Solution-derived sodalite made with Si- and Ge-ethoxide precursors for immobilizing electrorefiner salt

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

Pacific Northwest National Laboratory, Richland, WA 99352, USA

ABSTRACT

Chlorosodalite has the general form of $Na_8(AlSiO_4)_6Cl_2$ 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 $Si(OC_2H_5)_4$ or $Ge(OC_2H_5)_4$. Additionally, seven different glass sintering aids (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 treatments.

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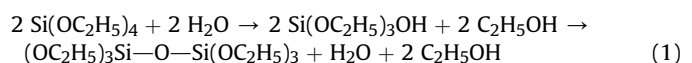
1. Introduction

The future of nuclear power production in the U.S. is uncertain, but, in order to maximize 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 $Na_8(AlSiO_4)_6Cl_2$. 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 (~500 °C), mix in ~25 mass% of a glass sintering aid, and then fire the mixture at ~900—950 °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., $Si(OC_2H_5)_4$ (also called tetraethyl orthosilicate or TEOS) and $Ge(OC_2H_5)_4$, which are also referred to as silicon ethoxide and germanium ethoxide, respectively. The $Ge(OC_2H_5)_4$ precursor was selected as a potential option to reduce the consolidation temperature of the product considering that GeO_2 melts at a much lower temperature (1116 °C [7]) than SiO_2 (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]. An example of how this process works for $Si(OC_2H_5)_4$ is shown in Equation (1).

$$2\ Si(OC_2H_5)_4 + 2\ H_2O \rightarrow 2\ Si(OC_2H_5)_3OH + 2\ C_2H_5OH \rightarrow$$
$$(OC_2H_5)_3Si\!-\!O\!-\!Si(OC_2H_5)_3 + H_2O + 2\ C_2H_5OH \tag{1}$$

While solution-derived minerals, including sodalite [39—44], are often found in the literature, it is not as common to see

* Corresponding author.
  E-mail address: brian.riley@pnnl.gov (B.J. Riley).

solution-based processes using alkoxides precursors. Latturner et al. [45] performed hydrothermal synthesis of sodalite using aluminum isopropoxide, TEOS, NaOH, and $AgNO_3$ or $TlNO_3$ but this account is rare in the literature. The work presented here shows a simplified low-temperature route for making sodalite precursors using $Si(OC_2H_5)_4$ or $Ge(OC_2H_5)_4$, a mixed chloride salt waste, and $NaAlO_2$ 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 $Na_8(AlSiO_4)_6Cl_2$. 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 to help drive the exchange of Na in the sodalite for Li and K into the glass phase. Also, the molar 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 $Si(OC_2H_5)_4$-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 $Si(OC_2H_5)_4$ (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 $Ge(OC_2H_5)_4$-based sample (called S5D), a ¼-scale batch was made. Here, 7.5 mL of salt solution was added to a 100 mL beaker. Then, 13.2 mL of $Ge(OC_2H_5)_4$ (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.

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**

2.2. Sintering aid 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 glasses evaluated was $\pm0.003 \times 10^3$ 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 $\eta \sim 100$ Pa 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-### glasses, 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 h, 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 and NaAlP glasses were provided by collaborators as powders and not made new for this study. The NBS-1 glass developed by Vienna et al. [6] was 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 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 of sodalite batches, ~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 °C min^{-1} up to the maximum firing temperature between 550 and 950 °C, held for 8 h, and then furnace-cooled at ~10 °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