Powder XRD, SEM, and Multinuclear MAS-NMR Investigations of the Interactions Between Glass and Crystalline Phases of Li, Na, or K Ceramic Waste Forms

Marsha J. Lambregts† and Steven M. Frank
Argonne National Lab West, Idaho Falls, Idaho 83403

Interactions between the glass and crystalline phases of ceramic waste forms were investigated via powder X-ray diffraction, scanning electron microscopy, and 

27Al, 23Na, 7Li, and 35Cl magic angle spinning nuclear magnetic resonance spectroscopy. LiCl, NaCl, or KCl waste form samples were made with or without glass. The waste forms containing glass consist of sodalite and glass phases with minor amounts of nepheline. Samples without glass form varying amounts of sodalite and nepheline. The glass frit, intended to bind the zeolite particles together, changes in composition, showing marked increases in aluminum and alkali content.

1. Introduction

AR GONNE National Laboratory, as part of the Spent Fuel Demonstration Project for the Department of Energy, has developed a glass-bonded sodalite ceramic waste form. This material immobilizes the fission product and transuranic actinide-containing salt from the electrometallurgical treatment of spent sodium-bonded nuclear fuel into a stable product suitable for a geological repository.1 Two of the standards for acceptance into a geological repository are that the concentration of lithium and sodium that leaches from the waste form during product consistency tests be less than that of the benchmark glass and that the chemical composition and crystalline phases be identified for elements which comprise more than 0.5 wt% of the waste form.2 Although these waste forms are not glasses, be identified for elements which comprise more than 0.5 wt% of glass and that the chemical composition and crystalline phases necessary into a geological repository are that the concentration of

This paper explored the alkali metal behavior within the waste form by describing the disposition of these cations among the three phases. These interactions have been studied via X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and solid-state nuclear magnetic resonance (NMR) spectrometry. XRD was utilized to identify crystalline phases and crystal unit cell parameters. This information was then correlated to empirical formulae. SEM was used to identify the bulk phase distribution and phase-specific elemental analysis. NMR chlorides, and sodium chloride. These surrogate waste forms were used to study the interaction between the glass and crystalline phases.

The three phases present in these samples are sodalite, nepheline, and glass. Sodalite, one of the few aluminosilicates that contains chloride within its matrix, is a cubic zeolite consisting of alternating rings of SiO₄ and AlO₄ tetrahedra joined at the corners to form four- and six-unit rings. These rings make up β-cages similar to those found in zeolite A (LTA),3 among others. For the sodium chloride form of sodalite (NaCl-SOD), a chlorine atom lies in the center of each cage tetrahedrally coordinated to four sodium atoms. The sodium atoms are further coordinated to three of the oxygen atoms of the six-unit rings. The empirical formula is M₈Al₆Si₆O₂₄X₂ (MX-SOD), where M is a +1 valence metal and X represents a halide. The halide in our samples is chloride.

Sodalite forms when the salt-occluded zeolite (SOZ), LTA (Na₄Al₆Si₆O₂₄X₂), is heated in an inert atmosphere. The reaction follows the following stoichiometry:

\[
Na_{12}Al_{12}Si_{12}O_{48} + 4 NaCl \rightarrow 2 Na_{8}Al_{6}Si_{6}O_{24}Cl_2
\]

This process calls for a deficiency of salt to be used to assure complete salt occlusion. The experiments studied here also follow this format, using the same molar ratio of salt to zeolite. (This ratio comes from the ceramic waste form process. The process uses a 10 wt% deficit of salt:zeolite to minimize free salt levels in the final product.) A secondary phase, nepheline, forms in the samples made without glass. Sodalite and nepheline are related to one another through the reversible reaction4–6

\[
Na_{10}Al_{6}Si_{6}O_{24}Cl_2 \rightarrow 6 NaAlSiO₄ + 2 NaCl
\]

Ohgushi et al.7 also show that LTA forms nepheline upon heating. Thus, it is not surprising that nepheline is an alternative phase in these materials.

Nepheline has the empirical formula, MAISiO₄, but its “ideal” formula is KN₃Al₃Si₃O₁₂.8 It also consists of alternating SiO₄ and AlO₄ tetrahedra. These are joined at the corners to form distorted six-unit rings. Its overall structure is a distorted hexagonal (P₆₃), stuffed derivative of the high-tridymite framework. Layers of six-unit hexagonal and oval rings form channels that run parallel to the c-axis. The charge-balancing cations are located in two distinct sites within the channels. A large cation site generally accommodates potassium, while a smaller site holds the sodium cations.

This paper explored the alkali metal behavior within the waste form by describing the disposition of these cations among the three phases. These interactions have been studied via X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and solid-state nuclear magnetic resonance (NMR) spectrometry. XRD was utilized to identify crystalline phases and crystal unit cell parameters. This information was then correlated to empirical formulae. SEM was used to identify the bulk phase distribution and phase-specific elemental analysis. NMR
was applied to explore the shorter range structural information on a by-element basis.

II. Experimental Procedure

Reagent-grade lithium chloride, sodium chloride, and potassium chloride were used. Dry sodium LTA (UOP) was obtained as a size fraction from 45 to 250 μm. Moisture content was found via Karl Fischer analysis to be less than 0.5%. Appropriate amounts of the salts and dry zeolite were transferred to a small v-mixer and heated to 550°C under argon while mixing to achieve salt occlusion. The extent of salt occlusion was checked by washing a sample of the SOZ with water, filtering it, and measuring the chloride level in the filtrate with an ion-selective electrode. The chloride level in the wash water was found to be less than 0.1% of the sample by weight. Samples were mixed with borosilicate glass frit (Bayer: 66.5% SiO₂, 19.1% B₂O₃, 6.8% Al₂O₃, 7.1% Na₂O, 0.5% K₂O, Pemco Corp., Baltimore, MD) at 3:1 SOZ to glass ratio by weight. Approximately 35 g of the mixture was transferred to graphite crucibles and heated to 915°C for 4 h and cooled. All process steps were performed under an argon atmosphere.

X-ray scans were made over a 10°–60° 20 range at 0.1°/min with a powder X-ray diffractometer (Scintag, Cupertino, CA) utilizing CuKα radiation. Unit cell dimensions were determined by peak fitting the data, indexing the peaks to reference sodalite and nepheline patterns, and then using Scintag’s lattice parameter calculation program.

Chemical analysis was performed by dissolving approximately one-tenth gram samples in a mixture of reagent-grade hydrofluoric, hydrochloric, and nitric acids. Solutions were stabilized with 2% boric acid/EDTA solutions to eliminate any residual hydrofluoric acid and analyzed via inductively coupled plasma atomic emission spectrophotometry (ICP-AES).

29Si, 31Al, 7Li, 35Cl, and 23Na nuclei were studied using Avance NMR spectrometers (Bruker, Germany) at 7.04 and 11.7 T field strengths and NMR spectrometers (Chemagnetics/Varian, Palo Alto, CA) at 7.04 and 9.1 T. Chemical shifts of 29Si spectra are given in parts per million (ppm) from tetramethylsilane (TMS). 27Al chemical shifts are in ppm from aqueous field strengths and NMR spectrometers (Bruker, Germany) at 7.04 and 11.7 T. No cross-polarization or proton decoupling was used. Pulse delays of 60–6–8 kHz and 15–17 kHz on the 11.7 T instrument. No cross-polarization or proton decoupling was used. Pulse delays.

The chloride level in the wash water was found to be less than 0.1% of the sample by weight. Samples were mixed with borosilicate glass frit (Bayer: 66.5% SiO₂, 19.1% B₂O₃, 6.8% Al₂O₃, 7.1% Na₂O, 0.5% K₂O, Pemco Corp., Baltimore, MD) at 3:1 SOZ to glass ratio by weight. Approximately 35 g of the mixture was transferred to graphite crucibles and heated to 915°C for 4 h and cooled. All process steps were performed under an argon atmosphere.

X-ray scans were made over a 10°–60° 20 range at 0.1°/min with a powder X-ray diffractometer (Scintag, Cupertino, CA) utilizing CuKα radiation. Unit cell dimensions were determined by peak fitting the data, indexing the peaks to reference sodalite and nepheline patterns, and then using Scintag’s lattice parameter calculation program.

Chemical analysis was performed by dissolving approximately one-tenth gram samples in a mixture of reagent-grade hydrofluoric, hydrochloric, and nitric acids. Solutions were stabilized with 2% boric acid/EDTA solutions to eliminate any residual hydrofluoric acid and analyzed via inductively coupled plasma atomic emission spectrophotometry (ICP-AES).

29Si, 31Al, 7Li, 35Cl, and 23Na nuclei were studied using Avance NMR spectrometers (Bruker, Germany) at 7.04 and 11.7 T field strengths and NMR spectrometers (Chemagnetics/Varian, Palo Alto, CA) at 7.04 and 9.1 T. Chemical shifts of 29Si spectra are given in parts per million (ppm) from tetramethylsilane (TMS). 27Al chemical shifts are in ppm from aqueous field strengths and NMR spectrometers (Bruker, Germany) at 7.04 and 11.7 T. No cross-polarization or proton decoupling was used. Pulse delays of 60–6–8 kHz and 15–17 kHz on the 11.7 T instrument. No cross-polarization or proton decoupling was used. Pulse delays.

The second use of the XRD data was to index the patterns and calculate lattice parameters. In Table I, the lattice parameters calculated from the refinement of the XRD patterns for both phases as well as representative reference examples for comparison are shown.

The lattice parameters for the sodalite phase of the Na-CWF samples, both with and without glass, are very close to the reference sodalite (Na₈Al₆Si₂O₁₆Cl₂) shown in Table I. The sodalite and nepheline phases of the K-ng and Li-ng samples reflect the accommodation of the crystal lattice for the differently sized Li⁺ and K⁺ cations.

In a previous paper,10 we explored the application of Vegard’s law to the calculation of the cation content of Li/Na and K/Na mixed cation sodalites such as these. Vegard’s initial

III. Results and Discussion

The elemental composition of the processed material was determined by the combination of XRD via interpretation of the unit cell lattice parameters, SEM/EDS analysis, and elemental analysis via ICP-AES. NMR was then used to characterize the short-range order present in the phases.

(1) XRD

XRD was first used for identification of the crystalline phases. Figures 1 and 2 show the XRD patterns for the samples. In both the glass-bonded and “no-glass” samples, the major phases were sodalite and nepheline. In the glass-bonded samples, sodalite was the major phase. Nepheline was a very minor phase, particularly in the sodium chloride sample. In the samples with no added glass, the behavior was more complex. Sodalite was the major phase in the lithium chloride and sodium chloride samples as it was in the glass-bonded versions, but in these samples the nepheline phase was more pronounced. In the potassium chloride sample without glass, nepheline and sodalite are both major phases. No salt phases were detected in any of the samples.

The second use of the XRD data was to index the patterns and calculate lattice parameters. In Table I, the lattice parameters calculated from the refinement of the XRD patterns for both phases as well as representative reference examples for comparison are shown.

The lattice parameters for the sodalite phase of the Na-CWF samples, both with and without glass, are very close to the reference sodalite (Na₈Al₆Si₂O₁₆Cl₂) shown in Table I. The sodalite and nepheline phases of the K-ng and Li-ng samples reflect the accommodation of the crystal lattice for the differently sized Li⁺ and K⁺ cations.

In a previous paper,10 we explored the application of Vegard’s law to the calculation of the cation content of Li/Na and K/Na mixed cation sodalites such as these. Vegard’s initial
mulations for the four samples are shown. In Table II, the calculated parameter for the mixed sodalite. By utilizing these equations, it was possible to calculate an approximate formulation for the empirical formula of Na$_{0.80}$K$_{0.20}$AlSiO$_4$. This was close to KCl-ng sample had a potassium content of 0.20 mol% that gave found in his paper, we estimated that the nepheline phase of the tion presented in Hovis the “ideal” form of nepheline discussed above and to a formula-

For K/Na and Li/Na sodalites, an equation relating the lattice parameter to the molar fraction of the Li or K substituted into the base Na sodalite was established:

\[ K/Na : y = 0.0505x + 0.88686 \]

\[ Li/Na : y = -0.0541x + 0.88857 \]

where \( x \) was the molar fraction of K or Li and \( y \) was the lattice parameter for the mixed sodalite. By utilizing these equations, it was possible to calculate an approximate formulation for the sodalite phases in the samples. In Table II, the calculated formulations for the four samples are shown.

Hovis et al.\textsuperscript{12} used similar calculations for nephelines containing varying amounts of potassium. Using the calculations found in his paper, we estimated that the nepheline phase of the KCl-ng sample had a potassium content of 0.20 mol% that gave an empirical formula of Na$_{0.80}$K$_{0.20}$AlSiO$_4$. This was close to the “ideal” form of nepheline discussed above and to a formulation presented in Hovis et al.’s\textsuperscript{12} paper: Na$_{0.70}$K$_{0.30}$AlSiO$_4$ (\( a = 0.99993 \text{ nm}, c = 0.83849 \text{ nm} \)). The nepheline phase unit cell parameters calculated for LiCl-ng and NaCl-ng were essentially the same as that of sodium nepheline, Na$_2$AlSiO$_4$.

(2) SEM

SEM micrographs are shown in Fig. 3 for the samples containing glass, and EDS analysis provided some elemental information. The more mottled areas are the sodalite phase and the more smooth areas are the glass phase. X-ray mapping of chlorine content spots in the Li-PC sample led to the identification of small crystallites of sodium chloride. These were not seen in the other samples. The EDS composition of sodalite was not used because of high variability in the compositions obtained across the sample.

The SEM–EDS information was combined with elemental analysis and the sodalite compositional information obtained from the XRD-calculated lattice parameters shown in Table III. Also shown in this table is compositional analysis of glass and zeolite starting materials. The glass composition shown is normalized without boron for comparison with the EDS data that cannot detect boron. The lithium content of the glass also had to be estimated because it is undetectable via SEM/EDS. The estimate was based upon calculating the amount of aluminum dissolved in the glass versus initial concentration in the glass frit, the amount of lithium determined to be in the sodalite phase, and the total lithium content of the sample.

Using the elemental analysis in Table III, an estimation of the amount of zeolite dissolved in the glass was obtained. This was done by calculating the Al/(Al+Si) ratio for the final glass phase, the sodalite phase, the starting SOZ, and the starting glass phase. Based on the as-batched ratios, 25 wt% of the starting material was glass and 75% was SOZ. Then, the following calculation was carried out:

\[ 25\% (\text{Al}/(\text{Al} + \text{Si}))_{\text{glass}} + 75\% (\text{Al}/(\text{Al} + \text{Si}))_{\text{SOZ}} = (75\% - x) (\text{Al}/(\text{Al} + \text{Si}))_{\text{sodalite phase}} + (25\% + x) (\text{Al}/(\text{Al} + \text{Si}))_{\text{glass phase}} \]

The equation was solved for \( x \), the amount of sodalite phase dissolved in the glass phase. This yielded 14.7%, 12.8%, and 13.5% for the lithium chloride, sodium chloride, and potassium chloride samples, respectively. The glass phase had the M$_4$O$_2$:Al$_2$O$_3$:SiO$_2$ composition: 0.23:0.23:1 for Li-PC, 0.12:0.15:1 for Na-PC, and 0.18:0.12:1 for K-PC.

(3) NMR

NMR chemical shifts are directly related to the shielding of the nucleus by the electronic structure of its immediate environment. Thus, they will be influenced by the identity and position of nearby atoms. $^2$Si has a spin of \( I = 1/2 \) and is the only non-quadrupolar nucleus in the samples. Its spherical charge distribution makes spectral interpretation relatively simple in that the chemical shifts are isotropic. Figure 4 shows the $^2$Si solid-state NMR spectra for all the samples. Two peaks are seen in each spectrum. In all the samples, the peak at approximately –85 ppm with respect to TMS is because of both NaCl-SOD and nepheline, both of which exhibit a peak near this chemical shift: \(~ –85,13–17 \text{ ppm} \) for sodalite, \(~ –83.5 \text{ ppm} \) for sodium nepheline, and \(~ –84.5 \text{ ppm} \) for a nepheline containing potassium (Na$_{0.70}$K$_{0.30}$AlSiO$_4$).\textsuperscript{12} Nepheline and sodalite are 1:1 Al:Si ratio compounds in which the silicon atoms are tetrahedrally coordinated through oxygens to four aluminum atoms. A notation has been developed for discussing the various silicate structures, wherein \( Q \) denotes a silicon bonded to four oxygen atoms.\textsuperscript{8,18} Superscripts, 0 to 4, designate the number of \( Q \) units attached to the primary silicon. Bonding to 0 to 4 AlO$_4$ groups is designated as \( Q^0(\text{Al}) \), although most of the time when aluminosilicates are discussed, the superscript is acknowledged as 4 and left out. Thus, both sodalite and nepheline exhibit $^2$Si NMR peaks in the \(~ –92 \text{ to } –92 \text{ ppm} \) range characteristic of the Q$^0$(Al)-type silicons (see Table IV).\textsuperscript{19}

Several of these papers give correlation formulae for relating the $^2$Si Al bond angle to chemical shift.\textsuperscript{13–17,20} As the most accurate correlation would be one for only chloride sodalites containing Li, Na, and K, we chose to calculate a correlation based on the data presented in Weller and Wong’s\textsuperscript{21} paper for chloride sodalites. This yields the formula

\[ \delta(\text{Si}) = -0.64350 + 3.544 \text{ (ppm)} \]
The calculated bond angles for the sodalite phase in the CWF’s are presented in Table V.

The mean bond angle given in the literature is 138° for NaCl-SOD, but the range for LiCl-SOD to KCl-SOD is 125.7°–156.5°. Changes in bond angle track the amount of expansion or contraction that the cages within sodalite experience because of the changing alkali cation content. This expansion or contraction has also been correlated to chemical shift for sodalites through the unit cell lattice parameter, $a$:

$$\delta(Si) = -22.59a + 115.71 \text{ (ppm)}$$

This yields 0.8818(5)±0.0041 nm for the Li-ng sample to 0.8893(8)±0.0041 nm for the K-ng sample. This can then be compared with the values as calculated from the XRD data presented in Table I of 0.878(2) and 0.891(5) nm for the same samples, respectively. These measurements are essentially the same within the associated error.

Sodium nepheline, NaAlSiO$_4$, also exhibited two peaks at approximately 83.5 and 89 ppm. The two peaks of nepheline were assigned by Hovis et al. to the two crystallographically unique sites in the nepheline structure. They were described as in a ratio of 3:1, with the “general site” having two Na neighbors and one K neighbor and a “special site” with three Na neighbors. “Ideal” nepheline, Na$_3$KAl$_4$Si$_4$O$_{12}$, has two peaks at approximately −85 and −88 ppm. Hovis et al.’s paper showed the shifting of the $^29$Si NMR peaks of nepheline with changes in potassium content. This behavior is clearly present in the samples without glass. If the peak at −88 to −89 ppm were present in the samples with glass, it would be very low in intensity and was probably masked by the glass peak.

The glass peak is a very broad peak whose maximum shifts from −97.7 ppm for KCl-gb to −95.3 ppm for NaCl-gb to −93.3 ppm for LiCl-gb. This shift reflects the changes in silicon environments in the glass in both the connectivity—governed by the alkali content and the next nearest neighbors—governed by the aluminum content. With an aluminum content of approximately 20%–25%, most of the silicon tetrahedra will be close to only 1 Al, with a small fraction experiencing no aluminum neighbors. The Q$_4$(1Al) range is about −97 to −107 ppm. The alkali oxides modify the glass by decreasing the polymerization. This leads to silicon atoms in the Q$^2$ configuration. These silicon nuclei have chemical shifts in the range −90 to −100 ppm overlapping that of the Q$_4$(1Al) region. Thus, dispersion in the chemical shifts for the silicon nuclei in the glass because of both effects leads to the rather broad Gaussian peak seen in the spectra for samples with glass.

Table III. Elemental Composition of the Phases in Weight Percent

<table>
<thead>
<tr>
<th>Li-PC sodalite phase (±0.1%)</th>
<th>Na-PC sodalite phase (±0.1%)</th>
<th>K-PC sodalite phase (±0.1%)</th>
<th>Glass/Zeolite $^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si 18.2</td>
<td>17.3</td>
<td>17.7</td>
<td>23.25 18.7</td>
</tr>
<tr>
<td>Al 17.0</td>
<td>16.7</td>
<td>16.5</td>
<td>2.40 18.8</td>
</tr>
<tr>
<td>Na 16.4</td>
<td>19.0</td>
<td>17.9</td>
<td>6.22 14.9</td>
</tr>
<tr>
<td>K 1.44</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li 0.85</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Li-PC glass phase $^g$ (±3%) Na-PC glass phase $^g$ (±3%) K-PC glass phase $^g$ (±3%)

| Si 28.1                     | 31.1                        | 28.9                        |
| Al 12.5                    | 8.95                        | 6.38                        |
| Na 6.97                    | 6.13                        | 2.74                        |
| K 9.48                     |                             |                             |
| Li (1.13) $^g$             |                             |                             |

Li-ng $^h$ (±5%) Na-ng $^h$ (±5%) K-ng $^h$ (±5%)

| Si 19.9                     | 18.4                        | 18.4                        |
| Al 17.0                    | 15.8                        | 16.7                        |
| Na 14.4                    | 16.6                        | 12.5                        |
| K 5.41                     |                             |                             |
| Li 1.14                    |                             |                             |

$^i$X-ray diffraction (XRD) analysis. $^g$Elemental analysis. $^h$Scanning electron microscopy (SEM) analysis. $^i$Estimation, see text. PC, pressureless consolidation of the material; ng, no glass.
Figure 5 shows the $^{27}$Al solid-state NMR spectra for nuclei at 11.7 T are 60.1 and 63.1 in nepheline and 64.2 in sodalite. Literature values for the peak positions of aluminum resonances at 11.7 T are not far from the isotropic values and isotropic values. For the sodalites found in this study, $^{27}$Al symmetry is present in these samples, narrow peaks appear at more than 1 ppm different from the measured value at 11.7 T. As mentioned above, the isotropic chemical shift was not calculated in these samples and the peak positions with respect to aqueous Al$^{3+}$ findings were used.

Table V. $^{29}$Si Chemical Shifts (ppm) and Calculated Bond Angles

<table>
<thead>
<tr>
<th>CWF's</th>
<th>$\delta$ (Si)</th>
<th>$\theta$ (Si-O-Al) (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl-PC</td>
<td>-85.9</td>
<td>139.0</td>
</tr>
<tr>
<td>NaCl-PC</td>
<td>-85.1</td>
<td>137.8</td>
</tr>
<tr>
<td>LiCl-PC</td>
<td>-84.8</td>
<td>137.3</td>
</tr>
<tr>
<td>KCl-ng</td>
<td>-86.2</td>
<td>139.5</td>
</tr>
<tr>
<td>NaCl-ng</td>
<td>-85.5</td>
<td>138.3</td>
</tr>
<tr>
<td>LiCl-ng</td>
<td>-84.5</td>
<td>136.8</td>
</tr>
</tbody>
</table>

Table VI. $^{27}$Al Isotropic Chemical Shifts (ppm)

<table>
<thead>
<tr>
<th></th>
<th>$^{27}$Al (iso) C.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-PC</td>
<td>64.1</td>
</tr>
<tr>
<td>Na-PC</td>
<td>64.5</td>
</tr>
<tr>
<td>Li-PC</td>
<td>65.2</td>
</tr>
<tr>
<td>K-ng</td>
<td>64.7, 60.3</td>
</tr>
<tr>
<td>Na-ng</td>
<td>64.8, 59.6</td>
</tr>
<tr>
<td>Li-ng</td>
<td>66.6, 59.6</td>
</tr>
</tbody>
</table>

$^{27}$Al, $^{23}$Na, $^7$Li, and $^{35}$Cl are all quadrupolar nuclei. With the exception of $^{27}$Al, which is $I = 5/2$, all are $I = 3/2$ nuclei. The high natural abundance of all the nuclei (75% or greater) and fast relaxation times make these nuclei favorable to NMR spectroscopy; but the spectra of quadrupolar nuclei are complex if some site symmetry is not present. Nuclei with nuclear spins greater than 1/2 have a nuclear quadrupole moment that interacts with the electric field gradients within the samples causing line-broadening, distortion of the peaks, and displacement of the resonance from the isotropic (or true) chemical shift. The compounds under study exhibit some of these effects to a lesser or greater extent. Far from being simply a complication, these changes in peak shape can reveal relative information on site symmetry.

Tetrahedrally coordinated aluminum nuclei in aluminosilicate materials containing only Al–O–Si linkages typically exhibit chemical shifts in the range 50–70 ppm. If ideal tetrahedral symmetry is present in these samples, narrow peaks appear at isotropic values. For the sodalites found in this study, $^{27}$Al resonances at 11.7 T are not far from the isotropic values and fairly narrow. Literature values for the peak positions of aluminum nuclei at 11.7 T are 60.1 and 63.1 in nepheline and 64.2 in sodalite.

Figure 5 shows the $^{27}$Al solid-state NMR spectra for the samples and the peak positions with respect to aqueous Al$^{3+}$ found at a field strength of 11.7 T and are listed in Table IV. The samples show that, in a manner similar to the $^{29}$Si data, the peaks at 64.2 and 63.1 for sodalite and nepheline overlap. The second peak in the nepheline system is seen at approximately 58–60 ppm in our samples. As seen in the work of Hovis et al., for nepheline and Engelhardt et al. on sodalite, the charge-balancing guest ions in the cages of these structures affect the Al–O–Si bond angles and thus the peak positions of the aluminum nuclei. In our samples, this is seen in the shift of the peak maxima over a 63.9–66.0 ppm range for the various compositions.

The measurement of the $^{27}$Al solid-state NMR spectra for each sample at three different field strengths allowed the calculation of the isotropic chemical shifts, shown in Table VI. Note, that as mentioned above, the isotropic chemical shift was not more than 1 ppm different from the measured value at 11.7 T.

Although we know that a substantial amount of the aluninum dissolves in the glass, it only shows up in the $^{27}$Al NMR spectra as an underlying low broad peak at approximately the same maximum as the sodalite. As all the aluminum nuclei are also tetrahedrally coordinated, and contain only Al–O–Si linkages, this is understandable. This does not contribute to the full-width at half-height (FWHH) as the samples containing glass have smaller widths than those that do not contain glass. The increase in cations other than sodium in the cages increases the width of the peaks as both samples containing lithium and potassium exhibit this effect. The disorder this creates causes an increase in the dispersion of chemical shifts.

The $^{25}$Na solid-state NMR spectra are shown in Fig. 6, and the peak positions are given in Table IV. There are at least two effects being shown. Consider the $^{23}$Na spectrum taken at a field strength of 11.7 T of Na–PC as the baseline. It shows that a narrow peak occurs at $-2.76$ ppm with respect to solid NaCl with an FWHH of 161 Hz. This peak arises from the sodium cations within the sodalite cages that surround the chlorine anion. (Jelinek et al. observed an isotropic peak at $-0.9$ ppm for NaCl–SOD.) They are in a relatively symmetric tetrahedral environment—hence the narrow symmetric peak. When potassium is introduced into this system, a slight increase in the width of the peak to 275 Hz is noted and it becomes slightly asymmetric. As indicated by the formula calculated from the XRD data of...
K0.36Na7.64Al6Si6O24Cl2 for the K–PC sample, there would be relatively few sodalite cages containing potassium, therefore the alteration would be minor. The low broad peak seen at approximately −20 ppm is because of sodium nuclei in the nepheline phase and/or glass phase. (Stebbins et al.24 observed a single asymmetric peak at −17.6 ppm for Na0.75K0.25AlSiO4, and a synthetic sodium sodalite showed two peaks in the same range.) When lithium is introduced, the peak is far broader and clearly asymmetric. There are more lithium nuclei in the sodalite phase with a formula of Li1.17Na6.83Al6Si6O24Cl2, therefore more cages are affected. This peak is probably because of overlapping peaks from sodalite cages without lithium and broader peaks because of cages containing one lithium cation. Jelinek et al.23 observed a similar effect upon the exchange of silver into sodium sodalite. The broad peak in the Li–PC23Na spectrum is believed to be the sodium in the glass phase, as very little nepheline is seen in the XRD pattern.23Na peaks for glass also occur in this region.25,26

Starting again with the Na–ng sample, we noted that the peak is broader, indicating more disorder within the sodalite. Small peaks because of nepheline are seen at −20 ppm and −30 ppm. The K–ng samples showed an obvious increase in the nepheline phase. It was clear that a large amount of the sodium present in this sample was in the nepheline phase. The symmetry of the sodium nuclei in the sodalite cages of the Li–ng sample changed again with the additional amount of lithium present. From the formula for the sodalite phase, Li1.92Na6.08Al6Si6O24Cl2, it was recognized that nearly every cage in the sodalite phase contains at least one lithium cation.

7Li spectra are shown in Fig. 7. In the sample without glass, two peaks are present. We assigned the larger peak to lithium in the sodalite and the smaller one to lithium in the nepheline phase. The single broader peak present in the Li–PC sample was indicative of the overlap of lithium in the glass phase with that of lithium in the sodalite phase.25,26

35Cl solid-state NMR spectra were obtained at all three field strengths, in all cases within measurement error; there was no change in the peak positions of any of the peaks with field strength, indicating that this value is the isotropic chemical shift. Spectra are shown in Fig. 8. Peaks at −73.5 to −78.2 ppm were assigned to chlorine nuclei inside the sodalite cages. Variance in the peak position is related to the amount of non-sodium content within the cages. Jelinek et al.27 found a peak position of −78 ppm for NaCl–SOD. The resonance shifted downfield from that of the NaCl–SOD with increasing lithium content and upfield from the NaCl–SOD with increasing potassium content. Jelinek et al. did not observe a shift in the peak at −78 ppm upon exchanging silver for the sodium atoms even at high loading. This may have been because of the similar size and charge density of the silver cation to that of sodium. Both lithium and potassium had much different characteristics versus sodium in these respects.

Peaks at −0 ppm were assigned to NaCl. An anomaly appeared in the 35Cl spectrum of K–ng in that it appeared that two overlapping peaks were present close to 0 ppm at −0.9 and −4.2. We were unsure as to what caused the second peak at −3.1 ppm. (Peaks for LiCl and KCl would be present at peak positions of 31 ppm and 49–50 ppm, respectively.)19

IV. Conclusions

The elemental compositions of the three phases, sodalite, nepheline, and glass, have been defined for each sample. The changing cation content within the aluminosilicate phases was tracked via 29Si, 27Al, 23Na, 7Li, and 35Cl NMR, XRD, and
SEM, in particular, a change in the position of the $^{35}$Cl chemical shifts was noted in relation to type of cation. The disorder created by the changing cation content of the sodalite cages was also tracked using $^{27}$Al NMR.

The glass phase, when present, plays an interesting role in the overall composition of the waste form. It promotes the formation of the sodalite phase over the nepheline phase. In samples where potassium and glass are present, most of the potassium lies in the glass phase, showing that the sodalite phase favors sodium and lithium over potassium. By tracking the aluminum content of the glass phase, it is evident that a substantial portion, ~13%–15%, of the sodalite phase dissolves in the glass phase. Similar behavior was seen in a previously published study by our group where cesium chloride was the salt used. Cesium is found to have exchanged into the glass phase of a similar CWF.

When ng is present, the amount of sodalite formed increases and depends upon the cation makeup of the sample. In samples that contain potassium (a necessary component of the “ideal” formula for nepheline), nepheline became the predominant phase over sodalite.

Acknowledgments

Part of this research was performed in the Environmental Molecular Sciences Laboratory (a national scientific user facility sponsored by the U.S. DOE Office of Biological and Environmental Research) located at Pacific Northwest National Laboratory, operated by Battelle for the DOE. Special thanks are due to Tanya M. Barber and Tom O’Holleran for operational assistance with the EM, to Dr. Thomas Luther, Dr. Sarah Barton, and Dr. Alexander Blumenfeld for their operational assistance with the NMR spectrometers, Pamela Crane for her analysis of the NMR samples, and Dr. Chien M. Wai for his support of this work as part of a doctoral project.

References