*Solution-Derived Sodalite Made with Si- and Ge-Ethoxide Precursors for Immobilizing
Electrorefiner Salt*

Brian J. Riley,* William C. Lepry, Jarrod V. Crum

Pacific Northwest National Laboratory, Richland, WA 99352

Abstract

Chlorosodalite has the general form of $\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$ and this paper describes experiments conducted to synthesize sodalite with a solution-based approach to immobilize a simulated spent electrorefiner salt solution containing a mixture of alkali, alkaline earth, and lanthanide chlorides. The reactants used were the salt solution, NaAlO_2 , and either $\text{Si}(\text{OC}_2\text{H}_5)_4$ or $\text{Ge}(\text{OC}_2\text{H}_5)_4$. Additionally, seven different glass binders at loadings of 5 mass% were evaluated as sintering aids for consolidating the as-made powders using a cold-press-and-sinter technique. This process of using alkoxide additives for the Group IV component can be used to produce large quantities of sodalite at near-room temperature as compared to a method where colloidal silica was used as the silica source. However, the small particle sizes inhibited densification during heat treatment.

Keywords: sodalite, electrochemical waste forms, eutectic salt, ethoxide, alkoxide

1 Introduction

The future of nuclear power production in the U.S. is uncertain, but, in order to maximize

* Corresponding author: brian.riley@pnnl.gov; (509)372-4651 (phone), (509)372-5997 (fax)

the efficiency of the nuclear fuel cycle, the fuel will likely have to be recycled through a series of reprocessing steps. Several potential recycle methods have been proposed and one of them requires that the fuel be dissolved in a LiCl-KCl eutectic salt within an electrorefiner. Once this salt is saturated with fission products released from the fuel, these components must be removed or the salt must be replaced to maintain separations efficiency.

The current baseline approach for immobilizing the spent salt is chlorosodalite, which has the general formula of $\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$. The baseline sodalite developed by Argonne National Laboratory and Idaho National Laboratory is the most commonly studied waste form in the US for encapsulating the entire spent salt [1, 2]. The typical method for making this waste form is to occlude the salt in zeolite 4A at elevated temperatures ($\sim 500^\circ\text{C}$), mix in ~ 25 mass% of a glass sintering aid, and then fire the mixture at $\sim 900\text{--}950^\circ\text{C}$.

An alternative way to making the sodalite is with a solution-based approach [3-5]. One solution-based method [3, 4] used colloidal silica, NaAlO_2 , and a salt solution to make sodalite at near-room temperature (65°C), and those samples were referred to as S5A pellets. This process had some limitations where the sodalite production was limited at the elevated firing temperatures required to get high density pellets and the high processing temperatures usually led to chloride volatility and, subsequently, nepheline formation. However, even small amounts (1–7 mass%) of a borosilicate glass sintering aid (NBS-1 [6]) improved these results and these samples are referred to as S6 pellets [3].

The current work presents a modified approach to the S5A/S6 technique with organic forms of Group IV additives, i.e., $\text{Si}(\text{OC}_2\text{H}_5)_4$ (also called tetraethyl orthosilicate or TEOS) and $\text{Ge}(\text{OC}_2\text{H}_5)_4$, which are also referred to as silicon ethoxide and germanium ethoxide, respectively. The $\text{Ge}(\text{OC}_2\text{H}_5)_4$ precursor was selected as a potential option to reduce the

consolidation temperature of the product considering that GeO₂ melts at a much lower temperature (1116 °C [7]) than SiO₂ (1710 °C [8]). Both of these compounds hydrolyze in the presence of water and undergo polycondensation reactions. This process can be controlled by adjusting the ratio of water to the organic precursors (on a molar basis), and this was studied previously in acid- and base-catalyzed reactions [9-12] and an example of how this process works for Si(OC₂H₅)₄ is shown in Equation (1).

While solution-derived minerals, including sodalite [39-44], are often found in the literature, it is not as common to see solution-based processes using alkoxides precursors. Lattur et al. [45] performed hydrothermal synthesis of sodalite using aluminum isopropoxide, TEOS, NaOH, and AgNO₃ or TiNO₃ but this account is rare in the literature. The work presented here shows a simplified low-temperature route for making sodalite precursors using Si(OC₂H₅)₄ or Ge(OC₂H₅)₄, a mixed chloride salt waste, and NaAlO₂ that can be combined with a glass powder and then fired to produce a glass-bonded sodalite monolith. The primary reason for investigating the organic precursors was to see if their reactivities would be different from colloidal silica, leading to a difference in the sodalite yield or a more preferred morphology in the as-made product. Also, seven different glass sintering aids were evaluated for improving sodalite yield and minimizing porosity in the fired pellets.

2 Methods

2.1 Solution-based process

The basic process for making all of the samples was similar with a few exceptions for each batch. In all cases, the goal was to achieve sodalite, nominally Na₈(AlSiO₄)₆Cl₂. However,

the stoichiometry used in these experiments was not batched as nominal and additional NaAlO_2 was added to make up for the lack of Na in the salt and help drive the exchange of Na in the sodalite for Li and K into the glass phase. Also, the ratio of Cl to cations in the salt was not 1:1 because of the LnCl_3 and BaCl_2 (see Table 1) so this additional Na was also present to supplement the alkali content to balance the Cl. The residual Al_2O_3 from the excess NaAlO_2 was expected to incorporate into the glass phase.

For the $\text{Si}(\text{OC}_2\text{H}_5)_4$ -based samples (called S5C), 30.0 mL of salt solution (see Table 1) was added to a 250 mL beaker with a serpentine platinum stirring wire and this was heated to 75 °C while stirring. Then, 52.8 mL of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (99.0% purity, Sigma-Aldrich, St. Louis, MO) was added to the beaker while stirring. This was followed by the addition of 51.0 mL of NaAlO_2 (38% solution, USALCO, LLC, Baltimore, MD) and 13.8 mL of absolute ethanol. For the S5C pellets, 2.05 g of glass sintering aid (5 mass%) was added into the solution and stirred. After the glass was added, the viscosity sharply increased through the process of an exothermic reaction (~30 s). Each beaker was placed in a drying oven overnight at 105 °C and the resulting products were powdered for homogenization.

For the $\text{Ge}(\text{OC}_2\text{H}_5)_4$ -based sample (called S5D), a 1/4-scale batch was made. Here, 7.5 mL of salt solution was added to a 100 mL beaker. Then, 13.2 mL of $\text{Ge}(\text{OC}_2\text{H}_5)_4$ (97% solution, Alfa Aesar, Ward Hill, MA) was added to the beaker while stirring as was done previously. Then, 12.75 mL of NaAlO_2 was added followed by 3.45 mL of absolute ethanol. The beaker was placed in a drying oven overnight at 105 °C and the resulting product was powdered for homogenization.

2.2 *Glass binder preparation*

The compositions of all glass sintering aids are presented in Table 2 as well as the

predicted properties (if known) of viscosity (η)-temperature relationships, melting temperature (T_M), and bulk density (ρ_b). Each glass was added as a powder during the solution-based process discussed in the previous section. The volume of each glass powder was measured using a He pycnometer (Micromeritics AccuPyc II 1340, Norcross, GA) through a series of 5 purges and 10 measurements that were averaged. Mass values were measured with an analytical balance (PR2003 DeltaRange, Mettler-Toledo, Inc., Columbus, OH; ± 0.003 g precision) and then the pycnometer calculated the average ρ_b . The average standard deviation of all 7 binders evaluated was $\pm 0.003 \times 10^3 \text{ kg m}^{-3}$.

The sodium borosilicate glass sintering aids, denoted as SA-###, were formulated based on their lower T_M 's compared to NBS-1 and were labeled based on the temperatures (i.e., 700, 750, 800, and 850 °C) at which $\eta \sim 100 \text{ Pa}\cdot\text{s}$ based on predictions with SciGlass models (v 7.0, ITC, Inc., Newton, MA). A melt-quench technique was used to make 250 g of each of the SA-### glass binders, which were batched from SiO_2 , Na_2CO_3 , and H_3BO_3 . The as-batched powders were mixed in an agate mill, melted in a lidded Pt/10%Rh crucible at various T_M 's (see Table 2) for 1 hr, and quenched on an Inconel plate. This glass was ground in a tungsten carbide mill, remelted, requenched, and then ground to the final powder.

The NBS-1 glass developed by Vienna et al. [6] was also used in previous work with the S6 pellets [3]. The NaAlP glass was selected based on past success as a sintering aid (NaAlP-B4) for an apatite mineral waste form [13]. The NBS-1 and NaAlP binders were provided by collaborators as powders and not made new for this study. The TePbO glass was selected because it has a high loading for the same mixed salt waste that was used in this study [14-17]. The TePbO glass was made by mixing TeO_2 and PbO with a composition of 78% TeO_2 /22% PbO (by mass) in a mortar and pestle and melting in a covered Pt/10%Rh crucible for 20 min at

700 °C. The melt was quenched on an Inconel plate and powdered.

2.3 Pellet Preparation and Firing

Following drying and homogenization, ~2.5 g of the as-dried powders were weighed and uniaxially pressed into pellets at 2.5×10^7 Pa (3.6×10^3 pounds per square inch) in a stainless steel die. The unfired “green” densities were calculated by measuring volume with a set of calipers and applying the aforementioned mass. Then, the pellets were placed on a dense alumina sintering plate and loaded into a Lindberg furnace (Thermal Product Solutions, Rochester, NY). Specimens were heated at $1 \text{ }^\circ\text{C min}^{-1}$ up to the maximum firing temperature between 550–950 °C, held for 8 h, and then furnace-cooled at $\sim 10 \text{ }^\circ\text{C min}^{-1}$. Following firing, pellets were broken into quadrants and characterized.

2.4 Density and Porosity

The ρ_b was measured by taking accurate mass and geometric volume measurements (average height and diameter) of the pellets before firing (green density) and after firing (sintered density). Pellet masses were measured with the PR2003 DeltaRange analytical balance and volumetric measurements were taken using digital calipers with a precision of ± 0.01 mm. Archimedes’ method was also performed to measure ρ_b using ethanol (EtOH).

Here, the specimen masses were measured dry (m_{dry}) on the PR2003 DeltaRange analytical balance and then submerged in absolute EtOH within a vacuum desiccator where the air was removed from the open porosity and these voids were back-fill with absolute EtOH. After ≥ 20 min of sitting in the ethanol under vacuum (1.3–6.7 Pa), the submerged mass (m_{sub}) was measured using an Archimedes apparatus. Then, the pellet was removed from the EtOH and the excess EtOH on the surface of the pellet was removed by blotting it on an EtOH-soaked

cloth, and then the pellet saturated with EtOH was weighed (m_{sat}). The temperature of the EtOH was monitored and used to calculate the ρ_b of the pellet according to Equation (2) where the ρ_{EtOH} was the density of ethanol ($\rho_{\text{EtOH}} = -8.54 \times 10^{-4} T + 0.806$; $T = 15\text{--}25\text{ }^\circ\text{C}$ [18]).

$$\rho_b = (m_{\text{dry}} * \rho_{\text{EtOH}}) / (m_{\text{sat}} - m_{\text{sub}}) \quad (2)$$

From these data, the open porosity (ϕ) of the specimens was measured based both on mass differences (ϕ_m) and the ratio of ρ_b to the theoretical density (ρ_t) of sodalite ($\sim 2.27 \times 10^3 \text{ kg m}^{-3}$) (ϕ_p) as seen in Equation (3) [19]. The ρ_t values were calculated using Equation (4) where ρ_i and m_i were the calculated density and mass fraction of the i -th crystalline phase, respectively, determined using X-ray diffraction (XRD). This approach does not account for the amorphous fraction so it is considered an estimation of the true ρ_b .

$$\phi_m = (m_{\text{sat}} - m_{\text{dry}}) / (m_{\text{sat}} - m_{\text{sub}}) \quad (3a)$$

$$\phi_p = 1 - (\rho_b / \rho_t) \quad (3b)$$

$$\rho_t = \sum_{i=1}^n \rho_i m_i \quad (4)$$

2.5 X-Ray Diffraction

Specimens of as-made and fired materials were powdered in a tungsten carbide milling chamber and then analyzed with XRD. A Bruker® D8 Advance (Bruker AXS Inc., Madison, WI) equipped with a Cu K α target set to a power level of 40 kV and 40 mA was used to collect diffraction patterns. The detector used was a LynxEye™ position-sensitive detector with a scan range of $3^\circ 2\theta$. Typical scan parameters used for specimen analysis were $5\text{--}70^\circ 2\theta$ with a step of $0.015^\circ 2\theta$ and a 0.3-s dwell at each step. Bruker AXS® EVA (v14) and Topas (v4.2) software were used to identify and quantify phase assemblages. A standard was not added to the samples prior to analysis so the amorphous (or nanocrystalline) portion in each sample was not included

in the phase distribution analysis.

2.6 *Scanning Electron Microscopy and Energy Dispersive Spectroscopy*

Both fractured and cross-sectioned specimens were observed with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). A JSM-7001F with a field emission gun (JEOL USA, Inc. Peabody, MA) was equipped with an EDAX Apollo II 30 mm² Si drift detector (AMETEK, Berwyn, PA) for compositional analysis. Specimens were coated with palladium prior to analysis. Both secondary electron and backscattered electron detectors were used for imaging.

3 Results and Discussion

3.1 *Phase Distribution and Morphology*

As shown in Table 3 [20-26], the as-made S5C (Si-based) samples had high sodalite fractions at ~82–98% (of the crystalline content). In contrast to previous work where colloidal silica was used instead of TEOS [16], the use of TEOS may be the preferred silica precursor for maximizing sodalite yield in the as-made product without having to prolong the mixing duration.

Figure 1 provides a comparison of the phase distribution in S5C pellets made with different sintering aids and fired at different temperatures. All of the SA sintering aids behaved quite similarly with a maximum sodalite concentration at the lower sintering temperatures (550–600 °C) and an inverse correlation between the mass% of sodalite and Na-Al-Si-O phases (e.g., nepheline, carnegieite) with increasing firing temperatures. This inverse relationship was similarly observed with S5C-TePbO and S5C-NBS1 but was more pronounced in the data for S5C-NaAIP. This was attributed to Cl-volatility with increased firing temperatures.

Figure 2 shows the XRD spectra for the as-made S5D (Ge-based) sample as well as the

product after a heat-treatment at 750 °C for 8 h. The primary phase (~81.4 mass%) in the as-made sample was $\text{Na}_8(\text{AlGeO}_4)_6\text{Cl}_2$ (Ge-sodalite, ICSD#65664 [27], where ICSD is the Inorganic Crystal Structure Database). The minor components included unreacted NaCl (7.0 mass%, ICSD#61662 [28]), KCl (6.5 mass%, ICSD#28938 [29]), and LiCl (1.9 mass%, ICSD#26909 [30]) as well as $\text{KH}_3\text{Ge}_7\text{O}_{16}\cdot 3\text{H}_2\text{O}$ (3.2 mass%, ICSD#34094 [31]).

For the heat-treated S5D sample, not all of the phases could be quantified because of unfit peaks but the primary phase was $\text{Na}_8(\text{AlGeO}_4)_6\text{Cl}_2$. An *hkl* phase based off of $\text{Na}_{1.74}\text{Mg}_{0.79}\text{Al}_{0.15}\text{Si}_{1.06}\text{O}_4$ [32] with the orthorhombic *Pbca* space group ($a = 10.5$, $b = 10.4$, $c = 5.25$ Å) was created during Reitveld refinement to fit several of the unfit peaks as per a peak location and intensity fit with the diffraction pattern using EVA phase identification (International Centre for Diffraction Data database 1999). Several minor components were found in the fired pellet including unreacted salts (i.e., NaCl [28] and KCl [29]), KAlSi_3O_8 (ICSD#73416 [33]), and GeO_2 (ICSD#158589 [34]) as well as several structural (not chemical) matches for phases like lithium silicates (i.e., Li_2SiO_3 ICSD#100402 [35] and $\text{Li}_2\text{Si}_2\text{O}_5$ ICSD#15414 [36]). This shows that the Ge-sodalite can be synthesized with this salt composition and the $\text{Ge}(\text{OC}_2\text{H}_5)_4$ precursor. Although the substitution of Si for Ge, in theory, should reduce the required consolidation temperatures, the ϕ in the fired pellet was ~40%. Thus, with the added disadvantage of the $\text{Ge}(\text{OC}_2\text{H}_5)_4$ precursor being notably more expensive than $\text{Si}(\text{OC}_2\text{H}_5)_4$, this process was abandoned but might warrant further investigation with a new glass binder optimized for this particular formulation if lower processing temperatures were a limitation for a given waste due to selective volatility of salt constituents.

Figure 3 provides some microstructure comparisons between solution-based materials made with colloidal silica from a previous study [3, 14] and some from the current study with

TEOS as the silica source. It is apparent by comparing the scales of the microstructure that the TEOS-based product has a smaller grain size by an order of magnitude (~10-fold difference). Also, a clear distinction can be found between the sodalite and nepheline fractions based on the Cl EDS map. The presence of free lanthanides is denoted by the La map where this fraction appears to be present at the grain boundary between the nepheline and sodalite phases. This suggests that a larger fraction of glass binder might be required to fully incorporate the lanthanide fission products into the glass phase.

3.2 *Pellet Densities and Porosity*

The full data set for density and porosity measurements on the alternative sintering aids is presented in Table 4. The ρ_t for sodalite varies slightly depending on the true composition of the sodalite ($2.27 \times 10^3 \text{ kg m}^{-3}$ [37] ICSD#98812 to $2.30 \times 10^3 \text{ kg m}^{-3}$ [38] ICSD#166827). It should be noted that Equation (4), which is used for calculating ρ_t , contains a source of error in that it does not account for the density and mass fraction of the amorphous fraction. The glass sintering aids have higher ρ_b values (see Table 2) than sodalite ($\sim 2.29 \times 10^3 \text{ kg m}^{-3}$), which will inflate the true ρ_t values, although this will only be a minor contribution due to the low mass of glass added (5 mass%). Also, some of the data for “% of ρ_t ” are probably artificially inflated and the data for ϕ_p values in Table 4 must be considered in comparisons. The maximum density observed was at 92% of ρ_t (S5C-SA700 at 750°C).

The optimum heat-treatment temperature to achieve maximum density for specimens with the sintering aids was ~750–850 °C for all except NBS-1, which was ~950 °C (possibly higher). Adding NaAlP or TePbO sintering aids did not increase pellet densities where maximum achieved % of ρ_t values were 55% (at 750 °C) and 56% (at 850 °C), respectively. Thus, these sintering aid compositions were not as reactive with the as-made materials as the SA#### and

NBS-1 glasses.

Figure 4a provides a summary of the pellet densities at different firing temperatures for the S5C pellets and Figure 4b provides a comparison of both sodalite mass% (of crystalline fraction) and the % of ρ_t values for all samples fired at 750 °C. Here, we see that the maximum density with the NBS-1 glass sintering aid was not confirmed over the temperatures tested. This is attributed to the fact that the glass has the highest SiO₂ content (60 mass%) as well as a higher η and T_M than all of the other sintering aids evaluated here. From Figure 4, it can be seen that the SA-### sintering aids were effective at closing the pores and allowing for moderate sodalite fraction to form during firing at lower temperatures than are normally used for producing the baseline ceramic waste form (~915 °C). It should also be noted that the NaAlP and TePbO samples showed the highest sodalite fractions following the 750 °C firing at 81.8 and 79.7 mass%, respectively.

Figure 5 provides a comparison of the “% of ρ_t ” and “mass% of sodalite in the crystalline fraction” for each sintering aid at different firing temperatures. Figure 5 also includes data from a previous study [3] where sodalite samples were made using colloidal silica instead of Si(OC₂H₅)₄. Here, the most promising candidates are towards the upper right corner of the plot where both target properties are maximized. From this plot, it is evident that the SA### sintering aids performed well to close the porosity while still allowing sodalite to form during firing although all of the data seem to settle along a boundary shown by the dotted arc revealing the limitations of the current work.

The effect of increased viscosity for NBS-1 over the SA### sintering aids was evident by the high ϕ for these samples at temperatures ≤ 750 °C. When comparing all of the data obtained with the NBS1 sintering aid, i.e., S6 made with colloidal silica and S5C-NBS1 made with

$\text{Si}(\text{OC}_2\text{H}_5)_4$, it is apparent that the colloidal silica formulations had comparable values of % of ρ_t but noticeably higher sodalite fractions. This could be a result of the size of the starting as-made sodalite material but is also likely related to the sodalite fraction in the as-made starting material.

4 Conclusions

The work presented here demonstrates the syntheses of sodalite using either $\text{Si}(\text{OC}_2\text{H}_5)_4$ or $\text{Ge}(\text{OC}_2\text{H}_5)_4$ along with NaAlO_2 and a simulated electrefiner salt solution containing a mixture of alkali, alkaline earth, and lanthanide chlorides at near-room temperature. The as-made products showed high sodalite yields of ~82–98 mass% for the Si-based materials and ~81 mass% for the Ge-based sample. The seven glass binders that were evaluated performed quite differently from one another. The four SA### binders all performed similarly with maximum densification achieved at temperatures of 750–850 °C whereas the NBS-1 glass densified at much higher temperatures (≥ 950 °C) and the NaAlP and TePbO glasses did not show evidence of densification at any of the temperatures evaluated. These binders were not optimized and so further improvements could be made to densify at reduced temperatures with modifications to the glass compositions. The primary limitation to densification time and temperature is the volatility of Cl, which results in sodalite decomposition to nepheline.

5 Acknowledgements

Pacific Northwest National Laboratory is operated by the U.S. Department of Energy under Contract Number DE-AC05-76RL01830. The authors thank Jared Kroll for his help with measuring density on the NaAlP glass binder, Nathan Canfield for helpful comments, and Josef Matyáš for helpful discussions. This work was conducted with funding support from the Department of Energy Office of Nuclear Energy under the Fuel Cycle Research and Development Program with partial support from a subcontract from Idaho National Laboratory

through the Korean Atomic Energy Research Institute.

6 References

- [1] K.J. Bateman, C.J. Knight, C.W. Solbrig. 2007. Current Status of Ceramic Waste Form Development. INL/INT-06-11736, Rev. 1. Idaho National Laboratory, Idaho Falls, ID.
- [2] W.L. Ebert. 2005. Testing to Evaluate the Suitability of Waste Forms Developed for Electrometallurgically-Treated Spend Sodium-Bonded Nuclear Fuel for Disposal in the Yucca Mountain Repository. ANL-05/43. Argonne National Laboratory-East, Argonne, IL.
- [3] B.J. Riley, J.V. Crum, J. Matyáš, J.S. McCloy, W.C. Lepry, J. Am. Ceram. Soc. 95 (10) (2012) 3115-3123.
- [4] B.J. Riley, D.A. Pierce, S.M. Frank, J. Matyáš, C.A. Burns, J. Nucl. Mater. 459 (2015) 313-322.
- [5] E.R. Vance, J. Davis, K. Olufson, I. Chironi, I. Karatchevtseva, I. Farnan, J. Nucl. Mater. 420 (1-3) (2012) 396-404.
- [6] J.D. Vienna, J. Luey, P.R. Huma, D.E. Smith, R.D. Scheele, H.L. Wigent, J.V. Crum. 1998. Proc. of the Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries IV, 93, pp. 399-407, Ed. J. C. Marra and G. T. Chandler. The American Ceramics Society, Westerville, OH.
- [7] A.W. Laubengayer, D.S. Morton, J. Am. Chem. Soc. 54 (1932) 2303-2320.
- [8] J.N. Wilson, Sand. Clay Miner. 2 (3) (1935) 127-130.
- [9] C.J. Brinker, K.D. Keefer, D.W. Schaefer, C.S. Ashley, J. Non-Cryst. Solids 48 (1982) 47-64.
- [10] C.J. Brinker, K.D. Keefer, D.W. Schaefer, R.A. Assink, B.D. Kay, C.S. Ashley, J. Non-

- Cryst. Solids 63 (1984) 45-59.
- [11] I.M. Thomas, "Method for producing glass precursor compositions and glass compositions therefrom," patent number 3799754, 1974.
- [12] C.J. Brinker, S.P. Mukherjee, J. Mater. Sci. 16 (1981) 1980-1988.
- [13] I.W. Donald, B.L. Metcalfe, S.K. Fong, L.A. Gerrard, D.M. Strachan, R.D. Scheele, J. Nucl. Mater. 361 (1) (2007) 78-93.
- [14] B.J. Riley, B.T. Rieck, J.V. Crum, J. Matyas, J. McCloy, S.K. Sundaram, J.D. Vienna. 2010. Alternative Electrochemical Salt Waste Forms, Summary of FY2010 Results. FCRD-WAST-2010-000129. Pacific Northwest National Laboratory, Richland, WA.
- [15] B.J. Riley, B.T. Rieck, J.S. McCloy, J.V. Crum, S.K. Sundaram, J.D. Vienna, J. Nucl. Mater. 424 (1-3) (2012) 29-37.
- [16] B.J. Riley, J.S. McCloy, J.V. Crum, C.P. Rodriguez, C.F. Windisch Jr., W.C. Lepry, J. Matyas, M.P. Westman, B.T. Rieck, J.B. Lang, D.A. Pierce. 2011. Alternative Electrochemical Salt Waste Forms, Summary of FY/CY2011 Results. FCRD-SWF-2012-000028. Pacific Northwest National Laboratory, Richland, WA.
- [17] B.J. Riley, J.S. McCloy, J.V. Crum, W.C. Lepry, C.P. Rodriguez, C.F. Windisch Jr., J. Matyas, M.P. Westman, B.T. Rieck, J.B. Lang, M.J. Olszta, D.A. Pierce. 2012. Alternative Electrochemical Salt Waste Forms, Summary of FY11-FY12 Results. FCRD-SWF-2013-000025. Pacific Northwest National Laboratory, Richland, WA.
- [18] S.W. Stratton, Standard density and volumetric tables, 6th ed. Washington: Government Printing Office (1924).
- [19] D.J. Lacks, R.G. Gordon, Phys. Rev. B 48 (5) (1993) 2889-2908.
- [20] B. Beagley, C.M.B. Henderson, D. Taylor, Mineral. Mag. 46 (1982) 459-464.

- [21] I. Hassan, H.D. Grundy, *Acta Cryst. C* 39 (1983) 3-5.
- [22] S. Hansen, L. Fálth, *Zeolites* 2 (3) (1982) 162-166.
- [23] J.J. Pluth, J.V. Smith, *J. Am. Chem. Soc.* 102 (14) (1980) 4704-4708.
- [24] S. Cartlidge, E.B. Keller, W.M. Meier, *Zeolites* 4 (3) (1984) 226-230.
- [25] H. Ott, *Z. Krystallogr.* 63 (1926) 222-230.
- [26] P. Stegmüller, "Strukturelle Untersuchungen an Verbindungen $\text{Yb}_m\text{Cl}_{2m+1}$ ($m=6,8$) und Chloroaluminaten von Sr und Ba sowie Yb, Sm und Eu," Ph.D. dissertation Thesis, Universität Karlsruhe, 1997.
- [27] M.E. Fleet, *Acta. Cryst C.* 45 (1989) 843-847.
- [28] J.E. Nickels, M.A. Fineman, W.E. Wallace, *J. Phys. Chem.* 53 (1949) 625-628.
- [29] W.T. Barrett, W.E. Wallace, *J. Am. Chem. Soc.* 76 (1954) 366-369.
- [30] A.F. Levin'sh, M.E. Straumanis, K. Karlsons, *Z. Phys. Chem. B.-Chem. E.* 40 (1938) 146-150.
- [31] G.I. Sturua, E.L. Belokoneva, M.A. Simonov, N.V. Belov, *Dokl. Akad. Nauk. SSSR* 242 (1978) 1078-1081.
- [32] R. Withers, C. Lobo, J. Thompson, S. Schmid, R. Stranger, *Acta Cryst. B* 53 (1997) 203-220.
- [33] J.-M. Zhang, J.-D. Ko, R.M. Hazen, C.T. Prewitt, *Am. Mineral.* 78 (1993) 493-499.
- [34] J. Haines, J.M. Leger, C. Chateau, A.S. Pereira, *Phys. Chem. Miner.* 27 (2000) 575-582.
- [35] H. Völlenkne, *Z. Kristallogr.* 154 (1-2) (1981) 77-81.
- [36] F. Liebau, *Acta Cryst.* 14 (1961) 389-395.
- [37] I. Hassan, S.M. Antao, J.B. Parise, *Am. Mineral.* 89 (2004) 359-364.
- [38] G.O. Siqueira, É.G. Gravina, J.A.L.C. Resende, N.G. Fernandes, *Am. Mineral.* 24 (2009)

41-43.

[39] N.C. Nielsen, H. Bildsøe, H.J. Jakobsen, P. Norby, *Zeolites* 11 (6) (1991) 622-632.

[40] J.O. Dickson, J.B. Harsh, M. Flury, W.W. Lukens, E.M. Pierce, *Environ. Sci. Technol.* 48 (21) (2014) 12851-12857.

[41] S. Bachmann, J.C. Buhl, *Micropor. Mesopor. Mater.* 28 (1) (1999) 35-47.

[42] J.M. Newsam, J.D. Jorgensen, *Zeolites* 7 (6) (1987) 569-573.

[43] J.C. Buhl, J. Löns, *J. Solid State Chem.* 112 (2) (1994) 243-250.

[44] V.I. Srdanov, W.T.A. Harrison, T.E. Gier, G.D. Stucky, A. Popitsch, K. Gatterer, D. Markgraber, H.P. Fritzer, *J. Phys. Chem.* 98 (17) (1994) 4673-4676.

[45] S.E. Latturner, J. Sachleben, B.B. Iversen, J. Hanson, G.D. Stucky, *Zeolites* 19 (34) (1999) 7135-7144.

TABLES

Table 1. Composition of spent electrochemical salt simulant where the representative fission products include all components except KCl, LiCl, and NaCl.

Component	Mass Fraction	Concentration (g L⁻¹)	M (moles L⁻¹)
KCl	0.3799	68.43	0.9179
LiCl	0.2985	53.77	1.2683
NaCl	0.1171	21.09	0.3609
NdCl ₃	0.0537	9.66	0.0386
CsCl	0.0395	7.12	0.0423
CeCl ₃	0.0352	6.34	0.0257
LaCl ₃	0.0229	4.13	0.0168
BaCl ₂	0.0202	3.63	0.0174
PrCl ₃	0.0169	3.05	0.0123
SmCl ₃	0.0160	2.88	0.0112
Sum:	1.0000	180.11	2.7116

Table 2. Compositions (in mass%) of glass sintering aids. Properties are listed and include the temperature at which predicted $\eta \sim 100$ Pa·s, the melting temperature (T_M), and the bulk density (ρ_b) measured with a He pycnometer. Some of the data was not available for TePbO or NaAlP for comparison.

Components	NBS-1	SA-700	SA-750	SA-800	SA-850	NaAlP	TePbO
SiO ₂	60.00	28.57	40.83	42.5	48.31	-	-
Na ₂ O	15.00	38.32	37.49	32.88	34.89	24.57	-
B ₂ O ₃	10.00	33.11	21.68	24.62	16.80	1.38	-
Li ₂ O	5.00	-	-	-	-	-	-
Al ₂ O ₃	5.00	-	-	-	-	19.20	-
ZrO ₂	5.00	-	-	-	-	-	-
P ₂ O ₅	-	-	-	-	-	54.85	-
TeO ₂	-	-	-	-	-	-	78.00
PbO	-	-	-	-	-	-	22.00
T where $\eta = 100$ Pa·s	963	700	751	805	850	^(b)	<600 ^(a)
T_M , °C	1250 ^(a)	850	900	950	1000	742 ^(c)	650 ^(a)
ρ_b , $\times 10^3$ kg m ⁻³	2.561	2.527	2.542	2.551	2.544	2.490	6.169

^(a)These values are estimated

^(b)These values are unknown

^(c)This is the measured liquidus temperature (T_L)

Table 3. Phase distribution of as-made S5C sodalite samples as determined with XRD whole pattern fitting where ρ_b is the calculated bulk density of the crystalline phase.* Note that the amorphous fraction was not determined.

Crystalline phase	ICSD[†] [Ref.]	ρ_b ($\times 10^3 \text{ kg m}^{-3}$)	NBS1	SA700	SA750	SA800	SA850	TePbO	NaAIP
$\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$	41188 [20]	2.30	93.2%	96.3%	97.8%	98.2%	87.9%	-	96.3%
$\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	36050 [21]	2.29	-	-	-	-	-	82.2%	-
$\text{Na}_3(\text{AlSiO}_4)_3(\text{H}_2\text{O})_{1.8}$	201460 [22]	2.36	4.9%		0.6%	0.0%	2.4%	3.8%	1.6%
$\text{Na}_{0.96}\text{AlSiO}_4$	34100 [23]	1.52	-	-	-	-	-	11.3%	-
$\text{K}_9\text{Al}_{9.7}\text{Si}_{26.3}\text{O}_{72}$	201596 [24]	1.86	-	-	-	-	7.5%	-	-
KCl	18014 [25]	1.99	1.9%	2.2%	1.6%	1.8%	2.2%	2.7%	2.1%
$\text{Ba}(\text{AlCl}_4)_2$	56735 [26]	2.35	-	1.5%	-	-	-	-	-
SUM	-	-	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

*Note that some of these phases might not be chemistry matches but are structure matches and thus these values might not be exact but estimates

[†]ICSD is the Inorganic Crystal Structure Database reference number from FindIt (v2014-2).

Table 4. Measured porosity (ϕ_p), calculated ρ_t based on phase distribution, and % of theoretical density (% of ρ_t) for several specimens. The error associated with ϕ_p is associated with that of the analytical balance (<1%). The error associated with ρ_t and % of ρ_t are higher because the mass fraction was not determined and the density of the amorphous phase could not be determined. Additionally, the ρ_i values used for each phase to calculate ρ_t using Equation (4) were estimated based on data in the ICSD. *The heat-treatment temperatures resulting in the maximum % of ρ_t are shown in bold type.

Binder	Firing temperature (°C)	ϕ_p	ρ_t	% of ρ_t
NBS-1	550	56%	2.32	46%
	600	55%	2.32	47%
	650	51%	2.32	52%
	700	39%	2.33	65%
	800	26%	2.38	76%
	950	15%	2.43	87%
SA-700	550	49%	2.32	54%
	600	34%	2.31	68%
	650	13%	2.35	90%
	750	11%	2.37	92%
	850	14%	2.37	90%
SA-750	550	51%	2.31	50%
	600	45%	2.32	57%
	650	35%	2.34	67%
	700	28%	2.34	74%
	750	18%	2.38	85%
	800	20%	2.36	84%
	850	16%	2.37	87%
SA-800	550	56%	2.32	46%
	600	48%	2.32	55%
	650	27%	2.33	75%
	700	15%	2.35	87%
	750	12%	2.36	91%
	800	15%	2.36	89%
	850	18%	2.39	85%
SA-850	550	56%	2.32	46%
	600	44%	2.32	58%
	650	24%	2.34	78%
	700	19%	2.33	83%
	800	18%	2.36	86%
	850	23%	2.41	79%
TePbO	550	59%	2.33	44%
	600	58%	2.32	45%
	750	52%	2.27	54%
	850	51%	2.33	56%
NaAlP	550	55%	2.29	46%
	600	55%	2.30	47%
	650	58%	2.29	44%
	750	48%	2.30	55%
	850	50%	2.48	50%
	950	54%	2.54	50%

FIGURES

Figure 1. Phase distribution for the various S5C formulations with the different sintering aids fired at different temperatures. The legend presented in the lower right is valid for all.

Figure 2. XRD on Ge-sodalite (S5D) samples both (a) as-made and (b) after firing at 750 °C for 8 hr. The “salt phases” include NaCl, KCl, and LiCl and the “Other phases” include a variety of different phases discussed in the text.

Figure 3. SEM micrographs of as-made sodalite samples S4 (from a previous study [3, 14]) and S5C (both without glass binders) as well as an EDS dot map on S5C showing elemental distribution and a clear distinction between the sodalite and nepheline phases by the chloride distribution.

Figure 4. (a) Summary of pellet density as a function of firing temperature for S5C series specimens with 5 mass% sintering aid. (b) Column chart comparing the mass% of sodalite in each specimen with the % of ρ_t for all S5C specimens fired at 750 °C (note that in some cases, data at 750 °C was obtained by taking an average between data at 700 and 800 °C).

Figure 5. Comparison of sodalite and % of ρ_t for the S5A [3, 14], S6 [3, 14], and S5C specimens at different firing temperatures. The S5A specimens are shown with and without the NBS-1 sintering aid (1–7 mass%) at different temperatures. Each sample is denoted with a different symbol and the firing temperature is denoted by the color as defined in the legend. The dotted blue line outlines the maximum density/sodalite attained for $\text{Si}(\text{OC}_2\text{H}_5)_4$ -based pellets in this study.