Road Map for Developing Iron Phosphate Waste Forms for Salt Wastes

Nuclear Technology Research and Development

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SUMMARY

In this report, issues that must be addressed to advance the technology readiness level of phosphate glass waste forms being developed to immobilize high-level radioactive salt waste streams are identified, the states of understanding various technical aspects of formulation, processing, and performance are summarized, and approaches supporting further development are recommended. Processing results in dehalogenation of the waste salt, capture of the gaseous halide-bearing species, and immobilization of the residual salt components in a phosphate waste form. The approach is suitable for high-level salt wastes from electrochemical reprocessing and molten salt reactors. The technology has been demonstrated for chloride-based salts and may also be suitable for the treatment and immobilization of fluoride-based and iodide-bearing waste salts. Aspects of the process requiring further development are identified and approaches recommended.

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ACRONYMS AND ABBREVIATIONS

A^+	alkali
ADP	ammonium dihydrogen phosphate ($NH_4H_2PO_4$)
AE^{2+}	alkaline earth
An^{3+}	actinides (3+ valence)
ARPA-E	Advanced Research Projects Agency–Energy
BS	borosilicate (glass waste form)
BSE	backscattered electron (SEM imaging)
CCC	canister centerline cooling (cooling profile at the centerline of a 0.61-m diameter canister)
CTE	coefficient of thermal expansion
DHP	diammonium hydrogen phosphate [$(NH_4)_2HPO_4$]
DOE	Department of Energy
DPF	dehalogenated phosphate forms
DWPF	Defense Waste Processing Facility
EBR-II	Experimental Breeder Reactor II
EDS	energy dispersive X-ray emission spectroscopy
ER	electrorefiner (electrorefining)
ER(SF)	electrorefiner salt simulant version 1 (electrochemical salt simulant)
ERV2	electrorefiner salt simulant version 2 (electrochemical salt simulant)
GBS	glass-bonded sodalite
GBP	glass-bonded perovskite
Ha^-	halide anions
HLW	high-level waste
MSR	molten salt reactor
NE	Office of Nuclear Energy
NL	normalized release
NRC	Nuclear Regulatory Commission
OR	oxide (electro)reduction
RE^{3+} or REE	rare earth element
SEM	scanning electron microscopy (or microscope)
TC	thermocouple
TRL	Technology Readiness Level
WF	waste form

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A Round Table Workshop was held on August 4th and 11th, 2020 under the support of DOE-NE in which participants from U.S. universities, national laboratories, industry, and representatives of different DOE offices participated in discussions on phosphate-based processes for treating salt waste streams, alternative waste forms, large-scale production and accountancy. The authors thank these participants and several descriptions and recommendations in this report resulted from that Round Table Workshop. A summary of the agenda and list of participants in the Round Table Workshop are provided in Appendix A.

1. INTRODUCTION AND BACKGROUND

Phosphate glass-based waste forms are being developed under the auspices of the U.S. Department of Energy (DOE) Office of Nuclear Energy's (NE) Nuclear Technology Research and Development Program that can be used to immobilize salt wastes from the electrochemical reprocessing of used nuclear fuel. These waste forms are appropriate for oxide-fuel or metal-fuel (electro)reduction (OR) and electrorefining (ER) waste salts. The reaction of chloride salt with various phosphates results in dehalogenation of the salt waste and dissolution of the remaining salt cations in a phosphate glass. The phosphate glass is not chemically durable and iron oxide is added to generate a waste form with acceptable chemical durability. The halogen-bearing species in the off-gas (primarily chlorides) can be recovered for recycle or disposal. The iron phosphate waste form may potentially be suitable for immobilizing end-of-life chloride salt wastes from molten salt reactors (MSR) and possibly end-of-life fluoride salt wastes. The use of phosphates for salt processing is not a new idea but has not been investigated at the level of rigor required for fully evaluating and qualifying an approach for waste processing and waste form disposal. In this report, we identify technology gaps that must be addressed to advance this waste processing and immobilization approach towards a higher Technology Readiness Level (TRL) in the form of an idealized flowsheet, or Road Map, starting from a waste stream and generating a disposable waste form.

Figure 1-1 summarizes the high-level issues and interfaces that are considered when developing a high-level radioactive waste form. These include interrelated issues regarding waste form formulation, production, and disposal. The *Waste Composition* box defines the waste stream to be immobilized and the *Matrix/Additives* box defines the materials used to immobilize it. The *Waste Processing* method is selected based on the immobilizing matrix and the capacity to retain radionuclides present in the waste stream within the waste form during processing. The matrix material(s) and processing method(s) are usually selected based on the compatibility of the waste stream with the immobilizing matrix and waste loadings that can be achieved. The waste loading is often limited by waste stream constituents other than radionuclides of concern or limits established by storage or disposal of the waste form. For example, Cl concentration in the waste form may be more limiting than fission product loading. The storage, transportation, and disposal concepts may add additional constraints on waste loading, such as those from decay heat, that can be generally managed by loading limitations in the waste form, waste form size, and/or decay storage.

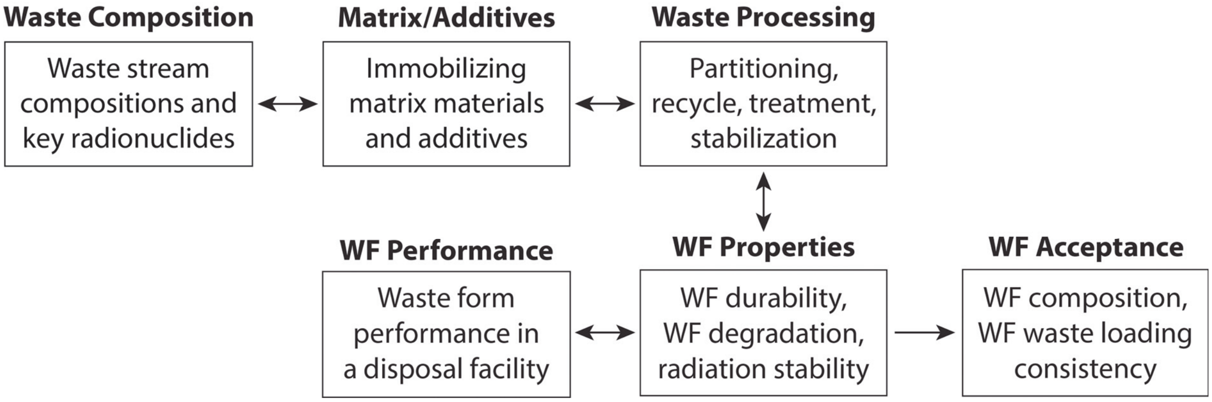


Figure 1-1. Simplified diagram showing aspects of waste form development with emphasis on the preprocessing.

Following the diagram in Figure 1-1 from left to right shows how waste forms are developed based on the waste stream composition and selected immobilizing matrix, the methods developed to produce waste forms, and the testing and modeling activities used to evaluate waste form behavior in a disposal system.

These steps are summarized below with specific consideration for application to electrochemical salt high-level waste streams.

Waste Streams

Generally, the physical, chemical, and radioactive characteristics of the waste stream are all considered important when designing the waste form. Both the nominal or average characteristics and their range of variation within the targeted stream are important. For those characteristics that strongly influence the immobilization process or product performance either narrow variation or precise analyses are required. In the case of halide salt wastes, characteristics such as

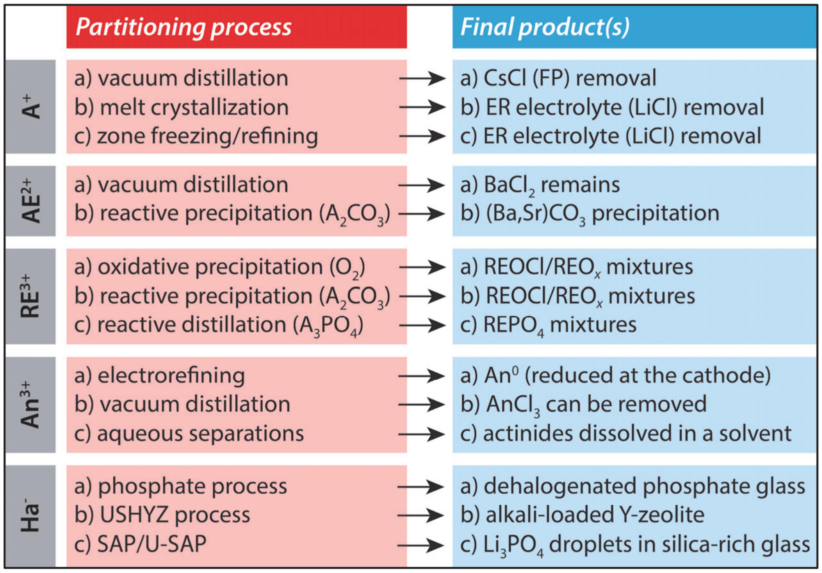
- decay heat;
- concentrations of total halogen, alkali, alkaline earths, rare earths, transition metals, U, Pu, and other actinides;
- ratios of different halogens (e.g., Cl:F:I) and alkalis (e.g., Li:Na:K:Cs) and, to a lesser extent, alkaline earths, rare earths, and transition metals;
- concentration of long-lived isotopes (e.g., I-129, Cl-36, Se-79, Tc-99, Pu-242, Np-237); and
- fissile content (e.g., U-233, U-235, Pu-239, Pu-241).

are important considerations for waste form formulation and processing. Each of these will depend on the fuel being processed and the details of the electrochemical process being performed. Example ER salt waste streams were reported by Vienna et al. (2015). Generally, these estimates assume low fissile contents as part of a closed fuel cycle. However, other salt waste streams may contain significant fissile materials (e.g., end-of-life molten salt reactor fuel).

Immobilizing matrix and process

Alkali-chloride-based wastes can be immobilized either directly or in combination with salt partitioning. Riley (2020b) summarized several of those options. Unpartitioned salt contains relatively high concentrations of alkali-halide salts. Waste forms that are rich in alkali and halides were the natural focus including: glass-bonded sodalites (GBS), glass-bonded perovskites (GBP), cancrinites, and tellurite glasses. The GBS waste form is typically formed by occluding the salt waste into a porous zeolite, mixing with a borosilicate glass frit, and sintering (either pressurelessly or under hot-isostatic pressing) together to form a final dense product (Periera et al. 1999; Simpson et al. 2001; Priebe and Bateman 2008; Morrison and Bateman 2010; Ebert et al. 2016; Riley et al. 2017b). By this process, the sodium from the salt waste or borosilicate glass combines with the alumina and silica from the zeolite to form a sodalite crystal. Rare earths, lithium, and actinides partition to the glassy phase, which completely encapsulates the sodalite crystals. Alkali- and halide-containing perovskites were formed by precipitation from solution (either aqueous or organic) (Scott et al. 2018). The perovskites were then densified by mixing with a glass frit and sintering (Yang et al. 2021). The TeO_2-based glasses were melted and cast into containers (Riley et al. 2012, 2017a).

Several options exist to immobilize portions of the partitioned salt waste. Riley (2020b) summarizes those options as a function of which components are partitioned as reproduced in Figure 1-2. The options include partitioning of alkali (A^+), alkaline earths (AE^{2+}), rare earths (RE^{3+}), actinides (An^{3+}), and halides (Ha^-). Example partitioning processes are shown in the figure. Some of the products from each of these partitioning methods are intended to be immobilized. Generally, the immobilized waste stream differs significantly in characteristics from the original salt stream. Therefore, both the immobilizing matrix and process will change to match the new waste characteristics; again, examples are described by Riley (2020b).



	Partitioning process	Final product(s)
A^+	a) vacuum distillation	a) CsCl (FP) removal
	b) melt crystallization	b) ER electrolyte (LiCl) removal
	c) zone freezing/refining	c) ER electrolyte (LiCl) removal
AE^{2+}	a) vacuum distillation	a) $BaCl_2$ remains
	b) reactive precipitation (A_2CO_3)	b) $(Ba,Sr)CO_3$ precipitation
RE^{3+}	a) oxidative precipitation (O_2)	a) REOCl/REO_x mixtures
	b) reactive precipitation (A_2CO_3)	b) REOCl/REO_x mixtures
	c) reactive distillation (A_3PO_4)	c) $REPO_4$ mixtures
An^{3+}	a) electrorefining	a) An^0 (reduced at the cathode)
	b) vacuum distillation	b) $AnCl_3$ can be removed
	c) aqueous separations	c) actinides dissolved in a solvent
Ha^-	a) phosphate process	a) dehalogenated phosphate glass
	b) USHYZ process	b) alkali-loaded Y-zeolite
	c) SAP/U-SAP	c) Li_3PO_4 droplets in silica-rich glass

Figure 1-2. Example salt waste partitioning processes and associated final products (Riley 2020b).

The focus of this document is on the process of dehalogenation (i.e., Ha^- partitioning) followed by immobilization of the residual waste stream in iron phosphate glass. A generalized process flow diagram for treating a chloride-based ER salt using this process is shown in Figure 1-3. This diagram identifies the additives, processing conditions, intermediate products, off-gases, and secondary waste streams generated during the process. Note that chloride-based salt wastes will likely contain small amounts of other halides as impurities or dissolved fuel constituents that will be present in the off-gas. Figure 1-3 also shows the use of ammonium dihydrogen phosphate (ADP) and the optional recovery and recycle of NH_4Cl to generate UCl_3. Similar diagrams can be generated for other additives and salt compositions including fluoride salts.

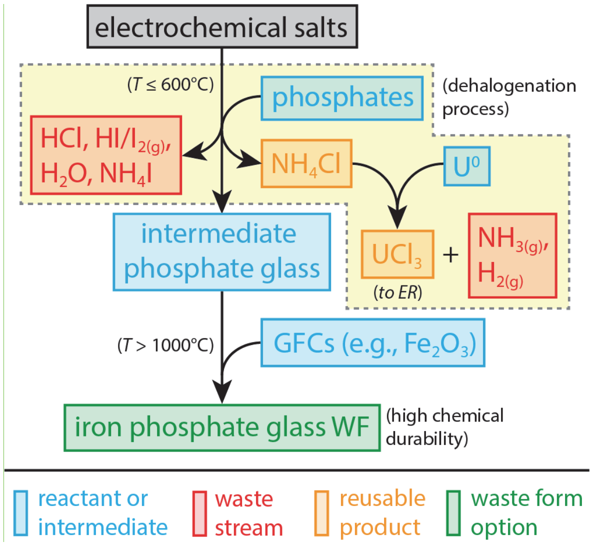


Figure 1-3. Proposed general process flow diagram when reacting ADP with chloride salts (Riley et al. 2020c).

The *Waste Processing* box in Figure 1-1 indicates control of the production process to generate waste forms with sufficiently consistent physical, radiological, and chemical properties. Secondary wastes must be successfully managed during the process through recycle, treatment, and/or immobilization. The physical and radiological properties of the waste form must be controlled for accountancy, handling, transport, temporary storage, and disposal purposes and chemical properties must be controlled to ensure adequate durability in the disposal facility.

Performance, Durability, and Consistency

Waste form consistency is achieved by first appropriately controlling waste loading and matrix material composition, then controlling processing conditions that may include temperature ranges, gas composition and flow rates, pressures, durations, and cooling rates, depending on the matrix material and waste composition. If the durability of the waste form is deemed to be inadequate, changes to the immobilizing matrix, waste loading, or processing method or conditions must be modified. The generation of secondary waste streams during processing is an important issue for the dehalogenation processes addressed in this report but are not shown in the diagram. If those waste streams are to be disposed, they would serve as the waste stream in the top left-hand box and an appropriate matrix and process identified.

The *WF Performance* box in Figure 1-1 addresses the predicted behavior of the waste form in a disposal facility and is used to determine the required waste form durability. Degradation of the matrix used to immobilize radionuclides in the waste stream will occur during disposal for geologic time periods when contacted by groundwater and the radionuclides may be transported by diffusive and convective processes. The dispersal of radionuclides released from a degrading waste form will depend on solubilities, colloid formation, sorption to engineered and natural materials, etc. The performance of the disposal system is regulated to ensure that the release to the biosphere is acceptably low, and the efficiency of natural and engineered barriers (including waste forms) will provide the required containment. Models are being developed to predict waste form degradation rates under the range of conditions anticipated in disposal facilities. Those models provide source terms for radionuclide release that are used in simulations of disposal facility performance conducted to ensure regulatory limits are met throughout the regulated service life. Most models are based on a mechanistic understanding of how the immobilizing matrix degrades and how radionuclides are released. This provides confidence in the calculated degradation kinetics and radionuclide release rates in different disposal environments.

The role of the waste forms in disposal facility design and performance assessment is based on the modeled degradation kinetics and the inventory of radionuclides in the waste forms that are disposed. These establish the acceptance criteria for disposal and required combination of waste form chemical durability and waste loading (both from migration and heat source requirements). Those criteria then establish threshold values for waste form characteristics (*WF Properties* in Figure 1-1) that can be used to demonstrate the consistency and acceptability of all waste form products that are produced (*WF Acceptance* in Figure 1-1). Those characteristics can be used to determine acceptable ranges of processing conditions.

Summary

The diagram in Figure 1-1 shows how waste forms are developed based on the waste stream composition and selected immobilizing matrix, the methods developed to produce waste forms, and the testing activities used to evaluate waste form behavior in a disposal system. Following the diagram from right to left shows how analyses of disposal system behavior and waste form degradation under disposal conditions are used to determine the required chemical durability of the waste form and waste loading restrictions. Those requirements are used to determine acceptable waste loading and processing conditions that can be used to generate consistently acceptable waste forms. For an established waste form, controlling formulation and processing conditions ensures that consistently acceptable waste forms are generated. Tests with the consistent waste form can provide a mechanistic model to predict waste form degradation and radionuclide release. A disposal system is engineered considering barrier properties of the natural system and engineered barriers including backfill, metallic waste containers, and engineered waste forms. The design and performance of repository systems in generic natural systems and safety assessments are being addressed within the DOE Spent Fuel and Waste Disposition campaign. Work done during the development of waste forms and waste form degradation models provides insights used to assess facility designs, inform regulators, and establish acceptance requirements for waste form durability and other characteristics.

This general approach is being followed to develop and evaluate iron phosphate waste forms. A significant amount of work has been conducted to identify candidate processes and immobilization forms for anticipated ER and OR salt stream, but significant effort is needed to address processing and disposal issues before a baseline waste form, process, and performance source-term can be determined.

The perceived advantages of the phosphate process are described hereafter. First, it can be used to dehalogenate the salt to enable the recovery and recycle of economically valuable isotopes (e.g., ^{37}Cl, ^{7}Li). Second, it facilitates production of waste forms with high waste loadings that are suitable for disposal (e.g., fluorine removal opens up more waste form options for fluoride salts). Third, the phosphate waste form can be produced using existing technologies designed for large-scale production (off-gas systems, Joule-heated melters).

Some perceived disadvantages to phosphate glass waste forms pertain to the relative immaturity of this technology. First, phosphate glasses are known to chemically attack refractories and their low viscosity makes vitrification challenging. Second, very few composition-property models exist for phosphate glasses, making glass property predictions more difficult for glasses made with different waste streams. Third, common glass properties are more sensitive to minor changes in the composition of phosphate glasses than borosilicate glasses. For example, small changes in the Fe:P molar ratio can have a significant impact on the chemical durability of the final waste form (Ma et al. 2017).

On August 4th and August 11th of 2020, the authors hosted a virtual Round Table Workshop to discuss the state of knowledge regarding the phosphate process for immobilizing salt wastes and to identify and assess the remaining technical gaps in several areas. The Round Table Workshop included invited participants from national laboratories, universities, industry, and representatives from DOE-NE and Advanced Research Projects Agency–Energy (ARPA-E). The agenda and participants are provided in Appendix A. The agenda included key issues identified by the organizers for which several experts from national laboratories, universities, and industry were invited to make prepared presentations. Discussions held after each presentation were used to assess the current states of various topic areas relevant to phosphate glass waste forms, assess the current state of technology in these areas, identify remaining research gaps in these areas, and suggest possible ways to close those gaps. The following issues were addressed:

- Radionuclides and chemical constraints
- Immobilizing matrix materials
- Waste form material production (lab scale development)
    - Chemical reactions
    - Off-gas hazards, capture, and recycle
    - One-step vs two-step processing
- Waste form attributes
    - Crystalline phase content
    - Chemical and physical robustness
    - Thermal and radiological stability
    - Waste loading
- Waste form product production (full scale production)
    - Waste form product consistency and regulatory acceptability
    - Production complexity and remote operations
    - Security and safeguards
    - Material balance and secondary wastes
    - Production rates and throughput
    - Intermediate storage and transport
- Performance in disposal system

  - Performance tests and degradation modeling

The status and results of these discussions are summarized in Table 1-1. The following sections address each bullet point listed above in greater detail based on existing data, information presented during the Round Table Workshop, and follow-on review of the literature.

Table 1-1. Summary of areas of needed research, potential issues for pursuing these areas of research, the current state of the art, as well as identified gaps and possible ways to fill those gaps (more information is provided in subsequent sections for each topic area). See footnote for abbreviations.

Topic area	Issues	Current state	Gaps/approaches to fill
Waste Compositions (Section 2)	The range of ER and OR salt waste compositions that will ultimately be produced has not been clearly defined. The waste composition and characteristic ranges are needed to support waste form, process design, and disposal qualification activities.	Current electrochemical salt wastes are dominated by LiCl (OR) and LiCl/KCl eutectic mixtures (ER), and include fission products, other fuel constituents, such as sodium, and trace actinides. The salts are anticipated to be used until reaching some limiting factor that may be related to the physical properties of the salt (e.g., liquidus temperature) the decay heat management of salt waste forms, impacts on product purity, or other limiting factors.	Electrochemical process development, waste form design, waste processing, and disposal requirements need to be developed concurrently due to the potential feedback effects of each technology component on the others. By doing so, the ranges of key waste component concentrations and waste characteristics will be refined.
	Several chloride and fluoride salt mixtures are being considered by MSR designers. For MSRs, salt compositions vary depending on vendor design and operating strategy. The range of halide salt wastes generated from prototypical MSRs are needed.	Several different fuel/coolant salt compositions have been proposed by MSR vendors. These include both chloride-based salts (primarily for fast reactors) and fluoride-based salts (primarily for thermal reactors). The salt constituents, the fission and activation products, and the fuel burnup prior to processing differ.	Work with other organizations within DOE-NE and the potential MSR vendors to develop a database of fuel compositions and characteristics. Select from the list example salt composition for use in waste form and process development activities.
Matrix and Additives (Section 3)	Alkali- and alkaline earth-phosphate glasses are not sufficiently durable to serve as a waste form. Additive such as Fe_2O_3 and Al_2O_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.	Iron phosphate and alumino-phosphate glasses have been formulated and tested for a number of nuclear waste streams in the U.S. and abroad. Several iron-phosphate glass compositions were developed specifically for dehalogenated ER salt waste. To the best of the authors knowledge, phosphate glasses were not developed for a range of the dehalogenated salt wastes generated from ER, OR, and MSRs.	Design and test phosphate-based glasses with a range of different salt compositions, additives, and waste loadings to survey the boundaries of acceptable glass formation.

Topic area	Issues	Current state	Gaps/approaches to fill
Matrix and Additives (continued) (Section 3)	Nuclear waste glass design, qualification, and process control all rely heavily on the ability to predict glass properties as functions of key composition and processing related parameters. Few if any such models are available for iron-phosphate based glasses.	Models available for iron-phosphate glass properties are few (e.g., density, CTE) and are aimed at Hanford tank waste compositions rather than dehalogenated salt wastes.	Develop glass property-composition data and associated models over the range of likely glass compositions. These data and models should include properties such as durability response (see Section 7), processability related properties (Section 4), and glass forming ability (Section 3).
Waste Processing (Section 4)	A single-step process is preferred for simplicity and scale-up, but the system does not operate as desired during single-step scoping tests.	Scoping tests with 1-step vs 2-step tests show that the 2-step dehalogenation/ vitrification process is more effective for Cl-based salts.	Evaluate alternative options for making the 1-step process work effectively.
	Reactant optimization for different chloride salt wastes (e.g., H_3PO_4 vs ADP; different Fe additives).	Preliminary tests with ADP and H_2PO_4 have shown some success for two stage process.	Evaluate different phosphate precursors for different chloride salt streams.
	Dehalogenation and immobilization reactions require evaluation for fluoride salts.	It is theoretically possible to dehalogenate fluoride based MSR salts using phosphate precursors, it has not yet been demonstrated.	Perform initial dehalogenation tests with H_3PO_4 and ADP. Evaluate other potential reactions.
	Integrated process tests are needed to determine adequacy of materials flows and determine partitioning between process streams.	No integrated process tests have yet been performed.	Perform laboratory/bench-scale integrated process tests, develop reaction rates and process flow sheets. Separate tests may need to be done for waste forms made with different salt types.
	Evaluate off-gas stream compositions, treatment requirements, and treatment methods.	Off-gas compositions are unknown and potentially problematic. For example, $HF_{(g)}$ can be generated with fluoride salts, which will attack most glassware; chlorides: off-gases require neutralization; iodides: N-I compounds (e.g., NI_3, NH_4I_3) are contact explosives so ADP or DHP are not good choices for I-containing salts. Off-gas	Evaluate off-gas generation, neutralization, and need for recycle and treatment. Develop and test off-gas treatment/recycle methods.

Topic area	Issues	Current state	Gaps/approaches to fill
Waste Processing (continued) (Section 4)	Process ranges are not determined.	No data on processing ranges available (temperature, time, composition, gas flow, etc.).	Perform integrated process tests over range of key processing parameters. Determine processing success boundaries and develop process models. (may need to be done for different salt types).
	Process equipment remote operation and maintenance.	No process equipment yet developed.	Evaluate methods to remotize process equipment and demonstrate effective hands-off operations and control.
	Scale-up testing is required to evaluate overall system performance (e.g., process rates, component partition factors)	No scale-up data exists.	Scale-up integrated process tests from laboratory-scale to pilot scale (may need to be done for different salt types).
	Determine process equipment lifetime and replacement requirements.	No process equipment yet developed. Salt waste streams and their byproducts are highly corrosive adding challenges to equipment design and materials lifetime.	Study materials corrosion processes at laboratory scale. Design equipment and test equipment lifetime thought scaled testing of individual components and integrated systems.
	Determine safety concerns from processes required to make iron phosphate waste forms.	Current precursors used for iron phosphate waste form production evolve toxic gases, e.g., NH_3, HCl, HF.	Determine how/if can these hazards be effectively mitigated.
	Safeguards and materials accountancy.	Some radionuclides may need to be tracked throughout process for accountancy.	Regulations established by NRC.
WF Properties (Section 5)	Waste glasses tend to crystallize during slow cooling after melting.	Few data exist for canister centerline cooling (CCC) treatments of phosphate glasses with relevant ER/MSR salt waste compositions.	More data are needed to evaluate properties of CCC-treated WFs including what crystals form and how they affect glass properties of interest.
	Crystallization can occur during CCC, which can lead to cracking and embrittlement of the WF.	Little is known about how CCC treatments affect crystallization in these WFs, and therefore, chemical and physical robustness.	Evaluate the chemical and physical robustness of CCC-treated phosphate glasses.

Topic area	Issues	Current state	Gaps/approaches to fill
WF Properties (continued) (Section 5)	Few studies exist in the literature on the thermal stability of phosphate glasses (including compositions expected from these salt streams).	Little is known about the thermal stability of these glasses.	Evaluate thermal stability of these glasses.
	Few studies exist in the literature on the radiological stability of phosphate glasses (including compositions expected from these salt streams).	Little is known about the radiological stability of these glasses.	Evaluate radiological stability of these glasses.
	Determine if waste form should remain in crucible and be placed into a canister or be poured into a canister. Determine if radiation dose and heat from waste form with high waste loading require a special storage facility or longer cooling times before transport and disposal.	Only generic thermal properties and limits of iron phosphate glasses are known.	Determine thermal properties and thermal limits of iron phosphate waste forms.
WF Acceptance (Section 6)	The chemical durabilities of phosphate glasses vary significantly with minor differences in composition.	Literature shows that targeting an O:P molar ratio of 3.4–3.5 and maximizing Fe:P ratios improves chemical durability of Fe-P-O glasses.	Evaluate consistency and regulatory acceptability for phosphate glasses made with different salt waste streams.
WF Performance (Section 7)	Understanding composition effects on quenched glass chemical durability are limited. Need to determine the mode of radionuclide release and WF degradation. Determine if WF acceptance criteria developed for BS glass WFs are appropriate for iron phosphate WFs. Determine the effect of dissolved phosphate species on solubility limits and transport behaviors of radionuclides used to assess repository performance.	The effects of composition (i.e., O:P molar ratio, Fe:P molar ratio) on quenched glass chemical durability are limited. Tests with developmental DPF materials indicate BS glass WF model is appropriate; Stage 3 behavior not expected.	More work is needed to evaluate the chemical durability of quenched and CCC-treated glasses of varying WLs and compositions. Also, the effects of phosphate on seepage water and chemistry of radionuclides should be studied.

ADP = $NH_4H_2PO_4$; BS = borosilicate (glass); CCC = canister centerline cooling; CTE = coefficient of thermal expansion; DHP = $(NH_4)_2HPO_4$; DPF = dehalogenated phosphate forms; NRC = Nuclear Regulatory Commission; WF = waste form; WL = waste loading.

2. WASTE COMPOSITIONS

The waste streams that are being considered for iron phosphate waste forms include OR and ER waste salts from electrochemical reprocessing as well as chloride- and fluoride-based salts that are being evaluated by developers for use in different MSR designs. As an example, a representative ER waste salt composition for once-through processing of 300 driver rods of Experimental Breeder Reactor II (EBR-II) sodium-bonded U-15Zr fuel is provided in Table 2-1 (Ebert 2005). Simplified compositions ER(SF) (version 1) and ERV2 (version 2) that have been used to make prototype iron phosphate materials are provided in Table 2-2. Those prototype materials were made to study the efficacy of the process for chloride salt waste streams, the distributions of surrogate radionuclides in the waste form, and the waste form degradation behavior.

Table 2-1. Composition of 300 driver salt.

Salt	Mass%
$BaCl_2$	1.20
$CeCl_3$	2.33
CsCl	2.51
$EuCl_3$	0.05
KI	0.15

Salt	Mass%
$LaCl_3$	1.22
LiCl-KCl	69.82
NaCl	14.95
$NdCl_3$	3.90
$PrCl_3$	1.15

Salt	Mass%
RbCl	0.33
$SmCl_3$	0.69
$SrCl_2$	1.00
YCl_3	0.70

Table 2-2. Compositions of ER(SF) (Riley 2017) and ERV2 (Ebert et al. 2017) salt simulants (mass%, based on measured values from chemical analysis of the as-made salts).

Additive	ER(SF)	ERV2
LiCl	33.09	32.32
KCl	40.52	38.68
NaCl	9.88	9.00
CsCl	5.18	-
CsI	-	7.00
KI	3.09	-
$SrCl_2$	3.13	3.00
YCl_3	1.55	-
$LaCl_3$	1.55	-
$CeCl_3$	0.002	5.00
$NdCl_3$	2.01	5.00

Molten salt reactors are being designed to use various mixtures of chloride fuel salts (e.g., NaCl, $ZrCl_4$, UCl_3/UCl_4, $PuCl_3$) or fluoride fuel salts (e.g., LiF, BeF_2, ZrF_4, UF_4, ThF_4); most compositions remain proprietary so examples are not provided in this report.

3. IMMOBILIZING MATRICES AND ADDITIVES

Alkali phosphate glasses are not sufficiently durable to serve as waste forms and stabilizing reagents must be added. Several additives have been shown to be effective in increasing chemical durability as measured in standard immersion tests, including PbO, Fe_2O_3, and Al_2O_3 (Ma et al. 2017; Rajaram and Day 1986; Sales and Boatner 1984). The use of PbO is not appropriate for waste forms due to the inherent toxicity and Fe_2O_3 has been used in most studies, including proof-of-principle tests. The addition of Fe_2O_3 is economical and effective.

The chemical durability of phosphate glasses varies several orders of magnitude depending on glass composition. Based on several studies, it is clear that optimizing the chemical durability of iron phosphate glasses can be achieved by starting with O:P molar ratios of ~3.4–3.5 and high Fe:P molar ratios (see Figure 3-1 and Figure 3-2) (Day and Ray 2013; Ma et al. 2017; Zhang et al. 2011).

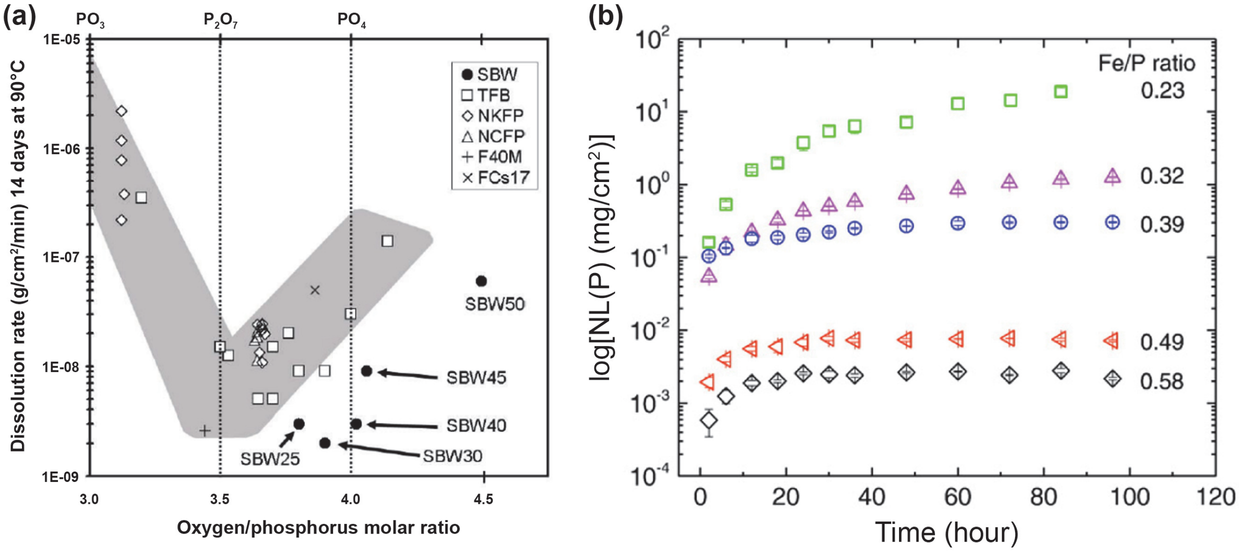


Figure 3-1. (a) Summary of dissolution rate (chemical durability) of phosphate glasses as a function of O:P ratio (Day and Ray 2013). (b) Summary of iron phosphate glass dissolution behavior for different Fe:P molar ratios at a fixed O:P of 3.40±0.03 (Ma et al. 2017).

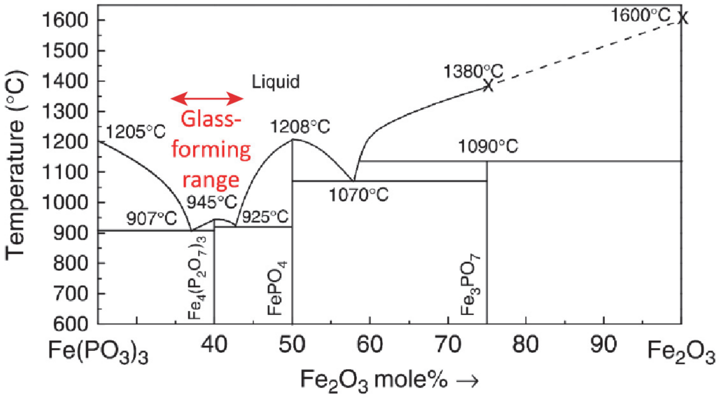


Figure 3-2. Glass-forming region (arrow region) for the $Fe(PO_3)_3$-Fe_2O_3 binary system according to (Zhang et al. 2011).

Another aspect of glass composition to consider is the choice of the source chemicals during batching. For instance, the choice of phosphate precursor(s) [e.g., H_3PO_4, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$] used during phosphate glass synthesis can affect the properties of the melt as well as the final glass. Figure 3-3 shows the impact on Fe^{2+} and Fe^{3+} in the glass when using H_3PO_4 vs $NH_4H_2PO_4$, where H_3PO_4 results in a more oxidized glass (i.e., higher Fe^{3+}/Fe_{tot}) (Bai et al. 2020). Additionally, glass-forming additives can drastically change the properties of the final glass (e.g., Fe_2O_3, Al_2O_3).

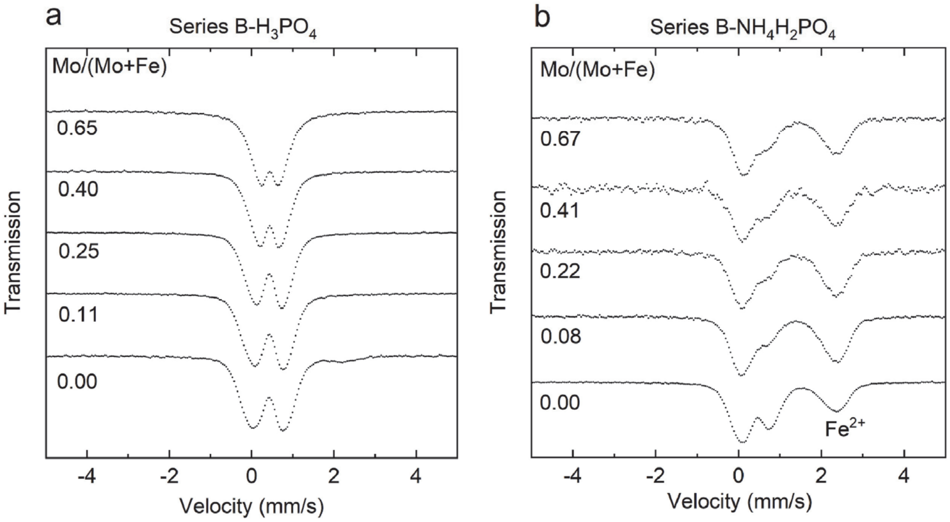


Figure 3-3. Summary of Mössbauer spectroscopy of $15Cs_2O$-$y$$MoO_3$-(28.75-$y$)$Fe_2O_3$-$56.25P_2O_5$ glasses showing Fe^{2+} and Fe^{3+} in glasses with similar targeted composition batched with either (a) H_3PO_4 (5% Fe^{2+}) or (b) $NH_4H_2PO_4$ (53% Fe^{2+}) (Bai et al. 2020). The doublet between 0 and 1 mm/s denotes the Fe^{3+} region.

4. WASTE PROCESSING

4.1 Chemical Reactions

Some of the chemical reactions are known for mixing phosphates with various salts, but these studies have mainly focused on chloride salts. More work is needed to fully evaluate reactions with fluoride salts.

The phosphate glass waste forms evaluated for immobilizing ER salt wastes were made by reacting H_3PO_4, $NH_4H_2PO_4$, or $(NH_4)_2HPO_4$ with the salts of interest at elevated temperatures. This process results in dehalogenation wherein the cations are retained in phosphate glass and halides come off the melt as a volatile byproduct at temperatures below 600°C. Examples of reactions for individual salt constituents using $NH_4H_2PO_4$ provided by Donze et al. (2000) and by using H_3PO_4 provided by Siemer (2012) are shown in Reactions (4-1) and (4-2) below, respectively (*M* denotes a 1+, 2+, or 3+ metal).

$$2\ NH_4H_2PO_4 + 2\ M\mathrm{Cl} \rightarrow M_2O{\bullet}P_2O_{5(\mathrm{glass})} + 2\ NH_4Cl_{(\mathrm{g,l})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}1a)$$

$$2\ NH_4H_2PO_4 + M\mathrm{Cl}_2 \rightarrow MO{\bullet}P_2O_{5(\mathrm{glass})} + 2\ NH_4Cl_{(\mathrm{g,l})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}1b)$$

$$6\ NH_4H_2PO_4 + 2\ M\mathrm{Cl}_3 \rightarrow M_2O_3{\bullet}3\ P_2O_{5(\mathrm{glass})} + 6\ NH_4Cl_{(\mathrm{g,l})} + 6\ H_2O_{(\mathrm{g})} \qquad (4\text{-}1c)$$

$$2\ H_3PO_4 + 2\ M\mathrm{Cl} \rightarrow M_2O{\bullet}P_2O_{5(\mathrm{glass})} + 2\ HCl_{(\mathrm{g})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}2a)$$

$$2\ H_3PO_4 + M\mathrm{Cl}_2 \rightarrow MO{\bullet}P_2O_{5(\mathrm{glass})} + 2\ HCl_{(\mathrm{g})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}2b)$$

$$6\ H_3PO_4 + 2\ M\mathrm{Cl}_3 \rightarrow M_2O_3{\bullet}3\ P_2O_{5(\mathrm{glass})} + 6\ HCl_{(\mathrm{g})} + 6\ H_2O_{(\mathrm{g})} \qquad (4\text{-}2c)$$

The resulting products from these reactions are phosphate glasses or glass ceramics and the cations associated with the phosphate (e.g., H^+, NH_4^+) as well as any associated H_2O are removed as off-gas products that can be collected or scrubbed and neutralized. The resulting phosphate product can then be treated in a subsequent vitrification step where other components are added to aid in achieving suitable glass properties, e.g., Fe_2O_3 to improve chemical durability.

Thermodynamic calculations of the Gibb's free energy of formations (ΔG_f°) for different ammonium halides as well as hydrohalic acids reveal trends with more spontaneous reactions occurring for lighter halides vs heavier halides where formation favorability decreases as $NH_4F > NH_4Cl > NH_4Br > NH_4I$ and $HF > HCl > HBr > HI$ as shown in Figure 4-1. Also, the favorability for the formation of each compound increase (i.e., ΔG_f° decreases) with increases in the reaction temperature. Based on these reactions and the thermodynamic data, it expected that the same processes developed for the chloride salt simulants would translate well towards other salts like fluorides.

For fluoride salts, similar reactions are expected as are shown below in Reaction (4-3) for $NH_4H_2PO_4$ as the phosphate reactant and Reactions (4-4) for H_3PO_4 as the phosphate reactant. It is known, however, that NH_4F decomposes around 100°C.

$$2\ NH_4H_2PO_4 + 2\ M\mathrm{F} \rightarrow M_2O{\bullet}P_2O_{5(\mathrm{glass})} + 2\ NH_4F_{(\mathrm{g,l})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}3a)$$

$$2\ NH_4H_2PO_4 + M\mathrm{F}_2 \rightarrow MO{\bullet}P_2O_{5(\mathrm{glass})} + 2\ NH_4F_{(\mathrm{g,l})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}3b)$$

$$6\ NH_4H_2PO_4 + 2\ M\mathrm{F}_3 \rightarrow M_2O_3{\bullet}3\ P_2O_{5(\mathrm{glass})} + 6\ NH_4F_{(\mathrm{g,l})} + 6\ H_2O_{(\mathrm{g})} \qquad (4\text{-}3c)$$

$$2\ H_3PO_4 + 2\ M\mathrm{F} \rightarrow M_2O{\bullet}P_2O_{5(\mathrm{glass})} + 2\ HF_{(\mathrm{g})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}4a)$$

$$2\ H_3PO_4 + M\mathrm{F}_2 \rightarrow MO{\bullet}P_2O_{5(\mathrm{glass})} + 2\ HF_{(\mathrm{g})} + 2\ H_2O_{(\mathrm{g})} \qquad (4\text{-}4b)$$

$$6\ H_3PO_4 + 2\ M\mathrm{F}_3 \rightarrow M_2O_3{\bullet}3\ P_2O_{5(\mathrm{glass})} + 6\ HF_{(\mathrm{g})} + 6\ H_2O_{(\mathrm{g})} \qquad (4\text{-}4c)$$

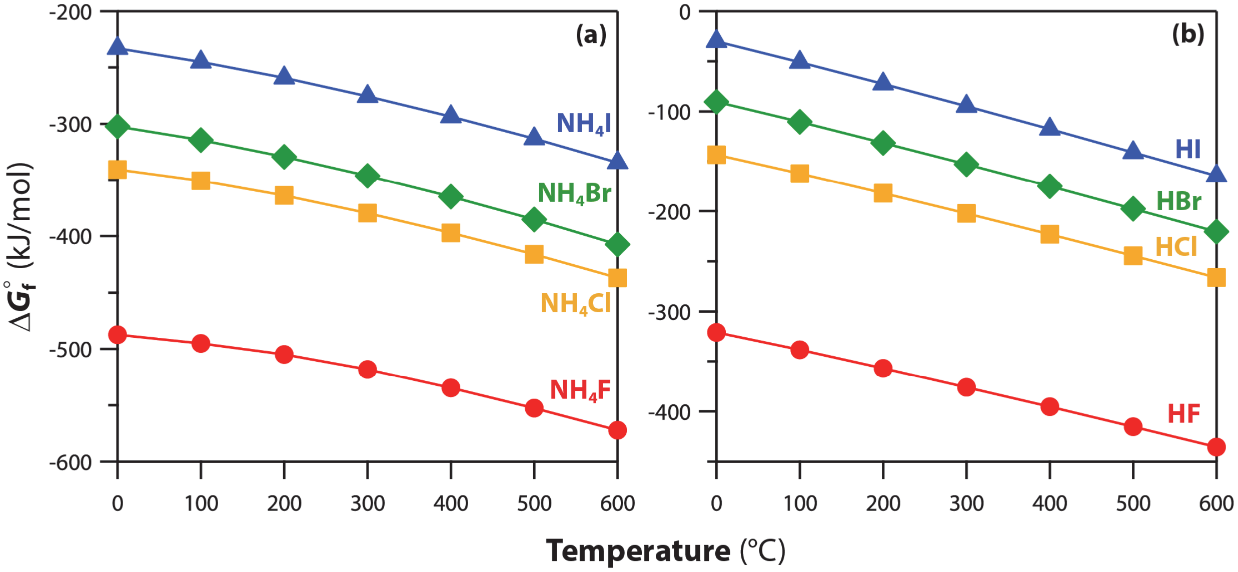


Figure 4-1. Summary of ΔG_f° as a function of temperature for (a) ammonium halide salts (i.e., NH_4F, NH_4Cl, NH_4Br, and NH_4I) from (Riley et al. 2020c) and (b) halide acids (i.e., HF, HCl, HBr, and HI) calculated by using HSC software (v9.9.0.1).

4.2 Off-Gas Hazards, Capture, and Recycle

Dehalogenation reactions discussed in this report generate off-gas products that require management. More work is needed to better understand the specific off-gas hazards, methods for capture and/or neutralization, and potential recycle of gaseous byproducts coming off the melt during dehalogenation (e.g., NH_4Cl). The specific pieces of data that are needed in this area include the following (described below in more detail):

- reaction rates for dehalogenation, i.e., ideal heat-treatment schedule for achieving full dehalogenation including both temperatures and times;
- precursor composition that allows for full dehalogenation while maximizing waste loading and other glass properties such as chemical durability, e.g., O:P molar ratio, Fe:P molar ratio; and
- effects of the heat treatment process (e.g., heating rates, dwell temperatures) and reactants on the production of acidic gases. In some cases, acidic byproducts have been observed when using ADP as the phosphate precursor suggesting reaction pathways other than those presented in Reaction (4-1).

While the dehalogenation approach works for chloride-based salts, it has not yet been thoroughly evaluated for other halide salts, i.e., F, Br, I. Thus, more data is needed with these other salt systems to fully evaluate the applicability of these techniques for dehalogenating these other salt wastes. In some cases, the halides could be recovered and recycled, when in other cases (e.g., F, I), recycle is likely not beneficial. Table 4-1 provides a summary of the potential value in recycle of the halogens and the expected radioactivity of different halogens. Some of these halides can be recovered and recycled, while others do not need to be recycled. However, in all cases, removing the halides opens more waste form possibilities with these salt streams.

Fluoride salts would be applicable for molten salt reactor waste streams and should be considered with the dehalogenation approach. Additionally, it is possible that this process could be used to remove I or Br from salt mixtures or pure streams. In the case of ^{129}I, this is important because this is a major long-term dose contributor to a repository dose requirement due to the long half-life ($t_{1/2}$) of 1.57×10^7 y. However, one of the most important benefits of dehalogenation is the ability to use this approach for ^{37}Cl recovery. It is likely that the chloride salts in an MSR will be enriched in ^{37}Cl to minimize the neutron activation of natural ^{35}Cl to ^{36}Cl, which is a long-lived ($t_{1/2} = 3.01\times10^5$ y) radioisotope posing issues for waste form disposal in a geological repository.

Table 4-1. Options for various halides present in salt waste streams.

Species	Value in recycle	Radioactive
F	No	No
Cl	Yes(a) (^{37}Cl)	Maybe(b)
Br	No	Yes
I	No	Yes

(a)If chlorine is present in these salts as ^{37}Cl, value can be obtained through recycle.

(b)If chlorine is present as ^{35}Cl, some ^{36}Cl might be present through neutron activation.

Halide salts can be somewhat soluble in phosphate melts under certain conditions such as in alkali-rich silicophosphate melts (Tsai and Greenblatt 1988). However, they are only sparingly soluble in iron phosphate melts and tend to decompose during vitrification as the halide or halide compounds formed through reaction with phosphate precursors are released as gases above the melt. Once this dehalogenation process occurs, if these reactions are performed in air, it is common that the cations associated with the initial halides (e.g., Na^+ from NaCl) are converted to oxides and incorporated into the glass network as such (Mesko et al. 2000; Kim and Day 2003). It is unclear how these reactions would proceed in the absence of air or $O_{2(g)}$.

Figure 4-2 provides a conceptual process flow diagram for potential off-gas products generated in different scenarios when reacting chloride salts with H_3PO_4, $NH_4H_2PO_4$, or $(NH_4)_2HPO_4$. Depending on the compositions of the reactants, different processing temperatures will be required, and a range of off-gas products are expected. Table 4-2 provides a partial list of potential off-gas products generated during reactions between halide salts and phosphate precursors along with melting and boiling temperatures of pure species, e.g., H_3PO_4, $NH_4H_2PO_4$, or $(NH_4)_2HPO_4$.

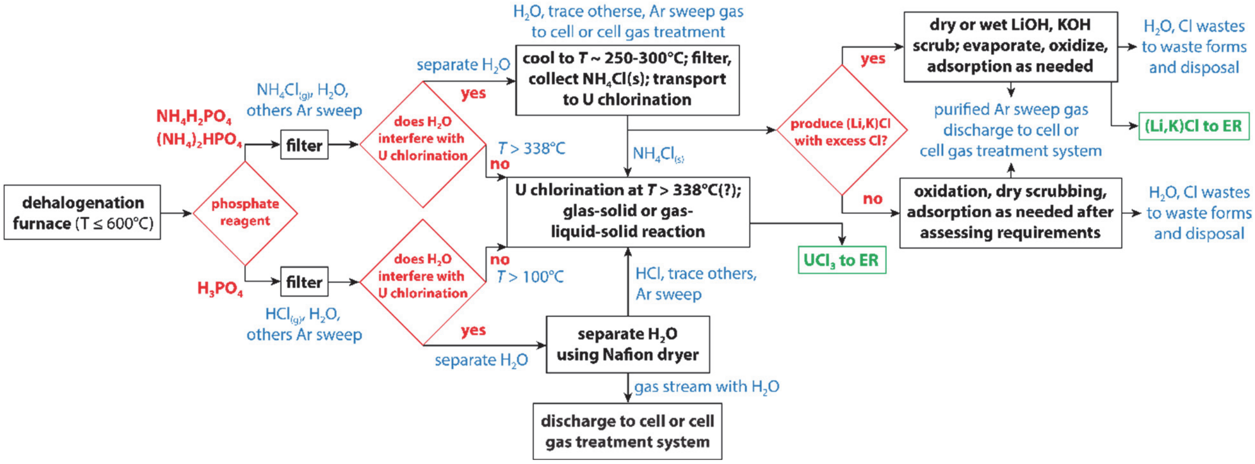


Figure 4-2. Conceptual process flow diagram for treating chloride salts with phosphates showing different off-gas products based on decisions (in red) made during the processing (courtesy of Nicholas Soelberg of Idaho National Laboratory and Stephanie Bruffey of Oak Ridge National Laboratory).

Table 4-2. Summary of melting temperatures (T_m) and boiling temperatures (T_b) for halogens, hydrohalic acids, and ammonium halides. Note that (a) = triple point, (b) = decomposition temperature, and (c) = sublimation point.

Chemical	T_m (°C)	T_b (°C)
F_2	-219.67[(a)]	-188.12
Cl_2	-101.5	-34.04
Br_2	-7.2	58.8
I_2	113.7	184.4
HF	-83.36	20
HCl	-114.17	-85
HBr	-86.80	-66.38
HI	-50.76	-35.55
NH_4F	238	–
NH_4Cl	520.1[(a)(b)]	338[(c)]
NH_4Br	542[(b)]	396[(c)]
NH_4I	551[(b)]	405[(c)]

4.2.1 Reaction Rates for Effective Dehalogenation

Effective dehalogenation is not only full removal of the halides in the starting salt mixtures, but also preventing volatile losses of the salt cations into the off-gas system. To achieve successful dehalogenation, several parameters require optimization including (1) the temperature of the reactions, (2) heating rates, and (3) the molar ratio of phosphate precursors to halide present in the salt. These types of parameters should be evaluated so that a range of optimum parameters can be established. These reactions are producing off-gas products, so heating at too fast of a rate could result in excessive bubbling and volatile losses of critical salt cation component from the salt into the gas-phase.

4.2.2 Optimizing Precursor Compositions for Achieving Optimum Product

It is important to select the precursor composition so that the fully dehalogenated product will have the ideal properties. The reason that this in the off-gas section is because one of the critical parameters here is the H:Cl or NH_4:Cl molar ratios in the starting material, which should be H > Cl or NH_4>Cl to make sure that enough cations are present to react with the halides. If the concentration of H^+ or NH_4^+ cations in the starting mixture are lower than the halides, it is likely that some halides will remain in the glass. From a previous study, it was shown that residual halides in iron phosphate glasses can lead to significantly reduced chemical durability in the final glass product. Other parameters that can be adjusted in the starting mixture include the O:P molar ratio and the Fe:P molar ratio.

4.2.3 Effects of the Heat Treatment Process and Reactants on Off-Gas Products

The off-gas products and evolution rates from reacting halide salts with phosphate precursors will be different depending on several factors including the heating rate, dwell temperatures, dwell times, and the phosphate precursor selection. The use of ammonium-containing phosphates [e.g., $NH_4H_2PO_4$, $(NH_4)_2HPO_4$] will result in ammonium halide off-gas products (e.g., NH_4Cl) while using H_3PO_4 will result in hydrohalic acids (e.g., HCl). These different products will require different capture mechanisms and treatment systems for recovery, recycle, and or treatment for disposal.

4.3 One-Step vs Two-Step Process for Dehalogenation and Vitrification

To date, the most effective method for full dehalogenation and vitrification of chloride salts has been a two-step process in which the salts are dehalogenated through a gentle heating process ($T \leq 600°C$) followed by adding Fe_2O_3 and a separate vitrification step ($T \sim 1050°C$). To further simplify this approach, exploration of one-step processes should be explored to react salt wastes where the dehalogenation and vitrification steps can be combined in a way that does not require cooling to room temperature between the two steps.

In scoping experiments to evaluate a one-step process, the mixture of a chloride salt simulant ER(SF), ADP, and Fe_2O_3 did not melt at $T \leq 600°C$ (Riley et al. 2020c). Rather, the mixture was a porous sintered mass resembling a pumice stone with large open pores. Also, the condensate was visibly yellow due to the presence of I and Fe, which were observed in this material during analysis with scanning electron microscopy and energy dispersive spectroscopy (see Figure 4-3). If the glass-forming additives (e.g., Fe_2O_3) are included in the batching process for the initial dechlorination heat treatment process, it will be difficult to balance a full dechlorination reaction with the chloride salts while minimizing volatile losses of additional components in the glass (e.g., P, Fe) and fission products from the salt (e.g., Cs). A comparison of the details from the one-step and two-step processes is provided in Table 4-3.

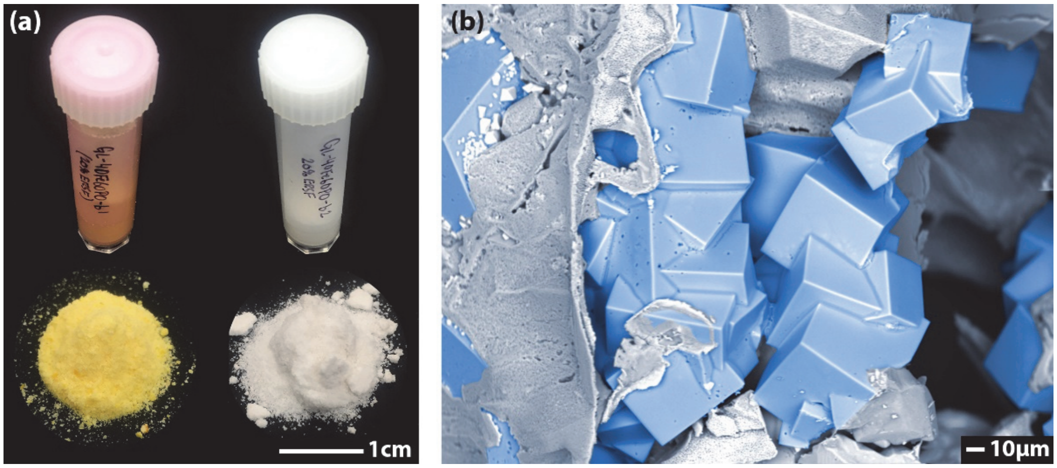


Figure 4-3. (a) Pictures of the condensates collected using (yellow) the one-step process where Fe_2O_3 was included in the batch during dechlorination and (white) the two-step process with no Fe_2O_3 present; the two-step process yielded a higher-purity NH_4Cl salt. (b) Pseudocolored scanning electron micrograph showing impurity crystals in the yellow condensate from the one-step process (these crystals contained N-P-Cl-K-Fe-I-Cs).

Table 4-3. Summary between scoping tests to evaluate differences between one-step and two-step processes for performing dehalogenation and vitrification for making phosphate waste forms from salt wastes.

Details	**One-step process**	**Two-step process**
Addition of Fe_2O_3	Before dehalogenation	After dehalogenation
Dehalogenation process ($T \leq 600°$)	Mixture does not melt	Mixture creates a homogeneous melt
Off-gas condensate	Yellow and contaminated with P, K, Fe, I	White and very pure NH_4Cl

Some options for accomplishing this could be including other additives in the initial formulation such as higher alkali, transition metals, or other intermediates (e.g., Al_2O_3). Each additive included in the glass composition will change the properties of the final form. It is straight forward to formulate a durable waste form for a large variety of borosilicate glasses due to a large database of composition-property data and models (Vienna et al. 2002). However, doing this same thing with phosphate glasses is difficult because this type of database does not exist for phosphate waste forms and the waste streams will vary.

4.4 Large Scale Production

Various aspects of these processes need to be considered when discussing a full-scale operation. One aspect that requires consideration is the water generated during decomposition of $NH_4H_2PO_4$. This could pose issues for hot cell environments. Additionally, the more steps required for a given process, the more difficult that process will likely be to implement in a radiological facility.

4.5 Process Complexity

Full-scale production requires facilities to store and mix reagents and waste, perform dehalogenation and capture off-gas for treatment and possibly storage for recycle, adding a stabilizing agent such as Fe_2O_3 to the phosphate glass intermediate material and vitrifying, then sealing the final iron phosphate waste form in a canister for storage to cool prior to transporting to a disposal facility. The operations must provide adequate throughput rates using remote operations and possibly robotics. The overall complexity of the process should be less than that developed for glass-bonded sodalite waste forms that are the current baseline waste forms for ER and OR waste salts and similar to that used to vitrify tank wastes at the Defense Waste Processing Facility (DWPF) at the Savannah River Site. Implementing the production processes represented in the flow diagram in Figure 1-3 and off-gas treatment options outlined in Figure 4-2 will be challenging and simplifications such as one-pot production of the final waste form will make the approach more practical.

4.6 Security and Safeguards

All waste forms should be evaluated from the perspectives of accountability and safeguards. This means that all separations activities and immobilization processes require consideration in ways that material could be diverted for nefarious purposes. Approaches developed for fuel reprocessing and production of vitrified waste forms from radioactive tank wastes can likely be directly applied to processes used to produce iron phosphate waste forms. Methods for labeling and tracking waste canisters during storage, transport, and disposal developed for other waste from production facilities will be applicable.

4.7 Material Balance and Secondary Wastes

Most radionuclides in the waste salt are retained in the phosphate glass formed during the dehalogenation step at moderate temperatures and the iron phosphate waste form produced by adding Fe_2O_3 and vitrifying at a higher temperature. Depending on the composition of the waste salt, the off-gas stream generated during dehalogenation may be subjected to several processes to recover NH_4Cl, HCl, or other volatilized species for recycle or remove hazardous species such as HF for further treatment.

4.8 Safety Considerations

Reactions between chloride salts and the phosphate precursors H_3PO_4, $NH_4H_2PO_4$, or $(NH_4)_2HPO_4$ will result in the production of toxic gases including $NH_{3(g)}$ and $HCl_{(g)}$. These can likely be mitigated using submerged bed scrubbers on the off-gas line coming from the melters processing these materials. Processing fluoride-based salts will likely result in the production of $HF_{(g)}$, which is very hazardous and corrosive to glassware commonly employed in off-gas systems. This will need to be taken into consideration when processing fluoride salts. Reactions for iodine-based salts are likely similar to those of chloride-based salts when combining with H_3PO_4. However, when combining nitrogen compounds with iodine vapors, it is possible to form NH_4I_3 or NI_3, both of which are contact explosives. Thus, if iodine-containing salts are present within the salt streams being investigated, the safety hazards of these potential byproducts need be considered.

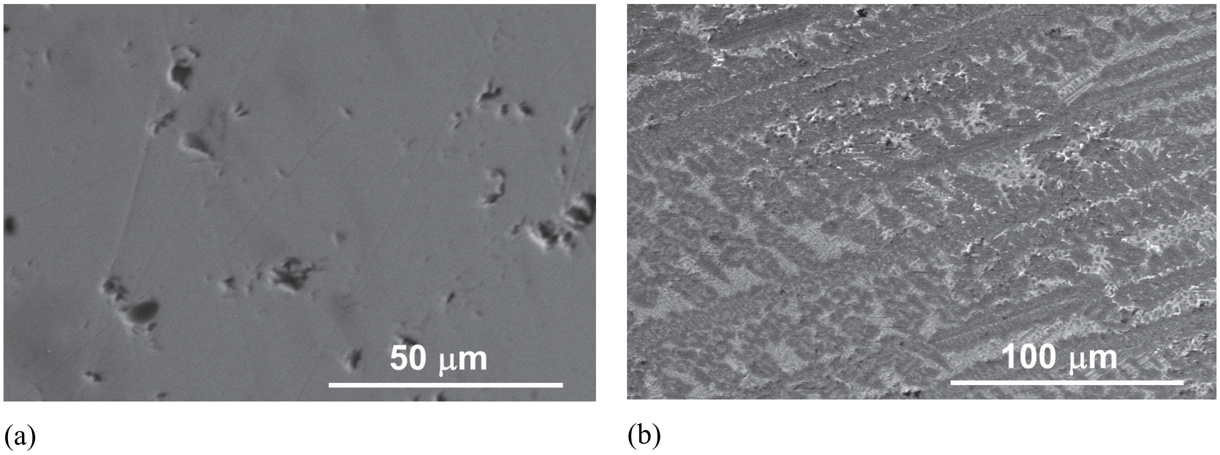
4.9 Production Rates and Throughput

Many of the reactions discussed in this report have only been demonstrated on a small scale. Scaling up these processes, in particular the dechlorination reactions, could indicate some issues that require further study, such as incomplete dehalogenation of the initial salt waste stream. Accelerating the dechlorination reaction in scoping studies resulted in splattering of the melt and volatility of some of the salt cations that should be retained in the final glass waste form. These operations will require optimization to achieve maximizing waste processing throughput.

5. WASTE FORM PROPERTIES

5.1 Crystalline Phase Content

Developmental iron phosphate materials made with different relative amounts of phosphate, salt, and iron oxide resulted in materials with different crystal contents, primarily alkali iron phosphates with dendritic structures. For example, Figure 5-1 shows the microstructures of materials DPF5-280 made with 40.1 mol% P_2O_5-26.3 mol% Fe_2O_3-33.6 mol% salt cations and DPF5-336 made with 43.5 mol% P_2O_5-28.5 mol % Fe_2O_3-28.0 mol% salt cation oxides. Material DPF5-280 was an essentially homogeneous glass and Material DPF5-336 contained a significant quantity of crystalline phases. The waste constituents of concern (primarily Cs, Sr, and rare earth elements in these materials) report to the glass phase. The Fe_2O_3 is added to improve the durability of the glass phase, but excessive amounts lead to the formation of crystalline phases that decrease the amount of glass available to sequester the radionuclides from the salt.



(a) (b)

Figure 5-1. Microstructures of (a) Material DPF5 280 and (b) Material DPF5 336.

While certain lab-scale samples of waste form options might appear acceptable when made by melt quenching, the typical waste form production process involves either pouring a melt into a canister or using an in-can vitrification technology and, in both cases, the melt slowly cools within the canister. Slow cooling of a melt can result in crystallization with detrimental effects on the final waste form composition and performance. For example, the melt can undergo phase transitions where unwanted crystalline materials precipitate leading to a residual glass of lower durability than desired. Because most radionuclides will be contained in the glass phase, waste form performance is determined by the chemical durability of the iron phosphate glass that encapsulates the crystalline phases.

Initial data on slow-cooling of DPF-5 (Riley 2020a) iron phosphate glass containing ER salt cations has shown that a wide variety of different phosphate phases can form during slow cooling. The slow-cooling temperature profile for canister centerline cooling (CCC) is shown in Figure 5-2, which is based off the centerline cooling profile for a standard 0.61-m diameter HLW canister.

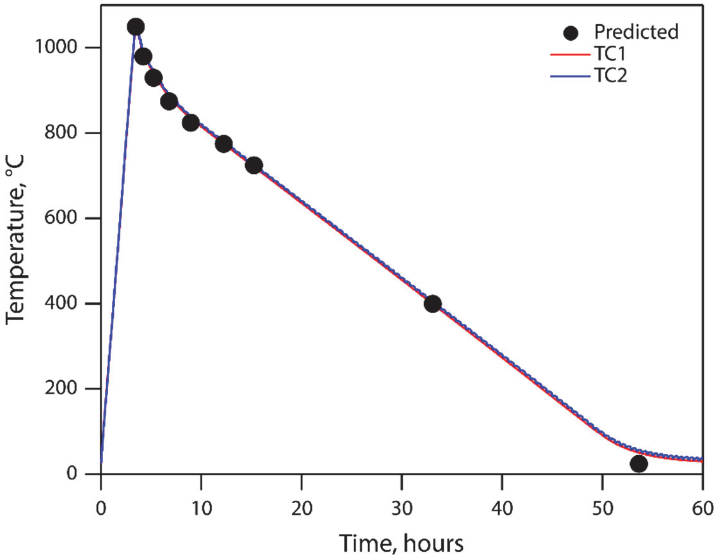


Figure 5-2. Summary of CCC treatment profile compared to what types of cooling rates can be achieved in a typical box furnace (Riley 2020a).

For these experiments, ERV2 salt was dehalogenated with $NH_4H_2PO_4$ at temperatures up to 600°C, then Fe_2O_3 was added and the mixture vitrified at 1050°C. Following vitrification, the melt was quenched onto an Inconel pour plate. Once cooled, the glass was ground to a powder within a tungsten carbide milling chamber. Portions of this powder were added to a quartz crucible and an alumina crucible and both were heated through the profile shown in Figure 5-2. Following the heat treatment process, the samples were cross sectioned, and pictures of these cross sections are shown in Figure 5-3. Both samples showed regions of blackish and reddish colored phases.

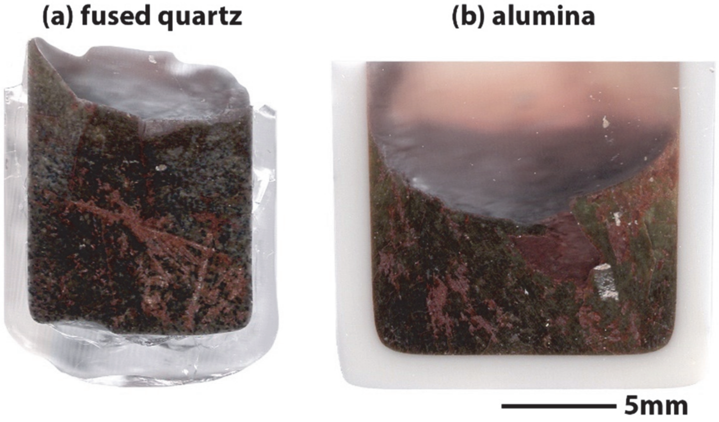


Figure 5-3. Pictures of cross-sectioned DPF5 samples following CCC treatments in (a) a fused quartz crucible and (b) an alumina crucible (Riley 2020a).

Both samples had regions of crystals rich in rare earth elements (REEs) at the base of the samples, which are shown in Figure 5-4 and Figure 5-5 for quartz and alumina crucibles, respectively. However, the layer thicknesses varied extensively between the different experiments with a value of 133±15 μm for the experiment in the alumina crucible and 805±97 μm for the experiment in the fused quartz crucible. It is also worth noting that the morphologies of the crystals were quite different between the samples where the experiment run in fused quartz had thin plate-like crystals and the experiment run in alumina showed more rectangularly shaped crystals. This is possibly due to the formation of oxyapatite-type crystals when SiO_2 was present.

This type of crystal settling is commonly observed when vitrified HLW is slow-cooled where spinel crystals are found on the bottom of cross-sectioned samples from crucible studies or even glass canisters (Rankin et al. 1982). This precipitation process can lead to settling of the crystals, if their density is higher than that of the melt, and these crystals can clog the melter pour spout (Jantzen 1982).

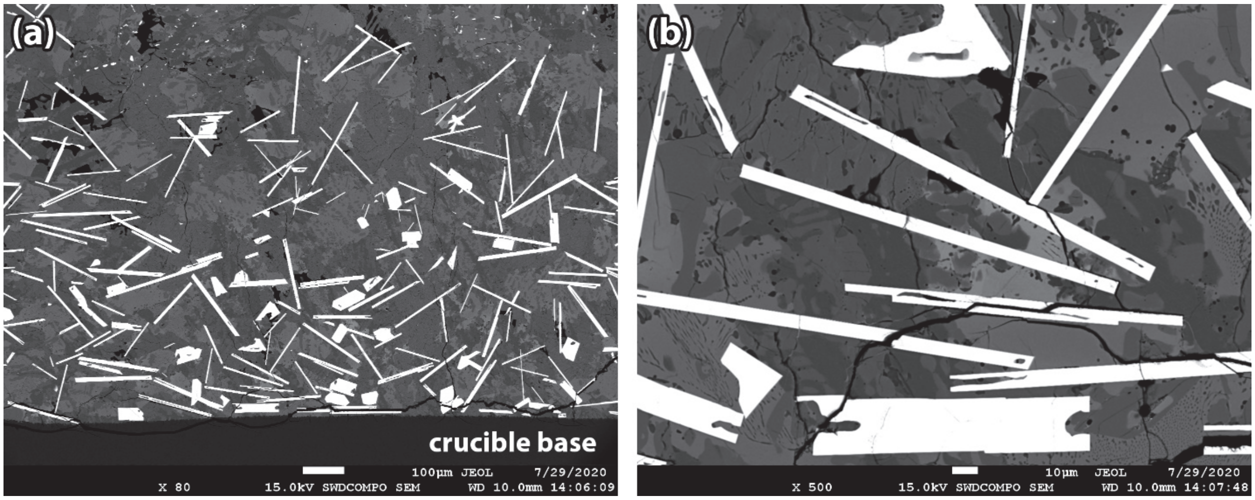


Figure 5-4. SEM collage of the base of cross-sectioned iron phosphate glass waste forms that were CCC-cooled in a quartz crucible, shown at different magnifications (Riley 2020a). These micrographs show the accumulation of REO_x-concentrated crystals.

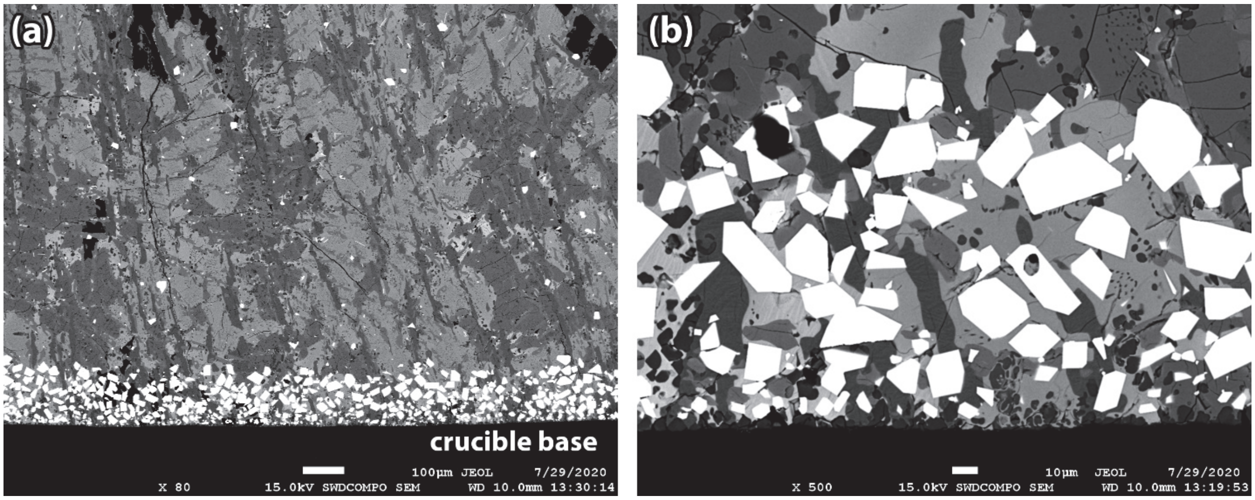


Figure 5-5. SEM collage of the base of cross-sectioned iron phosphate glass waste forms that were CCC-cooled in an alumina crucible, shown at different magnifications (Riley 2020a). These micrographs show the accumulation of REO_x-concentrated crystals.

A summary of the EDS elemental map on the sample made in the alumina crucible is shown in Figure 5-6. This shows elemental distributions and how they changed across the different phases observed. Additional analysis was performed on this EDS map to look at spot chemistry of different regions and this information is shown in Figure 5-7. Based on the comparison shown in Figure 5-7, it is clear that the compositions of many of the different phases were very similar in chemical composition with minor fluctuations in components including Al, K, Na, Sr, and Cs. The high-RE phase is one that stands out as being very different from the rest of the phases compositionally with values as high as 23.3 at% total RE cations. It should also be noted that these values do not include O or Li, based on limitations of the analytical technique. The Li distribution could affect the appearance of these phases in the SEM due to the very low atomic number, which would add a lot of contrast since all SEM micrographs were captured using backscattered electrons. Additional work could be done to track Li in these samples using a different analytical technique such as nano secondary ion mass spectrometry.

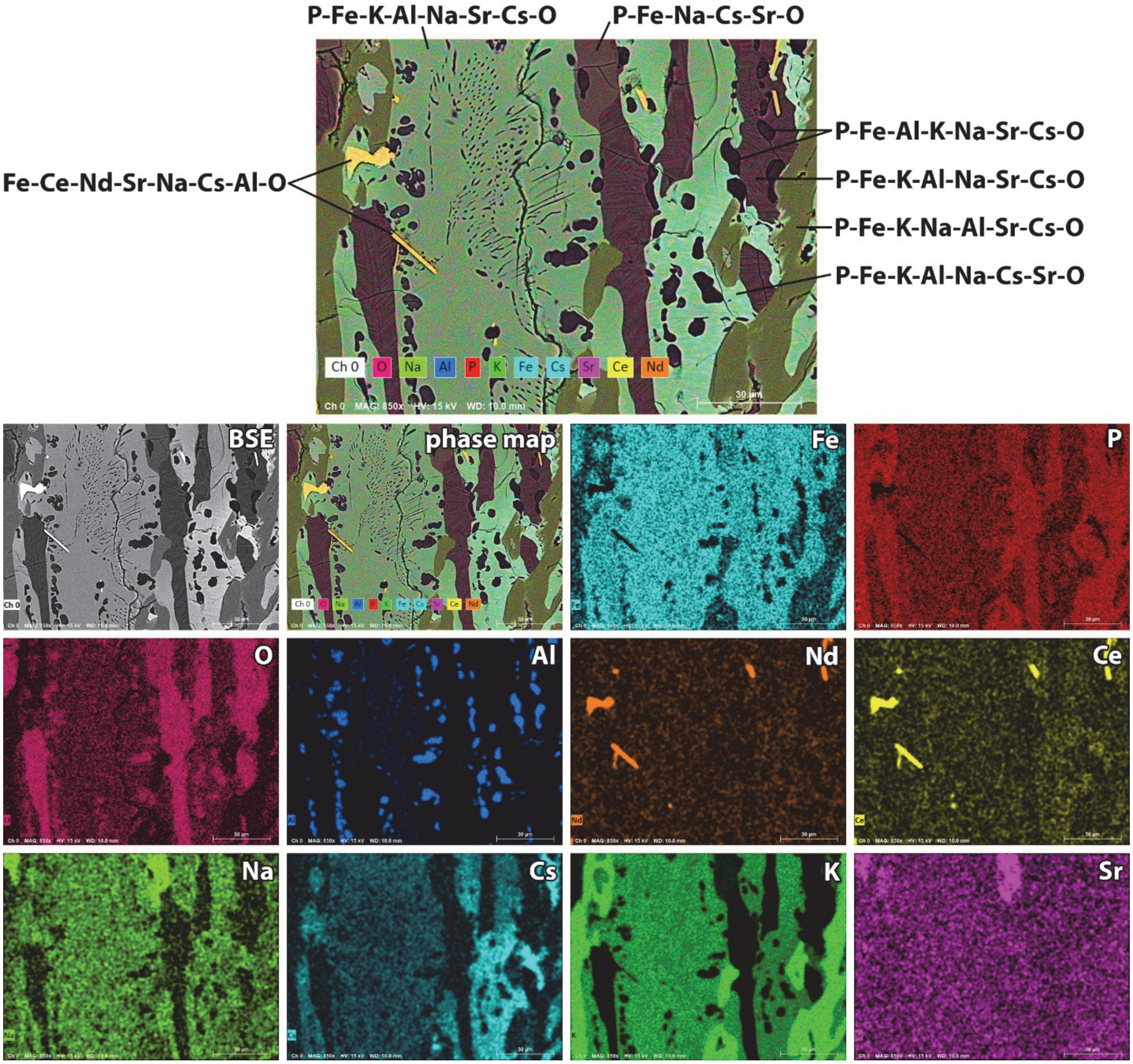


Figure 5-6. SEM-EDS collage taken at 850× of the DPF5-FY20-CCC2 sample run in an alumina crucible showing the backscattered electron (BSE) micrograph, the overlay map, and the elemental distribution maps (Riley 2020a). The top image shows the phase map with the most abundant species shown in descending order. The term FY denotes the fiscal year in which these samples were made.

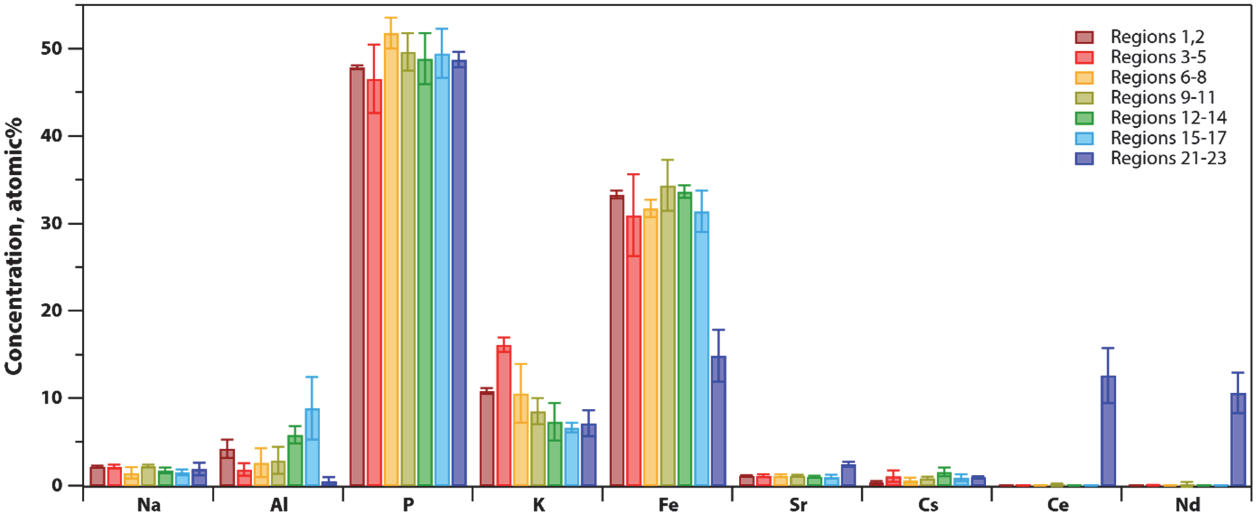


Figure 5-7. Summary of EDS compositions measured at different regions from Figure 5-6 including averages and standard deviation (±1σ) (Riley 2020a).

5.2 Chemical and Physical Robustness

The chemical durability and degradation behavior of developmental iron phosphate waste forms have been measured by using ASTM-International test methods C1308, C1220, and C1285 with minor modifications (ASTM 2014; ASTM 2017b; ASTM 2017a). The ASTM C1308 method is conducted with monolithic specimens in demineralized water at a low solid surface area-to-water volume ratio and the entire solution is replaced daily to maintain dilute conditions. These tests are used to measure the kinetic dissolution rate based on the release of soluble constituents Li, Cs, and P. The ASTM C1220 test is conducted under similar conditions except the solution is not replaced. Small samples are taken to measure the accumulation of Li, Cs, and P over time to detect saturation effects. The ASTM C1285 test is conducted with crushed material to achieve a higher solid surface area-to-water volume ratio to enhance saturation effects. Reacted specimens are examined after each test to detect preferential dissolution of different constituent phases and secondary phases generated during the test.

To date, the physical robustness of the prototype materials has not been quantified, but differences in the brittleness, the extent of cracking, release from casting crucibles, and resistance to polishing have been noted when preparing materials for corrosion tests. As with other vitrified waste forms, these characteristics are sensitive to processing and annealing procedures that have not yet been optimized for these materials.

The results of corrosion tests indicate the crystalline and glassy phases dissolve by surface dissolution mechanisms similar to borosilicate glasses. The dissolution rates of crystalline and glassy phases slow as dissolved constituents accumulate in the ASTM C1220 and ASTM C1285 test solutions but remain constant when solutions are maintained highly dilute in the ASTM C1308 tests. The affinity-based degradation model developed for borosilicate waste glasses will likely be appropriate for modelling the iron phosphate waste forms. However, two important aspects of borosilicate glass dissolution may not be relevant to the degradation of iron phosphate glass—the formation of surface alteration layers and secondary phases. The limited solubility of silica polymorphs results in the formation of highly porous clay-like layers on the glass surface and zeolites can precipitate from highly concentrated solutions (Vienna et al. 2013). The formation of both affect the dissolution rate of borosilicate glasses. Tests conducted with iron phosphate glass and glass-ceramic materials have not shown either surface layers or rate-affecting secondary phases to form, although tests may not have been conducted for sufficiently long durations to show these effects. Many phosphate compounds are sparingly soluble in water, but they might not form layers that affect glass dissolution or be coupled to the glass dissolution kinetics in a way the affects the dissolution rate. This would greatly simplify the iron phosphate glass dissolution model used in repository performance simulations.

5.3 Thermal and Radiological Stability

More work is needed to better understand the effects of thermal and radiological stability for phosphate glasses. Some data is available for these types of properties, but more in-depth analyses are needed.

The high waste loadings and high fission product loadings that can be achieved in iron phosphate waste loadings will result in high decay heats being generated by fission products within the waste form. This will affect the stability of the waste form itself and heat transferred to the storage and disposal facilities. These evaluations should be considered for a variety of possible waste streams. One of the primary issues that decay heat introduces into the qualification of a glass waste form is that, if the decay heat prohibits the waste form from rapidly cooling through critical phase transition temperatures (e.g., the glass transition temperature or T_g), this can lead to unwanted crystallization and, therefore, a lower chemical durability than desired. Heat loading calculations also take several other material properties into consideration such as the thermal diffusivity (α; defined in Equation (5-1)], thermal conductivity (k), specific heat capacity (c_p), and density (ρ), all of which will depend on the glass formulations and waste loadings. These intrinsic properties affect the rate at which decay heat can be transferred out of the waste form into the waste package and dissipated into the repository environment. In most engineered disposal facilities, the use of bentonite backfill material will impose thermal limits on disposed waste.

$$\alpha = k/(\rho \cdot c_p) \tag{5-1}$$

Radiation damage in a waste from can be manifested through the occurrence of several things including relaxation processes, diffusion processes, phase separation, devitrification, amorphization of crystalline phases, volume changes, cracking, as well as gas accumulation, bubble formation, and/or void formation. Specifically, very few studies have been done to evaluate the radiation stability of phosphate glasses and none have been directed at the types of compositions to be expected from treating or immobilizing salt streams from electrochemical reprocessing or molten salt reactors.

In iron phosphate glasses specifically, a few different studies have been conducted looking at radiation stability under different exposures from ion exposure (e.g., Kr^+, Ag^+, helium) to electron exposure (under transmission electron microscopy). Observations of glasses during post-irradiation analysis revealed bubbles, nanoparticle formation, phase separation, Fe redox changes, as well as depolymerization and other structural and chemical changes in the glasses.

Dube et al. (2016) evaluated radiation damage in iron phosphate glasses with the composition of 60 mol% P_2O_5 and 40 mol% Fe_2O_3 using either helium ions to simulate radiolysis and ballistic damage effects α decay from actinides. They discovered that “blisters” of ~ 1 µm were observed at helium energy of 30 keV (see Figure 5-8). Irradiation from 2 MeV bismuth ions showed that network depolymerization occurred in the form of breakage of Fe–O–P and P–O–P bonds. It is unclear how these types of effects would alter other glass properties such as the chemical durability.

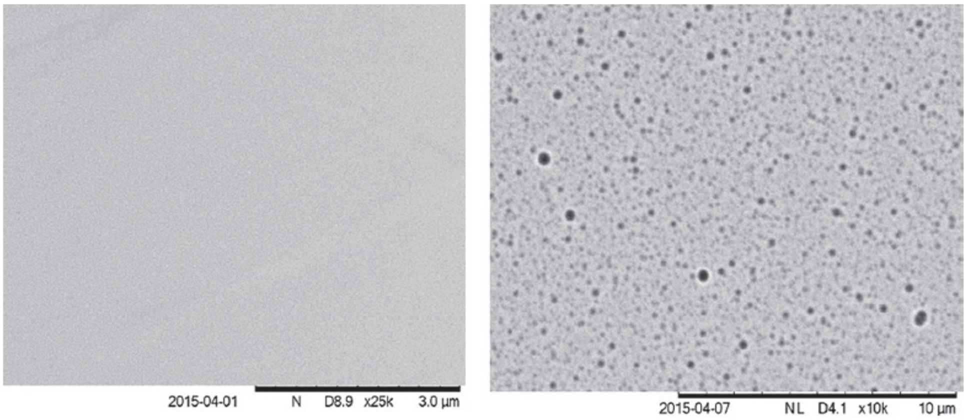


Figure 5-8. SEM micrographs of iron phosphate glasses showing (left) as-made and (right) after He ion irradiation on a pre-damaged specimen (Dube et al. 2016).

In a separate study by Gandy et al. (2015), analysis of 60 mol% P_2O_5 and 40 mol% Fe_2O_3 glasses irradiated with 2 MeV Kr^+ or Ag^+ ions showed additional damage to the glasses. To assess the progress of damage, X-ray absorption spectroscopy was performed looking at the Fe K-edge. Here, radiation-induced damage was observed in the form of (1) Fe^{3+} reduction to Fe^{2+}, (2) increases in average Fe–O distances, and (3) changes in local structure around the Fe^{2+} and Fe^{3+} ions.

5.4 Waste Loading and Durability

Two important aspects of waste form development are finding ways to maximize the waste loading and reduce the overall waste form volume. Both of these need to be considered when formulating and optimizing phosphate glass waste form compositions. More work is needed to determine these limits for phosphate glasses using a variety of additives.

Increasing waste loading in a waste form has several advantages including a lower overall waste form volume and potentially lowering costs for disposal in a repository. A comparison of waste form volume starting from a given amount of salt is shown in Figure 5-9 for glass-bonded sodalite, lead tellurite glass, and iron phosphate glasses; this comparison shows the benefit of research in the area of advanced waste forms. The plot is shown with salt cation loadings on the *x*-axis because the phosphate glasses do not contain any salt halides due to dehalogenation prior to vitrification. The y-axis is included to show how the waste form volumes change to immobilize a given starting mass of salt.

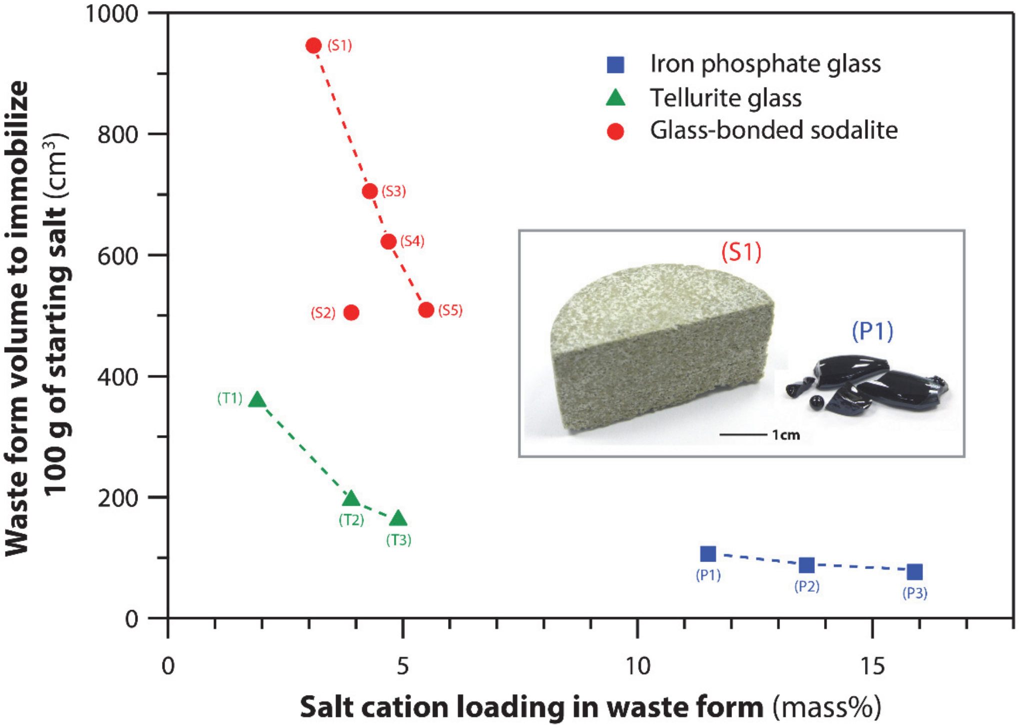


Figure 5-9. Summary of waste form volume as a function of salt cation loadings comparing glass-bonded sodalite with tellurite glass and iron phosphate glasses (Riley 2019b; Riley 2020b). The inset picture shows the difference in waste form volume to treat and immobilize the same starting mass of salt for GBS-CWF (S1) and iron phosphate glass (P1).

The waste loading within a given waste form is dependent on several factors. Depending on the waste composition, the overall waste loading will vary in each waste form matrix and this needs to be evaluated. The amounts of salt and Fe_2O_3 added to produce the iron phosphate waste form both affect the waste loading. The amount of salt directly increases the amounts of radionuclides retained in the waste form and the amount of Fe_2O_3 increases the mass and volume of the final waste form that immobilizes the radionuclides. It is desired to maximize the amount of salt waste and minimize the amount of Fe_2O_3 added to stabilize the waste form.

For initial and follow-on studies with iron phosphate glasses for these applications, several observations and recommendations lead to the formulation and production of several prototype waste forms for testing that are shown on the ternary diagram in Figure 5-10. Tests with glasses DPF-1 through DPF-6 were conducted in fiscal year (FY) 2018 and most of that work is documented in reports (Ebert et al. 2018; Ebert and Fortner 2019; Ebert and Fortner 2020; Stariha and Ebert 2020), memorandums to DOE-NE (Riley 2017; Riley 2018; Riley 2019a; Riley 2019b), and a journal article (Riley et al. 2020c). From those studies, the glasses with the best chemical durabilities were chosen for further study in FY2019 and FY2020 that included DPF-3 and DPF-5 where a glasses based on DPF-3 were made with varying Fe:P molar ratios (fixed salt loading) and glasses based on DPF-5 were made with varying salt loadings (fixed Fe:P molar ratios).

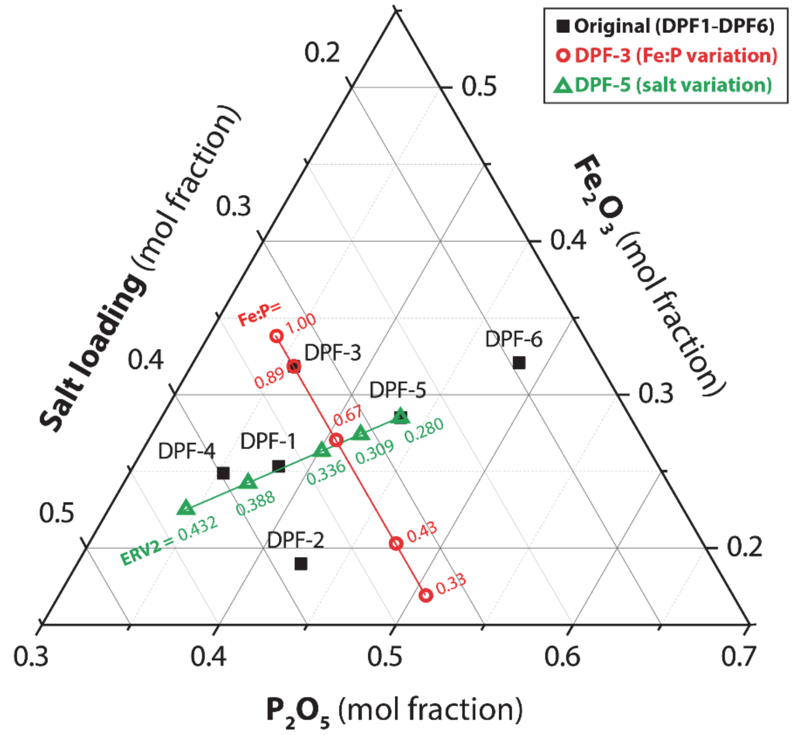


Figure 5-10. Phase diagram of the FY2018 and FY2019 glass matrices. Note that "salt loading" denotes salt cation oxide loading (e.g., while $NdCl_3$ is present in the original ERV2 salt, the Nd_2O_3 concentration in the final iron phosphate glass waste form was used to calculate the salt loading).

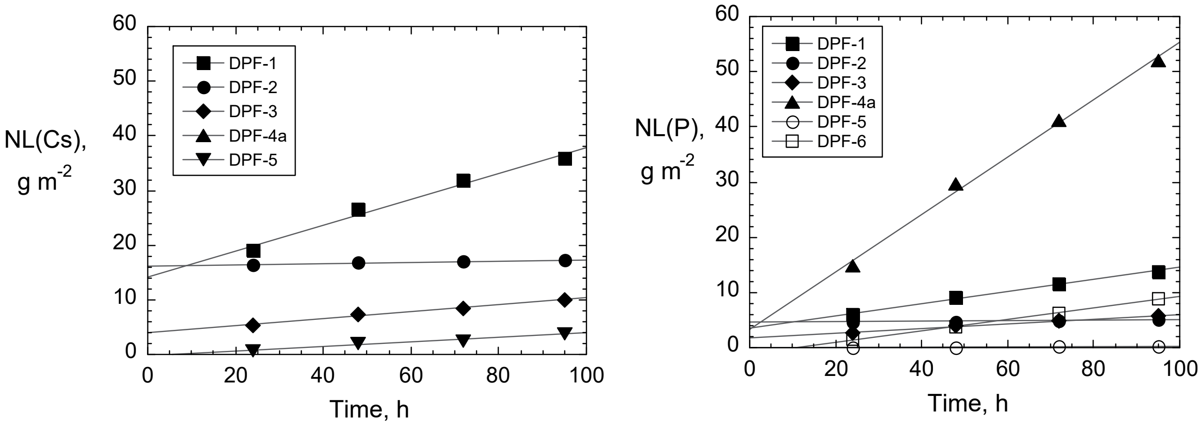
The first series of developmental materials DPF-1 through DPF-6 were formulated to evaluate the effects of the Cl^-/P and Fe/P ratios in the mixed reagents on the phase formation and chemical durability of the final waste form. The formulations are summarized in Table 5-1: DPF-1 was made using the ratios recommended in the literature; DPF-2 had a lower Fe content and DPF-3 had a higher Fe content; DPF-4 had a higher salt content and DPF-5 and DPF-6 had lower salt contents. Note that separate materials DPF-4a and DPF-4b were made using $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ to assess the effects on the dehalogenation efficiency and waste form durability. Use of the different reagents generates more or less NH_4Cl and water.

Table 5-1. As-batched reagents in developmental materials, in grams. Included are the molar ratios of Cl/P and Fe/P.

Sample ID	Mass, g			Mole ratio	
	ERV Salt	$NH_4H_2PO_4$	Fe_2O_3	Cl/P	Fe/P
DPF-1	11.8772	21.9954	10.1179	0.988	0.662
DPF-2	12.3169	24.1944	7.4784	0.931	0.445
DPF-3	10.5578	20.6752	12.7573	0.934	0.889
DPF-4a	13.1972	20.6754	10.1177	1.167	0.705
DPF-4b	12.3382	22.1929[a]	9.4599	1.167	0.705
DPF-5	8.7987	24.1955	10.9977	0.665	0.655
DPF-6	5.9388	26.0645	11.9877	0.417	0.662

[a] Mass $(NH_4)_2HPO_4$ or DHP

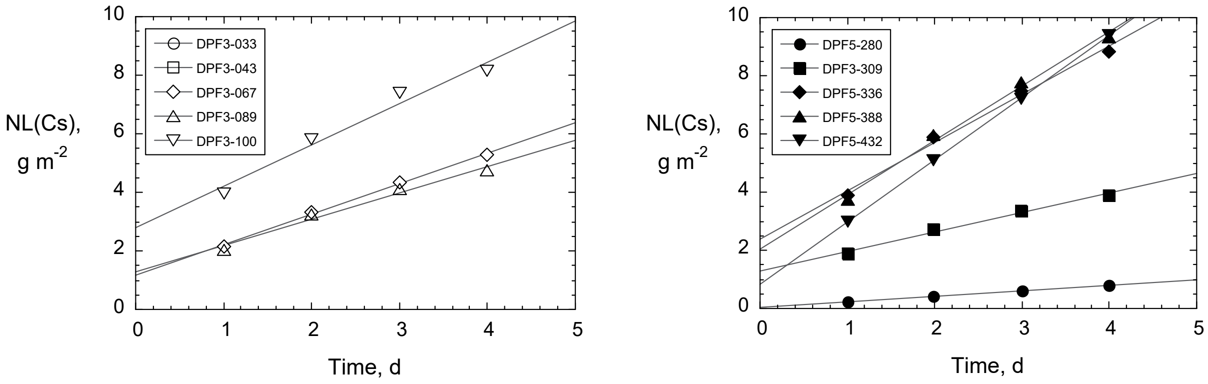
Figure 5-11 shows the results of ASTM C1308 tests conducted with the six developmental DPF materials. Tests were conducted at 90°C in demineralized water at a specimen surface area-to-water volume ratio of approximately 5 m^{-1}. The test solution was exchanged with fresh demineralized water every 24 hours to maintain dilute conditions. The solution concentrations measured in each recovered test solution were normalized to the surface area and elemental concentration in the DPF material to calculate the normalized elemental mass loss. The results based on cesium are shown in Figure 5-11 to indicate dissolution of the glassy phase and the results based on phosphorous represent dissolution of the glassy and crystalline phases (Ebert et al. 2018). The normalized release values of cesium [i.e., NL(Cs)] for the test with DPF-4a exceeded the range shown in the plot. Other major salt waste constituents show the same behavior as cesium. The linearity in the plotted results indicates both the glassy and crystalline phases dissolve by surface dissolution and the higher values of NL(Cs) and NL(P) in the test with DPF-4a (results for DPF-4b were identical) indicates material is much less durable than the others. The high *y*-intercepts of the regression fits may indicate the element was not effectively incorporated into the waste form or is present in a highly soluble phase. Material DPF-4 was formulated with an amount of salt that exceeded the stoichiometry of the dehalogenation reactions given in Equations (4-1a)–(4-1c). The salt constituents are most effectively immobilized in DPF-3 and DPF-5.



(a) (b)

Figure 5-11. Results of ASTM C1308 tests with developmental DPF materials based on (a) cesium and (b) phosphorous.

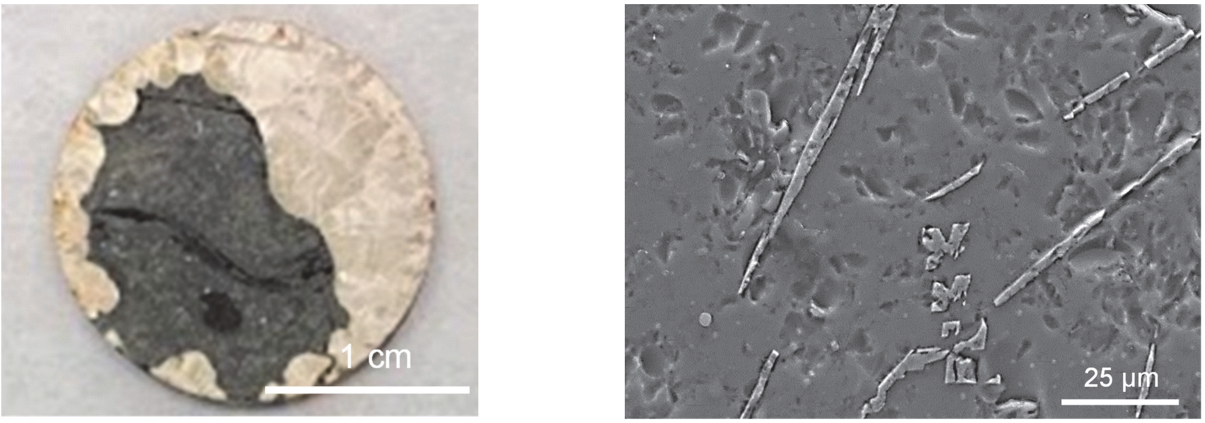
A second series of prototype waste forms were made to better quantify the effects of the reagent ratios by varying the iron contents in DPF-3 and varying the salt cation contents in DPF-5; the variations are shown by the red and green lines in Figure 5-10. The values for the symbols on the plot in Figure 5-10 represent the Fe:P ratio or the mass fraction of salt cations in the materials. Figure 5-12 shows the results of tests with the DPF-3 and DPF-5 series of materials based on NL(Cs). Materials DPF3-033 and DPF3-043 were non-durable and the NL(Cs) values were much higher than the scale of Figure 5-12a (values were approximately 100 and 400 g m^{-2} after the first test interval, respectively).



(a) (b)

Figure 5-12. Results of ASTM C1308 tests with prototype DPF materials made with (a) various iron contents and (b) various salt contents.

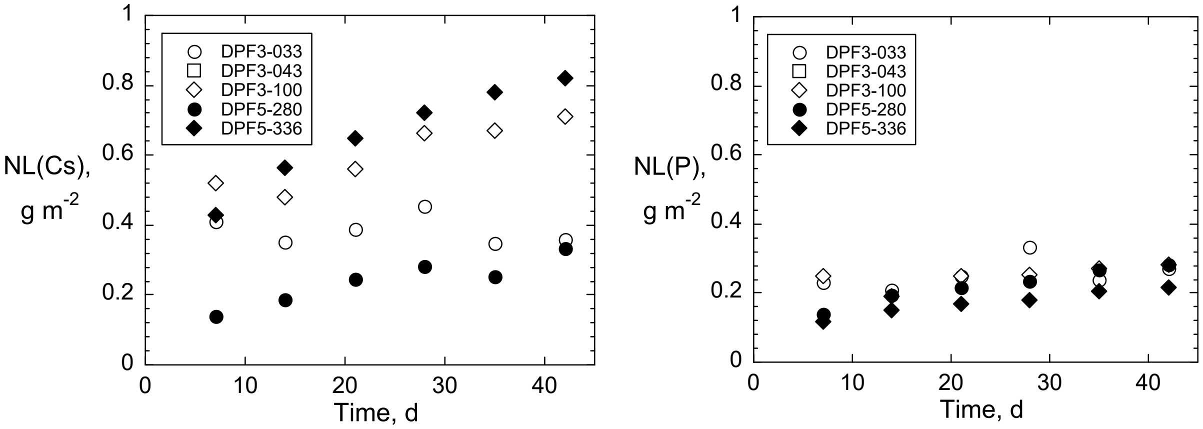
Materials DPF3-033 and DPF3-043 had visible phase separation of glassy and crystalline phases, as shown in Figure 5-13a, and material DPF3-100 had an abundance of iron laths, as shown by the SEM photomicrograph in Figure 5-13b. In contrast, the crystals formed in materials made with intermediate amounts of added Fe_2O_3 were more uniformly distributed throughout the glassy phase (see Figure 5-1b). Furthermore, material DPF3-100 made with the highest iron content was brittle and adding either too little or excessive Fe_2O_3 may be detrimental to waste form durability. These tests indicate waste forms with salt:phosphate ratios in the region between DPF5-388 and DPF5-280 in the ternary diagram in Figure 5-10 and the Fe_2O_3 contents in those materials will have similar chemical durabilities and are recommended for further consideration. Higher salt contents cannot be completely dehalogenated (based on currently known data) and higher Fe_2O_3 contents decrease the waste loading without improving the durability.



(a) (b)

Figure 5-13. (a) Photograph of DPF3-034 specimen and (b) SEM photomicrograph of DPF3-100 surface after ASTM C1308 test.

Modified ASTM C1285 tests were conducted to assess the effect of solution saturation on the dissolution rates. Figure 5-14 shows results of tests with several prototype materials based on the releases of cesium and phosphorous. Results for material DPF3-043 were higher than the scale of the plots (near 5 g m^{-2}) and are not shown, but the releases from other materials are similar and increase slightly during the tests. Cesium is only present in the glassy phase but phosphorous is present in both the glassy and crystalline phases. The slightly higher NL(Cs) values indicate that the glassy phase dissolves faster than the crystalline phases in the ASTM C1285 tests. More extensive testing to assess and quantify the effect of solution saturation on the degradation rate is needed to support long-term modeling and performance in a disposal system.



(a) (b)

Figure 5-14. Results of ASTM C1285 tests with prototype DPF materials made with different iron and salt contents (a) NL(Cs) and (b) NL(P).

6. WASTE FORM PRODUCT CONSISTENCY

A waste form must meet regulatory requirements addressing physical, chemical, and radiological attributes and be shown to perform acceptably in an engineered disposal facility. That is, the phases containing radionuclides must remain sufficiently durable under anticipated environmental conditions to adequately retain radionuclides throughout the service life of the repository. The degradation of most waste forms occurs through contact with groundwater and the degradation rate depends on the waste form composition. Confidence in waste form performance is provided by understanding the relationship between the composition and the degradation rate.

After a waste form material is accepted for disposal, the performance of waste forms made for disposal is ensured by careful control of the composition and processing conditions to provide product consistency. Therefore, it is important to determine acceptable ranges of composition and processing limits to ensure all waste forms that are produced for disposal meet regulatory requirements and will perform acceptably. All waste forms will not be identical because waste stream compositions will vary, but the chemical durability of all waste forms must meet an accepted threshold. An adequate understanding of the relationships between composition, processing conditions, degradation behavior, and other properties in possible disposal environments is required to establish production control limits that will provide consistently durable waste forms. The composition of the waste form is controlled during production based on knowledge of the waste stream composition and batching of waste, immobilizing materials, and additives. The phases generated in the waste form can be controlled through the batching and processing conditions. In the case of iron phosphate waste forms, the amounts of crystalline phases that form must be controlled, and it is likely that the cooling profile of full-size waste forms will be an important factor. The correspondence between the phase composition of the waste form and processing conditions must be established during waste form development.

The chemical durability of iron phosphate waste forms is expected to be controlled primarily by the durability of the glass phase, which will contain most or all of the radionuclides. The durability can be measured using the ASTM C1285 product consistency test, but the results will be affected by the crystalline content (ASTM 2014). The production controls can be used as evidence that the crystal content is acceptable if the relationships are established as part of waste form development. Product consistency tests with borosilicate glass include analyses of B and Si added as the immobilizing matrix in addition to soluble alkali metals from the waste. For iron phosphate waste forms, analyses of phosphorus and lithium can be used to represent the combined durability of the iron phosphate glass and phosphate crystalline phases. The P is provided by the immobilizing matrix and Li is provided by the waste, and both elements are present in both phases. The correspondence between the test results and the phase composition of the waste form must be established during waste form development.

7. PERFORMANCE IN A DISPOSAL SYSTEM

The HLW disposal systems are designed to mitigate contamination of the adjacent biosphere by the disposed waste during regulated periods of several hundred thousand years. This is done by utilizing natural geological and engineered barriers to first minimize contact of disposed waste by groundwater and then retard the migration of radionuclides released from engineered waste forms as they corrode. A mechanistic understanding of degradation and transport processes provides confidence in models used to predict waste form performance over the geological time scale pertinent to waste disposal. Laboratory tests cannot be run to empirically extrapolate responses over long times. Instead, tests are conducted to understand mechanistic aspects of material degradation processes and how they are affected by environmental conditions such as temperature, solution pH, and redox conditions. Several experimental parameters can be adjusted to accelerate waste form degradation behavior, such as running tests at elevated temperatures (e.g., ≥ 90°C), but it is important to understand how accelerating test conditions change the mechanism. Furthermore, different test methods and models will be appropriate for different waste materials. The ASTM International standard C1174 (ASTM 2020) provides guidance for using various testing approaches to develop reliable models for material degradation over long durations, including accelerating methods. That guide should be consulted before designing studies to develop a long-term degradation model for a reference waste form material.

The ASTM C1174 standard recommends types of tests needed to quantify waste form performance but does not identify specific tests methods because those will depend on the material of interest. Many standard test methods have been developed and different methods highlight different aspects of corrosion behavior. It is important to understand how the test response relates to the mechanism of the material being tested and the environment that is represented. Similar test methods are appropriate for glasses and crystalline materials relevant to the iron phosphate waste form, as described in Section 5.2. Disposal systems are engineered to prevent water from contacting the waste forms, but most test methods are water-dominated systems. The commonly used ASTM C1285 product consistency test (ASTM 2014) uses crushed material to establish a high surface area-to-solution volume ratio and generate a highly concentrated solution within a short test duration. The original objective of the method was to generate a saturated solution to measure the effective solubility of different waste forms. The test response does not provide a useful measure of the dissolution kinetics of the test material but has been used extensively (and incorrectly) for that purpose. The method does provide a valuable measure of dissolution under saturated solutions but is not very sensitive to the material composition. Test methods such as ASTM C1308 (ASTM 2017b) that maintain dilute solutions to eliminate saturation effects provide a reliable measure of the dissolution kinetics that is sensitive to the material composition. Other aspects addressed in ASTM C1174 include separate test series to quantify the effects of waste form composition, the disposal environment, interaction of co-located materials and waste forms.

Other aspects of waste disposal are being addressed within the DOE Spent Fuel and Waste Disposal Campaign, within which generic contaminant transport models are being developed that link radionuclide release rates from directly disposed waste and engineered waste forms to regulated dose limits at repository boundaries with the biosphere. Those models provide the range environmental scenarios under which waste forms degrade to provide radionuclide source terms needed for contaminant transport models. The environmental conditions may serve as inputs to the degradation model, such as temperature, pH, and dissolved chloride. The interface between waste form development and repository facility development will become important when the waste form characteristics become finalized. That interface will also inform specifications of waste form durability and consistency requirements.

The canistered waste will remain thermally hot for a long time due to high levels of heat-generating radionuclides and will probably need to be stored for many years before cooling sufficiently for transport and disposal. The waste will probably be thermally hotter than HLW glass and require storage facilities with active heat removal systems. The thermal limits for disposal or safe interim storage could establish maximum waste loadings for waste forms.

For now, and for the foreseeable future, engineered waste forms and directly disposable spent nuclear fuel are being stored near where they are generated in the U.S., including long-term dry storage of nuclear fuel and remote storage of HLW glass. Monitored retrievable storage near the final disposal site was recommended by the Blue Ribbon Panel in January 2012 and methods have been developed to assess storage and transport of commercial and government-owned spent nuclear fuel (SRNL 2016), HLW, and greater-than-Class C waste. The established requirements and practices for HLW will be relevant to iron phosphate waste forms.

8. SUMMARY AND CONCLUSIONS

Initial work to develop an iron phosphate waste form to dehalogenate and immobilize salt wastes from pyrochemical treatment of used nuclear fuels has been completed within the DOE fuel cycle program based on a fairly extensive literature review. Based on the results of these studies and input from technical experts from the national labs, universities, and industry during a 2-day virtual Round Table Workshop, this report identifies issues to be addressed and some recommended approaches for aspects starting from identifying waste streams to be immobilized for which the waste form may be suitable, technical bases for optimizing waste form formulation and possible processing methods, establishing durability requirements for acceptable performance and measuring durabilities with laboratory tests that also support the development of degradation models used to optimize formulations and predict radionuclide source terms for transport models. The development of durable waste forms includes interfacing with researchers developing separation methods that affect waste stream compositions, researchers developing engineered disposal systems, and regulators monitoring accountancy during production, storage, and disposal and establishing acceptance criteria for transporting and disposing the waste forms.

The initial considerations of production and disposal aspects summarized in this report indicate a pathway to the successful utilization of iron phosphate waste forms and a roadmap for the research needed to advance the TRL of all steps in the process towards implementation. For some of these production and disposal aspects, a lot of literature is available on the topics such as methods for dehalogenating chloride salts as well as glass formulation for optimizing chemical durability of phosphate glasses. However, little is known regarding other aspects, such as if the phosphate reactions given in Equations 4-1 through 4-4 would proceed effectively for fluoride salt wastes in an MSR waste stream. Overall, utilizing established phosphate technology holds promise for treating a wide range of halide salt waste streams to produce waste forms for disposal in a HLW repository and would be suitable for recycling ^{37}Cl and/or ^{7}Li.

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Appendix A

Round Table Workshop

Table A1. Participants in the Round Table Workshop in August 2020.

Hosts	***National Laboratories***		***Universities***	***Other participants***
Brian Riley (PNNL)	**Stephanie Bruffey** (ORNL)	**Joanna McFarlane** (ORNL)	**Richard Brow** (Missouri S&T)	**Ted Day** (MO-SCI Corp.)
William Ebert (ANL)	**Robert Finch** (SNL)	**Nick Soelberg** (INL)	**Krista Carlson** (Univ. Utah)	**CW Kim** (MO-SCI Corp.)
	Jeff Fortner (ANL)	**Sarah Stariha** (ANL)	**Delbert Day** (Missouri S&T)	**Darryl Siemer** (INL – retired)
Sponsors	**Steve Herrmann** (INL)	**Kevin Tolman** (INL)	**Levi Gardner** (Univ. Utah)	**Robert Ledoux** (ARPA-E)
Stephen Kung (DOE-NE)	**James King** (INL)	**John Vienna** (PNNL)	**Mike Simpson** (Univ. Utah)	
Kimberly Gray (DOE-NE)	**Morgan Kropp** (INL)	**Mark Williamson** (ANL)	**Ming Tang** (Clemson Univ.)	
Christina Leggett (DOE-NE)	**Ken Marsden** (INL)	**Jim Willet** (ANL)		

Table A2. Topics for discussion at the Round Table Workshop.

Topic	*Description*
1	Current process (PNNL-ANL-INL)
2	Phosphate glass history
3	Phosphate glass as a waste form
4	Phosphate glass chemical durability
5	Phosphate glass radiation stability
6	Electrochemical separations – salt waste chemistry
7	Alternative electrochemical waste forms
8	Off-gas perspective
9	Full-scale operations perspective (echem)
10	Accountancy & safeguards perspective
11	Waste disposal perspective
12	Advantages of phosphate process

Table A3. Agenda for Day-1 of the Round Table Workshop on August 4, 2020.

Time (PDT)	Topic #	Topic Description	Presenter(s)
8:00	–	Opening remarks and welcome	B. Riley, W. Ebert
8:05	(1)	Introduction to PNNL-ANL-INL phosphate process (general overview)	B. Riley
8:25	(1)	UCl_3 production using NH_4Cl	S. Herrmann, M. Kropp, K. Tolman
8:45	(2)	Phosphate glass history	T. Day, CW Kim
9:05	(2)	Phosphate glass history (US-DOE side)	J. Vienna
9:25	(4)	Phosphate composition-structure-properties (emphasis on glass chemical durability)	R. Brow
9:55		Break	
10:00	(3)	Phosphate glass as a waste form	T. Day, CW Kim
10:40	(3)	Phosphate glass (simplified approach)	D. Siemer
11:00	(4)	Phosphate glass microstructure and chemical durability (Fe-P-O)	W. Ebert
11:30	(5)	Radiation stability	M. Tang
11:55		Closing remarks	B. Riley, W. Ebert
12:00		Adjourn	

Table A4. Agenda for Day-2 of the Round Table Workshop on August 11, 2020.

Time (PDT)	Topic #	Topic Description	Presenter(s)
8:00	–	Opening remarks and welcome	B. Riley, W. Ebert
8:05	(6)	Electrochemical separations perspective (general overview)	J. King, K. Marsden
8:35	(7)	Baseline ACWF	W. Ebert
9:00	(7)	Alternative waste forms for salt streams (SAP)	B. Riley
9:20	(7)	Alternative waste forms for salt streams (USHYZ)	L. Gardner, K. Carlson, M. Simpson
9:40	(8)	Off-gas perspective (focus on this process)	S. Bruffey, J. McFarlane, N. Soelberg
10:10		Break	
10:15	(9)	Full-scale operations perspective	M. Williamson
10:45	(10)	Accountancy and safeguards perspective	R. Finch
11:05	(11)	Waste disposal perspective	W. Ebert
11:30	(12)	Advantages of phosphate process	B. Riley, S. Herrmann
11:50		Closing remarks	B. Riley, W. Ebert
11:55		Adjourn	