approximate</u>.
[2] Solid solution possible in the case of Magnesiochromite* (a spinel was definitely present; "Positive ID" refers to structure match).
[3] Two weak peaks could not be identified. These were ignored in the semi quant calculations.

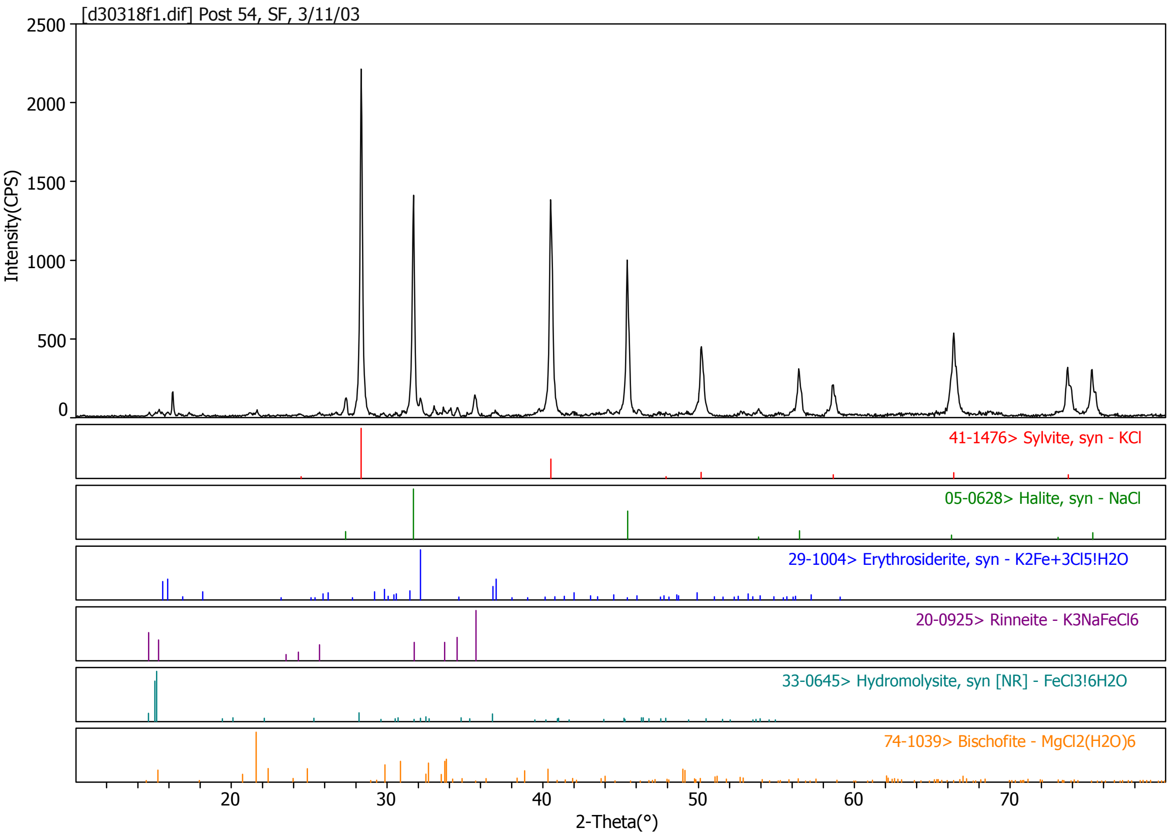

Figure B.6. Full-scale XRD Pattern for Cycle 54 Scrapings from Filter Element

Sample: Post 54, SF, 3/11/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30318F
Comments: "SF" above = Scrapings from Filter

<u>Phase/Qualification/Semi Quant</u>
Sylvite, KCl, PDF 41-1476/Positive ID/~60 wt%
Halite, NaCl, PDF 05-0628/Positive ID/~40 wt%
Erythrosiderite, K2FeCl5 **.** H2O, PDF 29-1004/Tentative ID
Rinneite, K3NaFeCl6/Tentative ID
Hydromolisite, FeCl3 **.** 6H2O, PDF 33-0645/Tentative ID
Bischofite, MgCl2(H2O)6, PDF 74-1039/Tentative ID

<u>Notes</u>
[1] Minor phases ignored in semi quant calculations.
[2] Several weak peaks could not be identified ("Residual Pattern")

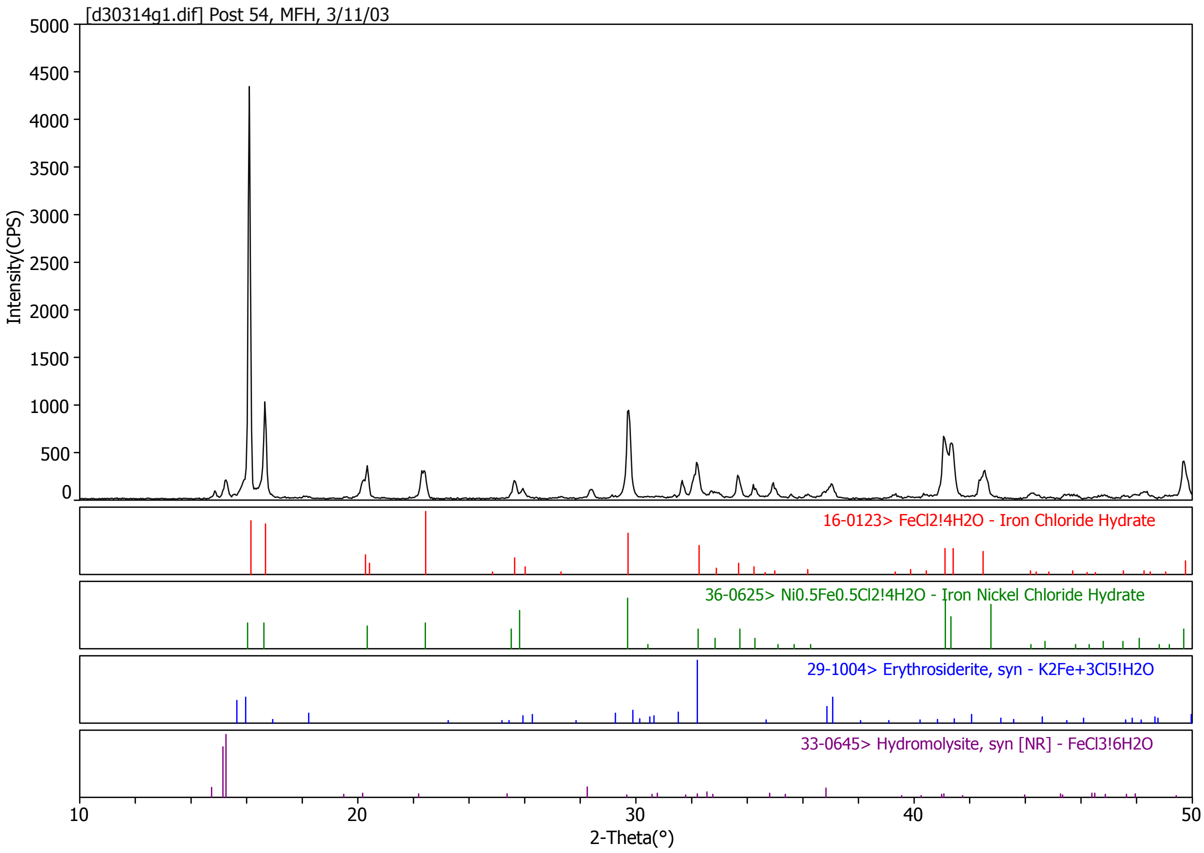

Figure B.7. Full-scale XRD Pattern for Cycle 54, Material from Filter Housing (Plus PDF 36-0625)

Sample: Post 54, MFH, 3/11/03
Scan: 2Theta-Omega, 2.00°-80.00° @ 0.04°/2s
File: D30314G
Comments: "MFH" above = Material from Filter Housing

Phase/Qualification/Semi Quant
FeCl2 **.** 4H2O, PDF 16-0123/Positive ID/~85 wt%
Erythrosiderite, K2FeCl5 **.** H2O, PDF 29-1004/Positive ID/~10 wt%
Hydromolisite, FeCl3 **.** 6H2O, PDF 33-0645/Positive ID/~5 wt%

Notes
[1] As shown, the major phase exhibited <001> preferred orientation.
[2] Also, as indicated by the similarity to PDF 36-0625, a solid solution with Cr was possible.
[3] Solid solutions possible.

Appendix C

Furnace and Boat Temperature Profiles

Thermocouple placement for Figures C.1 through C.4

The tips of thermocouples TC-100 and TC-105 were submerged in the simulant in the boat.
TC-100 was placed 2 to 3 in. from the front of the boat.
TC-105 was placed in the center of the boat.
"Furnace" = furnace control thermocouple, which was located on the back wall of the furnace.

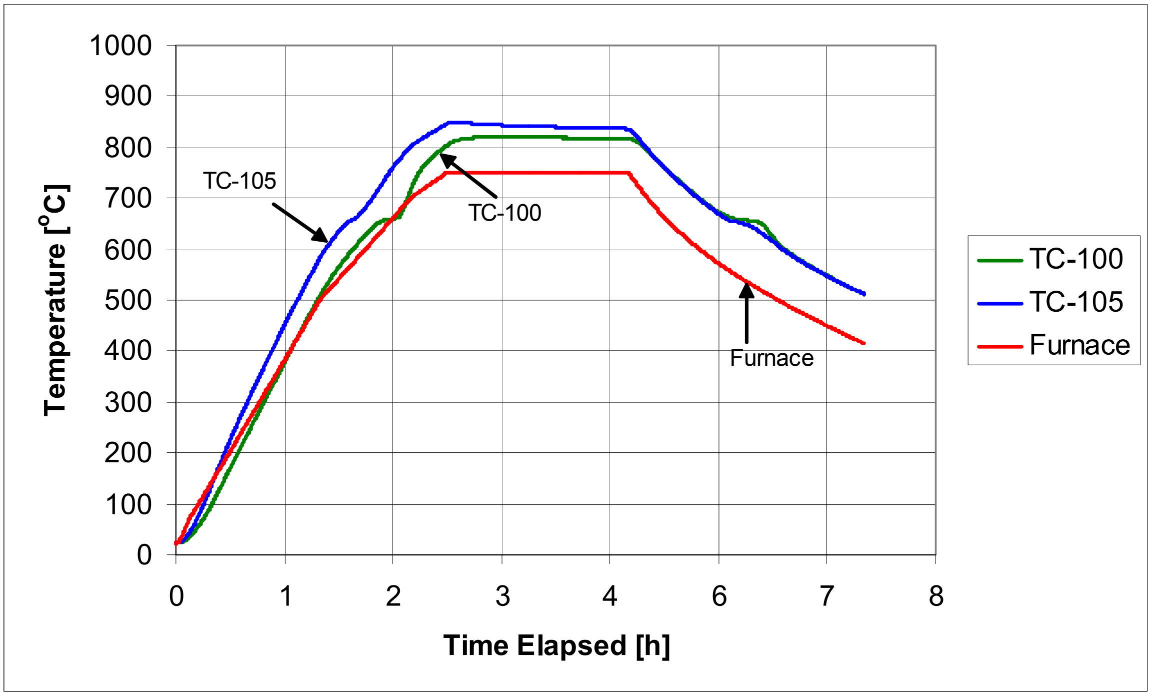

Figure C.1. Temperature Profile in Furnace and Boat During Cycle 51

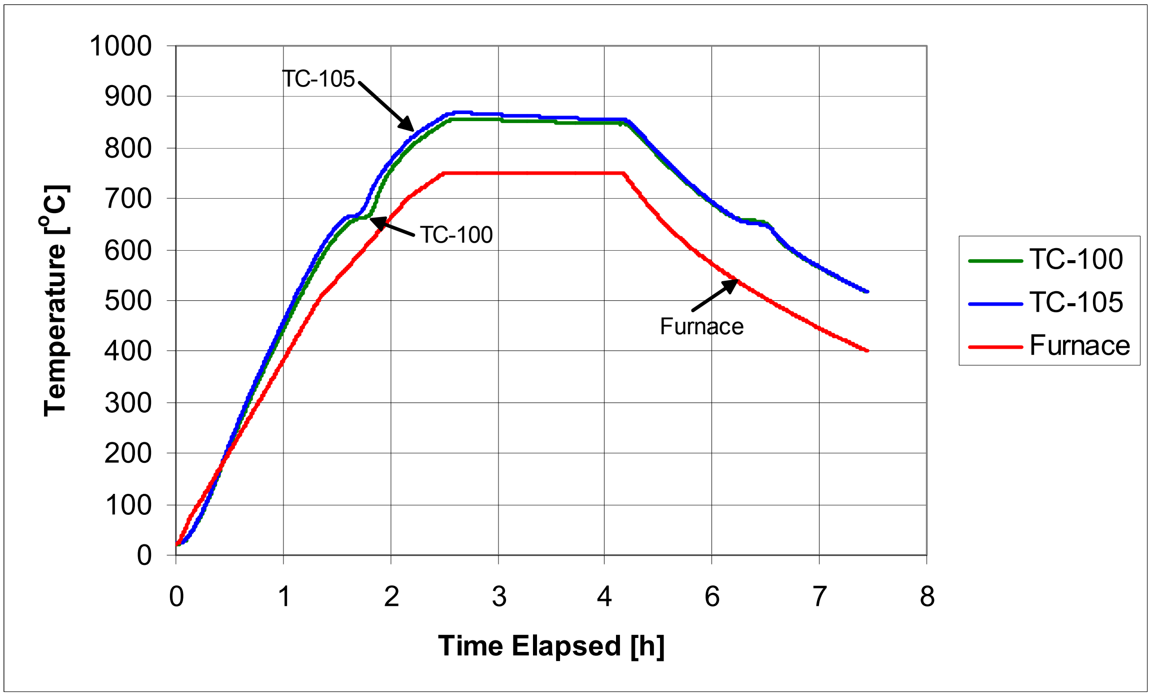

Figure C.2. Temperature Profile in Furnace and Boat During Cycle 52

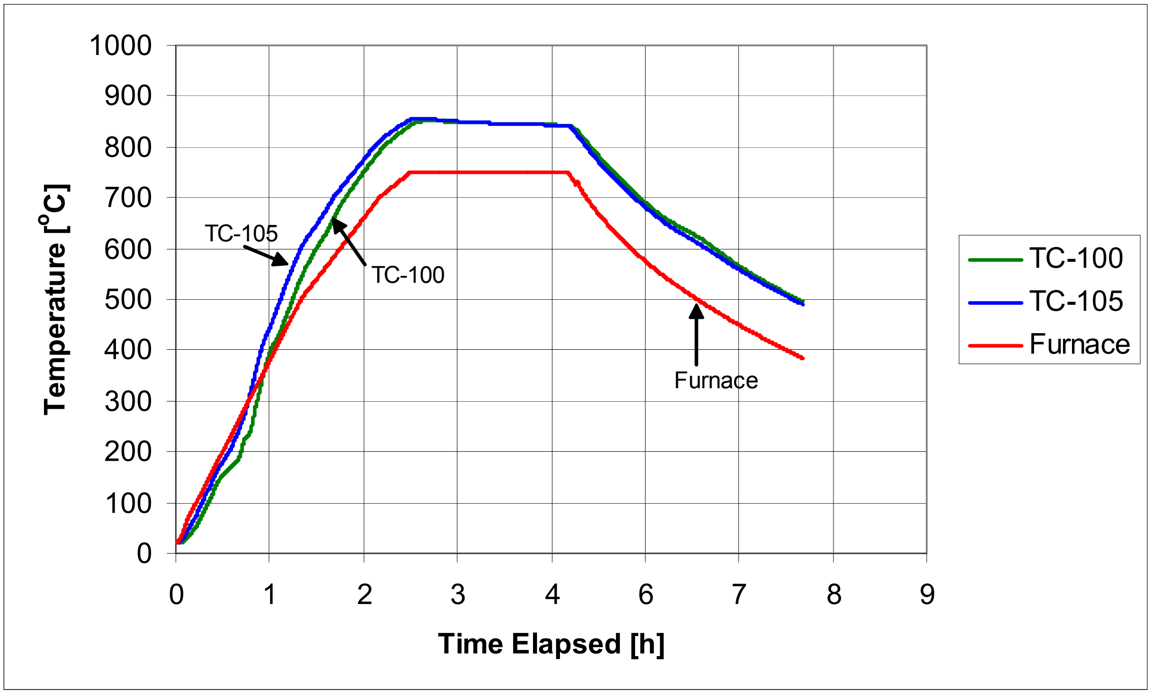

Figure C.3. Temperature Profile in Furnace and Boat During Cycle 53

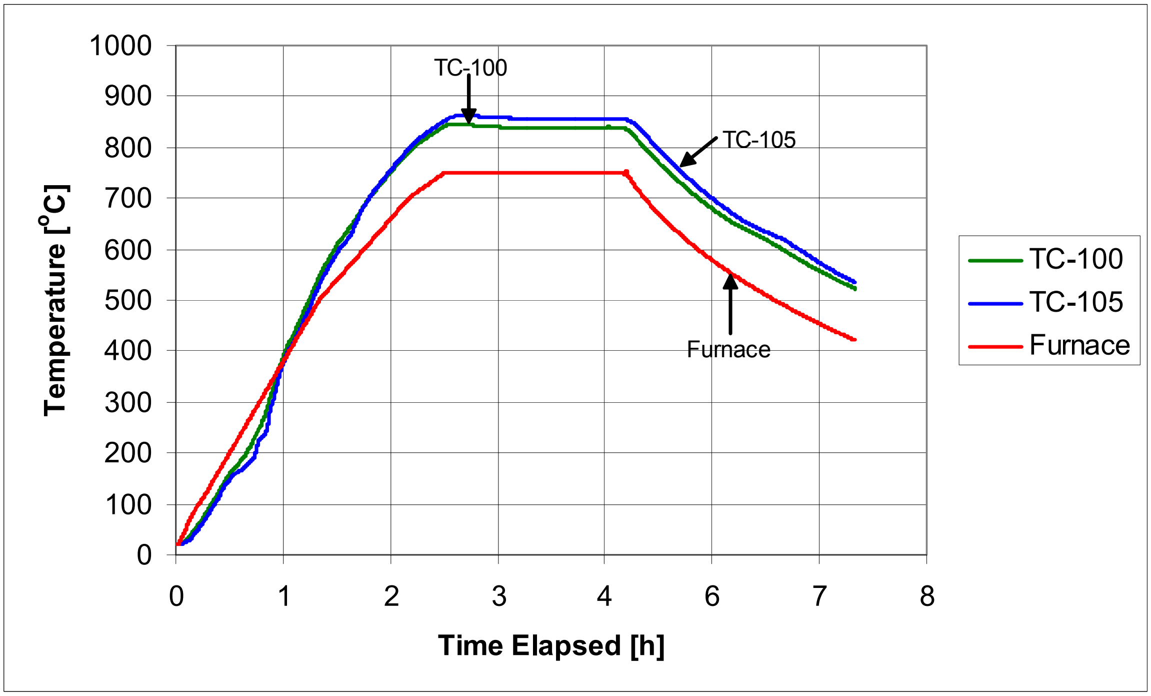

Figure C.4. Temperature Profile in Furnace and Boat During Cycle 54