

Phosphate-Based Approaches for Dechlorination and Treatment of Salt Waste from Electrochemical Processing of Used Nuclear Fuel: A Perspective on Recent Work

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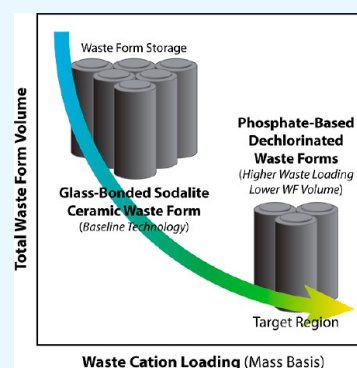


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ABSTRACT: Phosphate-based reagents are being considered by the U.S. Department of Energy (DOE) Office of Nuclear Energy to process halide salt-based nuclear wastes for stabilization prior to disposal. As evidenced by the Experimental Breeder Reactor-II (EBR-II) project, electrochemical processing (pyroprocessing) can be employed to recover uranium and other actinides for reintegration into the nuclear fuel cycle from metallic fuels. The resultant salt-based wastes generated from electrochemical processing of EBR-II fuel contains fission products within a LiCl–KCl eutectic salt that necessitate appropriate disposal. This paper provides an overview of recent efforts to support halide-based salt waste treatment for disposition, as well as a basis for comparison with other related efforts in salt waste treatment through salt partitioning initiatives. The U.S. DOE has selected a phosphate waste form reference material for further investigation and longer-term studies.



1. INTRODUCTION

The revival in nuclear energy as a recognized clean energy source, coupled with a significant increase in power demand, has brought a resurgence of innovations to the nuclear industry.¹ With the introduction of small modular reactors (SMRs) and molten salt reactors (MSRs), the ability to provide continuous power locally has become a reality; however, with this reality comes the environmental and regulatory responsibilities to ensure that used nuclear fuel (UNF) is managed accordingly.^{2–5} One of the considerations to improve the efficiency of and close the nuclear fuel cycle, is electrochemical processing of UNF, also referred to as pyroprocessing.^{6–14} The other option for recycling UNF includes a group of aqueous-based processing methods, including PUREX (plutonium uranium reduction extraction).¹⁵ In electrochemical processing of UNF, uranium and actinides may be recovered and separated from fission products through electrochemical reduction at a cathode. However, concentrations of fission products, including alkalis (A), alkaline earths (AE), and rare-earth (RE) elements, remain in the LiCl–KCl eutectic salt bath generating a secondary waste stream, which requires disposition.

One option for processing and immobilization of the product remaining in the electrorefiner after electrochemical processing is halide removal from the salt (dehalogenation) followed by immobilization of the salt cations within an iron phosphate waste form. Since the 1950s, phosphate-based glasses have been investigated and used for immobilization of high-level waste (HLW).¹⁶ Phosphate glasses have some advantages over traditional borosilicate HLW waste forms,

such as lower processing temperatures, lower thermal expansion coefficients, and improved solubilities for sulfur, aluminum, noble metals, and halides, which can cause unwanted crystallization in silicate glasses and reduced chemical durability.^{17–21} While phosphate glass may be advantageous for salt waste treatment, several limitations remain that need to be addressed, such as poor chemical durability due to crystallization and material compatibility with melter and storage containment vessels, which can cause premature melter component failure.²² Generally, chemical durability improvements to acceptable levels may be achieved through the additions of glass-forming chemicals (GFCs) like Fe₂O₃ and Al₂O₃ for long-term storage within geological repositories.^{22–26}

Another benefit of phosphate-based glasses for immobilization of fission products from electrochemical (echem) salt wastes is the ability to produce a dehalogenated product (DP). In the various processing approaches currently being investigated, phosphate-based precursors [e.g., H₃PO₄, NH₄H₂PO₄ (ADP), (NH₄)₂HPO₄ (DHP), and SiO₂–Al₂O₃–P₂O₅ (SAP)]^{11,26–36} are used to convert salt-waste anions (e.g. Cl) to gaseous chlorine species (e.g., HCl, NH₄Cl)

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Table 1. Timelin of Phosphate Waste Form Development Technologies and Events^a

timeline	critical historical event ^b	country ^c
1950s	development begins on Na–Al–P–O glasses for defense HLW	U.S.S.R.
1967–1970	Brookhaven National Laboratory develops phosphate waste forms for liquid metal fast breeder reactor (LMFBR)	U.S.
1960s–1970s	phosphate marbles in metal matrix are developed in Karlsruhe for the Pilot Anlage Mol zur Erzeugung Lagerfähiger Abfälle (PAMELA) in Belgium	Germany
1966–1972	the Pacific Northwest Laboratory (PNL) develops phosphate glasses for waste solidification engineering prototypes	U.S.
1978	the world's first full-scale HLW vitrification facility comes online in Marcoule producing borosilicate glass (BSG) waste form	France
1979–1981	Hench Panel recommends BSG for immobilizing US Defense HLW	U.S.
1982	record of decision for the Defense Waste Processing Facility (DWPF) (selecting BSG) (confirmed during National Environmental Policy Act in 1983)	U.S.
1982	West Valley Demonstration Project (WVDP) selects BSG as final waste form (preferred option following an Environmental Impact Statement)	U.S.
1984	WVDP analysis of alternative waste form options select BSG	U.S.
1977–1987	alternative waste form options are evaluated for Hanford double-shell tanks (DSTs) including phosphate, BSG, ceramic WFs, and other options	U.S.
1984–1986	Oak Ridge National Laboratory develops lead iron phosphate glass with improved durability for US Defense HLW	U.S.
1987	first HLW Na–Al–P–O waste form production at Mayak	U.S.S.R.
1987–1988	record of decision for Hanford DSTs, then all tank waste (selecting BSG for both)	U.S.
1990	Hanford reevaluates tank waste form selection, concurring with BSG selection	U.S.
1990s–present	Fe–P–O glasses evaluated by University of Missouri at Rolla (currently MUST) with lower tendency to devitrification and lower corrosion for various waste streams	U.S.
1995–1999	DOE Office of Materials Disposition (currently NA-233) evaluated waste forms for Pu immobilization including phosphate glass (they select Synroc)	U.S.
2008–2011	DOE Office of Environmental Management (DOE-EM) to develop next-generation melters and glass (include iron phosphate glass and cold crucible induction melting)	U.S.
2008–2010	crystalline silica aluminophosphate (SAP) ²⁹ and zinc-in-titania (ZIT) ¹⁰ waste forms developed for used electrorefiner salts	R.O.K.
2009–2012	MUST Nuclear Energy University Partnership (NEUP) on Fe–P–O glass corrosion	U.S.
2011	Siemer ³⁹ (formerly from Idaho National Engineering Laboratory) evaluates Fe–P–O glass for integral fast reactor (IFR) salt waste	U.S.
2012	DOE-EM decision not to further pursue next-generation melters and glass	U.S.
2013–2017	Mo-Sci Corporation initiates a Small Business Innovation Research contract on Fe–P–O nuclear waste glass development	U.S.
2015	DOE-NE defines baseline waste management technologies for advanced fuel cycle (focus on sodium-cooled fast reactor or SFR) (recommends BSG for aqueous HLW and ceramic waste form for electrochemical recycling salt for used nuclear fuel reprocessing) ⁴⁰	U.S.
2017–present	DOE-NE develops Cl recycle flowsheet for echem salt with FeP glass (based on literature data) ²⁶	U.S.

^aThis table was modified from the originally by Marcial et al.³⁸ and is reprinted with permission. Copyright 2024 Pacific Northwest National Laboratory. ^bBSG = borosilicate glass; DST = double-shell tank; echem = electrochemical; MUST = Missouri University of Science and Technology (formerly University of Missouri Rolla); SAP = silica aluminophosphate. ^cR.O.K. = Republic of Korea; U.S. = United States; U.S.S.R. = Union of Soviet Socialist Republics.

during dehalogenation processes, leaving radionuclides immobilized within a phosphate matrix. Since the H₃PO₄ and SAP dehalogenation processes are similar, only the H₃PO₄ is discussed in this paper. The GFCs are then added to the DP and vitrified at a higher temperature to produce a chemically durable waste form. The off-gas species are captured with potential for reuse (e.g., ³⁷Cl for MSRs) for pyroprocessing (e.g., to create UCl₃) or as an industrial reagent.^{31,32,37}

In 2021, an iron phosphate roadmap for developing iron phosphate waste forms for salt waste was published by the U.S. DOE to capture current progress, identify research and data gaps, and recommend future approaches to fill these gaps.³⁴ In the current paper, proposed dechlorination and vitrification solutions that seek to investigate dechlorination efficacy, material compatibility, crystallization during heat treatments, and chemical durability are reviewed and discussed.

This review has been organized to cover various aspects important to the development of the phosphate-based waste form process, including: a discussion on phosphate-based nuclear waste forms leading up to this work (Section 2), background and current state of electrochemical processing methods (Section 3), a summary and assessment of various dehalogenation procedures (Section 4), a review of iron-phosphate materials developed within the U.S. DOE Office of Nuclear Energy (NE) Material Recovery and Waste Form

Development (MRWFD) Campaign (Section 5), and concludes with a discussion and perspective on future outlook as well as updates to the phosphate waste form development roadmap (Section 6).³⁴

2. HISTORICAL PERSPECTIVE

The DOE-NE MRWFD Campaign builds upon decades of research on phosphate-based nuclear waste forms while addressing critical gaps in the existing literature, which largely predate modern issues including global energy demands, advanced reactor technologies such as molten salt reactors, and contemporary pyroprocessing methods for spent fuel treatment—challenges that necessitated this project's unique approach. A historical overview of phosphate waste form development technologies can be found Table 1 and the references therein.³⁸

3. ELECTROCHEMICAL PROCESSING (PYROPROCESSING)

Modern day electrochemical processing began development with the U.S. Integral Fast Reactor (IFR) Program at Argonne National Laboratory (ANL) in the mid-1980s, which employed an uranium electrorefining process, a molten cadmium anode, halide slagging, and cathode processing to

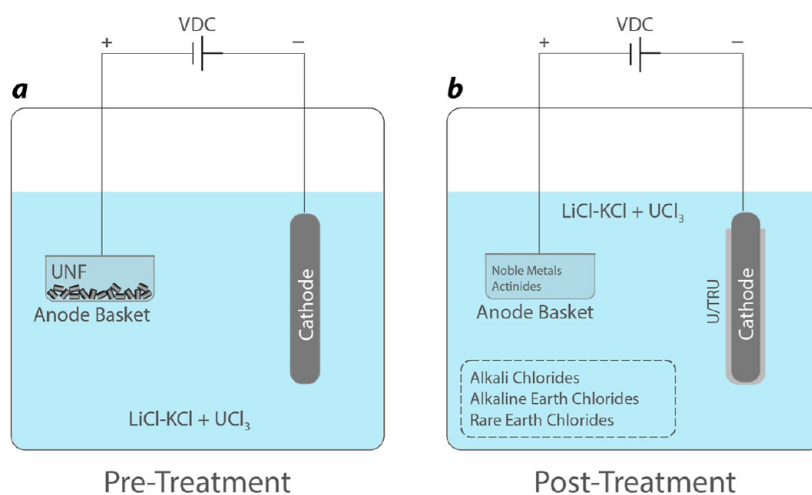


Figure 1. A representative schematic of ER operation, including (a) used nuclear fuel (UNF) prior to electrorefining and (b) following electrorefining. In (b), the remaining products following treatment are shown, including uranium metal adhered to the cathode, Group I and II elements, lanthanides, and transuranics (TRU) dissolved in the salt bath as chlorides.

	waste	Unpartitioned salt (e.g., LiCl+KCl+ fission products)	Partially dehalogenated salt (e.g., REOCl)	Fully dehalogenated salt (e.g., REO _x)
		dehalogenation →		
processes		a) phosphate process b) USHYZ process c) SAP/U-SAP process	a) USHYZ process b) phosphate process c) LABS process	
		a) GBS b) Pb-Te-O glass c) other glass systems	a) Pb-Te-O glass b) LABS glass c) Fe-P-O glass	a) LABS glass b) Fe-P-O glass c) SAP d) ZIT

Figure 2. Summary of ER salt processing and waste form options for different waste streams, including ultrastable H–Y zeolite (USHYZ), silica aluminophosphate (SAP), glass-bonded sodalite (GBS), lead tellurite (Pb–Te–O) glass, zinc-in-titania (ZIT), lanthanide (alumino)borosilicate (LABS) glass, and iron phosphate (Fe–P–O) glass. Note that RE denotes rare earth (elements). Reprinted in part with permission from Riley et al.¹² Copyright 2020 American Chemical Society.

demonstrate the feasibility of a pool-type sodium-cooled fast breeder reactor (SFBR) closed fuel cycle design, such as the Experimental Breeder Reactor-II (EBR-II).^{41–43} Following initial development, operational improvements were made where the anode was switched from liquid cadmium to a steel basket loaded with chopped fuel segments, and a liquid cadmium cathode was demonstrated for codeposition of U/TRU (TRU = transuranics) and removal of the halide slugging system. Following cancellation of the IFR program in 1994, pyroprocessing continued development under the Spent Fuel Treatment (SFT) disposition project for EBR-II used fuel.^{11,12,14,26,30,31,33,44–47} Under this project, the Mark-IV and Mark-V electrorefiners (ER) were used to treat EBR-II UNF using pyroprocessing technology.

Electrorefining is one of the key operations under pyroprocessing. In an ER, chopped metallic UNF is placed within a steel anode basket and immersed in a molten salt electrolyte (e.g., LiCl–KCl–UCl₃). An electric potential difference is applied between this anode basket and a steel cathode mandrel, leading to U and TRU actinide deposition onto the cathode (see Figure 1). Some of the fission products

in the UNF spontaneously react with UCl₃ to form metal chlorides that dissolve in the electrolyte. The equilibrium redox potential of the salt is set by the U/UCl₃ redox couple, which drives “active metal” fission products into the salt as chlorides, while “noble metal” fission products remain in the anode basket as metals. A design feature that has been incorporated in specific ER designs is a pool of liquid cadmium metal located below the molten salt electrolyte.⁴¹ U and TRU can be cathodically electrodeposited in the Cd pool or anodically electrooxidized out of the pool, depending on the electrochemical cell configuration. This affords several modes of electrotransport for U/TRU from the anode basket to a harvestable cathode. The cadmium pool is generally not harvestable because of its location under the pool of molten salt electrolyte. Another important function of the liquid cadmium is to collect U/TRU that falls from the anode basket or cathode mandrel in a form that can be electrochemically recovered. U/TRU can be electrotransported from the liquid cadmium pool back to the solid cathode mandrel.⁴⁸

During operation, active metal fission products (i.e., alkali, alkaline earth, and rare earth metals) remain dissolved in the

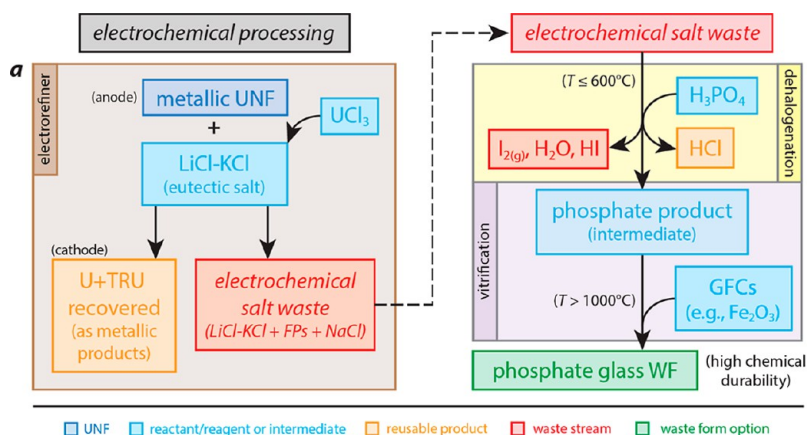


Figure 3. Process flow diagram showing (a) pyroprocessing as well as (b) the process of dehalogenating salt wastes and the process of vitrifying the dehalogenated product into a waste form for disposal. Reprinted in part with permission from Murray et al.²⁷ Copyright 2024 American Chemical Society. Licensed under CC-BY-NC-ND 4.0.

molten salt electrolyte while noble metals and some actinides remain in the anode basket. To keep the electrolyzer salt composition within its operating limits, a portion of the salt must be replaced with $LiCl-KCl$, which generates a secondary salt-waste stream that must be treated or discarded. UCl_3 may also need to be periodically added to the salt either directly or via oxidation of U metal from the UNF feed material. At the end of life, the whole ER salt bath is considered waste. Potential disposition pathways for the remaining salt waste range from direct disposal to immobilization of partitioned fission products in suitable waste forms, as shown in Figure 2.¹² In regard to waste form production before disposal, the demonstrated candidate (i.e., the baseline technology) for chloride salt waste immobilization is a glass-bonded sodalite ceramic waste form (GBS-CWF)⁴⁹ in which the entire waste salt in the ER is immobilized.

RE fission products can be recovered from the processing salt in a separate electrolysis step called lanthanide drawdown, and the volume of waste salt can be decreased by removing some of the solvent salt (e.g., purified $LiCl-KCl$ eutectic) by reactive distillation, oxygen sparging, and/or crystallization (or zone refining).^{50–53} The composition of the waste salt can differ significantly depending on the fuel burnup, the operations applied during pyroprocessing, and operation efficiencies where the remaining waste salt becomes enriched with active fission products (e.g., Cs, Sr, and Ba).⁵⁴ Thus, the formulation and processing of waste forms must be sufficiently flexible to accommodate a wide-range of waste salt compositions. Note that with higher concentrations of heat-generating isotopes in the waste salt, the heat loading of the waste form will also increase.

4. DEHALOGENATION

Halogen removal from ER salt wastes, referred to as *dehalogenation* (or specifically *dechlorination* when referring to chloride salts) is depicted in Figure 3 specifically for a H_3PO_4 dehalogenation reagent.^{55,56} Dehalogenation can be accomplished by reacting the salt waste with various reagents including phosphates [i.e., H_3PO_4 , $NH_4H_2PO_4$, $(NH_4)_2HPO_4$],^{26,28,29,32,35,39,57–61} organic acids,^{47,62} or other H-containing compounds (e.g., ultrastable H–Y zeolite).^{13,63,64}

The selection of appropriate dehalogenation reagents and processing parameters is critical for optimizing both waste

loading and final waste form performance, as illustrated in Table 2,²⁶ which shows the theoretical dechlorination reactions according to cation valence for ADP [eqs 1–3] and H_3PO_4 [eqs 4–6].

Table 2. Theoretical Dechlorination Reactions Based on Cation Valence of the Chloride Salt and Phosphate Precursor Species With Equations 1–3 for ADP and Equations 4–6 for H_3PO_4 ^a

cation valence	reaction equation	eq
Me^{1+}	$2NH_4H_2PO_4 + 2MeCl \rightarrow Me_2O \cdot P_2O_5 + 2NH_4Cl(g) + 2H_2O(g)$	(1)
Me^{2+}	$2NH_4H_2PO_4 + MeCl_2 \rightarrow Me_2O \cdot P_2O_5 + 2NH_4Cl(g) + 2H_2O(g)$	(2)
Me^{3+}	$6NH_4H_2PO_4 + 2MeCl_3 \rightarrow Me_2O_3 \cdot 3P_2O_5 + 6NH_4Cl(g) + 6H_2O(g)$	(3)
Me^{1+}	$2H_3PO_4 + 2MeCl \rightarrow Me_2O \cdot P_2O_5 + 2HCl(g) + 2H_2O(g)$	(4)
Me^{2+}	$2H_3PO_4 + MeCl_2 \rightarrow MeO \cdot P_2O_5 + 2HCl(g) + 2H_2O(g)$	(5)
Me^{3+}	$6H_3PO_4 + 2MeCl_3 \rightarrow Me_2O_3 \cdot 3P_2O_5 + 6HCl(g) + 6H_2O(g)$	(6)

^aReactions for other dehalogenation processes can be found in eqs S1–S9 in the Supporting Information.

For a two-step phosphate-based process, heating mixtures of salts and phosphate-based precursors leads to the formation of a dehalogenated product as salt cations incorporate into a phosphate glass with concurrent release of gaseous chlorine byproducts (i.e., HCl , NH_4Cl). The alkali-rich phosphate is then mixed with GFCs and vitrified at a higher temperature (typically $>1000^\circ C$) to maximize the chemical durability of the final product. If Fe_2O_3 is added in this process, an iron phosphate waste form will be produced; typically consisting of a mixture of both crystalline phases and glassy phases.^{11,65} In a single-step process, any additives for chemical durability enhancement are added to the salt-precursor mixture.^{26,34} Although a single-step process could potentially reduce processing complexity, initial studies have shown reduced dechlorination efficacy due to the increased melting temperature of the mixtures once the GFCs are added to the dehalogenation reagent (i.e., ADP, H_3PO_4).²⁶ Additionally, when Fe_2O_3 was added during the dehalogenation step in one study,²⁶ several additional elements (i.e., P, K, Fe, I, Cs) were

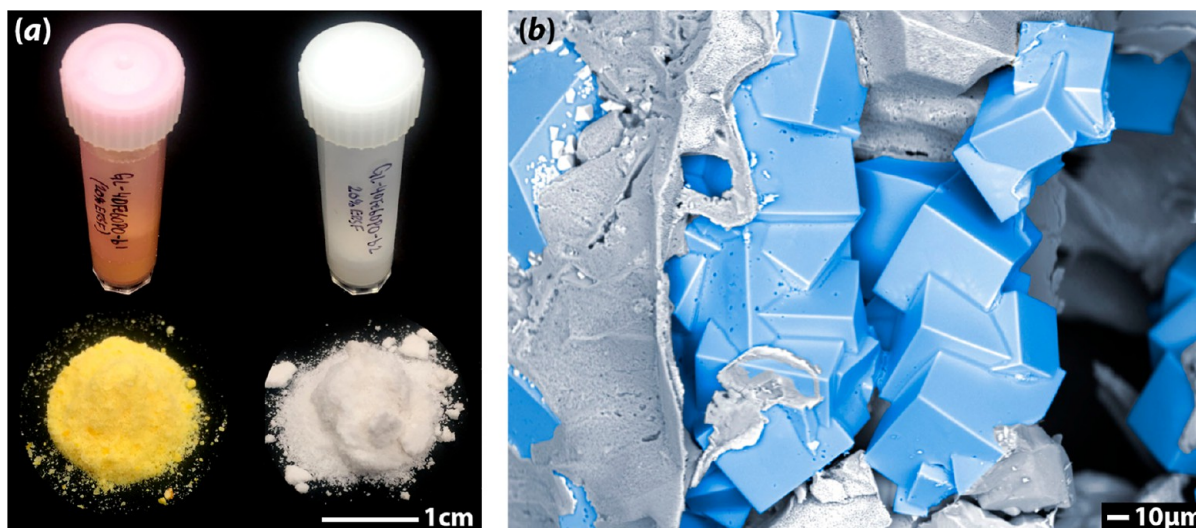


Figure 4. (a) Pictures of the solid condensates collected after salt dehalogenation showing (left) an attempted dehalogenation with Fe_2O_3 in the crucible with ADP and (right) a simple dehalogenation with only ADP. (b) Pseudocolored scanning electron micrograph of the recovered condensate product from the attempted one-step process. Reprinted with permission from Riley et al.³⁴ Copyright 2021 Pacific Northwest National Laboratory.

observed in the recovered NH_4Cl product (see Figure 4) and is likely yellow in color due to the Fe_2O_3 present.^{26,34}

For U.S. DOE-NE projects, salt waste simulants were designed to represent chloride-based waste salts from pyroprocessing of UNF with the representative fission product concentrations increased for traceability within waste forms during chemical durability tests. The actual salt waste stream will change based on the number of fuel batches processed within the electrolyzer. The waste salt composition for treated EBR-II fuel used to develop the glass-bonded sodalite ceramic waste form was based on a once-through processing of 300 driver rods.⁴⁹ Simplified salt simulants of simple salt mixture (SSM),⁶⁶ ER(SF),²⁶ ERV2,^{26,47,67} and ERV3^{68,69} were used in recent studies to evaluate the efficacy and performance of dehalogenation and radionuclide immobilization processes to generate iron phosphate waste forms with different dehalogenation reagents, GFCs, and heat-treatment processes (see Table 3).³⁴

For the simulant salts, some elements were used as surrogates for other elements expected to have similar distributions and release behaviors, e.g., NdCl_3 was used to represent mixed RE elements, CeCl_3 was used to represent

actinides. These salts have been reacted with phosphate precursors to study dechlorination efficiency, temperature requirements, and time requirements to reach reasonable end states for vitrification.^{26,32,68–71} The use of advanced methods during pyroprocessing, including electrolytic removal of trace actinides and lanthanides and melt crystallization, will change the waste salt composition significantly, but materials made with mixed simple salts indicate characteristic elemental distributions and release behaviors from phases comprising the waste form. Experiments performed with nonradioactive simulants can inform similar processes made with radioactive wastes but at a much lower cost to experimentalists.

In addition to the multicomponent simulants, single-salt studies using CsCl , KCl , LaCl_3 , LiCl , NdCl_3 , and SrCl_2 were conducted to determine element distributions and identify host phases in the resulting materials.⁷⁰ Results showed a variety of crystalline phases formed upon slow cooling, including some phases that were not observed during similar tests with the ERV2 simulant, e.g., $\text{K}_{7.33}\text{Fe}_{10}(\text{PO}_4)_{12}\text{O}_{0.66}$, $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$. These experiments built upon earlier foundational work by Donze et al.⁵⁷ with multicomponent chloride salt mixtures and Siemer³⁹ with H_3PO_4 treatment of alkali chloride salts.

4.1. Ammonium Hydrogen Phosphate (ADP & DHP)

Precursors. Using a furnace connected to a distillation apparatus, ADP can be reacted with a salt simulant such as ERV2 to produce an intermediate phosphate product that can be stabilized later with GFCs during vitrification (see Figures 3 and 5). Here the salt is reacted at $T \leq 600^\circ\text{C}$ to dehalogenate the fission product salts to their oxide form and the off-gas products are captured in a set of condensers. Off-gas reactions produce NH_4Cl , H_2O , and HCl as shown in eqs 1–3 (Table 2).²⁶ Effective dehalogenation is primarily dependent upon the $\text{NH}_4^+:\text{Cl}$ molar ratio but is also dependent upon heating rate and dwell times at different temperatures. Incorporating excess ammonium by reacting $(\text{NH}_4)_2\text{HPO}_4$ (DHP) with ERV2 salt simulant did not effectively dehalogenate the salt resulting in residual Cl left after that step.²⁶ This is partly due to the lower thermal stability of the $(\text{NH}_4)_2\text{HPO}_4$, which likely resulted in

Table 3. Summary of Mixed Salt Compositions (in Mass %) Evaluated to Date, Including SSM,⁶⁶ ER(SF),²⁶ ERV2,^{26,67} and ERV3^{68,69}

salt	SSM	ER(SF)	ERV2	ERV3
CeCl_3	-	0.002	5.00	5.00
CsCl	-	5.18	-	7.01
CsI	-	-	7.00	-
KCl	44.29	40.52	38.68	39.06
KI	-	3.09	-	-
LaCl_3	-	1.55	-	-
LiCl	36.29	33.09	32.32	32.05
NaCl	19.42	9.88	9.00	9.01
NdCl_3	-	2.01	5.00	4.87
SrCl_2	-	3.13	3.00	3.00
YCl_3	-	1.55	-	-

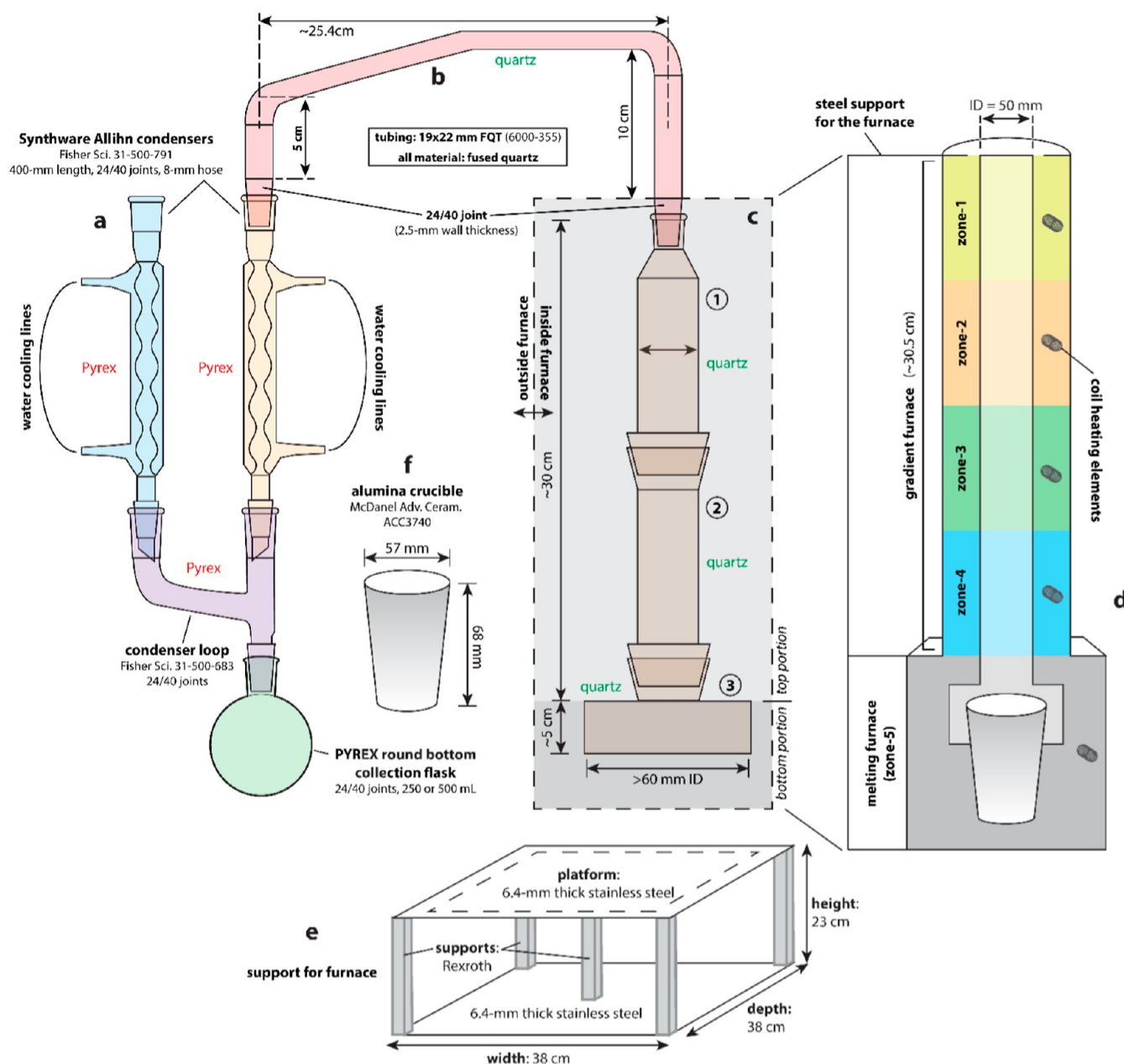


Figure 5. Schematic of the generation-2 dechlorination apparatus showing the (a) dual Allihn condenser system, (b) jumper piece between the condensers and the furnace glassware, (c) furnace with off-gas glassware (circled numbers are different pieces of glassware discussed in the text), (d) more detailed view of the furnace showing all five separately heated zones, (e) support for the furnace, and (f) 250 mL alumina crucible for holding the reactants. The drawings are not to scale. Reprinted in part with permission from Riley et al.³² Licensed under CC-BY-NC-ND 4.0.

decomposition prior to the dechlorination reactions. Thus, it is expected that maintaining a NH_4Cl molar ratio >1 will produce fully dehalogenated salts under the ideal heat-treatment process, but the ideal reagent for this is ADP compared to DHP due to the higher thermal stability of ADP. Different dehalogenation apparatus designs have been investigated to maximize system performance and efficiency, which include a single-zone furnace with dual Friedrichs condensers (Figure S1, Supporting Information)²⁶ and a five-zone gradient furnace with dual Allihn condensers (Figure 5).^{32,65} Second-generation modifications included a custom 5-zone gradient furnace and increased snorkel inner-diameter to mitigate clogging due to NH_4Cl buildup.³² These enhancements led to notable increases in NH_4Cl yield and a 2.5-fold mass increase in batch size.

4.2. Phosphoric Acid Precursor. In phosphoric acid-based dechlorination, the acid is combined with salt, forming an aqueous slurry that is heated to evolve H_2O and HCl off-gassed products [eqs 4–6]. The dechlorinated product is a solid alkali phosphate glass like other phosphate-based dechlorination methods described previously. A proof-of-concept study by Siemer first demonstrated single-step phosphoric acid-based dechlorination of LiCl – NaCl – KCl mixtures combined with Fe_2O_3 .³⁹ The ratio of alkali, iron, and phosphorus were noted as an important condition for complete dechlorination and chemical durability of the final glass. Recently, Murray et al.²⁷ and Werth et al.⁶⁶ have investigated the dechlorination efficacy and mechanisms during heating in detail. Their work considered the processing conditions for phosphoric-acid based dechlorination of SSM

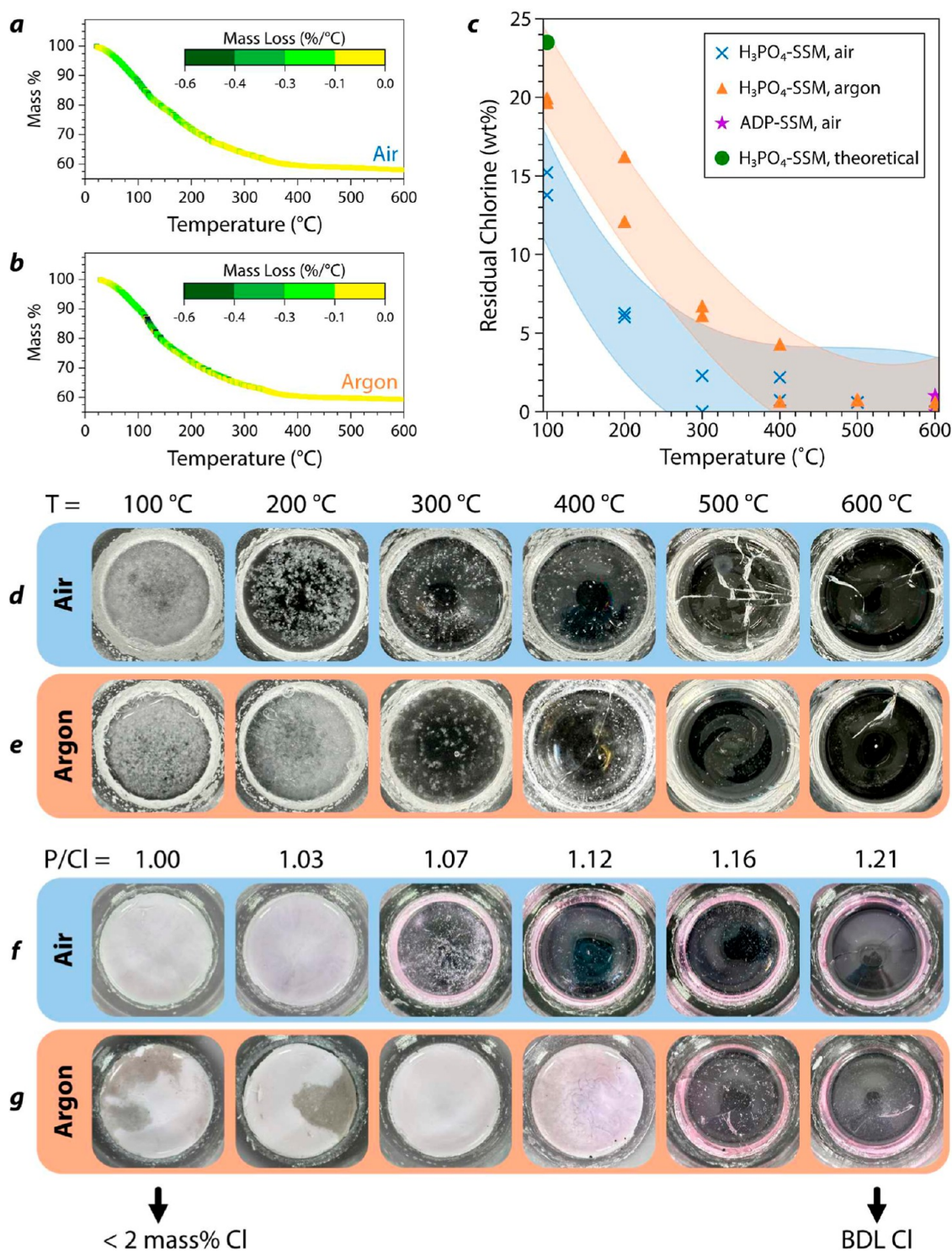


Figure 6. Results from dechlorination with a phosphoric acid precursor and the SSM simulant. Mass loss during dechlorination of a simple salt mixture in an (a) air and (b) argon environments. (c) Residual chlorine content in samples produced from phosphoric acid-based dechlorination of SSM simulant ($\text{P}/\text{Cl} = 1$). The legend labels samples by their salt mixture, phosphate precursor, and dechlorination environment. Sample appearance after dechlorination of the SSM simulant in (d) air and (e) argon environments. Sample appearance after dechlorination of the ERV3 mixture in (f) air and (g) argon environments. Callouts show the residual chlorine content for both the air and argon ERV3 samples. Reprinted in part with permission from Werth et al.⁷² Copyright 2025 American Chemical Society.

(48LiCl–33KCl–19NaCl mol %) and ERV3 salt mixtures (Table 3) in a two-step process. Dechlorination was performed in silica crucibles using a continuous heating profile to temperatures between 100 and 600 °C. Tests were conducted in air and in argon to account for the possibility of

implementation in an argon-atmosphere hot cell. The ratio of H_3PO_4 to Cl (P/Cl) was selected to provide the theoretical amount required for complete dechlorination [$\text{P}/\text{Cl} = 1$, eqs 4–6] and then increased as experimentally determined for complete dechlorination of the particular salt mixture. As the

processing temperature increased, the aqueous slurry transformed into an alkali metaphosphate-based melt.

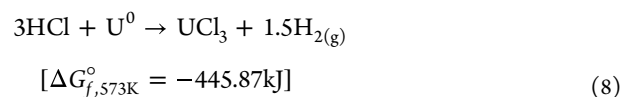
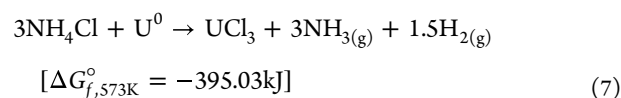
The most rapid mass loss in both environments occurred at $\approx 100^\circ\text{C}$ as shown in Figure 6a,b. Concurrent releases of HCl(g) and $\text{H}_2\text{O(g)}$ were detected in the off-gas. No additional gaseous species were detected. The majority of gas was released around $\approx 100^\circ\text{C}$ with additional spikes in gas release between 200 and 400°C . Figure 6c shows that, for SSM samples with $\text{P/Cl} = 1$, most of the chlorine was removed by 400°C , and complete dechlorination (i.e., below detection limit [BDL] of chlorine using ICP–MS) was consistently achieved after processing $\geq 500^\circ\text{C}$. Completely dechlorinated samples were X-ray amorphous and composed of metaphosphate units. For ERV3, a $\text{P/Cl} > 1$ was required to consistently achieve BDL of chlorine at 600°C , as shown in Figure 6f,g. Reactions between the acidic aqueous solution and ERV3 during heating are more complex than the SSM due to the presence of the trivalent lanthanides, which favor the formation of insoluble oxide crystals and retention of chloride anions. Oxygen in the environment appeared to play a role in dechlorination of both SSM and ERV3 salt mixtures at temperatures $\leq 400^\circ\text{C}$, where thermally driven dehydration and condensation reactions of phosphoric acid dominate. At higher temperatures, where reactions are dominated by polymerization of the glass structure, oxygen partial pressure (p_{O_2}) does not appear to play a major role in dechlorination.

4.3. Hot Cell Implementation for Waste Form Production. A study was performed at the Idaho National Laboratory in 2022–2023 to evaluate the option of producing a single system dechlorination and vitrification apparatus (called DeVA)⁷³ for use in a hot cell facility. The system design goals included evaluation of the system footprint requirement in a hot cell, estimates of total waste salt throughput, and estimates of waste form volumes for processing. Several additional options were conceptualized for this system, including a 1-step vs 2-step dechlorination + vitrification process (e.g., adding GFCs into the furnace remotely after dechlorination), options for introducing active cooling, as well as options for stirring the melt for improved homogeneity and decreased melting times required for full reactions to take place.

Some of the remaining unknowns for implementation of this type of prototype system include the maximum temperature requirements for such a furnace (i.e., dictated by maximum melting temperatures desired for processing) and the required materials of construction. The maximum temperature requirement is dictated by the need for melting refractory components in the glass, which includes high-melting GFCs (e.g., Al_2O_3) that might be needed for stabilizing certain waste stream compositions. The materials of construction include the melter containment shell and the possibility of a melter liner comprised of a refractory ceramic material (e.g., alumina, silica) to prevent corrosion of the containment. These types of conceptual design efforts are required to push the technology development of these systems to higher technology readiness levels.

4.4. Off-Gas Capture and Recycle. As previously mentioned, there is a motivation to recycle Cl removed from the salt in a dehalogenation process based on its value/radioactivity due to its isotopic concentration. Specifically, this means to return the Cl to either an electrorefiner or molten salt fuel (i.e., ^{37}Cl). Given that fissile materials (U, Pu, TRU) are not currently produced industrially as chlorides, there will be a

need to convert fissile material from available forms such as oxides or metals to chloride forms. Two of the chemical forms of dehalogenated Cl discussed in this review are HCl and NH_4Cl . Either of these compounds can be reacted with actinide metals to form actinide chlorides. Thus, two needs can be met by reacting the generated HCl or NH_4Cl with actinide metals. Consider the following reactions shown in eqs 7 and 8 using U as the model actinide. Both are spontaneous reactions up to 573 K , based on Gibbs free energies of formation thermodynamic calculations with HSC Chemistry (v9; Outotec, Finland).



The synthesis of actinide chlorides using NH_4Cl via eq 7 has been demonstrated by several research groups.^{74–79} Two distinct approaches have been reported: (1) production of pure actinide chlorides^{74–76} and (2) direct formation of actinide chlorides within molten salt mixtures.^{77–79} While pure actinide chlorides provide greater process flexibility, in-situ formation within molten salts offers better redox control by maintaining the preferred oxidation state during synthesis. This controlled environment can eliminate downstream processing steps, such as the reduction of UCl_4 to UCl_3 , which would otherwise be required when using alternative chlorination methods.

An example of preparation of UCl_3 in a mixed salt was reported by Herrmann et al.⁷⁹ where NaCl or LiCl–KCl was premixed with U or UH_3 powder and NH_4Cl powder. The powder was heated to 773 K for the reaction and higher if needed to melt the resulting salt mixture. Rood et al.⁷⁸ has recently reported a modification of this process in which NH_4Cl vapor is bubbled into premelted LiCl–KCl in which U metal is submerged.⁷⁸ NH_4Cl decomposes into NH_3 and HCl starting at about 338°C . Rood presented data that indicates the gases readily absorb in LiCl–KCl as NH_4Cl and react with U^0 to cause UCl_3 to dissolve in the salt ($\text{U} > 5$ mass % reported). This approach can be attractive for directly linking the off gas from a dechlorination unit to a molten salt pool in which the UCl_3 can be dissolved. Further research is needed to optimize this process for high efficiency of NH_4Cl utilization, given that it has limited absorption capacity in the molten salt and will condense on cold surfaces from the gas phase.

Similarly, HCl has been reported to rapidly react with U metal to form UCl_3 either as a pure product or a mixed salt.^{37,80,81} Given that anhydrous HCl remains in the gas phase even at room temperature, linking dechlorination and actinide chlorination processes is even more logical than it is for NH_4Cl . This motivated the study reported by Perhach et al.⁸⁰ on chlorination of U^0 in LiCl–KCl with HCl gas bubbled into the salt.⁸⁰ In very limited testing with U wire submerged in molten NaCl–CaCl_2 , 36% of the uranium was chlorinated over a 9 h process with the final U concentration equal to 0.65 mass %. HCl demonstrates much lower absorption in NaCl–CaCl_2 than NH_4Cl demonstrates in LiCl–KCl . Thus, it is more challenging to achieve a high efficiency of HCl utilization in the process reported by Perhach et al.⁸⁰ This approach of

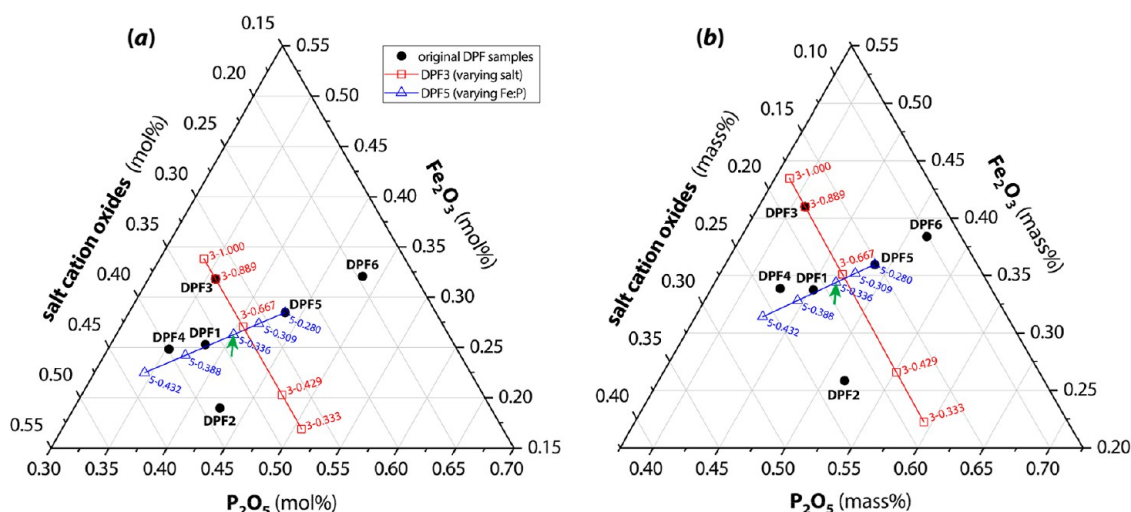


Figure 7. Expanded P_2O_5 – Fe_2O_3 –salt ternary diagram for DPFG3 (red) and DPFG5 (blue) series glasses in (a) mol % and (b) mass %. The location of the DPFG–336 reference material is shown as “0.336” and designated with the green arrow. This figure was modified from the original by Ebert and Fortner^{82,83} and is reprinted with permission. Copyright 2019 Argonne National Laboratory.

bubbling HCl into the salt needs to also be tested in LiCl–KCl.

4.5. Other Considerations. When selecting the dehalogenation precursor material, other considerations must be assessed. Something not mentioned until now is that unwanted secondary reactions can occur between halide salts and nitrogen (NH_4^+)-based compounds (e.g., ADP and DHP), which include contact explosives such as NCl_3 , NBr_3 , NI_3 , NH_4I_3 .³¹ Radioiodine (i.e., ^{129}I), a fission product, will be present in the ER salt, albeit in low concentrations, so these types of unwanted compounds could form if ADP or DHP are used as the dehalogenation reagent. However, the likelihood of these forming is quite low. This provides one very important justification for choosing H_3PO_4 over ADP or DHP. One benefit for using ADP or DHP is that these compounds are solid at room temperature whereas H_3PO_4 is a liquid and a strong acid that would require specialized handling.

5. IRON PHOSPHATE MATERIAL

As discussed in Section 4, dehalogenation of salt waste from pyroprocessing results in a dehalogenated waste form containing salt cations in phosphate and oxide forms. To improve durability, either (1) Fe_2O_3 or (2) Fe_2O_3 plus a sodium borosilicate glass (NBS) is added prior to vitrification.⁶⁵ To correlate iron phosphate waste form composition to final waste form properties, multiple studies have investigated the effects of varying Fe/P molar ratios and processing conditions such as cooling rates to the final microstructure and chemical composition.^{26,30,33,68–70} Samples described within this paper often include the prefix “DPFG” which describes dehalogenated phosphate samples with Fe_2O_3 .

5.1. Composition–Property Relationships. Initial studies used ER(SF) salt simulant with fixed mass ratio of ADP/ER(SF)/ Fe_2O_3 .²⁶ Differences included target masses, the step at which Fe_2O_3 was added, heating profile, and crucible material that was used. These initial experiments revealed that DPFG-A (31%) had significantly lower dechlorination efficiency than DPFG-B (64%), which was attributed to Fe_2O_3 being added after the dehalogenation (using a 2-step process for DPFG-B, rather than a 1-step process used for DPFG-A), a lower heating rate (allowing for a better reaction), and a smaller-

volume charge for DPFG-B.²⁶ Additionally, the appearance of DPFG-A suggested a second phase was present (see Figure 4), and X-ray diffraction (XRD) analysis showed that dechlorination was incomplete.

Based on the results of DPFG-A and DPFG-B, subsequent compositions were formulated to investigate the effects of NH_4/Cl and Fe/P molar ratios on dehalogenation efficiency and vitrification effectiveness. The compositional variation study used ERV2 salt simulant and included DPFG-1h, DPFG-2, DPFG-3, DPFG-4, DPFG-5, and DPFG-6 made with different amounts of salt, ADP, and Fe_2O_3 ,²⁶ where their locations on the P_2O_5 – Fe_2O_3 –salt ternary diagram are shown in Figure 7. DPFG-2 and DPFG-5 displayed a high amount of amorphous material due to their low Fe/P molar ratios. DPFG-3, which has a higher salt loading than DPFG-5, contained a mixture of dendritic phases and dendrite-free regions. The dendritic phases were primarily composed of $Li_3Fe_2(PO_4)_3$ as revealed by XRD analysis. DPFG-2 contained a minor amount of crystalline material comprised of $KFeP_2O_7$ and $Li_3Fe_2(PO_4)_3$. DPFG-6, with the lowest salt content, also exhibited a large amount of crystallization. No trends were observed between lithium iron phosphate phase formation and ERV2 mass fraction, Cl/P molar ratio, or the Fe/P molar ratio. Bulk densities of all annealed and quenched glasses were approximately 3×10^3 kg/m³. The apparent porosity in all quenched samples was <0.3 vol %. Annealed samples ranged from 0.21 to 4.58 vol % porosity.

Two variations on DPFG-4 were made: DPFG-4 was dehalogenated with ADP and DPFG-4b was dehalogenated with DHP. For these two DPFG-4 variations, the moles of P present in each phosphate additive were the same but the active dehalogenating cation (i.e., NH_4^+) differed by a factor of 2. These materials were used to assess the dehalogenating efficiency of these two reagents when the molar ratio was $NH_4^+:Cl < 1$ for DPFG-4 and $NH_4^+:Cl > 1$ for DPFG-4b. Two additional sets of waste form materials were produced based upon DPFG-3 with different Fe/P molar ratios and upon DPFG-5 with different salt loadings, which were documented by Ebert and Fortner.⁸⁴ The locations of these glasses on the P_2O_5 – Fe_2O_3 –salt ternary diagram are shown in Figure 7. DPFG-3 compositions maintained a consistent salt molar fraction while

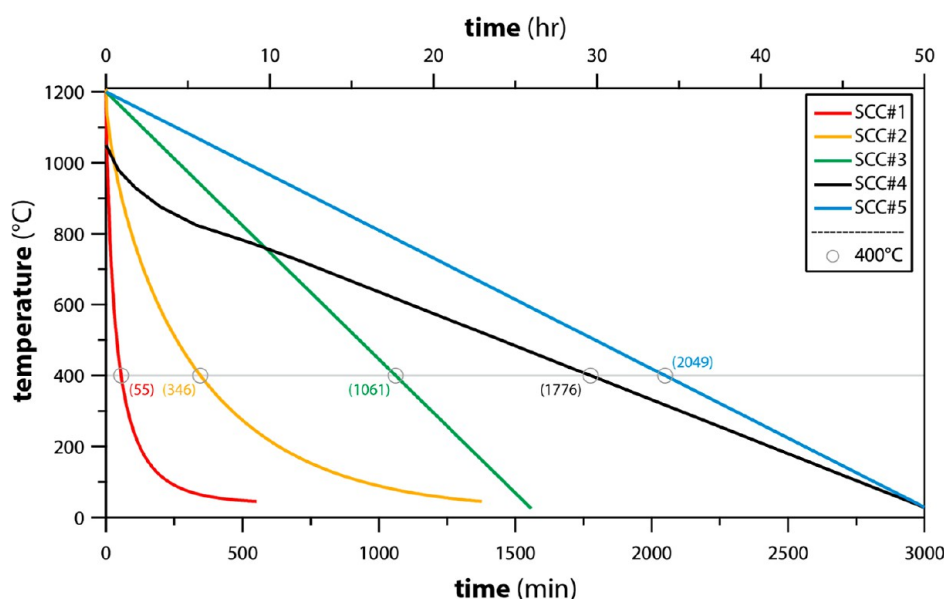


Figure 8. Cooling curves evaluated for processing DPF5–336. Curve SCC#1 is a theoretical curve. SCC#2, #3, and #5 results are found in Riley et al.⁶⁹ and SCC#4 results are found in Riley and Chong.⁷⁰ The numbers drawn on the horizontal line represent the time (minutes) required to get to 400 °C. Reprinted with permission from Riley et al.⁶⁸ Copyright 2023 Pacific Northwest National Laboratory.

DPF-5 compositions maintained a consistent Fe/P molar ratio. DPF-5 had a higher than stoichiometric P/Cl molar ratio of ≈ 1.5 while all formulations, except for DPF-4, were designed to completely dehalogenate the salt.

Reduced variable studies performed on materials made with fewer components, e.g. single-salt studies compared to a complex simulant like ERV2, can provide insights used to predict behaviors of materials with more complex compositions (i.e., glass + waste).⁷⁰ Waste form experiments on simple salts formulated with DPF-5 using a canister centerline cooling (CCC) (see Section 5.3 for further discussion on heat treatments) found that alkali metals and alkaline earths generally form an (alkali or alkaline-earth)-iron phosphate phase with varying stoichiometries, and REs form monazite or xenotime crystals (REPO_4).⁷⁰ However, there were several notable differences.⁷⁰ Single salt experiments with CsCl displayed good mixing of major components (P, Fe, Cs) while LaCl_3 phase separated into three distinct layered phases, which may be attributed to the higher melting temperature of the mixture than the CCC heat-treatment. While three layers were visible in the LaCl_3 phase, only two primary phases were identified by XRD, i.e., FePO_4 and monazite. The removal of Fe and P from the glass phase, despite the high chemical durability of monazite, diminishes the durability of the glass.

Following the initial study with DPF-1h through DPF-6, a series of additional materials were made that included variations of DPF-3 (varying salt loading at a 0.280–0.432 mole fraction of salts in oxide form with fixed Fe/P molar ratios) and DPF-5 (varying Fe/P molar ratio at 0.333–1.000 with fixed salt cation loadings) - see Figure 7. The goal of this work was to further optimize a starting point for expanded studies. From this study, the DPF5–336 glass was selected as the reference material for future work,⁸² which is discussed below in Section 5.2. This material had high salt cation loading (i.e., 13.9 mass % for ERV2 salt)⁸⁴ and reasonable chemical durability.^{34,82}

Crystalline phase formation, primarily induced by slow cooling, has been shown to deplete glass-forming elements like

iron and phosphorus from the glassy matrix, significantly compromising the chemical durability of the waste form.^{69,85,86}

To mitigate this issue, it is hypothesized that the addition of borosilicate glass can help stabilize the GFAs within the phosphate phase, preserving the integrity of the waste form.^{65,87} Preliminary studies found additions of 5 mass % sodium borosilicate (NBS) glass to DPF5–336 generates a waste form material comparable to the durability of a quench DPF waste form (see Section 5.5) with a high fraction of amorphous phase.⁶⁵ In all samples additions of NBS resulted in phase separation between the phosphate and silicate phases. Additions of 2.5 mass %, 15 mass % and 30 mass % NBS resulted in a highly crystalline material that performed similar to phosphate glasses with no iron or aluminum additions. Crystalline phases consisted primarily of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and undissolved Fe_2O_3 .

In addition to optimizing iron-phosphate material chemistry for salt waste immobilization, recent studies have explored the structure–property relationships of iron-phosphates with additions of glass modifiers, such as sodium, using machine learning and artificial intelligence (ML/AI)-based approaches.^{88–90} Studies found that, in sodium–iron-phosphate glasses, increasing the Fe_2O_3 molar concentration from 24 to 28.5 mol % maximized network connectivity and corner-sharing $[\text{PO}_4] - [\text{FeO}_x]$ became dominant when $\text{Fe}_2\text{O}_3 > 15$ mol %.^{89,90} Understanding structure–property relationships is critical for downselecting next generation material candidates with improved chemical durability following slow cooling, which it will undergo after melting and pouring into a canister or within the canister (if using an in-can melter approach) during the high-temperature vitrification process.^{68–70}

5.2. Iron Phosphate Reference Material. Based on these studies, a reference iron phosphate waste form (i.e., DPF5–336)⁸⁴ was developed in collaboration between various institutions including Pacific Northwest National Laboratory, Argonne National Laboratory, Idaho National Laboratory, University of Nevada, Reno, and Missouri University of Science and Technology (Figure 7). The experiments

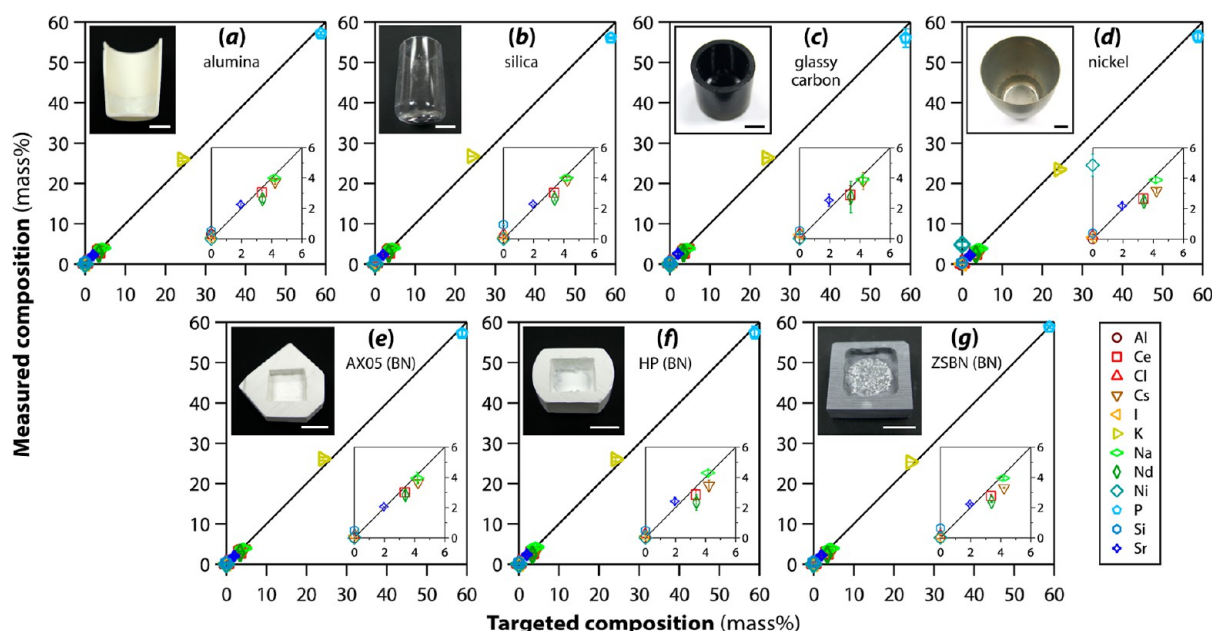


Figure 9. Summary of measured-versus-targeted glass compositions following dechlorination during crucible evaluation tests with (a) alumina, (b) silica (fused quartz), (c) glassy carbon, (d) nickel, (e) AX05 boron nitride, (f) HP boron nitride, and (g) ZSBN boron nitride. Each plot has an inset that is a magnified view of the 0–6 mass % window; the common legend is shown on the bottom right. Each data point is an average of three measurements and error bars are included as the standard deviation of those measurements. Each plot also has an inset showing a picture of the crucible used for these experiments; the scalebar shown for each represents 1 cm. Reprinted with permission from Riley et al.²⁶ Copyright 2020 Elsevier.

performed and ongoing data collection efforts are designed to fill technology gaps required to fully understand the extent of limitations with this type of waste form approach based on a recent roadmap documenting the required gaps that need to be addressed.³⁴ The primary technology topic areas with associated gaps identified in that roadmap include assessment of waste compositions, the effect of matrix and additives on acceptable glass formation, waste processing variables, waste form properties, waste form acceptance, and waste form performance. All of these are discussed below.

5.3. Heat Treatment Effects on Crystallization. Since waste forms will not be fast cooled through quenching processes in an actual industrial-scale implementation, assessing the properties of the waste form generated using the expected cooling profile of material made in full-size canister is important. Generally, waste form chemical durability is dependent upon the amount of crystallinity that occurs during slow cooling, what types of crystals form, and the elements pulled out of the glass for the crystals to grow leaving behind a residual glass.^{71,91} While uncontrolled crystallization can result in degradation of chemical durability diminishing waste form performance, controlled crystallization can be particularly beneficial.^{17,92} The results of several studies performed to evaluate slow cooling processing-related material properties are summarized within this section. The reference material, DFP5–336, was subject to cooling rates representative of various canister sizes (see Figure 8).^{68–70} Initial assessment of crystallization at cooling rates representative of a cooling profile for a 0.61 m diameter canister in DPF5–336 (CCC also represented by curve SCC#4 in Figure 8), found that alkali and alkaline-earth cations formed iron-phosphate-based phases, e.g., $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, $\text{K}_3\text{Fe}(\text{PO}_4)_2$, CsFeP_2O_7 , $\text{NaFe}(\text{PO}_3)_3$, and KFeP_2O_7 .⁶⁸ The RE elements in these samples formed monazite (REPO_4) phases.⁶⁸ REPO_4 can form

as monazite or xenotime, depending upon the RE element present in the structure; these crystalline forms are very effective final waste forms for RE elements due to their high chemical durability and mechanical integrity.^{93–95}

Samples cooled from 1200 °C using SCC#2, SCC#3 and SCC#5 cooling profiles found that undissolved Fe_2O_3 was present at the bottom of all alumina crucibles with large regions found in the bulk.⁶⁹ No undissolved Fe_2O_3 was found in samples cooled from 1050 °C using the SCC#4 cooling profile.⁶⁸ Monazite (REPO_4) was present in samples SCC#2, SCC#3 and SCC#5; however, the crystal size, shape, and morphology differed from the sample cooled using SCC#4, where the average monazite crystals were an order of magnitude smaller, $\approx 250 \mu\text{m}$ compared to $\approx 12 \mu\text{m}$ in length. Fe_2O_3 precipitated adjacent to the monazite crystals, suggesting that the precipitation of monazite depleted the surrounding region of P_2O_5 . Monazite formation resulted in a bulk region high in Fe_2O_3 and Al_2O_3 content leading to a reduction in chemical durability.⁶⁹ All samples contained Al_2O_3 due to dissolution of the alumina crucible. Crystalline fractions were similar in samples SCC#2, SCC#3 and SCC#5, ranging from 35.66–41.14 mass %. The quench sample (SCC#1) was primarily amorphous with small amounts of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.

5.4. Material Compatibility. Material compatibility tests have been conducted with phosphate melts over the last several years. These studies include traditional melter containment materials such as Monofrax K-3, different types of crucible construction materials (e.g., boron nitride, fused quartz, alumina), as well as different metals and metal alloys (e.g., Ni, Inconel 690, Inconel 693). These studies were conducted for different purposes including small-scale studies, larger-scale melter compatibility tests, and melter electrode compatibility tests. Most lab-scale phosphate glass samples documented in the literature are produced using traditional

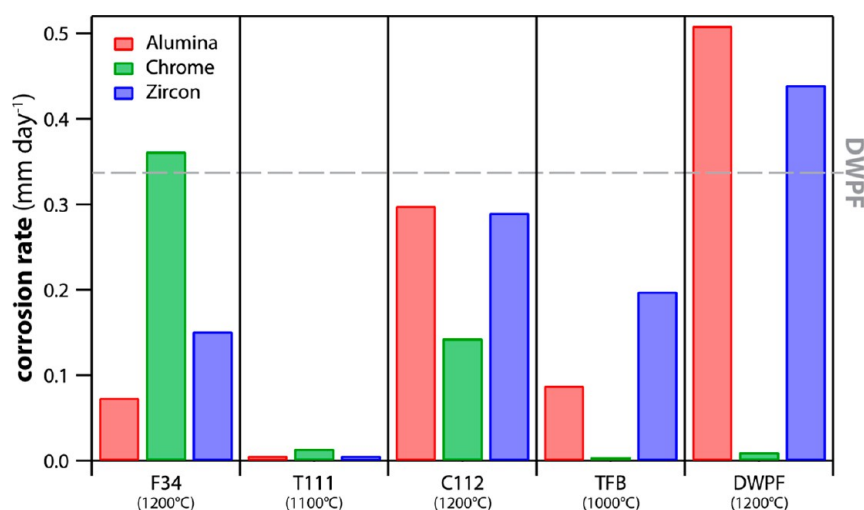


Figure 10. Corrosion rate, measured at the melt line, for three commercially produced refractories (cylindrical rods) rotated at 9.2 rpm for 24 h in an iron phosphate melt at the temperature shown. Reprinted with permission from Day and Ray.⁹⁶ Copyright 2013 Idaho National Laboratory.

refractory crucibles such as alumina, silica, or AZS (alumina-zirconia-silica) since it is known that the traditional metal alloy crucible materials used for making borosilicate glasses (e.g., Pt, Pt/Rh, Pt/Au) can dissolve in phosphate melts. This means that these refractory components can be dissolved, even if only in small amounts, into the phosphate melt.

Crucible compatibility tests documented in a recent study included the evaluation of seven different types of crucibles for dechlorination with ADP and ERV2 salt simulant (see Table 3) and a binary melt ($\text{Fe}_2\text{O}_3\text{--P}_2\text{O}_5$) quench: alumina, silica (fused quartz), glassy carbon (GC), Ni metal, and three types of boron nitride (i.e., AX05, HP, ZSBN).²⁶ In the dechlorination experiment with ADP, the Ni crucible dissolved into the melt showing ≈ 5 mass % incorporation into the sample, the product remained stuck to the BN crucibles, and there were indications of corrosion in the glassy carbon crucible. Among the materials investigated, fused quartz and alumina yielded the most favorable results, Figure 9. The binary melt quench experiment found that fused quartz and glassy carbon crucibles had superior performance compared to BN and alumina crucibles. From these experiments, the most promising crucible material for dechlorinating salts with ADP was determined to be fused quartz. Based on subsequent tests from that same study,²⁶ alumina crucibles worked well for the vitrification step, but Al_2O_3 did dissolve within the glass melt.

Iron phosphate corrosion behaviors in refractory materials were also documented by Day and Ray,⁹⁶ which includes K-3, high-purity alumina, and aluminosilicate (83% SiO_2 , 17% Al_2O_3) materials. They stated that corrosion was minimal in these materials.⁹⁷ Inconel 690 and Inconel 693 corrosion tests were conducted in iron phosphate melts to assess their applicability for melting Hanford waste compositions (i.e., AZ102 low-activity waste or LAW) using Joule-heated ceramic melters (JHCM) employed at the Hanford Waste Treatment and Immobilization Plant (WTP) in Richland, WA. These Inconel alloys are the typical compositions used for paddle electrodes in the JHCMs. The results, which are discussed in detail elsewhere,^{96,98} showed that the Inconel coupon corrosion behaviors were within acceptable limits to be implemented as electrodes for JHCMs processing these compositions. They also noted that Inconel 693 showed significantly less corrosion than the Inconel 690 alloy. Sevigny

et al.²² and Hsu et al.²⁴ documented <2.5 mm year⁻¹ and ≈ 1.6 mm year⁻¹ corrosion rates, respectively, for Inconel 693 electrodes in iron phosphate melts with 26% AZ102 LAW simulant. Day and Ray⁹⁶ noted that these corrosion rates were similar to those of borosilicate leach rates measured for JHCMs at Pacific Northwest National Laboratory (PNNL, in Richland, WA) and the Defense Waste Processing Facility (DWPF; Savannah River Site in Aiken, SC) ranging between 1.1 and 2.8 mm year⁻¹ (see Figure 10).^{96,97,99,100} In Figure 10, the F43 melt is $43\text{Fe}_2\text{O}_3\text{--}57\text{P}_2\text{O}_5$ (mass %). The T111, and C112 iron phosphate melts contain 35 and 50 mass % of simulated waste from Hanford tanks T111 and C112, respectively. The TFB iron phosphate melt contains 30 mass % of Hanford waste from Tank Farm B, average composition. DWPF is a borosilicate melt containing 28 mass % of a simulated waste, Savannah River.

Ten-day melting experiments at 1030 °C using Monofrax K-3 refractory material containing 26 mass % high sodium and high sulfate Hanford AZ102 waste concluded that melter component corrosion was acceptable.²² The corrosion of phosphate melts with traditional melter containment vessels (e.g., steel, Inconel alloys, Monofrax K3) is an issue for advancing the technology readiness level of these types of materials and requires additional study.

Interactions between molten iron phosphate and refractory materials have been further investigated by Werth et al.¹⁰¹ with a focus on potential crucible containment options, including alumina (Al_2O_3), Monofrax K3, fused quartz, and stainless steel 316L (SS316L). Bars of each material (≈ 5 mm $\times$ 5 mm $\times$ 50 mm) were suspended in molten DPF5–336 in an air or argon environment for 1 and 4 h time periods. Following each experiment, the bars were mounted in epoxy, cross sectioned, and polished. Corrosion was examined optically for material loss in the 13.8 mm region near the melt line, along with scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) of the corroded regions. The extent of corrosion and formation of secondary phases varied greatly depending on the material being tested. A summary of the key takeaways from this study is provided in Table 4 and a visual summary is provided in Figure 11. Additional data are provided in the previous report by Werth et al.¹⁰¹

Table 4. Summary of Iron Phosphate Corrosion Experiments on Alumina, Monofrax K3, Stainless Steel 316L, and Fused Quartz Coupons Documented by Werth et al.¹⁰¹

material	atmosphere influence	melt line corrosion	secondary phases	cracking	penetration
alumina	the maximum thickness of the iron oxide layer at the surface was greater in argon (20 μm) than air (5 μm)	melt line corrosion through the entire bar thickness after 4 h in air; <4 mm ² of material loss at the melt line of other samples; greater material loss at the melt line than other regions	iron oxide formed at the bar surface	no cracking	no penetration beyond the surface layer
Monofrax K-3	thicker oxide layer and deeper penetration in air compared to argon	<4 mm ² of material loss at the melt line; greater material loss at the melt line than other regions	chromium oxide formed a heterogeneous surface layer	no cracking	corrosion along Mg-rich and Al-rich phase boundaries; some areas of extensive subsurface penetration and corrosion (>1 mm penetration depth after corrosion in air for 4 h)
stainless steel 316L	the maximum thickness of the oxide layer was greater in air (1300 μm) than in argon (500 μm); corrosion in argon was concentrated at the melt line, while corrosion in air resulted in pockets of corrosion along the entire exposed surface	up to 14.2 mm ² of material loss at the melt line; greater material loss at the melt line than other regions	chromium oxide formed a heterogeneous surface layer; depletion and migration of SS components resulted in regions with disparate alloy compositions	no cracking	total penetration up to 1300 μm (oxide layer + intergranular corrosion) after 1 h
fused quartz	atmosphere did not impact corrosion	no observable difference between corrosion at the melt line compared to other regions (i.e., no "neck")	no secondary phases	transverse cracking at the surface up to 300 μm deep resulting from DPF5–336 penetration	multiple areas with penetration depth up to 200 μm into the bar along the entire exposed surface

Alumina bars exhibited resistance to the penetration of the molten DPF5–336 into the bulk of the bar, although degradation of the bar occurred at the glass melt line. After 1 h of exposure, material loss was similar in either environment ($\approx 1 \text{ mm}^2$ in argon and $<1.0 \text{ mm}^2$ in air). Exposure for 4 h in air resulted in corrosion through the entire thickness of the bar at the melt line, while the Ar sample remained intact (shown in Figure 11a). The molten DPF5–336 did not penetrate the thickness of the bar, as glass components were only detected at the surface. A layer rich in Fe and O (presumably Fe_2O_3) formed on all alumina bars on the surface that was exposed to the molten DPF5–336. Similar Fe_2O_3 layers that formed during alumina corrosion have been previously documented by members of this team.⁶⁸ The layer was typically thinnest (often $<1 \mu\text{m}$) at the melt line region, while a thicker layer was observed in the region below the location of the melt line. The greatest thickness of the layer in air samples was 5 μm compared to layer thicknesses of 10 and 20 μm in the 1 h and 4 h Ar samples, respectively.

Monofrax K-3 bar exhibited resistance to loss of material at the surface, although components from the DPF5–336 penetrated along the boundary of Al-rich and Mg-rich phases. A heterogeneous corrosion layer composed of chromium oxide and iron phosphate phases formed over the entire surface of the bar. Material loss measured from the cross section of the neck region was $<1 \text{ mm}^2$ in either environment after 1 h and 3.6 and 2.0 mm² after 4 h in air and argon, respectively. Although material loss was moderate, penetration of glass components into the bar was extensive as shown in Figure 11b. Penetration into the bar was especially prominent in the sample corroded in air for 4 h, with several regions of components from the glass at a depth $>1 \text{ mm}$. In comparison, the greatest penetration depth measured in the sample corroded in argon for 4 h was 520 μm .

The fused quartz bars degraded over the entire surface exposed to the molten DPF5–336, lacking the localized material degradation at the melt line that was observed in other samples. After 4 h, the molten DPF5–336 penetrated up to 200 μm into the bar in both air and argon. The transverse cracks that originated at the interface between the bar and the DPF5–336 are suspected to be the result of thermal stress during sample cooling. The surface cracking resulted in the loss of sections of the sample surface shown in Figure 11c during preparation.

Stainless steel 316L bars were especially susceptible to attack by molten DPF5–336 in either atmosphere, with the greatest material loss at the melt line. The samples developed regions with a heterogeneous corrosion layer composed of chromium oxide, components from the DPF5–336 (Fe- and P-rich residual glass and crystalline phases), and pockets of unoxidized metal consisting of Fe, P, Ni, and Mo. The layer measured up to 1300 and 100 μm thick in samples exposed for 1 h in air and argon, respectively. The DPF5–336 components penetrated the bars by intergranular corrosion. The greatest total penetration depths (oxide layer depth + intergranular corrosion depth) were 1300 μm in air and 500 μm in argon. EDS maps revealed that Mo and Ni migrated from the bulk of the bar to the region adjacent to the corrosion layer. The bar was depleted of Cr in the regions near the Cr-rich corrosion layer. While dispersed regions of extensive corrosion were observed along the entire surface of the sample corroded in air, corrosion of the bar in argon was concentrated at the melt line,

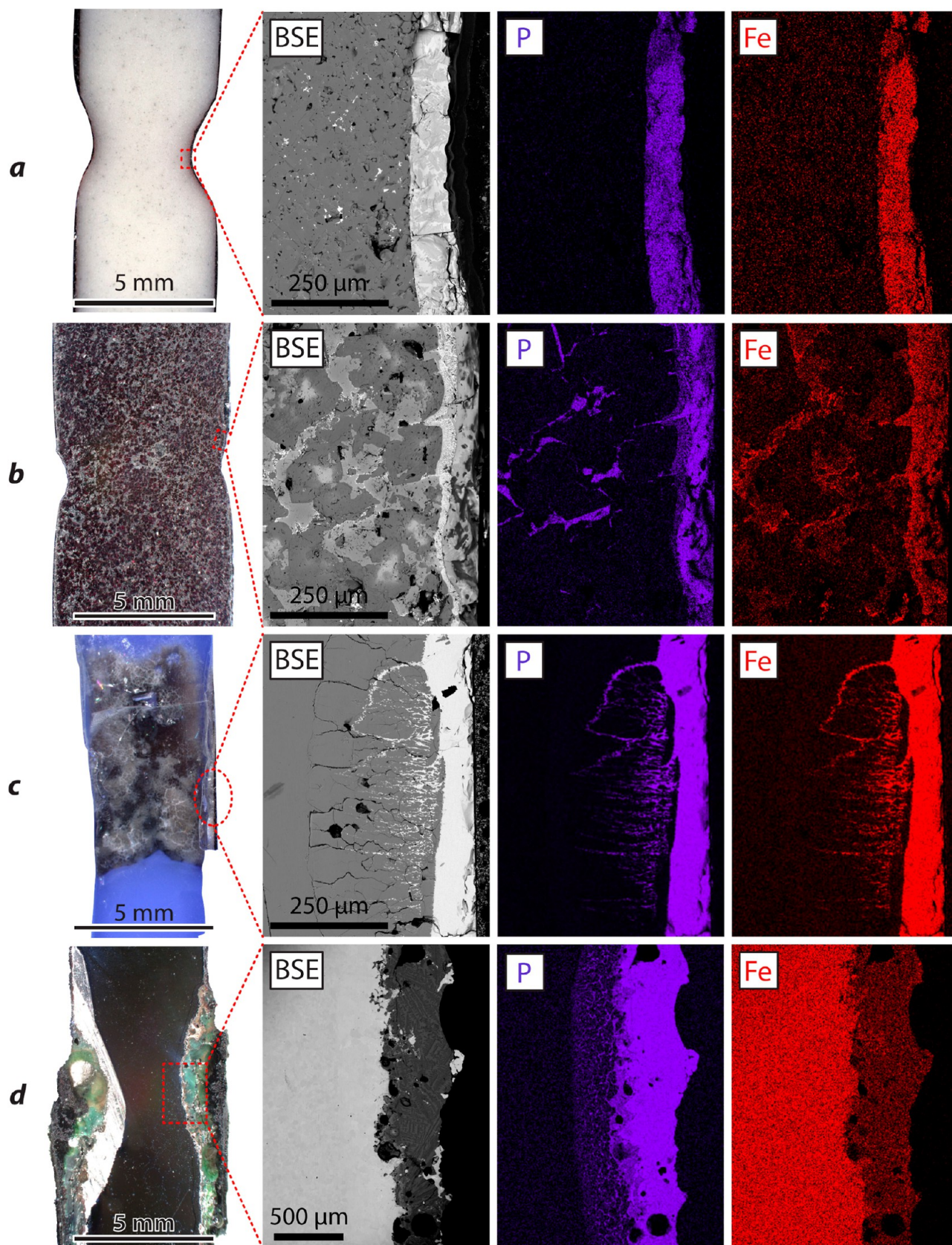


Figure 11. Results of corrosion by DPF5-336 of (a) alumina, (b) Monofrax K-3, and (c) fused quartz for 4 h and (d) stainless steel 316L for 1 h in an argon atmosphere are shown. The blue hue in the optical image in (c) is the epoxy behind the quartz bar. Column-1 represents optical micrographs, column-2 represents scanning electron micrographs, and the two right columns represent energy dispersive X-ray spectroscopy elemental dot maps for P and Fe. Reprinted in part with permission from Werth et al.¹⁰¹ Copyright 2025 Pacific Northwest National Laboratory.

as shown in Figure 11d. The samples exposed for 4 h were not sufficiently intact for analysis due to extensive corrosion.

5.5. Waste Form Chemical Durability. Regulatory acceptance of an iron phosphate waste form for disposal will be based on acceptable physical, chemical, and radiological properties that are controlled during production and the acceptable impact of disposing the waste form on the performance of an engineered repository. Confidence in predicting the retention of radionuclides during the regulated time is based on understanding the waste form degradation mechanism(s) and mode(s) of radionuclide release. Iron phosphate material testing results find that material dissolution behavior is similar to borosilicate glass, with preliminary models based on borosilicate glass, including stage I, II and III behavior (see Figure 12), which are discussed in more detail elsewhere.^{102–104}

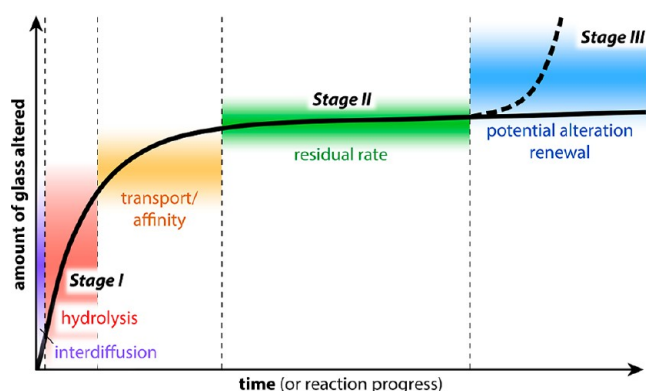


Figure 12. Figure showing the typical leaching progression of glass waste forms. Reprinted with permission from Marcial et al.³⁸ Copyright 2024 Pacific Northwest National Laboratory.

Chemical durability test methods used to determine the degradation mechanism and measure dissolution kinetics include ASTM C1308,¹⁰⁵ ASTM C1220,¹⁰⁶ ASTM C1663,¹⁰⁷ and ASTM C1285,¹⁰⁸ with a summary of these studies being presented in Table S1 (Supporting Information). Four-day ASTM C1308 tests are used to assess intrinsic dissolution rates of different materials under dilute conditions. ASTM C1220 tests are used to measure the effects of increasing dissolved concentrations of material constituents on the dissolution rate. ASTM C1663 vapor hydration tests are used to examine the long-term behavior of materials under drastically accelerated (200 °C) repository conditions, particularly resistance to hydration and corrosion in a humid environment by examining generation of secondary phases from saturated solution. The ASTM C1285 test, also referred to as the Product Consistency Test (PCT), provides insights into how solution saturation influences dissolution behavior and the production of secondary phases on the surfaces of particles.

Over the past five years, significant research has been conducted on the durability and salt retention of various waste form materials, emphasizing the role of composition and processing conditions in influencing their performance. Key findings highlight how increasing salt loadings adversely affect durability and retention, with waste forms containing 34 mass % salt demonstrating superior durability over glass-bonded sodalite with optimal salt waste loadings.⁸⁴ Materials enriched with 27 mol % Fe_2O_3 exhibit noticeably higher durability than

material with <27 mol % Fe_2O_3 , while materials with up to 34 mol % Fe_2O_3 resulted in iron-rich inclusions and lower effective salt waste loading.⁸⁴ Formation of alkali-iron-phosphate crystalline phases depletes the residual glass of both iron and phosphorus thereby reducing chemical durability of the resulting waste form.⁸⁶ Detailed studies at Clemson University, involving 25 samples with varying compositions, highlighted that moderate additions of Fe_3O_4 and Fe_2O_3 improved durability, whereas SnO_2 and high-salt loadings of BaO significantly reduced chemical durability.¹⁰⁹ This study also found that materials synthesized with a P_2O_5 reagent were less durable than those produced with ADP.

Processing methods also significantly impact the durability and performance of these materials. Temperature control during processing emerged as a crucial factor influencing crystal formation and subsequent material durability.⁶⁹ Slowly cooled materials exhibited higher dissolution rates, as the slow cooling process promoted the formation of primary crystalline phases that compromised the integrity of the waste form. This process of primary crystal formation during slow cooling depletes the glass phase of stabilizing elements like iron, leading to a weaker, less robust waste form. Conversely, quenching effectively “freezes” iron into the phosphate glass matrix, preserving the glass phase stability and enhancing overall durability. Materials produced using the CCC profile were found to be less durable and had inferior salt cation retention when compared to rapidly quenched materials lacking crystalline phases. The production environment was also critical; materials produced in fused quartz crucibles showed enhanced durability over those formed in alumina crucibles.⁶⁹

One effective strategy to improve the material durability is to limit the time spent within the 600–900 °C temperature range, thereby minimizing crystal growth.⁸⁵ Another suggestion involves reducing the waste form size, effectively increasing the CCC rate, to minimize unwanted crystal formation. Additionally, the inclusion of silicate glass frit has been recommended to act as a “sink” for cesium and salt cations, potentially preventing detrimental iron-crystalline phase formation. Recent studies have demonstrated that incorporating 5 mass % sodium borosilicate glass frit (NBS3) into DPF5–336 enhanced durability, aligning its performance with advanced glass-bonded sodalite materials (see Figure 13).^{65,87} The goal with this work was to assess differences in stabilities of the target high-activity fission products (i.e., Sr, Cs) within silica and phosphate matrices.

6. PERSPECTIVES AND FUTURE OUTLOOK

Significant progress has been made in electrochemical salt waste management methods in the past decade, which has resulted in several technologies suitable for technology readiness level (TRL) advancement. Each technology has its particular advantages and disadvantages at the commercialization level. For example, immobilizing salt waste within an ultrastable H–Y (USHY) zeolite is efficient with few byproduct waste streams.^{64,110} However, high sintering temperatures increase the overall cost, but may be ameliorated by using a low-temperature binding agent.⁶³ Similarly, dehalogenating using ADP requires high vitrification temperatures. Both zeolite exchange and ADP processes produce gaseous byproducts that have uses in other industrial applications such as the production of UCl_3 for use in electrorefiner operations,^{26,78} generating a closed process.

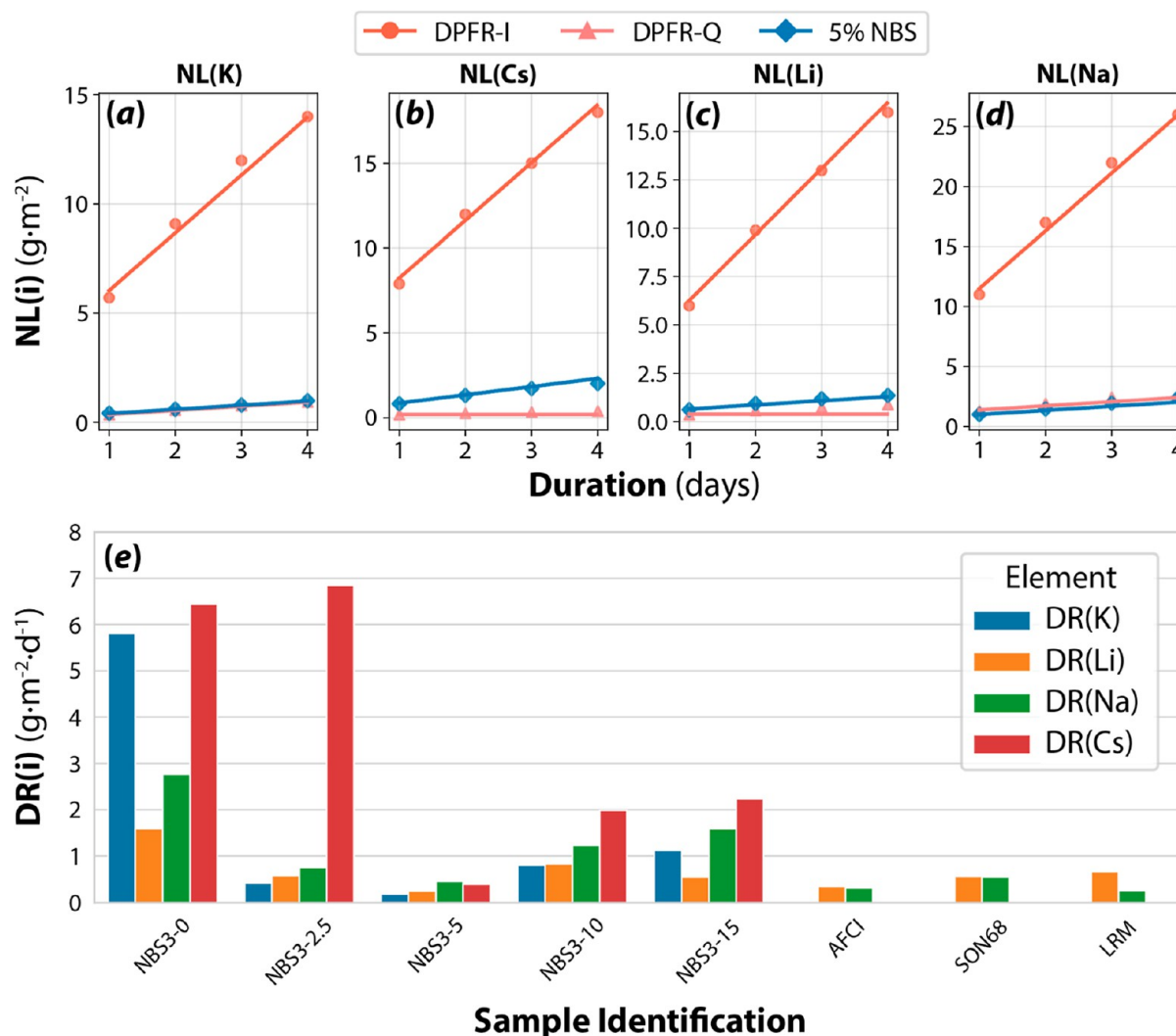


Figure 13. Cumulative normalized elemental release [NL(i)] for NBS3-5 compared to DPFR-I (DPF cooling rate most closely representing the NBS3-5 cooling rate) and DPFR-Q (quenched DPF5-336) waste forms showing values for (a) NL(K), (b) NL(Cs), (c) NL(Li), and (d) NL(Na). (e) Alkali metal dissolution rates [DR(i)] for samples in this study (NBS3-0, NBS3-2.5, NBS3-5, NBS3-10, NBS3-15), compared to waste glass standards, i.e., Advanced Fuel Cycle Initiative (AFCI), SON68, and Laboratory Reference Material (LRM). Reprinted with permission from Evarts et al.⁶⁵ Copyright 2025 American Chemical Society.

Organic acids, such as oxalic acid, produce HCl and H₂O byproducts,⁴⁷ and require high vitrification temperatures. Any methods using phosphates will require a detailed examination of the material compatibility as phosphates tend to corrode most materials as discussed previously. Table S2 (Supporting Information) provides a summary of electrochemical salt waste dehalogenation reactions, off-gas byproducts, and waste form properties discussed in this review.

In addition to treating metallic fuel, the back-end processes developed for pyroprocessing of UNF could be used to recover and recycle burnable actinides present in halide waste salts generated in MSRs. For MSRs, it is possible to recover resource materials from the waste salt, including U/TRU and noble metals with electrorefining, and ³⁷Cl using dehalogenation technology.¹¹¹ Removing halogens from salt wastes through dehalogenation creates additional gaseous waste streams that must be captured and managed.¹¹² However, dehalogenation provides significant benefits for waste management no matter which halide (or halide mixture) is present in the source waste. While the majority of this paper discusses chloride-based salt wastes, similar processes can be expanded

toward other types of salt wastes including fluoride salts from MSRs.²⁶ Dehalogenation converts the bulk halide salts (which constitute most of the waste on a molar basis) into manageable gaseous compounds, leaving behind a much smaller volume of electrolyte salt cations along with fission product residues for final disposal or further treatment for disposal. Additionally, converting the halides chemically stabilizes the remaining waste by preventing radiolytic decomposition that could otherwise generate volatile compounds such as F₂ and UF₆ during long-term storage of MSR wastes, including those from the Molten Salt Reactor Experiment at Oak Ridge National Laboratory.^{55,113}

As mentioned above, the chloride byproduct compounds captured from these reactions can be recovered and reused elsewhere as discussed in Section 4.4.²⁶ In consideration of chloride-based MSR fuels, recovered chlorine may be very valuable if it is enriched in ³⁷Cl or radioactive due to activation of ³⁵Cl to ³⁶Cl.¹¹⁴ The long half-life of ³⁶Cl (3.01 × 10⁵ y) will impact repository performance for disposal scenarios.

Critical gaps exist in iron phosphate waste form properties, including (1) a clear understanding of the relationship between

Table 5. Summary of Updates to the Roadmap Report^{3,4} for Developing Iron Phosphate Waste Forms for Salt Wastes^a

topic	issues	current state	gaps
waste compositions	the ranges of ER and oxide reduction (OR) salt waste compositions that will ultimately be produced have not been clearly defined; the waste composition and characteristic ranges are needed to support waste form, process design, and disposal qualification activities	ER(SF), ERV2, and ERV3 waste salt simulants have been developed and studied with several waste forms ^{26,32,66}	additional salt compositions need to be tested, including more advanced chloride simulants and fluoride simulants to represent fluoride-salt MSRs (e.g., LiF–BeF ₂)
matrix and additives	alkali- and alkaline earth-phosphate glasses are not sufficiently durable to serve as a waste form; additives such as Fe ₂ O ₃ and Al ₂ O ₃ can be used to improve chemical durability, but require higher-temperature vitrification in a separate processing step. Some composition regions are prone to crystallization and form phases that may be detrimental to processing or performance; adequate compositions are required for phosphate glasses that are processable and durable with dehalogenated salt wastes as major components of the glasses	developed reference material based on ternary study, DPFS–336; ⁸⁴ performed preliminary studies of DPFS–336 + silicate glasses to improve chemical durability (focus on NL _{Cs} and NL _{Sr}) ⁶⁸	develop formulations that have high salt cation solubilities and high chemical durabilities after a typical slow cooling curve
waste processing	reactant optimization for different chloride salt wastes (e.g., H ₃ PO ₄ vs ADP; different Fe additives)	multiple precursors have been tested including H ₃ PO ₄ , NH ₄ H ₂ PO ₄ , and (NH ₄) ₂ HPO ₄ ^{27,66}	while work has been done for certain simulants, similar work is needed on more complex simulants
	evaluate off-gas stream compositions, treatment requirements, and treatment methods	additional work is needed to understand the decomposition reaction and the reason(s) for pH change in the liquid condensates. For ADP, this is currently attributed to NH ₄ Cl decomposition to NH ₃ and HCl ^{65,82}	off-gas monitoring could be done using in-line spectroscopy; additionally, in-line chemical monitoring could be done for these reactions using methods like ICP–MS, laser-induced breakdown spectroscopy (LIBS), and/or auto-titration
	a single-step process is preferred for simplicity and scale-up, but the system does not operate as desired during single-step scoping tests	tested additions of Fe prior to and following dechlorination; Fe additions prior to degraded dechlorination performance; conceptual designs have been produced for consideration on how to implement continuous systems, but nothing has been built ^{73,121}	a continuous process is needed for dehalogenation of chloride salts with phosphate reagents
WF properties	determine process equipment lifetime and replacement requirements	material compatibility tests performed ²⁶	more tests are needed at a larger range of temperatures, times, and chemistries
	waste glasses tend to crystallize during slow cooling after melting	completed CCC and SCC experiments ^{68,69}	more data is needed to align the microstructure with initial chemistry and chemical durability
	few studies exist in the literature on the thermal stability of phosphate glasses (including compositions expected from these salt streams)	completed enthalpy of solution study on DPFR ⁶⁵	more work is needed in this area

^aCCC = canister centerline cooling (see Figure 8); ER = electrorefiner (salt); ICP–MS is inductively coupled plasma mass spectrometry; LIBS is laser-induced breakdown spectroscopy; OR = oxide reduction (salt); SCC = slow cooling curve (see Figure 8).

the glass forming additives and waste compositions, (2) crystalline phase formation during slow cooling and vitrification,^{68–70} and (3) waste form compatibility with refractory materials used for processing; see Table S for a summary of updates to the roadmap published previously.^{26,101} While some waste form-related properties (e.g., chemical durability) of several phosphate-based minerals (e.g., monazite,^{115–118} apatite^{119,120}) are known, most remain unstudied for these applications. In the Fe–P–O waste form system, a variety of crystal types have been observed in recent work, including A–Fe–P–O (A = alkali, e.g., NaFeP₂O₇, KFeP₂O₇, CsFeP₂O₇), monazites/xenotimes (REPO₄; RE = rare earths, e.g., Nd, Ce), and FePO₄. More work needs to be done to explore these crystalline phases so that waste-form formulations can be designed to target the formation of the most desired crystalline phases for maximum radionuclide stability (i.e., maximize chemical durability) and mitigate the formation of undesired phases that are highly water-soluble (e.g., A₃PO₄ such as trisodium phosphate).

Regarding the selection of the dehalogenation reagent for implementation of industrial-scale operations, three separate reagents were discussed in this paper, including H₃PO₄, NH₄H₂PO₄ (ADP), and (NH₄)₂HPO₄ (DHP), which can be used in liquid (H₃PO₄) or solid (ADP and DHP) forms and form liquid condensates (HCl forms from H₃PO₄ reactions) or solid condensates (NH₄Cl forms from ADP or DHP reactions). The reactions with H₃PO₄ appear to run toward completion at a much lower temperature ($T \approx 300$ °C) compared to the ADP/DHP reactions ($T \approx 600$ °C). Selection of the desired reagent for implementation of these processes with radiological salts depends upon the requirements of the facility where high-temperature acidic gases (i.e., HCl) might not be desired. However, capture and transportation of liquid HCl might be less problematic than capture and recovery of a solid NH₄Cl condensate.

In addition to the topics discussed above, the last topic to be discussed is the full capture and containment of volatile fission products from the dissolved UNF that could either volatilize out of the electrorefiner during operation, during dehalogenation, and/or during vitrification to the final waste form. To make sure that these are not lost, off-gas capture systems can be utilized above these unit operations to capture other volatiles through condensable traps and/or solid sorbent beds.

7. SUMMARY AND CONCLUSIONS

The content discussed within this paper provides an overview of recent efforts supported by the U.S. Department of Energy to evaluate phosphate reagents for treating salt-based nuclear wastes toward disposal pathways. The primary phosphate reagents considered in this review included H₃PO₄ (phosphoric acid), NH₄H₂PO₄ (ADP), and (NH₄)₂HPO₄ (DHP) to remove the halide portion of the salt in a process referred to as *dehalogenation* (or *dechlorination*, specifically, for Cl-based salts) through the generation of volatile halide-containing byproducts [e.g., NH₄Cl(g), HCl(g)] that can be captured, e.g., through condensation within a distillation column. The captured material can be used as a reagent to generate additional UCl₃ oxidant for the electrorefiner through reactions with metallic uranium (U⁰) dendrites. Following the dehalogenation process, the recovered products are (typically) not chemically durable and require further stabilization through the addition of GFCs and a high-temperature vitrification step. Through glass formation and characterization

iterations using salt simulants, a reference material (i.e., DPF5–336) was selected for further study. A large portion of the research discussed within this paper focused on studies performed before the selection of the reference material, which occurred in 2019.⁸⁴ Following that work, additional studies were done to understand the properties of this material under different conditions.

In conclusion, the phosphate processes discussed herein can be used to treat a wide range of salt compositions prior to waste form fabrication for disposal. Following dehalogenation, the selection of GFCs can be used to tailor the resulting properties of the final waste form. This approach shows promise for the future of salt waste treatment and immobilization with a recycling pathway for the byproducts from these reactions [e.g., NH₄Cl(g), HCl(g)] to create oxidant for the electrorefiner. While this work focused on treating electrorefiner salt wastes, the processes can also be extrapolated toward implementation of treating chloride-based MSR wastes.

■ ASSOCIATED CONTENT

Data Availability Statement

The data supporting this article have been included as part of the [Supporting Information](#). Additionally, Data are available upon request from the authors.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.5c08801>.

Dehalogenation reactions, dehalogenation apparatus design, chemical durability testing results from previous studies, methods for salt treatment and disposal ([PDF](#))

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Notes

The authors declare no competing financial interest.

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