Evaluation of the Generation-2 Dechlorination Apparatus for Treating Salt Wastes

Nuclear Technology Research and Development

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign

B.J. Riley and S. Chong
Pacific Northwest National Laboratory

July 21, 2021

PNNL-31646

SUMMARY

This document satisfies the requirements for two milestones (i.e., M2FT-21PN030103021 and M3FT-21PN030103026), which are described in detail below. Also, details for the work package at the Pacific Northwest National Laboratory (PNNL) are provided below. The goal of these milestones was to demonstrate the generation-2 dechlorination apparatus (G2DA) for removing Cl from chloride-based electrochemical salt simulants. The two salts chosen for this initial study were KCl to simulate a component from the eutectic salt (LiCl is harder to detect with analytical instruments) and CsCl to simulate a fission product chloride in these types of waste streams. The overall scope of this work included receiving, installing, and testing the G2DA. This new system was designed to address several shortcomings identified with the generation-1 apparatus (G1DA), which are described in detail within this document. The studies presented in this report show that the G2DA worked as intended and will help provide scaled-up batches for additional testing at Argonne National Laboratory.

Table S1. Summary of the milestones fulfilled by the work presented herein. Note that "NTD" and "FM" denote National Technical Director and Federal Manager, respectively.

Milestone#	Title	Due date	Milestone description	Criteria for completion
M3FT-21PN030103026	(Pre-M2) Demonstrate gen-2 dechlorination apparatus	07/30/21	This is a 1-month pre-check on the M2 milestone "Demonstrate gen-2 dechlorination apparatus."	An email will be sent to the NTD and FM with an update on the M2 milestone "Demonstrate gen-2 dechlorination apparatus"
M2FT-21PN030103021	Demonstrate gen-2 dechlorination apparatus	08/31/21	Demonstrate dechlorination apparatus for echem chloride salt. This will include a detailed description of the generation-2 apparatus along with testing data and results from the operation of the system with different salt simulants.	A memo or report will be sent to the NTD and FM summarizing these efforts.

Work package information:

- **Work Package Title**: Waste Forms - PNNL
- **Parent Work Breakdown Structure#**: 1.02.03.01.03
- **Work Package#**: FT-21PN03010302, Rev 1

CONTENTS

FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

ADP	ammonium dihydrogen phosphate ($NH_4H_2PO_4$)
FM	Federal Manager
G1DA	generation-1 dechlorination apparatus
G2DA	generation-2 dechlorination apparatus
in.	inches
l	liquid
NM	not measured
NTD	National Technical Director
OT	overtemperature (controller)
PNNL	Pacific Northwest National Laboratory
s	solid
SP	setpoint (controller)
TC	thermocouple
v	volatilized
XRD	X-ray diffraction
z#	(furnace) zone number

1. INTRODUCTION

The goal of this milestone was to demonstrate the generation-2 dechlorination apparatus (G2DA) for removing Cl from chloride-based salt wastes. For the demonstrations, KCl (Run-1) and CsCl (Run-2) were chosen as the simplified simulants. The specific tasks included receiving, installing, and testing the new dechlorination apparatus. This new system was designed to address several shortcomings identified with the generation-1 dechlorination apparatus (G1DA), which are described within Table 1 in more detail along with how those shortcomings were updated and fixed in the G2DA design. These types of salts are relevant to chloride salt wastes generated from electrochemical reprocessing and molten salt reactors.

Table 1. Summary of changes between G1DA and G2DA and how those changes were implemented for the redesign.

Attribute	Generation-1 dechlorination apparatus (G1DA)	Generation-2 dechlorination apparatus (G2DA)
Furnace size	A bigger furnace was needed to accommodate a larger crucible size and, therefore, a larger sample volume than the 100-mL crucibles used in the G1DA.	The G2DA furnace can easily accommodate 250-mL crucibles or perhaps even larger if custom-sized (diameter vs height) crucibles can be acquired.
Off-gas system design and NH_4Cl recovery	A larger-diameter off-gas port above the main furnace chamber (~32-mm) was needed. The snorkel system on top of the G1DA was made of fused quartz with an inner diameter of 28-mm. In nearly every experiment run in this system, plugging of the snorkel was observed resulting in incomplete NH_4Cl recovery. The glassware in the G1DA did not have tapered joints and often leaked at the seams, so a tighter-fitting system was also desired to help prevent NH_4Cl vapors from leaking into the furnace. An easier method for harvesting the NH_4Cl condensate was also needed. Smaller glassware sections were desired for better access to the inner surfaces of the off-gas lines for NH_4Cl recovery where they could be fit together using tight-fitting tapered joints.	The G2DA is comprised of four separate pieces of fused quartz with tapered joints that have a minimum inner diameter of 38 mm (at tapered ends). This should help prevent plugging from the NH_4Cl condensate but also make NH_4Cl recovery much easier. Also, all of the glassware pieces have tapered quartz joints to help prevent leaking of NH_4Cl into the furnace, which can damage the heating elements.
Temperature control	A better temperature control system for the off-gas lines before the condensers was needed. The heating pad and heating tape in the G1DA did not fully cover the glassware, leaving room for cooler regions where the NH_4Cl condensed. Also, the condensation region for the NH_4Cl was very narrow, so more control of the temperature gradient was desired to further span this region across a larger length to help prevent clogging of the off-gas lines and allow for higher NH_4Cl recoveries. Additionally, the temperature of the insulated region between the top of the furnace hot zone (inside the furnace) and the top of the furnace (outside the furnace) could not be controlled.	Where the G1DA off-gas lines were heated with heating pads and heating tape, the G2DA furnace is all inclusive within 5 separately heated hot zones. This drastic increase in temperature control should be much more effective at spreading out the region where the NH_4Cl condenses within the off-gas glassware system with less abrupt temperature fluctuations due to the furnace insulation (unheatable zone) that was present above the G1DA furnace.
Joints to condensers	More effective sealed joints were needed between the furnace glassware and the condensers to prevent leaking of NH_4Cl into the furnace or liquids out of the lines leading to the condensers.	All of the fittings between the furnace glassware and the condensers are tapered ground glass joints (i.e., 24/40 or 50/50).
Condenser system	A better condenser system was needed to capture off-gas vapors. The Friedrichs condensers are not the most efficient type of condenser for this type of application. Additionally, it is very difficult to clean solid condensates off the inner surfaces of these condensers.	The new system was designed with a dual Allihn condenser setup. These condensers are taller and have narrower diameters with more accessible inner surfaces for cleaning. This should allow for more contact area between the condensers and hot gases coming through the system (e.g., H_2O, HCl, NH_3). They are also much easier to clean than Friedrichs condensers.

The G2DA design schematic is presented in Figure 1 at a high level. This schematic shows the different components of the system, how these components are arranged, and an example of a 250-mL alumina crucible. Since the snorkel glassware sits on top of the crucible, the extension piece (Figure 1b) was designed to be longer at the portion that is inserted into the furnace to accommodate crucibles of different heights depending on the application. Wider crucibles could also be implemented if needed, but this could require a different piece of glassware (see Figure 1c3) to fully cover the crucible and help prevent NH_4Cl vapors from leaking into the furnace between the joint of the crucible and glassware. Other views of the G2DA at different orientations and showing other components are provided in Figure 2 and Figure 3. The water cooling was set up in series to cool the right condenser before the left one, where both are filled from the bottom ports and exit on the top ports, with a setpoint temperature of 10°C.

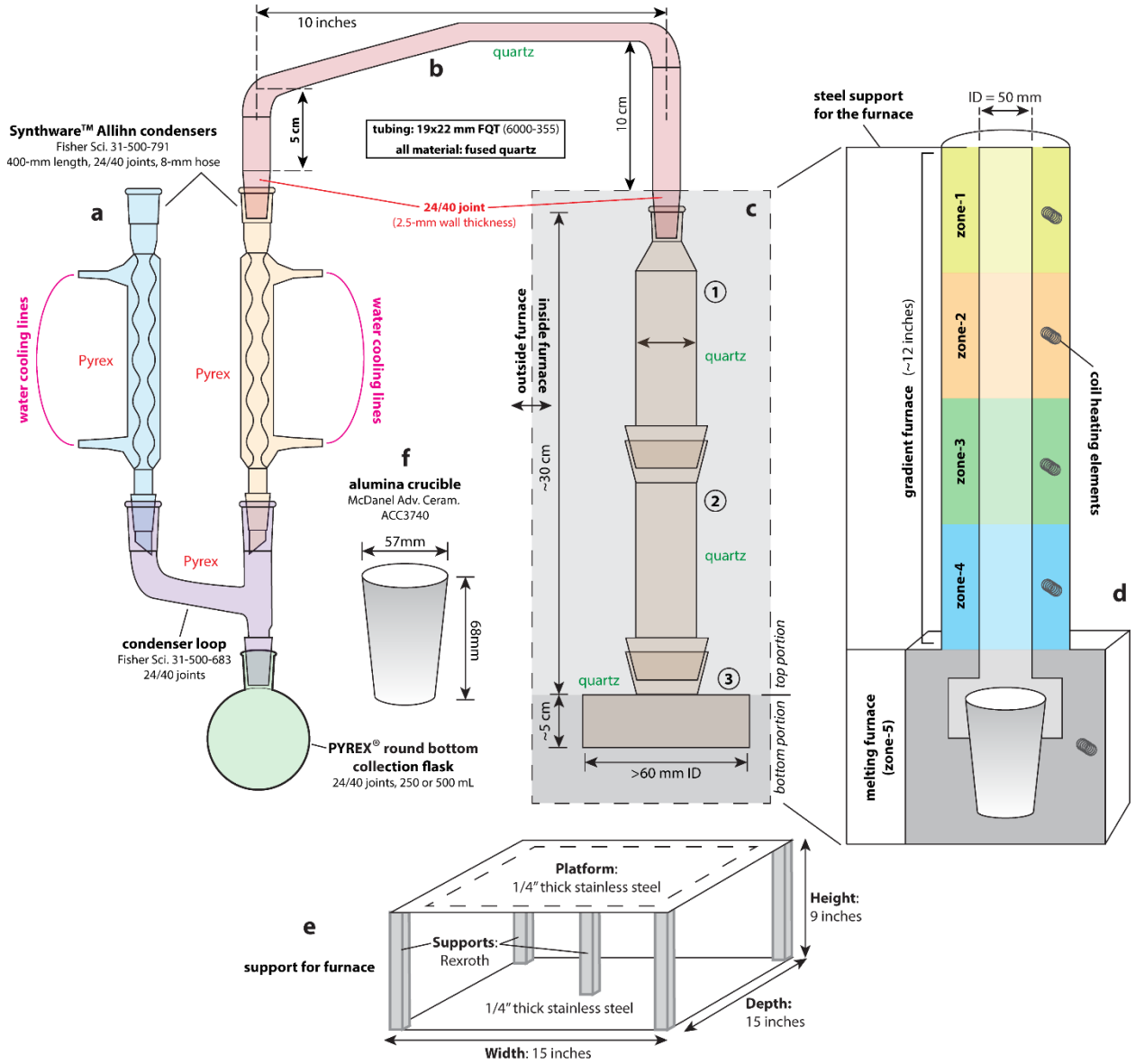

Figure 1. Schematic of the generation-2 dechlorination apparatus showing (a) the dual Allihn condenser system, (b) the jumper piece between the condensers and the furnace glassware, (c) the furnace, (d) a more detailed view of the furnace, (e) the support for the furnace, and (f) the 250-mL alumina crucible for holding the reactants. The drawings are not to scale.

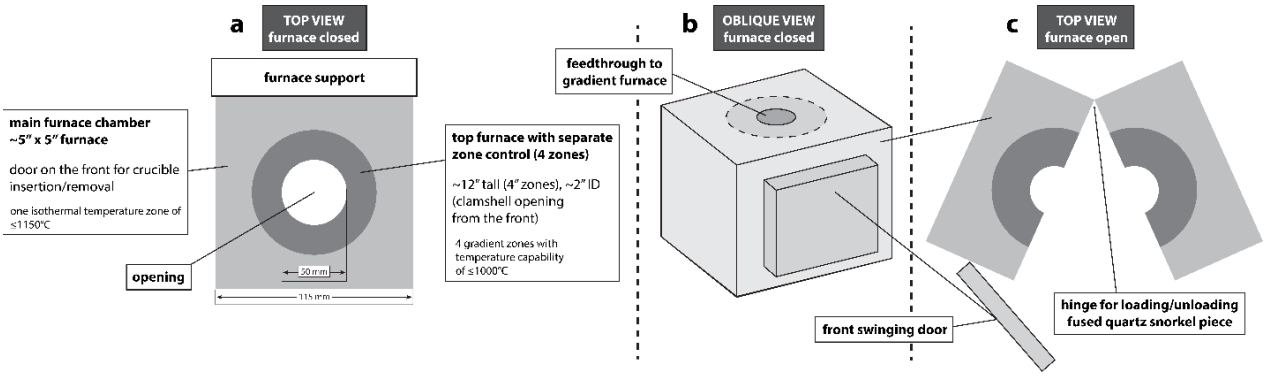

Figure 2. Different views of the G2DA melting furnace including (a) a top view with the door closed, (b) an oblique view with the door closed (gradient furnace not shown), and (c) a top view with both the door open and the main furnace shell open.

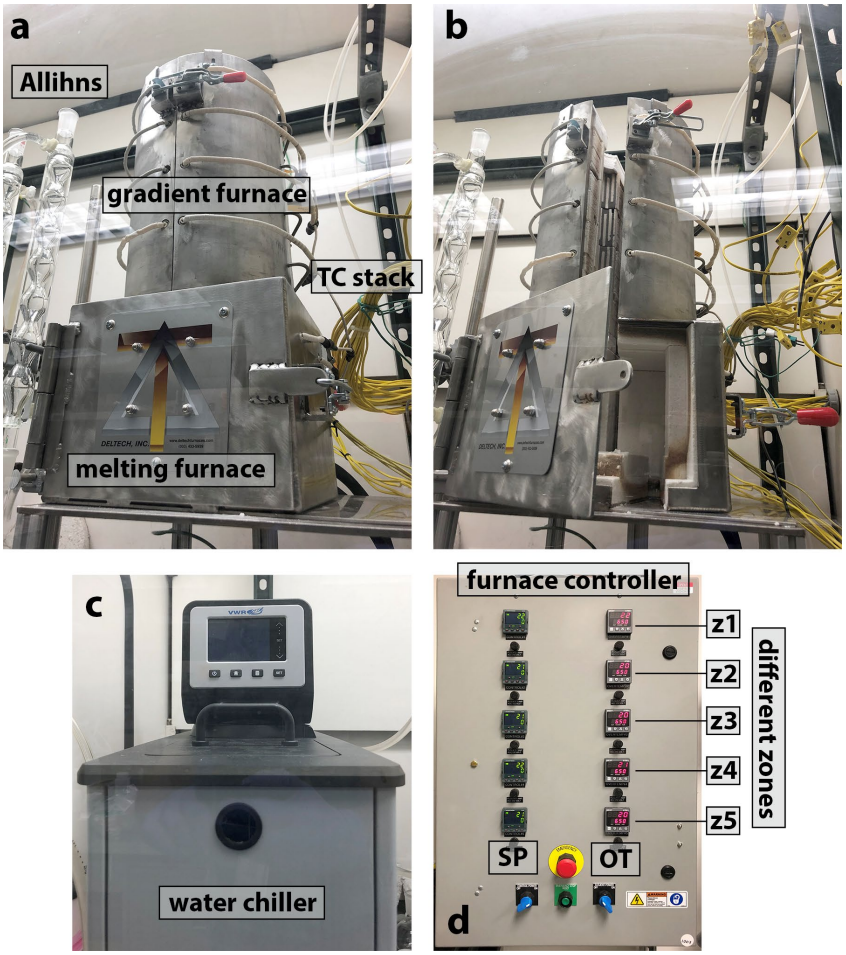

Figure 3. Pictures of the actual G2DA system and components including (a) furnace while closed with the Type-K thermocouple bank (TC stack) for temperature monitoring shown to the right, (b) furnace while partially open (unlatched), (c) the water chiller (in the fumehood to left of condensers), and (d) the furnace controller showing the different zones (i.e., z1–z5) with five Eurotherm 2416 setpoint (SP) and five WEST 6700+ overtemperature (OT) controllers. The TC stack is connected to a data acquisition system outside the fumehood (not shown).

2. TEMPERATURE TESTING AND FURNACE PROFILING

In order to evaluate the thermal tolerances of the furnace zones, several different heat treatments were performed with isothermal holds in the gradient furnace while the melting furnace was held at the 600°C, the typical maximum operating temperature for dechlorination. Based on the limitations of the Eurotherm 2416 controllers for these different furnace zones, the numbers of programmable segments were limited. Thus, a low-temperature test (T = 100, 150, and 175°C) was run as well as a higher-temperature test (T = 200, 250, and 300°C); the data for these are shown in Figure 4 and Figure 5, respectively.

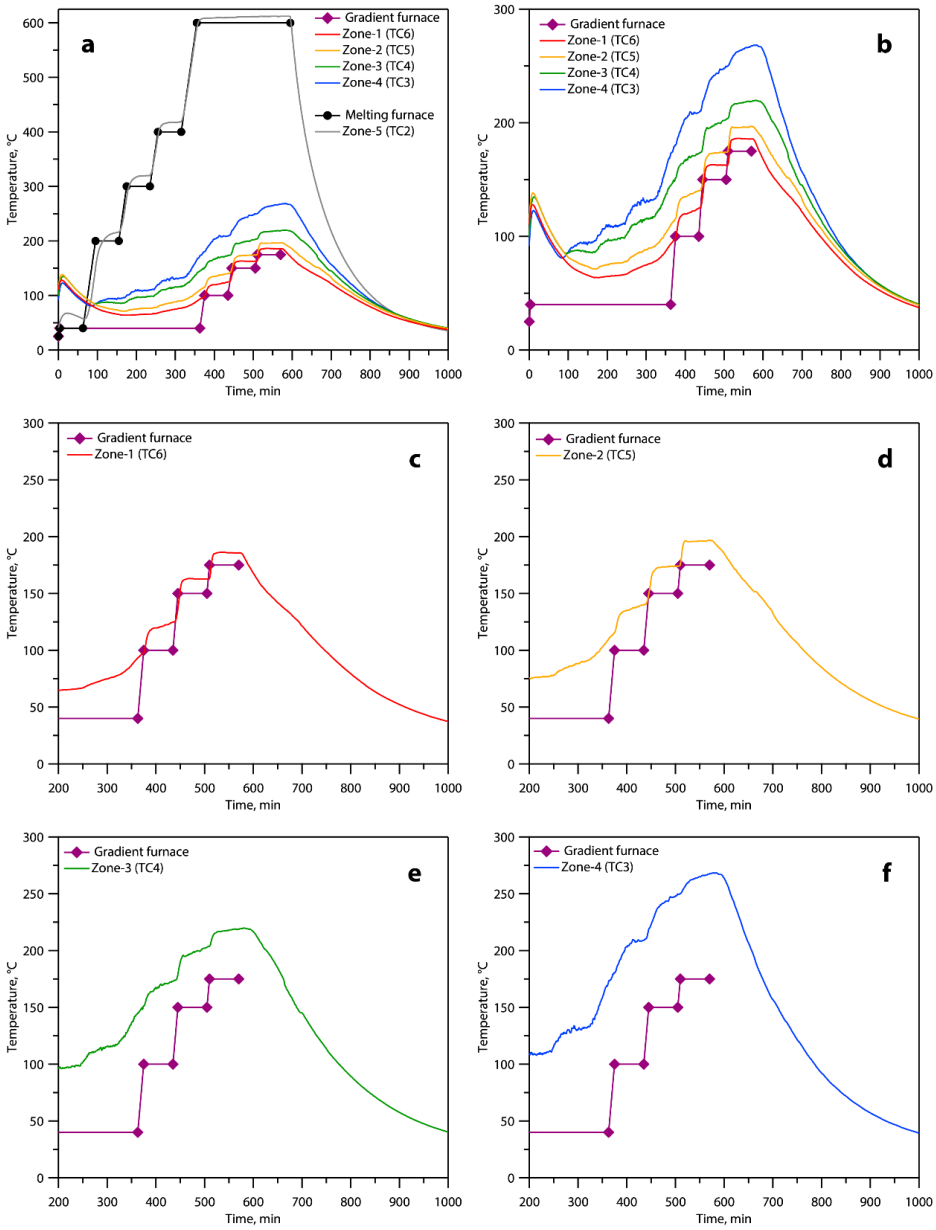

Figure 4. Summary of temperature logging data where data with points and lines represent target temperatures and the other lines (without points) represent measured temperatures. (a) Measured vs targeted temperatures for all zones where hold temps for gradient furnace zones (i.e., 1–4) were 100, 150, and 175°C, (b) same view as (a) but without zone-5 data, (c) zone-1 data, (d) zone-2 data, (e) zone-3 data, and (f) zone-4 data.

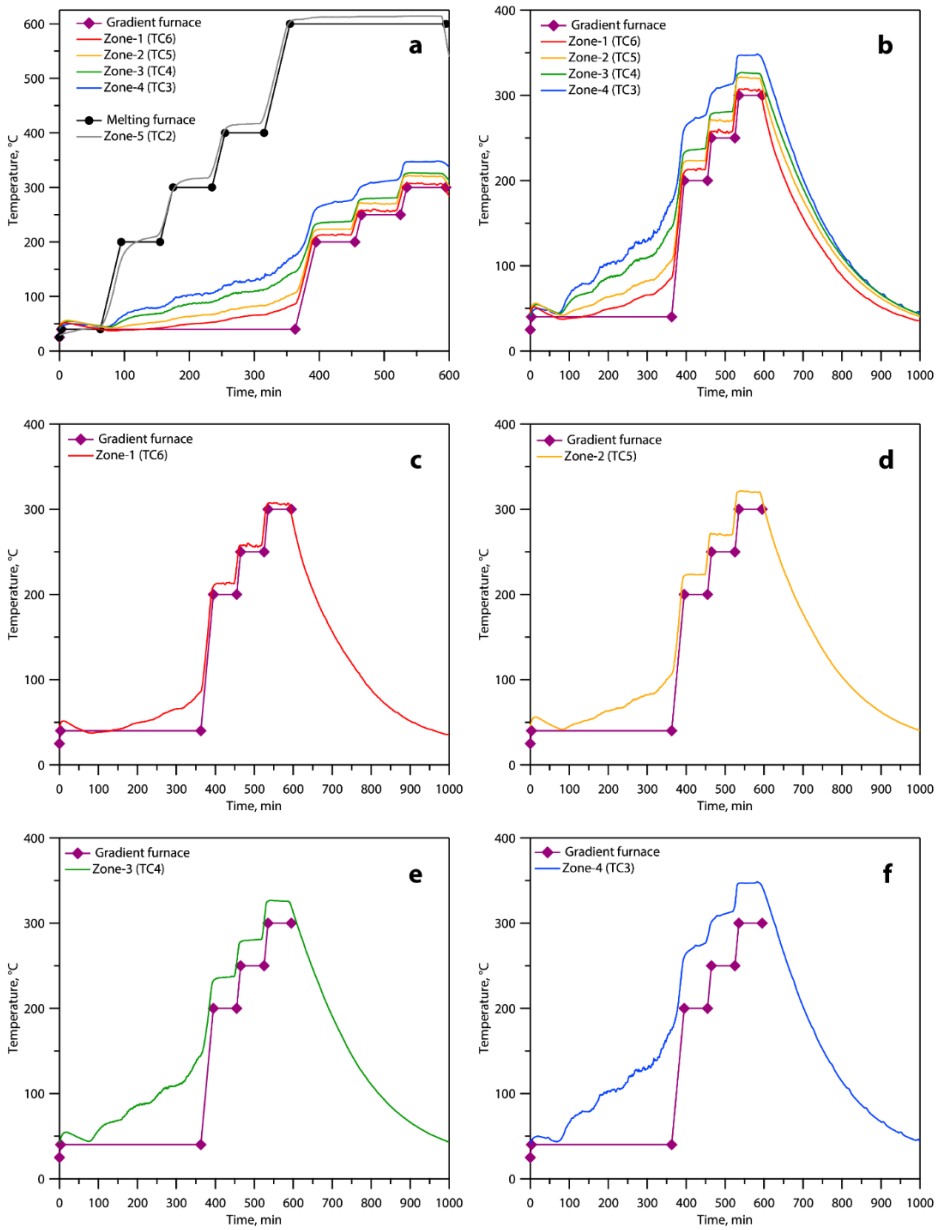

Figure 5. Summary of temperature logging data where data with points and lines represent target temperatures and the other lines (without points) represent measured temperatures. (a) Measured vs targeted temperatures for all zones where hold temps for gradient furnace zones (i.e., 1–4) were 200, 250, and 300°C, (b) same view as (a) but without zone-5 data, (c) zone-1 data, (d) zone-2 data, (e) zone-3 data, and (f) zone-4 data.

For these tests, the controllers were not autotuned beforehand and the top of the furnace where the glassware exited was insulated with Kaolwool to help prevent heat loss. Also, the Type-K TCs were connected to a separate quartz tube that was placed down the interior of the empty off-gas glassware and resided in the bottom of an empty 250-mL alumina crucible. This was done so that precise TC locations could be recorded. More detailed information is provided in Figure 6 and Figure 7 including the trends of the measured temperatures vs targeted temperatures for the different hold temperatures. The data shown in Figure 7b (differences) follow somewhat of a trend while the average measured temperatures follow a more

predictable trend (Figure 7c) with increasing target temperatures. Taking the locations inside the furnace as distances from the base of the melting furnace (or the bottom of the heated region), the average temperatures were plotted. These data were fit to Sigmoid equations of the format shown below [Equation (1)] where α, β, δ, and ε are all variables defined in Table 2. This equation format fit well for all datasets corresponding to different setpoint temperatures. When looking at these data, it was apparent that the gradient furnace could be set up to span a fairly wide range of different temperatures just by keeping all zones set up at the same temperature.

$$y = \alpha + \beta/[1 + \exp(-\{x - \delta\}/\varepsilon)] \quad (1)$$

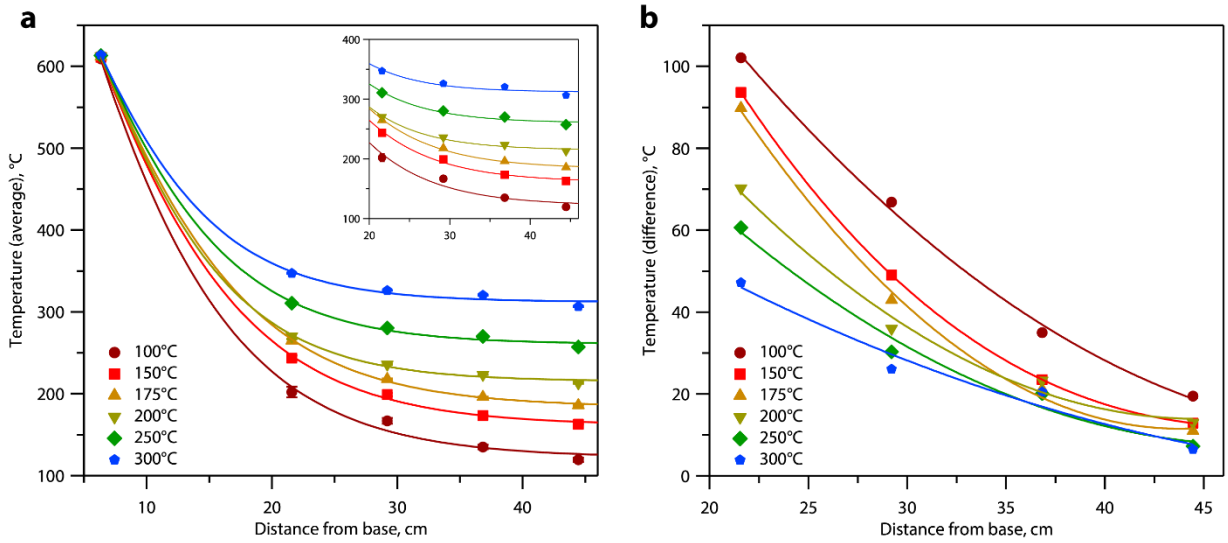

Figure 6. Summary of temperature in the furnace as a function of distance from the base of the melting furnace at different setpoint temperatures including (a) average temperatures with fitted Sigmoid equations and (b) temperature differences of measured (T_{meas}) minus targeted (T_{targ}).

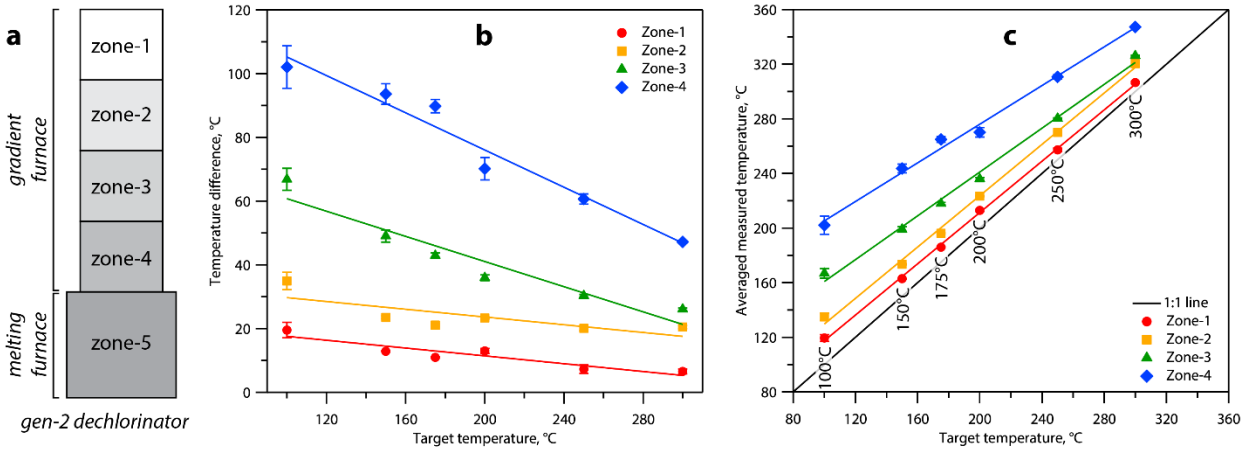

Figure 7. (a) Furnace zone layout, (b) ΔT values vs target temperatures for gradient zones 1–4, and (c) average temperatures for different setpoints within gradient zones 1–4 (zone-5 T_{SP} = 600°C).

Table 2. Fitting coefficients for Sigmoid equations presentend in Figure 6a for different gradient furnace setpoint temperatures.

Coefficient	100°C	150°C	175°C	200°C	250°C	300°C
α	1914.8	1554.4	1383.6	1305.1	1299.9	1216.2
β	-1793	-1393.3	-1200	-1090.1	-1039.5	-904.23
δ	-1.1962	0.6741	1.8865	2.7642	1.8905	2.0692
ε	7.6437	7.6626	7.571	6.4982	6.691	6.1976

3. EXPERIMENT WITH KCl (RUN-1)

In order to evaluate the effectiveness of the G2DA, an experiment was run similar to one performed previously in the G1DA (i.e., DPF5-Simple1) (Riley and Chong 2021) where only KCl was used as the salt simulant. This particular composition is based on the DPF-5 formulation from our previous work (Riley et al. 2020) and the targeted masses for this batch are shown in Table 3. The target reaction shown in Reaction (2) assumes equal molar salt (KCl) and $NH_4H_2PO_4$ (ADP), which is not the case since the NH_4:Cl molar ratio for this experiment was 1.782 (not 1.000). Here, ADP and KCl were dechlorinated in a 250-mL alumina crucible and the heating profile for the melting furnace was modified from 1-h dwells to 10-min dwells at 200, 300, and 400°C with a 1-hr dwell at 600°C – this thermal profile is shown in Figure 8b. In the proposed Reaction (2) below, "*s*" denotes solid, "*l*" denotes liquid, and "*v*" denotes volatilized product. The target temperatures for all gradient furnace zones were 150°C.

$$2\ KCl(s) + 2\ NH_4H_2PO_4(l) \vec{\Delta} 2\ NH_4Cl(v) + 2\ H_2O(v) + P_2O_5{:}K_2O(l) \quad (2)$$

Table 3. Targeted composition for the KCl experiment (Run-1) in the G2DA along with the total expected oxide glass mass (30.9921 g).

Additive	Mass fraction	Targeted mass (g)	Component in glass	Mass in glass (g)
$NH_4H_2PO_4$	0.55	23.8165	P_2O_5	14.6951
Fe_2O_3	0.25	10.8257	Fe_2O_3	10.8257
KCl	0.20	8.6606	K_2O	5.4713

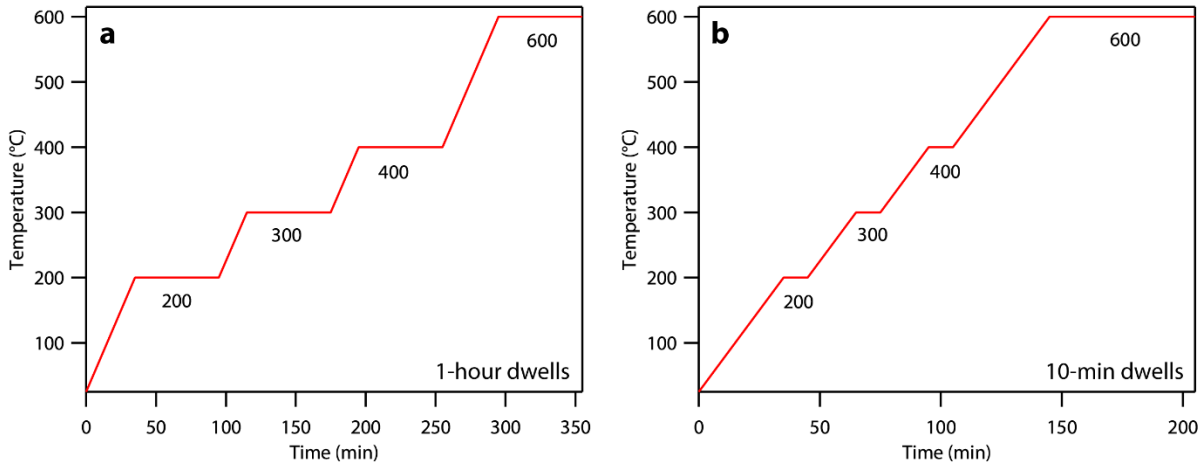

Figure 8. Furnace profiles used during (a) profiling runs as well as G1DA experiments and (b) for KCl experiment in G2DA. The shorter dwell times of 10 min at 200, 300, and 400°C were utilized to cut the total experimental time down by 150 min (2.5 h).

Following the dechlorination process, the off-gas glassware was removed from the furnace along with the crucible. A picture taken of the glassware with condensates is shown in Figure 9. The white condensation was not observed in any measurable quantity more than ~1 inch below the upper joint of piece-C2 and a majority of the salt was condensed at the tapered joint between piece-C1 and piece-C2 which equates to a predicted temperature (based on thermal profiling) of 200–246°C (Figure 10). The NH_4Cl condensate masses recovered from piece-C1, piece-C2, piece-C3, and from some material that fell into the crucible are presented in Table 4. From this, it is apparent the majority of the condensate mass was captured on piece-C1 on the inside of the bottom tapered joint.

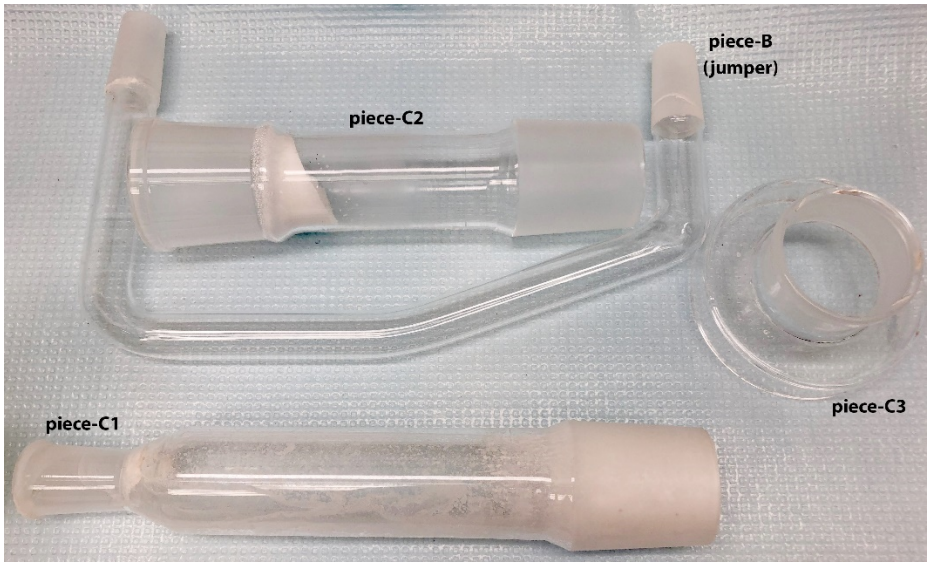

Figure 9. Pictures of glassware pieces after completion of the KCl experiment in the G2DA. The labels for each piece are the same as those provided in Figure 1.

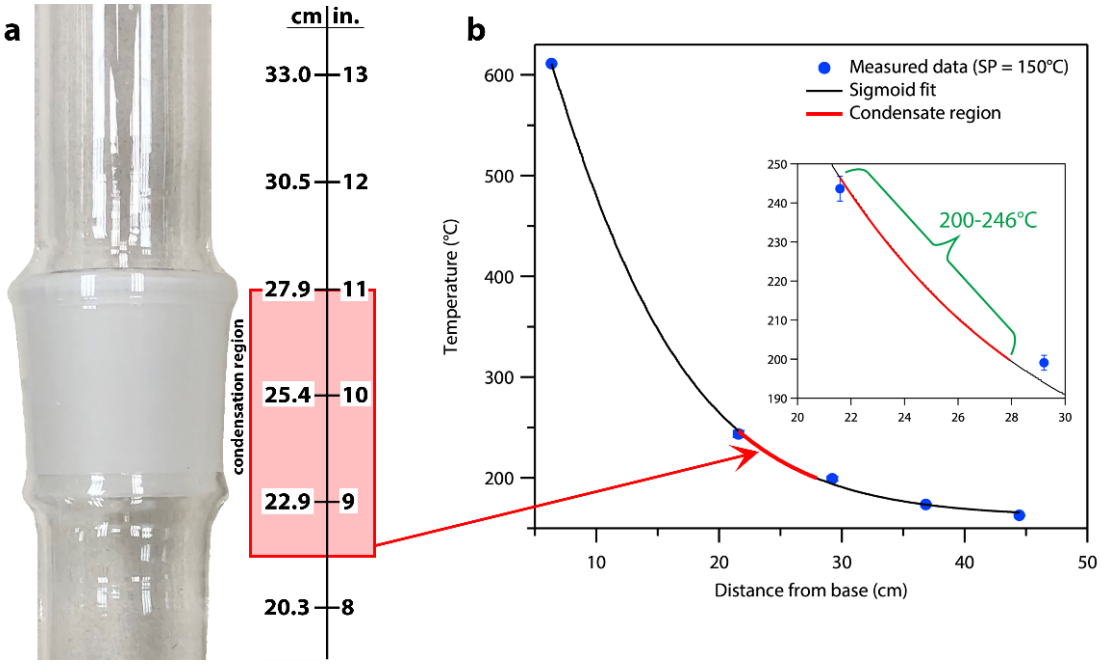

Figure 10. (a) Region where condensates were observed in the largest quantity showing piece-C1 and piece-C2 merged together at the tapered joint; a ruler is provided that shows the distances from the base of the melting furnace in both centimeters (cm) and inches (in.). (b) Plot showing the temperatures at these locations based on the Sigmoid fit (inset shows the relevant region magnified).

Table 4. Summary of condensate masses collected after the KCl experiment in the G2DA from different components of the system. Note that some NH_4Cl was observed in the crucible (it fell down off the wall of the glassware) and Piece-B was not weighed before/after (NM = not measured) and only contained a negligible mass of NH_4Cl. Here, m_i, m_f, and m_c denote the initial mass of each piece, the final mass of each piece, and the mass of condensate recovered, respectively.

Vessel piece	m_i (g)	m_f (g)	m_c (g)
Piece-C1	153.31	157.38	4.07
Piece-C2	145.10	146.16	1.06
Piece-C3	95.64	95.65	0.01
Piece-B	NM	NM	NM
Crucible	–	–	0.04

While almost all of the condensates were bright white in color, some condensates near the exit of piece-C1 (heading to the condensers) had some light gray discoloration. X-ray diffraction (XRD) analysis on both sets of condensates showed that they were pure NH_4Cl (see Figure 11). The source of the observed discoloration is likely an impurity in the KCl reactant.

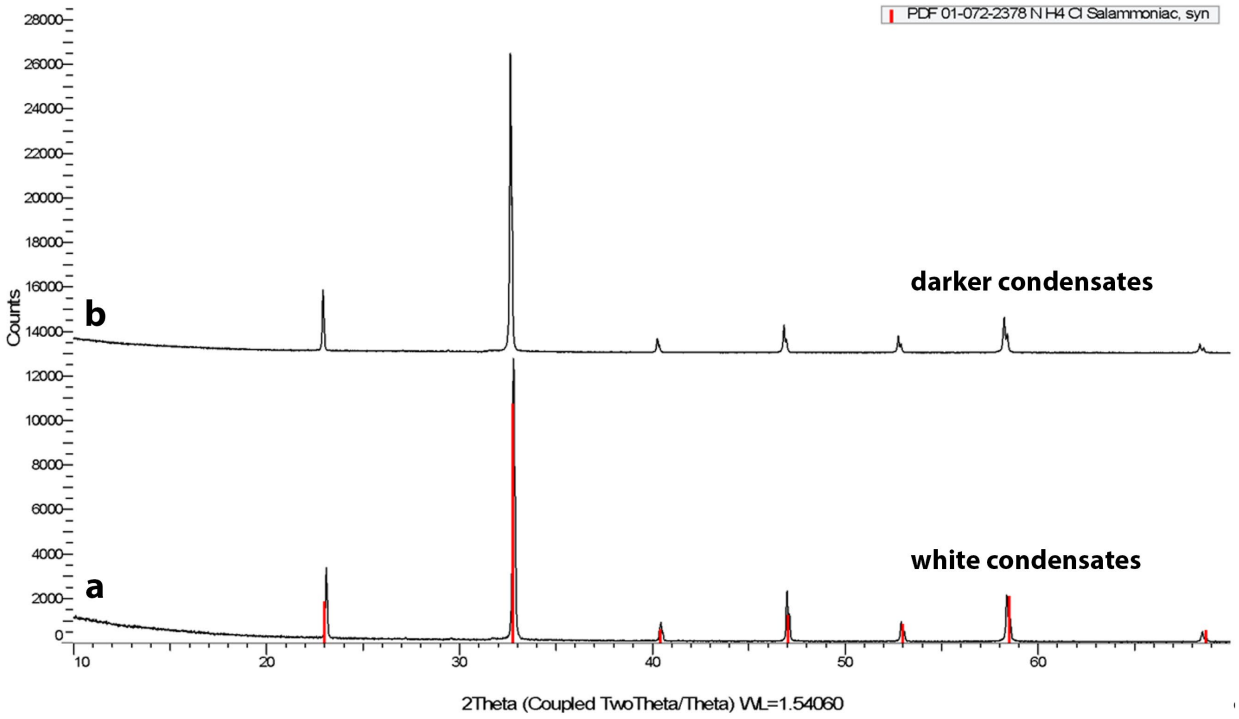

Figure 11. Powder XRD data for the condensates from both the (a) white and (b) white/gray salts. The red lines fit NH_4Cl (PDF01-072-2378, also called salammoniac).

The overall mass yield of NH_4Cl was much higher for the G2DA experiment (83.4 mass%) than that recovered from the identical G1DA experiment (13.8 mass%) – see Figure 12 for a yield comparison. The main source of loss from the G1DA was gaseous NH_4Cl leaving the crucible due to clogging in the off-gas glassware where these vapors left the crucible and vented into the furnace. This is a problem from many viewpoints including potential corrosion of the heating elements and furnace shell as well as NH_4Cl loss. Since no clogging was observed in the G2DA, no loss of NH_4Cl was observed. The missing mass of NH_4Cl from the G2DA experiment is likely due to the production of ammonia (NH_3), based on the pH (~8) of the liquid (~5 mL) present in the collection flask after the experiment. Ammonia has been demonstrated in the

literature as a potential byproduct of ADP decomposition at temperatures above 150°C (Pardo et al. 2017); see Equation (3). Instead of generating unreacted H_3PO_4, this compound likely reacts to form P_2O_5 and water shown in Equations (3) and (4). In Equations (3) and (4), "*s*" denotes solid, "*l*" denotes liquid, and "*v*" denotes volatilized product (these reactions require heat, hence the use of Δ).

$$NH_4H_2PO_4(s) \xrightarrow{\Delta} NH_3(v) + H_3PO_4(l) \quad (3)$$

$$H_3PO_4(l) \xrightarrow{\Delta} P_2O_5(l) + 3\ H_2O(v) \quad (4)$$

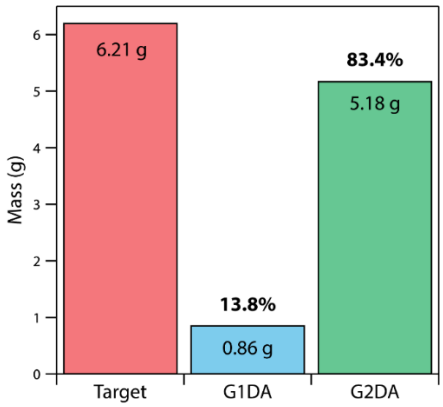

Figure 12. Comparison between NH_4Cl condensate mass recovered during KCl experiments in G1DA and G2DA with the target value (6.21 g) including the mass% recovered from total. The values above the blue and green bars assume full conversion of all available Cl to NH_4Cl.

Following dechlorination, Fe_2O_3 was added to the resulting product and melted without a lid at 1050°C for 55 minutes in a high-temperature melting furnace (Deltech Inc.). Following this melt process, the crucible was removed, and the glass was poured onto an Inconel quench plate. A picture of the glassy product is shown in Figure 13. The glass was visually free of inclusions or crystalline materials but was not analyzed with XRD.

Figure 13. Picture of quenched glass after the vitrification process was completed for the KCl sample (Run-1).

4. EXPERIMENT WITH CsCl (RUN-2)

For the second run in the G2DA, CsCl was used instead of KCl and the target masses of ADP, salt, and Fe_2O_3 were doubled from the KCl batch. This experiment was run similar to an experiment run previously in the G1DA (i.e., DPF5-Simple6) (Riley and Chong 2021) where only CsCl was used as the salt simulant and targeted masses are shown in Table 5. The target reaction shown in Reaction (5) assumes equal molar salt (CsCl) and $NH_4H_2PO_4$ (ADP), which is not the case since the NH_4:Cl molar ratio for this experiment was 4.025 (not 1.000). In the proposed reaction [Reaction (5)] below, "*s*" denotes solid, "*l*" denotes liquid, and "*v*" denotes volatilized product. Here, ADP and CsCl were dechlorinated in a 250-mL alumina crucible and the heating profile was the same as the one used for the KCl run (see Figure 8b). Again, the target temperatures for all gradient furnace zones were 150°C.

$$2\ CsCl(s) + 2\ NH_4H_2PO_4(l)\ \vec{\Delta}\ 2\ NH_4Cl(v) + 2\ H_2O(v) + P_2O_5{:}Cs_2O(l) \quad (5)$$

Table 5. Targeted composition for the CsCl experiment (Run-2) in the G2DA along with the total expected oxide glass mass (65.5383 g).

Additive	Mass fraction	Targeted mass (g)	Component in glass	Mass in glass (g)
$NH_4H_2PO_4$	0.55	47.6334	P_2O_5	29.3902
Fe_2O_3	0.25	21.6520	Fe_2O_3	21.6514
CsCl	0.20	17.3203	Cs_2O	14.4967

A picture of the glassware after the dechlorination experiment is shown in Figure 14. The condensates recovered from the walls of the glassware were verified to be pure NH_4Cl with XRD analysis shown in Figure 15. Based on the limiting reagent to form NH_4Cl, the target yield of the solid condensate was 5.50 g and 4.70 g were recovered resulting in a yield of 85.4 mass% of the target value. This mass recovery was even higher than that recovered for the KCl run (83.4%), albeit by only a small margin of improvement. The pH of the solution recovered in the collection flask was 12 and the liquid smelled of ammonia verifying what was predicted based on Reaction (3) and Reaction (4) (see Section 3 for more information). It should also be mentioned that piece-C3 and piece-B both lost mass between the m_i and m_f values, albeit these were only small values; see Table 6. For this experiment, the insulation was not added to the top of the furnace where the glassware exited the hot zone towards the condensers; this resulted in a downward shift in the gradient furnace temperatures and thus, the NH_4Cl condensates were observed at lower heights than those seen for Run-1 (i.e,. comparing Figure 9 with Figure 14c).

Table 6. Summary of condensate masses collected after the CsCl experiment in G2DA from different components of the system. Note that some NH_4Cl was observed in the crucible (it fell down off the wall of the glassware) and Piece-B was weighed this time. The values of m_i, m_f, and m_c denote initial mass, final mass, and mass of condensate recovered, respectively.

Component	m_i (g)	m_f (g)	m_c (g)
Piece-C1	153.32	156.03	2.71
Piece-C2	145.12	147.27	2.15
Piece-C3	95.84	95.66	-0.18
Piece-B	122.80	122.77	-0.03
Crucible	–	–	0.05

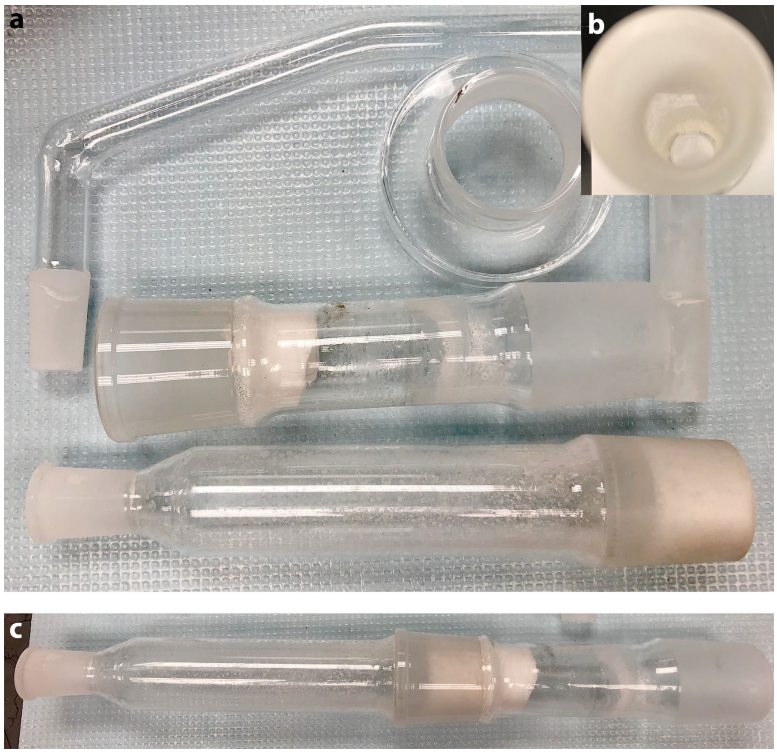

Figure 14. Picture of off-gas glassware after CsCl dechlorination experiment in G2DA showing (a) all of the pieces separately, (b) a view down the view of (c) from the top showing how the inside is open (not clogged), and (c) piece-C1 and piece-C2 joined together where the primary condensation region is shown as the white material on the inside of the pieces.

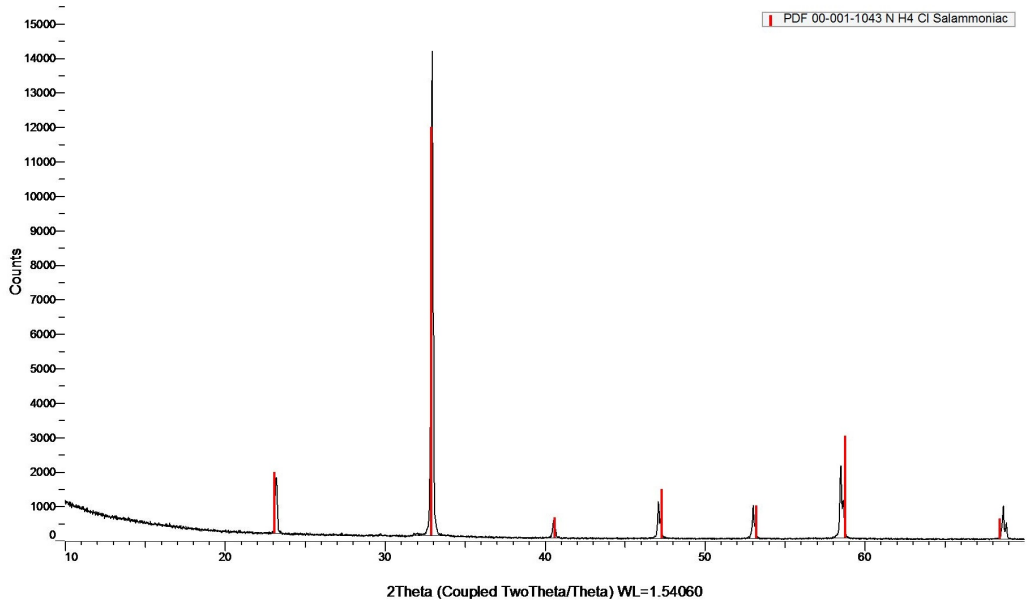

Figure 15. Powder XRD data of the white condensate collected from the CsCl dechlorination run. This product was pure NH_4Cl.

A picture of the glass removed from the quench plate is shown in Figure 16. The melt poured well, and no undissolved material was observed on the inside of the crucible. In the picture, the rougher surfaces are those that were in contact with the quench plate while the smoother surfaces are those that were not.

Figure 16. Picture of quenched glass after the vitrification process was completed for the CsCl sample (Run-2).

5. THOUGHTS AND CONSIDERATIONS FOR FUTURE DECHLORINATOR DESIGN IMPROVEMENTS

The G2DA was designed to meet the improvement needs identified during testing of the G1DA, but it is certainly not the most effective design for high-throughput processing and is not designed for continuous throughput processing. First, a horizontal orientation might be more efficient at performing the dechlorination process because the condensed NH_4Cl crystals cannot fall back into the crucible if they flake off the snorkel glassware. Having this horizontal orientation could also allow for a purge gas to sweep the condensate away from the melting furnace whereas if this was done in the vertical orientation, the NH_4Cl condensates could fall back into the crucible or be transported to the condensers where recovery would be more difficult. One limitation to having a horizontal assembly is that the apparatus footprint would be much larger. The chosen design and footprint for the G2DA was based on available fumehood space. Between the furnace/stand, the condenser system, and the water chiller/circulator, the fumehood where this work is being conducted is already full. The horizontal system would work well in a walk-in style fumehood with a large horizontal footprint. This arrangement might also work well for scaling up the system for processing larger batches since a larger melting furnace could be implemented.

Neither the G1DA nor the G2DA utilized any sort of purge gas to drive condensates out of the furnace. The main reason for this is that purging would likely result in a thin layer of NH_4Cl across a larger surface leading to more difficulty in harvesting the condensates. If so desired, it could be possible to draw all condensates through a liquid scrubber bed (e.g., NaOH) where any acidic gases (e.g., HCl) would be neutralized. This type of system could be introduced into future designs of the apparatus if so desired.

Another improvement would be a way to conduct the vitrification step in the same furnace as the dechlorination step. There are several reasons why this was not done in the G1DA and is not done in the G2DA described below.

- The tops of both furnaces are open and finding a way to close these ports while the furnaces are energized would be difficult as both would require the removal of the off-gas glassware. Not removing the glassware before heating the furnace to higher temperatures would almost certainly result in removal of the NH_4Cl. Also, the G2DA furnace cannot be easily opened without unlatching and opening the gradient furnace section. This is due the way that the insulation seals the furnace and the electrical hazards of the exposed heating elements deeming it unsafe to open while energized. Finding a way to plug the top of the furnace in an automated way (e.g., using a swing-style rotation mechanism) might be one way to plug the top of the furnace without opening it but again, this would require removing the off-gas glassware from the furnace while it is energized and at operating temperatures.
- An issue not mentioned until now is that alumina crucibles used in these studies are susceptible to thermal shock (cracking) so heating or cooling them rapidly is a problem. Thus, finding a way to keep the dechlorinated melt at moderate temperatures (~600°C) would be ideal to help prevent this from occurring, but that means that the other glass-forming chemicals (e.g., Fe_2O_3) would have to be charged into the crucible while the system is at these temperatures. One way to do this would be to insert the chemicals down the off-gas glassware to prevent contaminating the inside of the furnace, but this would mean contaminating the NH_4Cl with these chemicals. This is an engineering challenge that should be addressed and could potentially include the installation of a secondary system connected to the crucible snorkel on the crucible (Figure 1c3), separate from the off-gas port, for charging chemicals into the crucible. Of course, if this were done, that port would have to remain plugged during dechlorination or it could fill, or even plug, with NH_4Cl condensates unless it was kept at high temperatures.
- Another reason that this was not implemented has to do with the temperature limitations of coil heating elements, which are rated to 1150–1200°C. Some of the phosphate glass formulations

require vitrification temperatures in excess of these temperatures making it difficult to successfully vitrify these formulations in this type of furnace setup. Alternate types of heating elements are available (e.g., $MoSi_2$) for achieving higher temperatures, but these pose additional challenges such as the way they are installed with electrical-bus connections on the top of the furnace chamber (where the current gradient furnace sits) and greater exposure to any potential NH_4Cl vapors (the current coil elements are less exposed) that might escape the crucible during the dechlorination process, potentially leading to corrosion of the elements.

- Finally, performing the vitrification step without cooling the dechlorinated melt would be a better way to achieve homogeneity in the vitrified product. The current approach is to put Fe_2O_3 powder on top of the solidified dechlorinated product. These two react well during vitrification, but it is common to see a small amount of unreacted Fe_2O_3 in the crucible after vitrification.

The G1DA and G2DA were both comprised of separate pieces made out of fused quartz or alumina. Neither of these construction materials are ideal from a scale-up perspective. The fused quartz is very fragile to handle and 'frosts' (i.e., turns cloudy) over time when exposed to compounds containing chemicals like alkalis and halides. This frosting effect also makes the fused quartz more brittle over time. Also, alumina is not ideal as a crucible material due to the thermal shock susceptibility (described previously), because they are expensive to fabricate, because they can only be used once, and they are very susceptible to corrosion by phosphate melts (i.e., all of the vitrified products contain Al_2O_3 from the crucible). It should also be mentioned that iron phosphate glasses made in fused quartz crucibles are more durable than those made in alumina crucibles, suggesting that alumina could be negatively affecting these properties (unpublished data). An ideal system, including both the crucible and off-gas lines, should be made of a less reactive materials such as a metal alloy like Inconel 690 or 693. While these Inconel alloys have been demonstrated to work well for iron phosphate glasses (Hsu et al. 2013; Hsu et al. 2014), it is unclear how they would perform with the dechlorination melts that have much lower melting temperatures ($T_m < 600°C$) and very low viscosities.

Lastly, exploration of a cold finger system to highly concentrate the solid NH_4Cl condensates should be explored. It is possible that the condensates could be easily collected in this manner, without a flow-through-type solid-condensate-collection system in a separate chamber while the more volatile byproducts (e.g., H_2O, HCl, NH_3) travel to a liquid condenser system like the ones employed in both the G1DA and G2DA designs. If something like this were implemented, it is possible that the cold finger could be removed periodically for harvesting NH_4Cl and replaced with a clean cold finger for future condensate collections.

6. SUMMARY AND CONCLUSIONS

The generation-2 dechlorination apparatus worked much better than the generation-1 system at (1) preventing NH_4Cl from clogging the off-gas glassware using the same batch size,[a] (2) controlling the temperature of the primary NH_4Cl condensation region (spread over >2.5 inches vs <1 inch) by utilizing the gradient furnace, and (3) preventing splattering of the melt onto the snorkel glassware. Having the NH_4Cl condensates spread across a wider region of the glassware helped with the NH_4Cl recovery process as well. For the KCl (Run-1) and CsCl (Run-2) experiments run in the G2DA, the NH_4Cl recoveries were 83.4 mass% and 85.4 mass%, respectively, which are much higher than those achieved in the G1DA.

The changes in the generation-2 system drastically improved the process flow and should work well for scaling up the salt processing rate and throughput compared to the generation-1 system. Discussion was also provided to describe some changes that could be made in a future redesign if the generation-2 dechlorination apparatus was to be upgraded. These included: (1) using a horizontal off-gas system design to help prevent NH_4Cl from falling into the crucible, (2) using a purge gas to drive condensates out of the furnace more effectively, (3) performing the vitrification step without cooling down the dechlorinated melt, (4) using different construction materials for the crucible and off-gas lines such as metal alloys instead of fused quartz and alumina, and (5) using a cold finger system to collect NH_4Cl condensates in a way that they are easier to recover for recycle.

[a] The off-gas glassware clogged during the KCl experiment (DPF5-Simple1) in the generation-1 dechlorination apparatus.

7. REFERENCES

Hsu, J.-H., J. W. Newkirk, C.-W. Kim, R. K. Brow, M. E. Schlesinger, C. S. Ray, and D. E. Day. 2014. "The performance of Inconel 693 electrodes for processing an iron phosphate glass melt containing 26wt.% of a simulated low activity waste." *Journal of Nuclear Materials* **444**(1):323-30.

Hsu, J.-H., J. W. Newkirk, C.-W. Kim, C. S. Ray, R. K. Brow, M. E. Schlesinger, and D. E. Day. 2013. "Corrosion of Inconel 690 and Inconel 693 in an iron phosphate glass melt." *Corrosion Science* **75**:148-57.

Pardo, A., J. Romero, and E. Ortiz. 2017. "High-temperature behaviour of ammonium dihydrogen phosphate." *Journal of Physics: Conference Series* **935**:012050.

Riley, B. J. and S. Chong. 2021. "*Completion of Milestone M4FT-21PN030103022 "Evaluate fission product effects on phase distribution in slow-cooled iron phosphate waste forms".*" Pacific Northwest National Laboratory, Richland, WA.

Riley, B. J., J. A. Peterson, J. D. Vienna, W. L. Ebert, and S. M. Frank. 2020. "Dehalogenation of electrochemical processing salt simulants with ammonium phosphates and immobilization of salt cations in an iron phosphate glass waste form." *Journal of Nuclear Materials* **529**:151949.