Alternative Waste Forms for Electro-Chemical Salt Waste

Advanced Fuel Cycle Initiative

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SUMMARY

This study was undertaken to examine alternative crystalline (ceramic/mineral) and glass waste forms for immobilizing spent salt from the Advanced Fuel Cycle Initiative (AFCI) electrochemical separations process (Echem). The AFCI is a program sponsored by U.S. Department of Energy (DOE) to develop and demonstrate a process for recycling used nuclear fuel (UNF). Echem is a molten salt process for the reprocessing of UNF in an electrorefiner and generates spent KCl-LiCl salt that is contaminated with alkali, alkaline earths, halide, and lanthanide fission products (FP) that must either be cleaned of FP and other contaminants or replaced with new salt to maintain separations efficiency. Currently, these spent salts are occluded on zeolite 4A, mixed with a borosilicate binder, and heat treated to form a glass-bonded mineral waste form. The focus of this study was to investigate alternative waste forms to immobilize spent salt. A condensed version of the calculated composition of a spent salt with 20 mass% fission products is given in Table S1.[1] On a mole basis, the spent salt is dominated by alkali chlorides with minor amounts of alkaline earth and lanthanide chlorides.

Table S1. Calculated elemental composition (condensed) of spent electrochemical salt with 20 mass% fission products.[1]

Elemental	Salt (20% FP) Mole fraction	Salt (20% FP) Mass fraction
Alkali	0.4539	0.3217
Alkaline Earth	0.0044	0.0166
Lanthanide	0.0198	0.0863
Halide	0.5219	0.5754
Total	1.0000	1.0000

Borosilicate glass is the most widely studied and accepted waste form for immobilizing radioactive waste.[2-5] However, the limited solubility of chloride in borosilicate glass leads to low waste loading of spent Echem salt. To address this issue, past work with spent electrochemical salt from the electrochemical processing of sodium-bonded nuclear fuel led to the development of a two-step process that resulted in a glass-bonded ceramic waste form consisting of ~ 75 mass% minerals (primarily sodalite) bonded in a borosilicate glass network.[6] The sodalite allows higher loadings of Cl. The glass matrix encapsulates the sodalite and other minerals, supplies silica for the formation of sodalite, and solubilizes some of the FP and impurities.

In the study reported here, we explored glass systems that are more compatible with Cl and have not been previously considered for use as waste forms. In addition, alternate methods were explored with the hope of finding a way to produce a sodalite that is more accepting of as many FP present in the spent salt as possible.

This study investigated two different options:

1. alternate glass families that incorporate increased concentrations of Cl
2. alternate methods to produce a mineral waste form.

A literature survey was conducted for each option to identify high halide-containing glasses and minerals. Available fabrication and characterization methods along with available waste-form performance data were gathered from the available literature and evaluated to determine the best candidate glass systems and mineral structures for scoping studies. Scoping studies were conducted based on the conclusions from the literature surveys.

Several glasses were successfully processed in three tellurohalide systems, TeO_2-*X*Cl-B_2O_3, TeO_2-*X*Cl-Li_2O, and TeO_2-*X*Cl-Na_2O, where *X*Cl stands for "mixed chlorides" simulant. We were able to incorporate about 19 mass% *X*Cl in the TeO_2-*X*Cl-B_2O_3 system. These glasses show higher product consistency test (PCT) responses than the Environmental Assessment (EA)[7] glass standard for high-level waste. However, they show promise and should be further developed by investigating other compositions to achieve optimized glass with improved durability. Future work will investigate the solubility of mixed chlorides and performance of tellurite binary and ternary systems including B_2O_3,[8-10] P_2O_5,[11] Al_2O_3,[12] and/or PbO[13,14] with or without modifiers, e.g., alkali oxides[13,15] or transition metal oxides (e.g., ZnO, WO_3, Nb_2O_5).[14]

Sodalite was successfully synthesized with the sol-gel process at the theoretical waste loading limit of 12.7 mass% for the 20% FP waste. Durability of the sodalite was not measured in these scoping studies because the main concern was to focus on a method to fabricate the sodalite phase from a simple sol-gel process. Performance data available in the literature indicate that sodalite, if properly fabricated, is durable.[6,16-19] Future work will optimize the sol-gel and heating process to produce a fully dense sodalite waste form that is phase-pure. The cancrinite structure (quadridavyne), which is less preferred by Cl^-, will be attempted in future work as it has a theoretical waste loading limit of 22.9 mass% and alkaline earth elements can be incorporated into the structure which we have not yet demonstrated in sodalite.

Comparing the results of the glass to the sodalite we find the following:

1. The tellurite glasses tested in this study outperform the theoretical loading of alkali chlorides in sodalite (i.e., 12.8 mass%).
2. Sodalite outperforms the glass in terms of waste form performance (i.e., higher durability according to the literature).

Different waste compositions were used for the glass (10% FP waste) and the mineral (20% FP waste) waste forms and the mineral waste form was only demonstrated with the LiCl, NaCl, and KCl as waste components. However, the 10% and 20% FP wastes remain very similar in composition.

The tellurite glasses studied have the potential to exceed the waste loadings possible in the sodalite structure if major improvements are achieved in terms of waste form performance. The maximum waste loading was achieved in sodalite. Future work will focus on incorporation of the full waste composition and determine if the cancrinite structure can be synthesized. The following suggestions are proposed in order to ensure sufficient information for comparison between the candidate waste forms:

1. Produce all waste form candidates using the same waste composition (i.e., 20% FP waste).
2. Perform compositional analysis on all waste form candidates after production to verify that volatile materials were not evolved during processing.
3. Perform durability on all candidate waste forms for performance comparison purposes.

Note that these results are preliminary and qualitative in nature. They serve the purposes of exploratory research that can guide future research. No quantitative analysis or interpretation is intended or attempted.

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FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

AFCI	Advanced Fuel Cycle Initiative
ARM	Approved Reference Material
ASTM	American Society of Testing and Materials, now ASTM International, Inc.
DIW	deionized water
DOE	U.S. Department of Energy
EA	environmental assessment
EBR	Experimental Breeder Reactor
Echem	electrochemical separations process
EDS	energy dispersive spectroscopy
FT-IR	Fourier transform infrared spectroscopy
FP	fission products
GDL	Glass Development Laboratory (at Pacific Northwest National Laboratory)
IC	ion chromatography
ICP-MS	inductive coupled plasma-mass spectrometry
INL	Idaho National Laboratory
IR	infrared
MLEF	Mickey-Leland Energy Fellowship
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
SEM	scanning electron microscope or scanning electron microscopy
T_g	glass transition temperature
TRU	transuranics
UNF	used nuclear fuel (commonly referred to as spent nuclear fuel)
XRD	X-ray diffraction

ALTERNATIVE WASTE FORMS ELECTROCHEMICAL SALT WASTE

1. INTRODUCTION

This study was undertaken to examine alternate crystalline (ceramic/mineral) and glass waste forms for immobilizing spent salt from the Advanced Fuel Cycle Initiative (AFCI) electrochemical separations process (Echem). AFCI (now the Fuel Cycle Research and Development Program) is a program sponsored by U.S. Department of Energy (DOE) Office of Nuclear Energy (NE) to develop and demonstrate a process for recycling used nuclear fuel (UNF). Echem generates spent salt that is contaminated with alkali, alkaline earths, halide, and lanthanide fission products from the UNF plus impurities (primarily Na used to facilitate heat transfer in the fuel assembly). The calculated composition of a spent salt with 20 mass% fission products (FP) is given in Table 1.[1] The spent salt is dominated by alkali chlorides with minor amounts of alkaline earth and lanthanide chlorides.

Table 1. Calculated composition of spent electrochemical salt with 20 mass% fission products.[1]

Element	Mole Fraction	Mass Fraction
Y	0.0007	0.0020
La	0.0029	0.0127
Ce	0.0045	0.0195
Pr	0.0022	0.0095
Nd	0.0067	0.0301
Pm	0.0003	0.0011
Sm	0.0020	0.0092
Eu	0.0002	0.0011
Gd	0.0002	0.0011
Tb	0.0000	0.0001
Li	0.2219	0.0477
K	0.1603	0.1942
Na	0.0630	0.0449
Rb	0.0006	0.0017
Cs	0.0081	0.0332
Sr	0.0013	0.0036
Ba	0.0030	0.0129
Cl	0.5212	0.5725
Total	1.0000	1.0000
Simplified	**Mole Fraction**	**Mass fraction**
Alkali	0.4539	0.3217
Alkaline Earth	0.0044	0.0166
Lanthanide	0.0198	0.0863
Halide	0.5219	0.5754

Borosilicate glass is the most widely studied and accepted waste form for immobilizing radioactive waste.[2-5] However, the solubility of chlorine in borosilicate glass is limited, which leads to low waste loading of spent Echem salt. To address this issue, past work with spent Echem salt from the processing of sodium-bonded nuclear fuel led to the development of a two-step process that resulted in a glass-bonded ceramic waste form that consisted of ~ 75 mass% minerals (primarily sodalite) encapsulated in a borosilicate glass network.[6] The sodalite allows higher loadings of Cl. The borosilicate glass was used to encapsulate the sodalite and other minerals, supply silica needed to form sodalite, and immobilize other spent salt components that don't precipitate into minerals.[6]

This study explored glass systems more compatible with Cl that have not been considered for use as waste forms to date. In addition, alternate methods were explored with the hope of finding a way to produce a sodalite that is more accepting of all fission products present in the spent salt.

Scoping studies presented in this report were performed to investigate two different options:

1. alternate glass families that incorporate increased concentrations of Cl
2. alternate methods to produce a mineral waste form.

A literature search was conducted for each option to identify high halide-containing glasses and minerals. Fabrication and characterization methods along with waste-form performance data were gathered from the literature and evaluated to determine the best candidate glass systems and mineral types for scoping studies. Scoping studies were conducted based on the conclusions of the literature surveys for each option. In the case of the glass option, scoping studies of the tellurohalide glass system focused on fabricating glasses in a selected glass system and on waste-form response to the product consistency test (PCT).[7] Literature data is available on simple binary and ternary glass systems with only limited Cl solubility data compared to the well-studied borosilicate and other oxide glass systems. Several glasses were formulated and fabricated to expand the understanding of the simple glass systems found in the literature. PCT was performed on selected glasses to determine the durability of these exploratory glass compositions.

For the mineral option, a limited number of scoping studies for mineral waste forms were performed. The results of the literature search supported the selection of sodalite as the primary mineral phase so scoping tests focused on advanced processing techniques that would allow for inclusion of more of the spent salt components. Performance testing is of less concern at this stage because it has been shown by others to be quite durable as a stand-alone waste form or encapsulated in a borosilicate glass.[6,8]

This report summarizes the progress made on the two options, preliminary results, discussions, and conclusions. Note these results are preliminary and qualitative in nature. They serve the purposes of exploratory research that can guide the future research. No quantitative analysis or interpretation is intended or attempted.

2. ALTERNATE GLASS SYSTEMS

This section is focused on immobilization of spent Echem salt, including lanthanides, alkalis, halogens, alkaline earths, plus trace transuranic (TRU) impurities left in the K-Li-Na-Cl salt. Based on a recent report,[9] this waste stream and the waste form options are briefly discussed in this section.

Table 2 shows the chemical makeup of the 10 mass% FP waste stream (see Table 1 for the composition of the 20 mass% FP waste stream). The highlighted items in the table constitute major components (> 1 mass%). High alkalis and chloride in this waste stream limit the solubility of this stream in glasses. Ebert's[6] concluded that glass-bonded sodalite is the preferred option. The waste processing steps are:

1. Occlusion of salt waste onto the zeolite 4A phase
2. Mixing of the zeolite with a binder glass in the zeolite-to-glass ratio of 3:1
3. Heating to 915 °C for 4 hours.

This process results in a monolithic waste form. The reaction cited in the literature[6] is as follows:

$$12\ CsCl\ (\textit{\textbf{salt}}) + 4Na_{12}(AlSiO_4)_{12}\ (\textit{\textbf{zeolite 4A}}) + 12\ SiO_2\ (\textit{\textbf{glass}}) \rightarrow \quad (1)$$

$$6Na_8(AlSiO_4)6Cl_2\ (\textit{\textbf{sodalite}}) + 12\ CsAlSi_2O_6\ (\textit{\textbf{pollucite}})$$

In this process, the lanthanides are encapsulated in the glass phase along with sodalite and pollucite while iodine dissolves in the glass. Chlorine stoichiometry in the sodalite and soda needed to form the sodalite determine the waste loading, which is low at about 2 to 10 mass% of FP in the final waste form. This waste form, developed for salt waste from Experimental Breeder Reactor II (EBR-II) processing at Idaho National Laboratory (INL), is being implemented at INL in 2010.

Table 2. Chemical composition of alkali halides waste stream for 10 mass% FP.[1]

Component	Mole Fraction	Mass Fraction
Y	0.0004	0.0010
La*	0.0013	0.0060
Ce*	0.0022	0.0101
Pr*	0.0011	0.0050
Nd*	0.0033	0.0158
Pm*	0.0001	0.0006
Sm*	0.0010	0.0048
Eu	0.0001	0.0006
Gd	0.0001	0.0006
Tb	0.0000	0.0000
Li*	0.2597	0.0601
K*	0.1877	0.2447
Na*	0.0261	0.0200
Rb	0.0003	0.0009
Cs*	0.0039	0.0175
Sr	0.0007	0.0019
Ba*	0.0015	0.0068
Cl*	0.5106	0.6035
Total	1.0000	1.0000
	Simplified	
Alkali	0.4778	0.3432
Alkaline Earth	0.0021	0.0087
Lanthanide	0.0060	0.0285
Halide	0.5106	0.6035

*Components included as waste simulant in tellurite glasses.

In the present task, a broader approach has been proposed to ***explore the glass chemistry space for development of a chloride-based (oxide- or non-oxide based) glass systems with higher waste loading than 10 mass% and acceptable chemical durability as a potential alternative waste form and to evaluate the status of this technology***. Major requirements for a suitable glass system for this waste stream are:

- Compositional flexibility
- Homogeneous glass (preferably no crystals or phase separation if that will lower the durability of the waste form)
- High solubility of chlorides (i.e., mixed alkali chlorides)
- Low volatility
- Low processing temperature (preferably << 1000 °C)
- Suitable T_g if crystallization upon cooling will affect durability (≥ 300 °C).

In the current section, a summary of the literature survey, experimental work, and results will be presented.

2.1 Glass Literature Survey

Halide glasses[10] comprise a class of relatively uncommon inorganic glass systems, because of processing difficulties, toxicity, and chemical instability. While halide glasses based on beryllium fluoride and zinc chloride are well-known, the glass-forming ability of ZrF_4, AlF_3, HfF_4, and more recently, PbF_2, have also been demonstrated. In this section, a brief survey of halide glass-forming chemistries with a focus on chlorides from the perspective of nuclear waste immobilization is presented.

Halophosphate glasses: Mesko et al.[11] made iron phosphate glasses with up to 26 and 31 mol% CsCl and SrF_2, respectively, and up to 34 mol% CsCl and SrF_2. Batches were combined and melted at temperatures as low as 950 °C for 2 hours to form fluid melts. The low melting temperature was used to keep the volatility low. These glasses had a total ion release in distilled water of approximately 10 mg/L. This value is ~ $^1/_{10}$ of the value measured for the Approved Reference Material (ARM-1),[12] a reference borosilicate glass. Analysis of the glasses produced in this study showed that very little, if any, Cs and Sr was volatilized from the batches, although ***the majority of the halides were released during melting***. This system is not likely to perform well for the waste stream targeted in this section since the goal of this study is to find a waste form that will incorporate all of the waste components.

Halotellurite glasses: Ding et al.[13] processed several glasses in lead halotellurite system (PbX_2 - TeO_2 [X = F, Cl, Br]) and measured their optical properties (e.g., refractive indices, absorption and emission processes) for application as a material for 1.5-µm broadband amplification. Materials in this system were found to readily form glasses with good properties. These glasses show some promise for our applications, but no chemical durability data are reported. Another investigation[14] reported glass formation in halide systems with $PbCl_2$, NaCl, KCl, $BaCl_2$, and TeO_2. Here, Ivanova determined ranges of glass formation at different cooling rates in two systems, TeO_2-$PbCl_2$-NaCl-KCl and TeO_2-$BaCl_2$-$CdCl_2$-NaCl. In the case of the TeO_2-$PbCl_2$-NaCl-KCl system, the TeO_2 content was varied over 50–80 mol%. An attempt was also made to replace $PbCl_2$ with PbO, partly to improve glass formation. In the TeO_2-$BaCl_2$-$CdCl_2$-NaCl system, the TeO_2 content was varied over 10–80 mol %, keeping the ratio of ($BaCl_2$+$CdCl_2$):NaCl at a constant value of 9:1. These systems produced glasses with a low melting temperature (500–800 °C). No chemical durability data were reported for this family of glasses. Ozen et al.,[15] Ozen et al.,[16] and Ovecoglu et al.[17] successfully produced Tm_2O_3-doped (< 0.5 mol%) TeO_2-LiCl glasses with up to 69.65 mol% of LiCl. Thermal, optical, and crystallization properties were investigated. These glasses were quenched between two graphite plates at room temperature (suggesting that a high rate of quench was needed for glass formation). Performance analysis was not performed on these glasses.

Halophosphotellurite glasses: Kozhukharov, et al.[18] investigated the TeO_2-P_2O_5-XCl system for glass formation, where XCl = $BaCl_2$ and $PbCl_2$. High glass formability was reported. Chemical durability data for glasses in these ternary systems was not reported in this paper. This study demonstrates the feasibility of solubility of various chlorides in phosphotellurite glasses and thus, these glasses might be explored as candidate waste forms though the durability and T_g data are unknown.

Chalcohalide glasses: Sanghera, et al.[19] reviewed the chemical, physical, electrical, and optical properties of known chalcohalide glass-forming systems. These glasses contain no alkalis, and they were investigated in the 1980s for their interesting electrical and optical properties for various applications, e.g., memory and switching in the infrared region. However, no chemical durability data were reported in this paper.

$ZnCl_2$-based glasses: Zhonghong, et al.[20] investigated the $ZnCl_2$-based halide glasses for glass formation and chemical durability. The authors studied two systems, $ZnCl_2$-$PbCl_2$-XCl (X = Ag, Cu, K, Li, Na) and $ZnCl_2$-KCl-$X'Cl_2$ (X' = Ba, Ca, Mg, Sr). They also compared glass formations of ZnF_2-$PbCl_2$-KCl and $ZnBr_2$-$PbCl_2$-KCl to that of $ZnCl_2$-$PbCl_2$-KCl and studied the effect of substituting KBr for KCl and $BaBr_2$ for $BaCl_2$. They tested for chemical durability by using absolute alcohol (C_2H_5OH), a C_2H_5OH:H_2O (95:5 by volume) mixture, and H_2O as the solvents at 25 °C. They immersed pieces of glass in the solvent for about 50 hours, measured the concentration of Cl^- in the solvent, and calculated the solubility of the glass based on the concentration data. Their results and observation were as follows:

- In the case of the XCl (X = Li, Na, K) series, the solubility decreased in the order of

$$\mathrm{LiCl} \rightarrow \mathrm{NaCl} \rightarrow \mathrm{KCl}$$

- In the case of the X'Cl (X' = Ba, Ca, Sr) series, the solubility decreased in the order of

$$\mathrm{CaCl_2} \rightarrow \mathrm{SrCl_2} \rightarrow \mathrm{BaCl_2}$$

- Glasses with $PbCl_2$ showed the highest chemical durability.
- $ZnCl_2$, the network former in this case, was the most soluble in this family of glasses. Other components, e.g., LiCl, NaCl, KCl, $CaCl_2$, $SrCI_2$, and $BaCl_2$, were network modifiers. The authors attributed the poor durability of these glasses to an argument that the solvent first attacked the network former ($ZnCl_2$).

CuX-based glasses: Kadono and coworkers[21] studied the CuX-MX-BaX_2 (X = Cl, Br, I; M = K, Rb, Cs) system for glass formation. Several glasses were formed with 50–60 mol% of CuX. However, these glasses have low T_g (< 30–87 °C), which is likely too low for our targeted waste stream.

Silver-containing halide glasses: Minami[22] reported glasses based on silver halides. The author studied two systems, AgX-Ag_2Ch-P_2Ch_5 (X = I, Br, Cl; Ch = O, Se) and AgX-Ag_2O-B_2O_3 (X = I, Br, Cl). These glasses were studied for their high ionic conductivity (superionic conductors). The author explained their electrical properties (mainly from the perspective of Ag^+ ion transport) using simple glass structure models. These glasses are not suitable for our targeted waste stream because this high ionic conductivity will necessarily reduce the chemical durability.

Oxyhalide (aluminoborosilicate) glasses: A recent patent[23] reported oxyhalide glasses. The target glass composition contained SiO_2 = 0–70 mol%, Al_2O_3 = 5–35 mol%, B_2O_3 = 1–50 mol%, X_2O = 0–12 mass% (X = Cs, Li, K, Na, Rb), F = 0–12 mass%, Cl = 0–12 mass%, and rare earth elements = 0–0.2 mol%. This work focused mainly on the spectral properties of these glasses. This system may not be suitable because (in addition to the chemistry being patented) these glasses need a higher processing temperature with more SiO_2 addition. Also, the maximum Cl content in these glasses is a relatively low 12 mass%.

Lead tellurite glasses: Stanworth[24] presented data on TeO_2-PbO glasses with the addition of glass formers (i.e., B_2O_3) and modifiers (e.g., MoO_3, P_2O_5, Nb_2O_3, WO_3, Na_2O, Li_2O, and BaO). The glasses were placed into a sealed chamber at 50-55 °C under saturated H_2O vapor and after 3 weeks, the glasses were dried and the weight loss determined. The most efficient glass was a binary TeO_2-PbO glass (83.2

and 16.8 mol% of TeO_2 and PbO, respectively) with a release rate of 0.005 g/m^2/day and the glasses were consistently worse with the addition of modifiers to the TeO_2-PbO binary system in the order listed above with MoO_3, P_2O_5, Nb_2O_5, and WO_3 though release rates were still really low at $\leq$ 0.4 g/m^2/day at the highest in this series, WO_3. These glass systems show promise as a candidate waste form.

Borotellurite glasses: a few different groups have looked at chloride solubility in borotellurite glasses. Burger, Vogel, and Kozhukharov[25] looked at the infrared properties of glasses in the TeO_2-B_2O_3 system. Rao et al.[26] and Bhat et al.[27] looked at alkali borotellurite glasses with the addition of up to 10 mol% of LiCl with T_g = 366 °C. These studies did not report glass durability.

2.2 Glass Scoping Studies

Based on the literature survey and database (SciGlass®) search, the tellurohalide family was selected as a candidate for scoping studies. This family of glasses met most of the requirements, i.e., good glass formation, low melting temperature (600–750 °C), modest T_g (>300 °C), and reported Cl-solubility.[13-17,28]

2.2.1 Experimental Work

To prepare glasses for the scoping studies, the “mixed chloride” simulant waste stream was batched according to the chemical makeup of the waste stream (shown in Table 2). Loadings of 5–30 mass% of the “mixed chloride” simulant were prepared with TeO_2 as the main glass former. About 5 mass% of B_2O_3 and Li_2O were added separately in attempts to improve glass processability. Batches were then placed in Pt crucibles for melting and quenching as shown in Figure 1(a). The glass batches were heated to 600–800 °C to verify the optimum melting temperature for the tellurite glasses. The Pt crucible containing the previously prepared batches was placed in the furnace with a Pt lid (as shown in Figure 1(b)). The lid was necessary to reduce out-gassing of the chlorides.

The melts were then left in the furnace for about 25 minutes to confirm adequate mixing of the materials and formation of homogeneous glasses. Various quenching methods were employed, including:

- Air quench: glass was poured onto a steel plate (25 °C).
- Water quench: glass was poured directly into water (25 °C).
- Plate quench: glass was poured onto a steel plate and immediately covered with a platinum sheet (25 °C).
- Cold plate quenched: a steel quench plate was cooled in ice water (0 °C), and then the plate was removed from the water bath, dried, and the glass was immediately poured onto the cool, dry plate (~ 0 °C).
- Copper cold plate quenched: a copper quench plate was placed directly on top of a steel container full of ice water (0 °C, the plate was directly in contact with the ice water), and the glass was poured onto the cool, dry plate.

Quenched samples (shown in Figure 1(c)) were used for characterization.

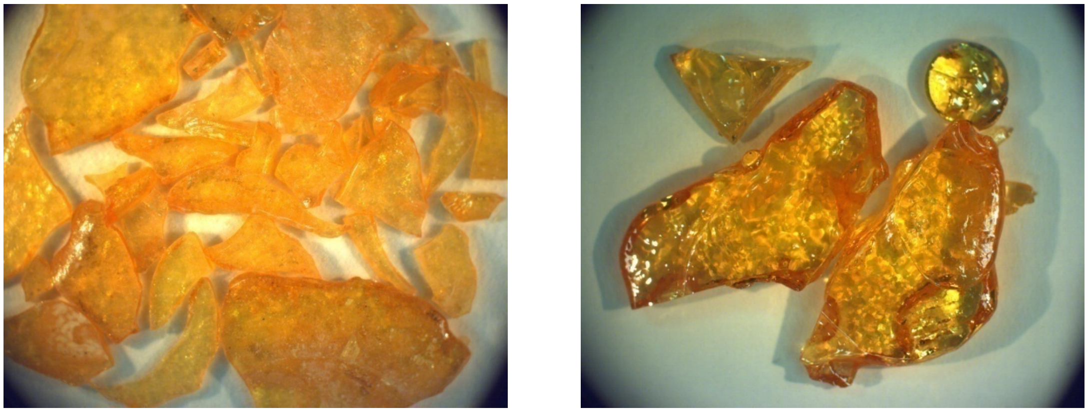

(a) (b) (c)

Figure 1. Process steps: (a) batching and placing in a Pt crucible, (b) melting inside a furnace, and (c) quenching (air quench) of glass melted in the Glass Development Laboratory (GDL) at the Pacific Northwest National Laboratory (PNNL).

Several different compositions were processed, and different quenching conditions were attempted. The results are summarized in Table 3. Selected glass samples are shown in Figure 2.

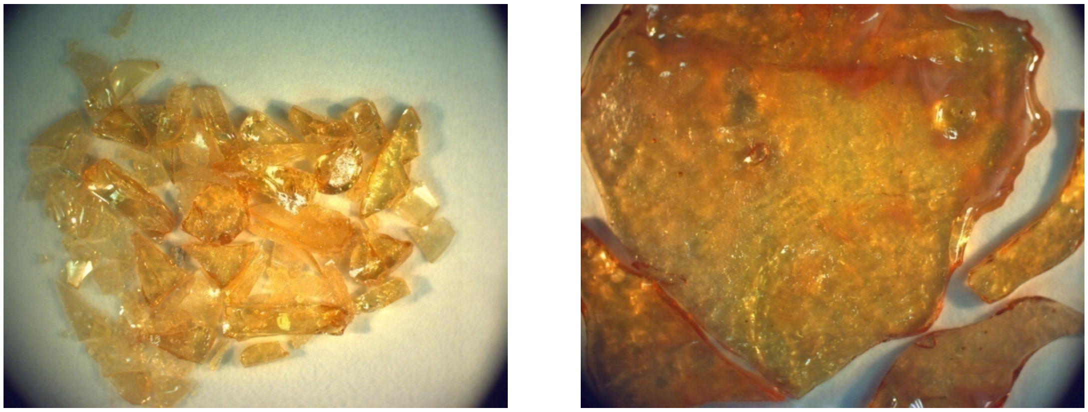
Table 3. Summary of quench method, glass compositions (mass%), and observations of glasses fabricated at 725°C. The simulant composition is found in Table 2 and it's concentration in glass listed below as *X*Cl%. The six glasses discussed below (see Table 4) that were analyzed using the PCT are called out under *Quenching Method*.

Quenching Method	*X*Cl%	TeO_2	B_2O_3	Li_2O	Na_2O	Observations
Water	30	70				Crystallized-a bit glassy
Water	20	80				Crystallized
Plate	5	95				Crystallized
Plate	30	70				Crystallized
Plate	20	80				Crystallized
Air	20	80				Crystallized
Plate	28.57	66.7	4.76			Crystalline
Plate **(Glass-4)**	19.05	76.2	4.76			Glass
Plate **(Glass-5)**	14.29	81	4.76			Glass
Plate **(Glass-6)**	9.52	85.7	4.76			Glass
Air **(Glass-3)**	19.05	76.1	4.76			Mostly Glass
Air	9.52	85.7	4.76			Top Glass Crystalline
Water	9.52	85.7	4.76			Mostly Glass
Cold Plate	19.05	76.2	4.76			Mostly Glass
Air	9.5	85.5		5		Glass
Air	23.8	71.3		5		Crystallized
Air **(Glass-2)**	19	76		5		Glass
Cu C Plate Q	9.5	85.5		5		Some crystals, black
Plate	9.5	85.5		5		Glass
Cold Plate	9.72	87.5			2.78	Slightly grainy crystals on top of glass-crystallized
Plate	19.45	77.8			2.78	Crystallized
Plate **(Glass-1)**	9.71	87.4			2.92	Some crystals



76.2% TeO_2, 19.05% *X*Cl, 5% B_2O_3 (725 °C, plate quenched)

85.5% TeO_2, 9.5% *X*Cl, 5% Li_2O (725 °C air quenched)



76.2% TeO_2, 19.05% XCl, 5% B_2O_3 (725 °C, plate quenched)

85.5% TeO_2, 9.5% *X*Cl, 5% B_2O_3 (725 °C plate quench)

Figure 2. Examples of as-fabricated tellurohalide glasses. Compositions are presented in mass%.

Overall progress is summarized as follows:

2.2.1.1 Glass Processing

- Batches heated to 600 °C did not fully melt. It was determined that the samples melted completely at about 725 °C.
- The highest waste loading (10% FP waste) composition, 70%TeO_2 - 30%*X*Cl, did not show glass formation. Other TeO_2-*X*Cl glasses did not show thorough glass formation but instead, a glass core (region that quenched first) surrounded by a severely crystallized shell. Even after quenching between two plates (one steel, one platinum) or directly into water, glasses of the binary system were not produced in contrast to the literature.[15-17]
- Approximately 20 mass% waste loading was demonstrated in some of the glasses in the ternary systems attempted.
- Less out-gassing was observed at the lower temperature heat treatments, possibly indicating that more of the Cl stayed in the material at the lower temperatures.

- Glass formed more readily at the lower *X*Cl content in the sample.
- Addition of 5 mass% of B_2O_3 or Li_2O to the composition resulted in significantly better glass formation.
- Sandwiching the melt between plates allowed for a more homogeneous dispersion of the glass in some samples and increased the waste loading capacity of the tellurite glass though that technique is unlikely to be developed into a simple process for radioactive wastes.

2.2.1.2 Glass Characterization

- PCT[7] leachates were analyzed for Cl by ion chromatography (IC), Rb, Y, Te, Cs, La, Pr, Nd, Sm, Eu, and Gd by inductively coupled plasma (ICP)-mass spectrometry (MS), and Ba, B, Li, Na, K, Si by ICP atomic emission spectroscopy (AES). The results are summarized in Table 4.
- These are preliminary results. No replicates or blanks were analyzed in conjunction with these tests. Target compositions were used for normalized release rate calculations.
- These results were used for planning the future work.

The normalized release, NL_i, was calculated with the following

$$NL_i = \frac{c_i(sample)}{(f_i)\cdot(SA/V)} \tag{1}$$

where $c_i(sample)$ is the concentration of element i in the solution (g_i/L, determined by ICP-AES, ICP-MS, or IC), f_i is the mass fraction of element i in the unleached waste form (unitless), and SA/V is the surface area of the final waste form divided by the leachate volume (m^2/L). The SA for -100/+200 mesh powders is reported as 1.99×10^{-2} m^2/g,[7] although since 2 g of glass were used for these experiments, the SA used to calculated NL_i was 3.98×10^{-2} m^2 and the V used was 0.02 L (20 mL). The normalized concentration, NC_i is expressed as

$$NC_i = \frac{c_i(sample)}{f_i} \tag{2}$$

where the result is in $g_{\text{waste form}}/L_{\text{leachant}}$. NC_i values were calculated to allow for comparison with an Environmental Assessment (EA) standard reference glass for durability.[29]

Table 4. Summary of composition and quench method for 6 of the most promising candidate glasses as well as the results of the normalized release rates, NL_i, performed on the PCT leachate.

	Compositions (mass%)					
Component	Glass-1	Glass-2	Glass-3	Glass-4	Glass-5	Glass-6
Quench	Plate	Air	Air	Plate	Plate	Plate
XCl	9.71	19.0	19.1	19.1	9.52	14.3
TeO_2	87.4	76.0	76.2	76.1	85.7	80.8
B_2O_3	N/A	N/A	4.76	4.76	4.76	4.76
Li_2O	N/A	5.00	N/A	N/A	N/A	N/A
Na_2O	2.92	N/A	N/A	N/A	N/A	N/A
	NL_i, (g/m^2) results on PCT leachate					
Component	Glass-1	Glass-2	Glass-3	Glass-4	Glass-5	Glass-6
Te	2.01E-01	1.56E-01	1.14E-01	9.58E-02	1.00E-01	1.02E-01
B	N/A	N/A	45.9	48.6	47.6	41.7
La	3.16E-03	1.64E-03	1.19E-03	1.11E-03	2.39E-03	1.19E-03
Ce	2.33E-03	1.04E-03	1.26E-03	1.15E-03	2.18E-03	1.40E-03
Pr	3.54E-03	1.33E-03	1.60E-03	1.45E-03	2.95E-03	1.87E-03
Nd	1.24E-02	2.90E-03	3.92E-03	3.60E-03	7.79E-03	4.79E-03
Sm	3.46E-03	1.44E-03	1.23E-03	2.01E-03	2.46E-03	1.71E-03
Cs	129	145	145	163	218	88.1
Ba	N/A	N/A	6.73E-01	5.66E-01	8.91E-01	7.08E-01
Li	18.2	33.1	36.9	38.7	28.5	18.5
K	69.4	65.8	72.7	70.4	111	44.7
Na	76.8	58.2	56.2	56.0	40.2	29.0
Cl	114	1605	956	811	403	582
	NC_i, (g/L) results on PCT leachate					
Component	Glass-1	Glass-2	Glass-3	Glass-4	Glass-5	Glass-6
Li	36.1	65.9	73.5	77.0	56.7	36.9
Na	153	116	112	112	80.0	57.6

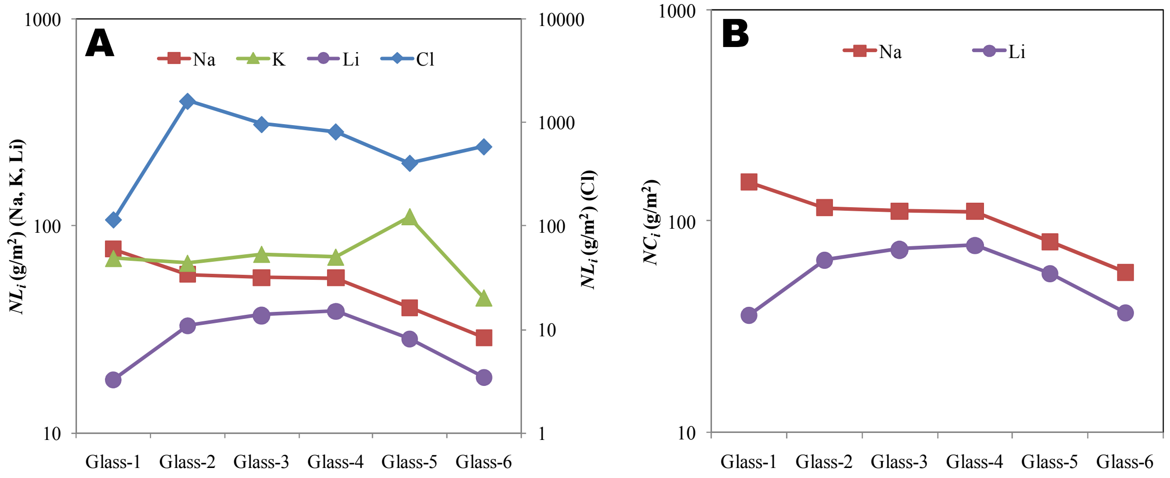


Figure 3. Normalized release (NL_i) and normalized concentration (NC_i) for the six tellurite glasses that underwent durability testing. The data were taken from Table 4.

2.2.2 Discussion of Results

The release values presented in Table 4 were higher by an order of magnitude in some glasses than the literature results for the EA glass,[29] a standard reference glass, for which the Li and Na releases are 9.565 ± 0.735 and 13.346 ± 0.902 g/L, respectively. However, some of the glasses showed promise. Based on our preliminary PCT results, the following observations were made:

- In the case of the TeO_2-XCl-B_2O_3 system, adding B_2O_3 improved glass formation over the four glasses tested (Glass-3 – Glass-6), and Glass-6 showed the lowest release of the following alkalis: Na (29.0 g/m^2), K (44.7 g/m^2), and Li (18.5 g/m^2). As would be expected, with the addition of XCl to this system with B_2O_3 = 4.76, the leach rates increased linearly, except for the anomaly in the data at XCl = 9.5 mass% where NL_{Cl} is at a minimum (403 g/m^2) and NL_K is at a maximum (111 g/m^2) (see Figure 4).
- In the case of the TeO_2-XCl-Na_2O system, substituting Na_2O for B_2O_3 (Glass-1) increases NL_{Na} (the highest of the glasses tested) and NL_{Te} but yielded the lowest measured value for NL_{Cl} (114 g/m^2) among the glasses tested in this study.
- In the case of the TeO_2-XCl-Li_2O system, substituting Li_2O for B_2O_3 increases NL_{Cl}, NL_{Li}, and NL_{Te}. These glasses had the highest NL_{Cl} releases among the glasses tested.

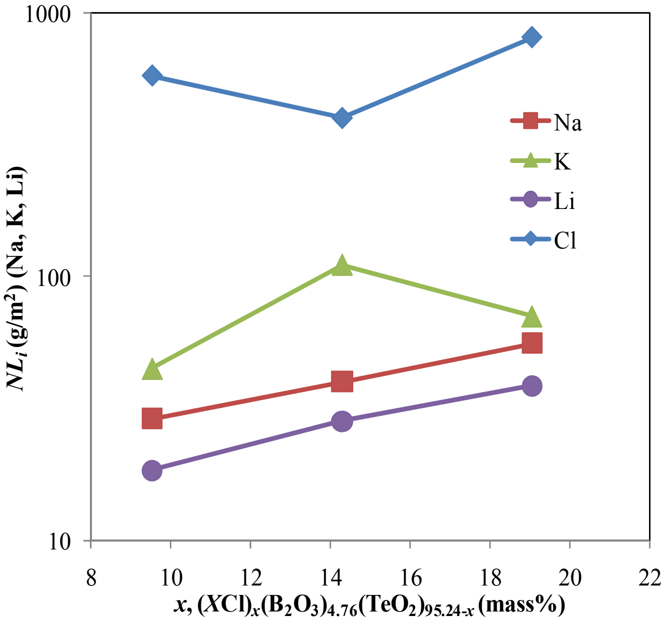


Figure 4. NL_i comparison for TeO_2-XCl-B_2O_3 system where B_2O_3 = 4.76 mass% and i = Na, K, Li, and Cl.

These results indicate that the TeO_2-XCl-Na_2O-B_2O_3 system needs to be more fully investigated for glass formation and chemical durability. Adding other suitable network modifiers (e.g., Al_2O_3) can potentially decrease leaching. Mixed-alkalis effect and the role of alkaline earths also need to be investigated.

2.2.3 Major Accomplishments

Our major accomplishments/outcomes of the work to date are:

- Good glass formation in the system of TeO_2-XCl-B_2O_3 with ~ 19 mass% of XCl. To our knowledge, this is the highest “mixed chloride” incorporated into a glass.

- An invention disclosure (IPID# 16472-E Tellurochloride-Based Glasses as Alternative Waste Form) was filed on the unique glass chemistry space that shows potential for immobilizing the target waste stream.
- An invited presentation was made at the Annual Meeting of the Society of Glass Technology, Lancaster, UK, September, 15–18, 2009.
- We hosted a summer student from Department of Materials Science and Engineering, University of Washington under the DOE Mickey-Leland Energy Fellowship (MLEF) program.

3. ADVANCED MINERAL WASTE PROCESSES

3.1 Mineral Literature Survey

The mineralogy database on Webmineral.com was used to search for high halide-containing minerals to identify likely candidate minerals for immobilizing the spent salt.[30] A short list of candidate minerals that contain high concentrations of Cl is given in Table 5. Minerals are ordered in decreasing mass% of Cl. Manganpyrosmalite and brokenhillite both contain significant concentrations of Cl; however, the lack of alkali does not lend them to be good candidates for the spent salt. Wadalite (sodalite group) is a closer compositional match to the spent salt, but again the lack of alkali in this mineral means it will be difficult, if not impossible, to make this mineral. Quadridavyne (cancrinite group) and sodalite are good matches, compositionally, with the spent salt because they contain a large fraction of Cl^- and alkali. Literature data on cancrinites and sodalites were gathered, which pointed to sodalite as a more natural fit for the Cl^- anion.[31-33] Good examples of synthesized cancrinite with Cl^- anion were not found in this literature survey; instead, cancrinite was the preferred structure when at least some amount of NO_3^-, CO_3^-, or OH^- anion was present.[31]

Table 5. Candidate minerals for spent electrochemical salt.[30] The values for theoretical waste loading limits (mass%) are listed in parentheses.

Mineral Name	Chemical Formula	Cl, Mass%	Alkali, Mass% (on Na basis)	Mineral Group
manganpyrosmalite	$(Mn,Fe^{++})_8Si_6O_{15}(OH,Cl)_{10}$	13.59 (24)	0.00 (0)	pyrosmalite
wadalite	$Ca_6Al_5Si_2O_{16}Cl_3$	13.40 (23)	0.00 (0)	sodalite
quadridavyne	$(Na,K)_6Ca_2Al_6Si_6O_{24}Cl_4$	13.20 (23)	12.84 (40)	cancrinite
brokenhillite	$(Mn,Fe)_{32}[Si_{24}O_{60}]OH_{29}Cl_{11}$	9.12 (16)	0.00 (0)	pyrosmalite
sodalite	$Na_8Al_6Si_6O_{24}Cl_2$	7.32 (13)	18.98 (59)	sodalite

In general terms, sodalites have been easily synthesized by reacting zeolite with salt, such as NaCl, in a wide concentration range of aqueous NaOH solutions at near ambient temperatures inside a reaction vessel. Many variations of this basic approach were found in the literature.[31-33]

Leachability data were available in the literature for natural sodalite and iodine sodalite. Sodalite was studied as a waste form for immobilizing the long lived ^{129}I isotope by Nakazawa et al, who measured a normalized release rate of ~ 10^{-4} g/m^2/d for the synthesized iodine sodalite and ~ 10^{-5} g/m^2/d for the natural sodalite.[6] The duration of the leachability testing was 70 days. There is no mention of temperature for the leaching experiments. Thus, it is assumed to be room temperature testing, which is less aggressive than the PCT method A,[7] which is conducted at 90 °C.

Based on the literature study, scoping studies for a mineral waste form will focus on synthesizing sodalite and/or cancrinite in a form that doesn't require a binder glass. The glass-bonded sodalite process starts by mixing spent salt with zeolite 4A. The zeolite does not incorporate some of the fission products, such as the lanthanides, into the cage structure and conversion of this zeolite to sodalite requires SiO_2 addition. Thus, a glass is needed to immobilize the spent salt, lowering the waste loading.

In this study, the sol-gel process was selected to synthesize a sodalite mineral from colloid suspension of silica and sodium aluminate solution because it provides a low-temperature route for preparing ceramic materials with excellent homogeneity and a low sintering temperature. In addition, the intimate mixing of colloid suspension and sodium aluminate solution with liquid waste containing the spent salt with 20 mass% FP will help incorporate chlorine as well as lanthanides (~ 2 mol% of the salt) into the sodalite structure during gel formation. If successful, there will be no need to immobilize the sodalite in a glass matrix, leading to increased waste loading. However, it would require the use of aqueous processing (both an advantage and disadvantage of this approach).

3.2 Mineral Scoping Studies

3.2.1 Sodalite Fabrication

Sodalite was fabricated by a sol-gel process followed with heating to convert the sol-gel into a sodalite ceramic waste form. The sol-gel was made by first adding the proper ratios of dissolved salt solution (see Table 6 for simplified waste simulant), 45 mass% sodium aluminate in solution, and 40 mass% colloidal silica in solution into a Pyrex® beaker maintained at a temperature of 67 ± 2.5 °C. In addition, a Pt stir rod was used to provide mixing during the entire process. A white gel formed immediately upon adding in the sodium aluminate solution and colloidal silica suspension. The gel was mixed for 30–60 minutes to homogenize the gel and drive off excess water.

After mixing, the material was placed in an oven and dried overnight at a temperature of 105 °C, which produced a bonded white mass. The dried material was removed from the beaker and ground and homogenized in a ceramic mortar and pestle. The powder was then placed into a Pt crucible and ramp heated at 3 °C/min to a temperature of interest (650 °C, 750 °C, or 850 °C), held for either 8 or 24 hours to form sodalite, and then the temperature was reduced at 3 °C/min to room temperature.

Four compositions were made with the sol-gel process to synthesize the sodalite structure, with the amounts given in Table 6. Sample S1 was made to observe the gel process with the proper ratio of sodium aluminate to colloidal silica and deionized water (DIW) to synthesize sodalite. Sample S2 was made with the same ratio of $NaAlO_2$ to SiO_2 as S1, but without the DIW to observe the effect of additional DIW on the gel process. S1 showed a more gradual gelling process than S2. As a result, S3 and S4 were designed after S1; however, DIW was partially replaced or fully replaced by salt solution, which served as a simulated spent salt waste.

Table 6. Sol-gel batch components in terms of concentration and solution volume.

		S1	S2	S3	S4
Component	Concentration	Volume added (mL)			
$NaAlO_2$ Solution	0.45 g/mL	54.8	54.8	54.8	48.8
SiO_2 Solution	0.40 g/mL	45.2	45.2	45.2	40.2
Salt Solution dissolved in DIW (waste simulant)	67.7 g/L LiCl 26.5 g/L NaCl 86.0 g/L KCl			125.0	27.9
DIW	NA	125.0			83.4
Total		225.0	100.0	225.0	200.3

3.2.2 Sodalite Characterization

3.2.2.1 Visual Observations of Alternate Mineral Waste Forms

All of the samples were loosely to moderately bound material after the heating process. Composition S-3 resulted in samples that were easily broken into powders on removal from the Pt crucible. Compositions S-1, S-2, and S-4 resulted in moderately bound materials that required reasonable force (~ 400 kPa) to crush into powder.

3.2.2.2 FT-IR Analysis on Alternate Mineral Waste Forms

Samples were first analyzed by Fourier transform infrared spectroscopy (FT-IR) to identify the presence of sodalite in the samples from the characteristic vibrational fingerprint given in the literature.[34,35] Sodalite alone is far too absorbing to perform FT-IR analysis without dilution in an IR transparent material (e.g., alkali halide salts). Instead, ~ 4 mg of each sample was mixed with ~ 400 mg of FT-IR-grade KBr and pressed into a pellet at ~ 75 kpsi. The IR spectra were collected in absorbance in the mid-IR (2.5–25 μm) as a function of wavenumber (cm^{-1}). Figure 5 shows the IR spectrum for compositions S1, S2, S3, and S4, heat-treated to 850 °C for 8 hours. Compositions S3 and S4 contain the three characteristic peaks at 665, 710, and 733 cm^{-1} associated with the sodalite structure according to the literature.[34,35] As expected, composition S4, stoichiometric match with sodalite, showed the strongest sodalite fingerprint of the four compositions tested. The IR spectrum was also collected for composition S4, which was heat-treated at a temperature of 650 °C and plotted along with specimen heat treated at 850 °C in order to compare the effect of temperature (see Figure 6). The S4 sample heat-treated at 650 °C appeared to have more pronounced sodalite peaks than the same sample heat-treated at 850 °C. In addition, the S4 sample heat-treated at 850 °C has a peak at 507 cm^{-1} and another faint peak at ~ 680 cm^{-1} that are absent from the same sample heat-treated at 650 °C. The additional peaks indicate that a second phase may be present in the S4 sample heat-treated at 850°C.

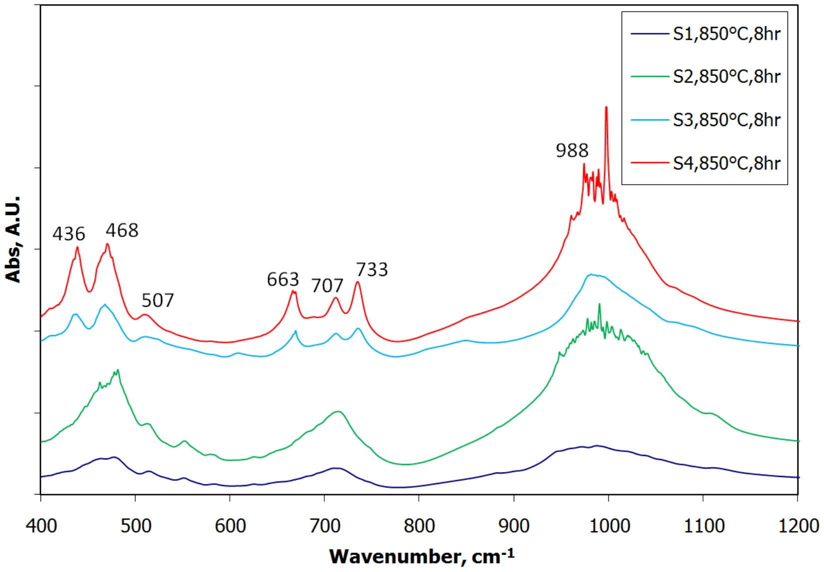


Figure 5. IR spectrum of 1 mass% samples spiked into KBr and pressed into pellets.

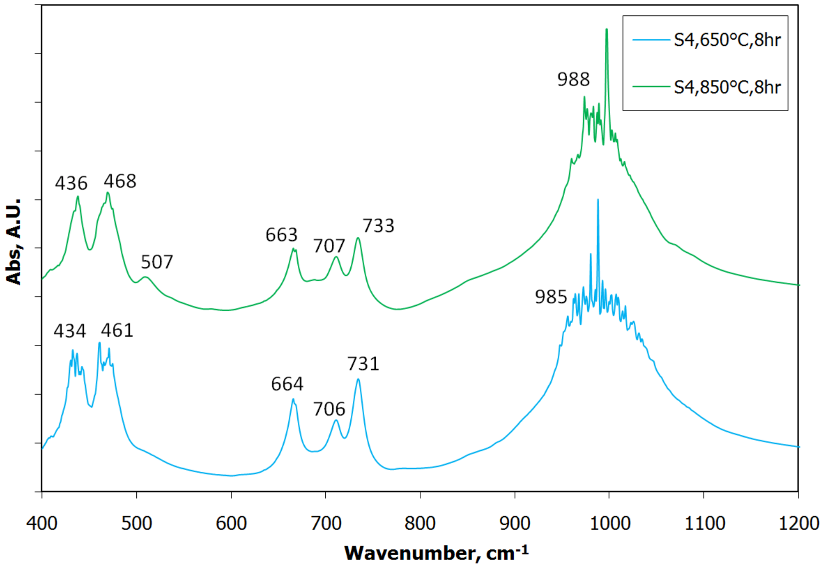


Figure 6. IR spectrum of 1 mass% sample spiked into KBr and pressed into pellets.

3.2.2.3 XRD Analysis on Alternate Mineral Waste Forms

Samples of S3 and S4, heat-treated at 850 °C for 8 hours, were then analyzed with X-ray diffraction (XRD) to identify the structures present in each sample. The XRD pattern confirmed the presence of sodalite that was found with FT-IR but also showed that nepheline ($(K,Na)AlSiO_4$) was present in both samples, S3 and S4 (Figure 7 and Figure 8, respectively). Composition S3, heat-treated at 850 °C for 8 hours, also contained lithium catena-silicate (Li_2SiO_3), halite ($Na_{0.9}K_{0.1}Cl$), and sylvine (KCl). The presence of halide-containing phases was expected in composition S3 with the excess salt added to the batch. FT-IR by the KBr pellet method most likely precluded the possibility of identifying any salt phases in the samples because of their very similar optical properties to KBr in the IR range, which are featureless with very high transmission at the small doping levels used.

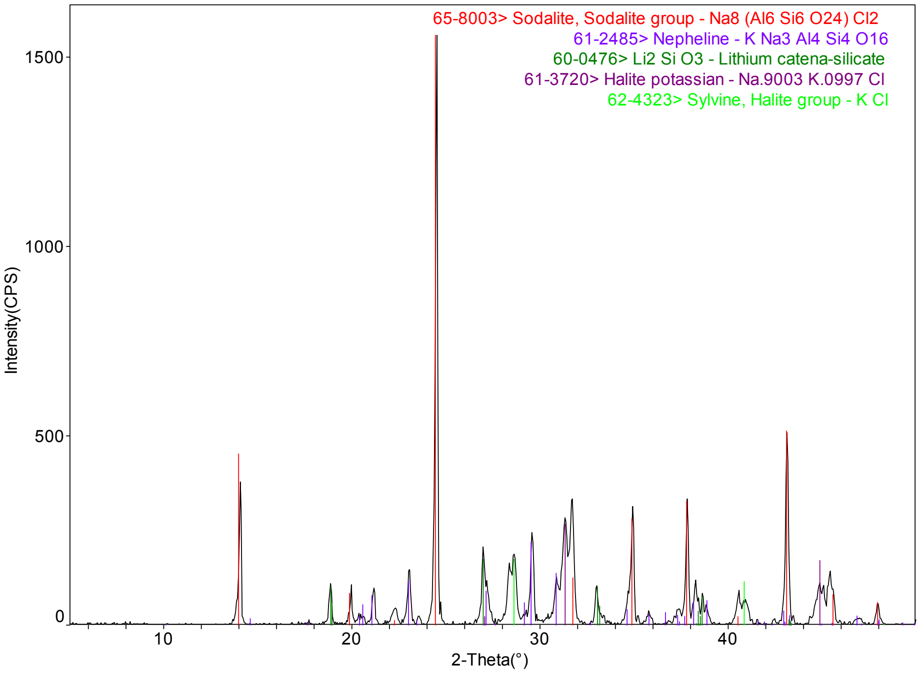


Figure 7. XRD scan of S3 sample heat-treated at 850 °C for 8 hours with phases identified.

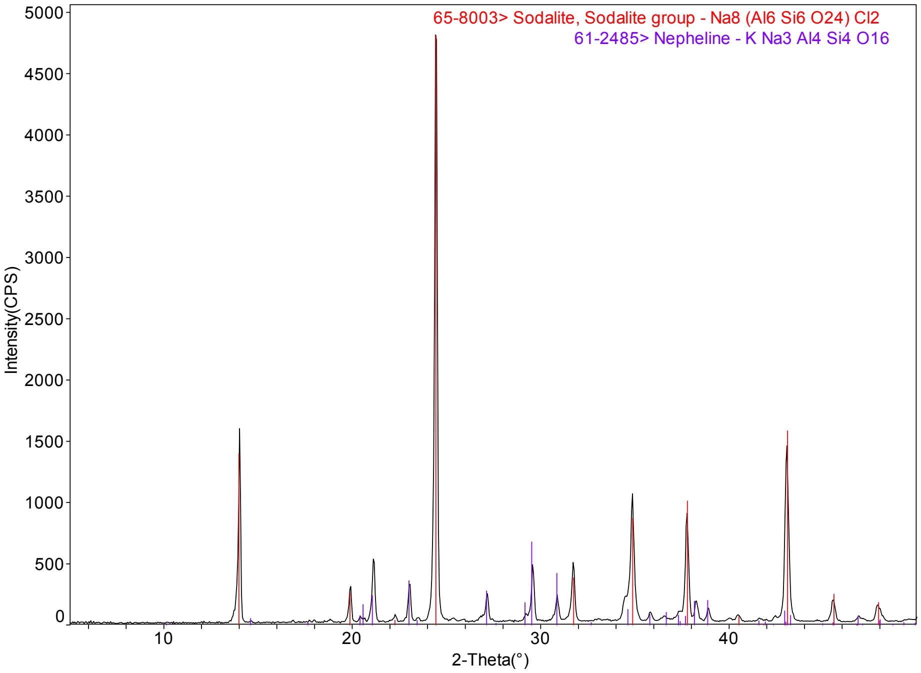


Figure 8. XRD scan of S4 sample heat-treated at 850 °C for 8 hours with phases identified.

3.2.2.4 SEM/EDS Analysis on Alternate Mineral Waste Forms

Samples of the S4 that were heat-treated at temperatures of 650 °C, 750 °C, and 850 °C were analyzed using a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) to examine the morphology and chemistry of the phases formed. Micrographs of the sodalite grains are shown in Figure 9. The sodalite grains are on the order of 0.5–2.0 µm in diameter and appear to become more rounded with increased temperature. Table 7 shows the tabulated EDS spot and the area analyses that were performed on each of the sodalite samples. The EDS analyses agree reasonably well with the "as-batched" compositions that were batched according to the stoichiometric composition of sodalite. The measured concentrations of Al are low, whereas the Si and Cl values are noticeably higher than the batched composition. The EDS system is not capable of measuring elements lighter than C, and hence measured concentrations are not given for Li.

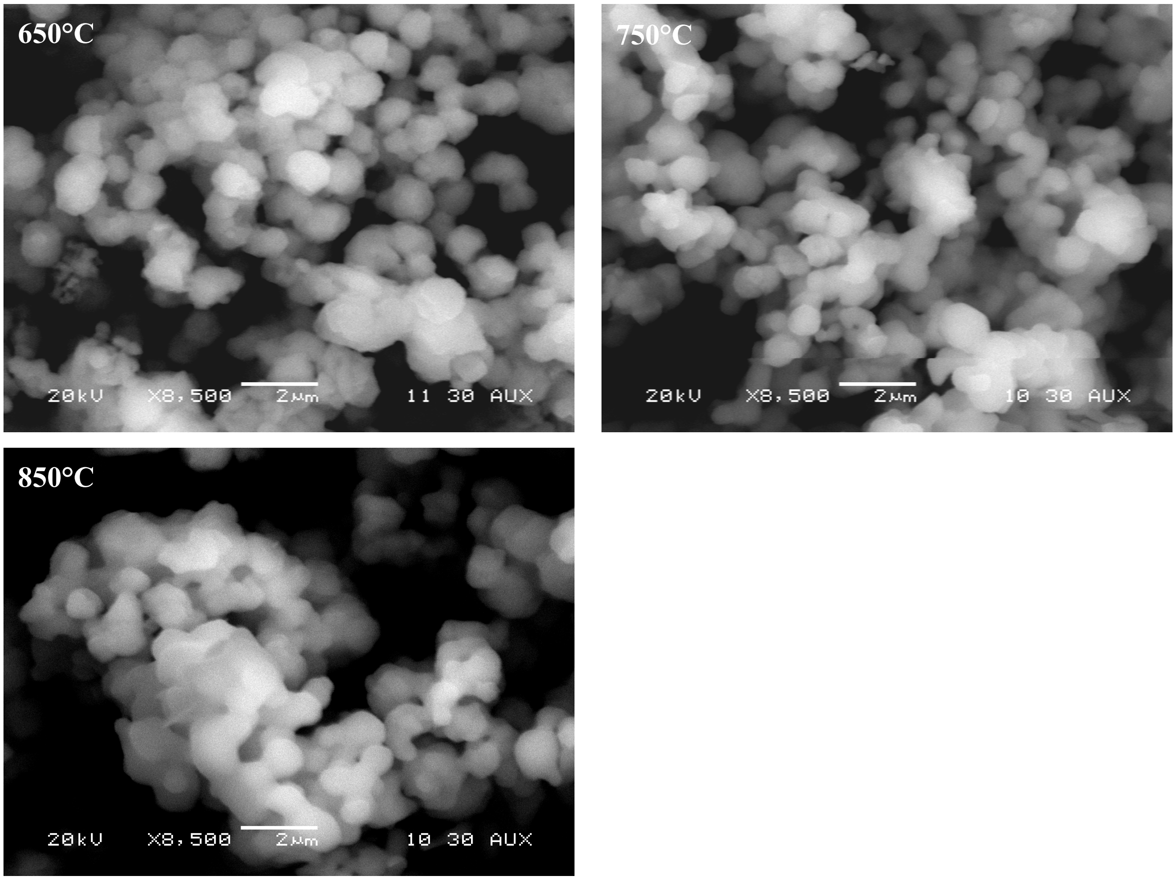


Figure 9. SEM micrographs of sodalite phase observed in composition S4 heat-treated at 650 °C, 750 °C, and 850 °C.

Table 7. EDS measured compositions of composition S4 heat-treated at 650 °C, 750 °C, and 850 °C. A predicted composition for as-batched S4 and a stoichiometric sodalite composition (neither analyzed by EDS) are included in the data for comparison purposes.

Sample ID	Condition	Li	Na	K	Al	Si	O	Cl	Total
S4	650 °C	*ND*	0.1584	0.0082	0.0899	0.1539	0.5260	0.0636	1.0000
S4	750 °C	*ND*	0.1587	0.0090	0.0906	0.1541	0.5280	0.0596	1.0000
S4	850 °C	*ND*	0.1590	0.0085	0.0904	0.1507	0.5207	0.0707	1.0000
S4	As-Batched	0.0217	0.1366	0.0157	0.1304	0.1304	0.5217	0.0435	1.0000
Sodalite	Ideal		0.1739		0.1304	0.1304	0.5217	0.0435	1.0000

4. CONCLUSIONS

4.1 Glass Waste Forms

These scoping studies revealed that we have formed homogeneous glass in the TeO_2-XCl-B_2O_3 system with up to 19 mass% of XCl. Although the leaching rates are generally high, these glasses show promise for the target waste stream and require further investigation. Small additions of glass formers (i.e., B_2O_3) and modifiers (i.e., X_2O where X = Li_2O, Na_2O, K_2O) to tellurite showed drastically different performance (i.e., durability) and these effects need be investigated should these glasses be optimized as a waste form for this application. Future work will investigate the solubility of mixed chlorides and performance of tellurite binary and ternary systems including B_2O_3,[25-27] P_2O_5,[18] Al_2O_3,[36] and/or PbO[24,37] with or without modifiers, e.g., alkali oxides[23,24] or transition metal oxides (e.g., ZnO, WO_3, Nb_2O_5).[37]

4.2 Alternate Mineral Waste Processes

Sodalite was successfully synthesized with the sol-gel process at the theoretical waste loading limit of 12.7 mass% for the 20% FP waste. Durability of the sodalite was not measured in these scoping studies because the main concern was to focus on a method to fabricate the sodalite phase from a simple sol-gel process. Performance data available in the literature indicate that sodalite, if properly fabricated, is durable.[6,8,38-40] Future work will optimize the sol-gel and heating process to produce a fully dense sodalite waste form that is phase-pure. The cancrinite structure (quadridavyne), which is less preferred by Cl^-, will be attempted in future work as it has a theoretical waste loading limit of 22.9 mass% and alkaline earth elements can be incorporated into the structure (see Table 5) which has yet to be demonstrated in sodalite.

4.3 Summary Conclusions

Comparing the results of the glass to the sodalite we find the following:

1. The tellurite glasses tested in this study outperform the theoretical loading of alkali chlorides in sodalite (i.e., 12.8 mass%).
2. Sodalite outperforms the glass in terms of waste form performance (i.e., higher durability according to the literature).

Different waste compositions were used for the glass (10% FP waste) and the mineral (20% FP waste) waste forms and the mineral waste form was only demonstrated with the LiCl, NaCl, and KCl as waste components (see Table 6). However, the 10% and 20% FP wastes remain very similar in composition (see Table 2 and Table 1, respectively).

The tellurite glasses studied have the potential to exceed the waste loadings possible in the sodalite structure if major improvements are achieved in terms of waste form performance. The maximum waste loading was achieved in sodalite. Future work will focus on incorporation of the full waste composition and determine if the cancrinite structure can be synthesized. The following suggestions are proposed in order to ensure sufficient information for comparison between the candidate waste forms:

1. Produce all waste form candidates using the same waste composition (i.e., 20% FP waste).
2. Perform compositional analysis on all waste form candidates after production to verify that volatile materials were not evolved during processing.
3. Perform durability on all candidate waste forms for performance comparison purposes.

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