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## EFFECTS OF HEATING ON SALT-OCCLUDED ZEOLITE

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### ABSTRACT

The electrometallurgical treatment of spent nuclear fuel generates a waste stream of fission products in the electrolyte, LiCl-KCl eutectic salt. Argonne National Laboratory is developing a mineral waste form for this waste stream. The waste form consists of a composite formed by hot pressing salt-occluded zeolite and a glass binder. Pressing conditions must be judiciously chosen. For a given pressure, increasing temperatures and hold times give denser products but the zeolite is frequently converted to sodalite. Reducing the temperature or hold time leads to a porous zeolite composite. Therefore, conditions that affect the thermal stability of salt-occluded zeolite both with and without glass are being investigated in an ongoing study. The parameters varied in this stage of the work were heating time, temperature, salt loading, and glass content. The heat-treated samples were examined primarily by X-ray diffraction. Large variations were found in the rate at which salt-occluded zeolite converted to other phases such as nepheline, salt, and sodalite. The products depended on the initial salt loading. Heating times required for these transitions depended on the procedure and temperature used to prepare the salt-occluded zeolite. Mixtures of glass and zeolite reacted much faster than the pure salt-occluded zeolite and were almost always converted to sodalite.

### INTRODUCTION

Two high level waste streams result from the electrometallurgical treatment of spent nuclear fuel. One of these consists of fission products accumulated in the electrolyte, LiCl-KCl eutectic salt. Argonne National Laboratory is developing a mineral waste form for this waste stream that consists of a two-phase composite: salt-occluded zeolite and a glass binder.[1] The thermal stabilities of the glass and, more particularly, the salt-occluded zeolite control the conditions for waste form production. Zeolite A was chosen to contain the waste salt because of its favorable sorption properties. In previous work, we showed that zeolite A preferentially sorbed the fission products from the waste salt and occluded up to 12 cation-anion (chloride) pairs within its molecular cages.[2] However, other work showed that salt-occluded zeolite A could be converted to sodalite and/or mixtures of salt and non-zeolitic aluminosilicates, such as nepheline or carnegieite, by heating salt-occluded zeolite A at 1000 K for at least 16 h.[3] The formation of these phases could adversely affect the leach resistance of the product. Nepheline and carnegieite do not have a cage structure to contain the salt, and sodalite's capacity for salt is about 1/3 that of zeolite A. Because the hot pressing temperature is typically around 1000 K, it is important to identify conditions where the zeolite does not react appreciably and convert rapidly to other crystalline phases. The

thermal reactivity of the glass binder is not expected to be an issue at 1000 K. A cursory examination was made of the thermal properties of several potential glass binders and the results are published elsewhere.[4]

More detailed information on the reactivity of salt-occluded zeolite would be useful in narrowing the selection of hot pressing conditions. Parameters other than temperature and heating time could affect the zeolite's reactivity and need to be identified. We have, therefore, started to measure the changes that occur during heat treatment of salt-occluded zeolite with various salt loadings, by itself and with glass. In the future, these results will be compared with results from hot pressing runs that use the same zeolite-glass mixtures. These data will allow us to determine the effect of pressure during hot isostatic pressing.

## EXPERIMENTAL

Blended zeolite was prepared by mixing dehydrated zeolite and simulated waste salt at 775 and 825 K. Three salt loadings were used: 12, 21, and 25 wt% of the total mixture. One or more batches of each loading were prepared. These salt loadings correspond to loading the unit cell of zeolite A with 4, 7.5, and 9.5 cation-anion equivalent pairs per unit cell, respectively. Because the salt is a mixture of chloride salts, we will refer to these loadings as 4, 7.5, and 9.5 chloride ions per unit cell (Cl/uc). (The number of cation equivalents is equal to the number of chloride ions for charge balance). One procedure at 775 K and a developmental procedure at 825 K were used to blend the salt with the zeolite.[5] The samples of blended zeolite are classified by their salt loading in Cl/uc and blending temperature. For example, blended zeolite with 4 Cl/uc that was mixed at 775 K is referred to as 4-775. The blended zeolite-and-glass samples were mixed in an analytical mill to reduce agglomeration.[6] Both the blended zeolite and the blended zeolite-and-glass were stored in an argon glovebox (oxygen content <1 ppm). Just before heating, the samples were removed from the glovebox and placed in alumina crucibles that had been dried previously at 775 to 975 K for at least 16 h. The samples were weighed in air and placed immediately into a muffle furnace at 575 K. The furnace was brought to the test temperature at a heating rate of 20 K per minute. The internal temperature of the furnace was checked with an independent thermocouple. The variation in the temperature at the different sample positions was less than 10 K. At the conclusion of the test, the samples were removed from the furnace, cooled in a desiccator, and weighed. X-ray diffraction (XRD) spectra were obtained with a RIGAKU diffractometer, Model D2400.

## Materials

Zeolite A powder (A50™) was obtained from UOP-Molecular Sieves Division, (Mt. Laurel, NJ). The zeolite was dried by heating to 798 K and purging with dry nitrogen gas. Two simulated waste salts were used in these experiments. Their compositions are given in Table I. The LiCl-KCl eutectic salt was obtained from Anderson Physics Laboratory, (Champaign, IL) and ultra dry grade fission product chlorides came from Johnson-Matthey. The salt solution was formed by heating

the mixture of salts in an argon atmosphere glovebox at 773 K. One proprietary commercial glass frit from Bayer Chemicals, (Baltimore, MD) was used in these experiments. Its composition is 9.7 wt% alumina, 13.9 wt% boria, 13.5 wt% calcia, 0.8 wt% potassium oxide, 6.5 wt% soda, and 55 wt% silica. Its properties are described elsewhere.[4]

Table I. Compositions of Salt 1 and Salt 2

Element	Salt 1 (wt%)	Salt 2 (wt%)	Element	Salt 1 (wt%)	Salt 2 (wt%)
CsCl	3.7	2.3	CeCl <sub>3</sub>	0.7	2.0
KCl	45.3	49.7	LaCl <sub>3</sub>	1.1	0.6
LiCl	39.6	39.5	NdCl <sub>3</sub>	1.0	3.2
NaCl	6.0	0	PrCl <sub>3</sub>	0	0.8
BaCl <sub>2</sub>	1.4	1.0	YCl <sub>3</sub>	0.1	0.1
SrCl <sub>2</sub>	0.6	0.4	KI	0.4	0.3

#### X-ray Diffraction Analysis

Experimental XRD patterns for hydrated zeolite A ( $\text{Na}_{12}(\text{AlSiO}_4)_{12}$ ) and blended zeolite 7.5-775 are given in Fig. 1A and B, respectively. The patterns are similar. However, blending causes some changes. For example, relative intensities have changed, peaks have shifted and, in some cases, become broader. Different cationic compositions are responsible for some of these changes. Work is ongoing to determine other causes for these differences.

Heat treatment also causes further changes in the XRD pattern. A typical pattern, in Fig. 1C, was obtained from blended zeolite 7.5-775 heated at 975 K for 23 h. Comparison of this pattern with Fig. 1B (blended zeolite 7.5-775 prior to heating) shows that positions of major peaks are about the same, but other features are different. Many of the weaker peaks vanished, the stronger peaks broadened and, in some cases, split. (The splitting is not shown in the pattern in Fig. 1C.) Relative intensities of several peaks are different. We believe that patterns similar to those shown in Fig. 1C represent a mixture of salt-occluded zeolite and a heat damaged phase. For this reason we refer to patterns of the type as "damaged zeolite."

New phases found in the heat-treated zeolites were sodalite, carnegieite, nepheline, and salt. These phases were identified by comparing the experimental patterns with those from the Powder Diffraction File.[7] Overall patterns were examined. Peak positions and normalized peak areas of the strongest lines were compared using the JADE program.[8] Relatively strong lines, or markers, for the blended zeolite and all of the new phases were found between  $d = 7.0$  and  $2.8 \text{ \AA}$ . The positions of the markers ( $d$ -spacings) and their normalized peak areas are given in Table II for each standard. The  $d$ -spacings that were measured for our samples were occasionally

shifted by as much as 0.3 Å, compared to the standard patterns. Some shift is expected because of the different compositions. Therefore, this shift did not negate the assignment if the overall patterns were similar. The choice of marker is governed primarily by the degree of overlap with other possible lines. As an illustration, carnegieite was assigned when there was a strong line at  $d = 4.16$  Å and no significant intensity at 3.83 and 3.00 Å (nepheline lines).[9,10] When the relative intensities were different from those listed in Table II, we assumed the overlap was due to two or more phases. For example, when the intensity of the 4.16 Å line was much greater than the 3.83 and 3.00 lines, both nepheline and carnegieite were assigned. The markers for sodalite, NaCl, and KCl are as shown in Table II.[11, 12, 13] A line at  $d = 2.89$  Å was assigned to a solid salt solution of  $\text{Na}_{0.8}\text{K}_{0.2}\text{Cl}$  [14]. Salt lines are evidence of a free salt phase.

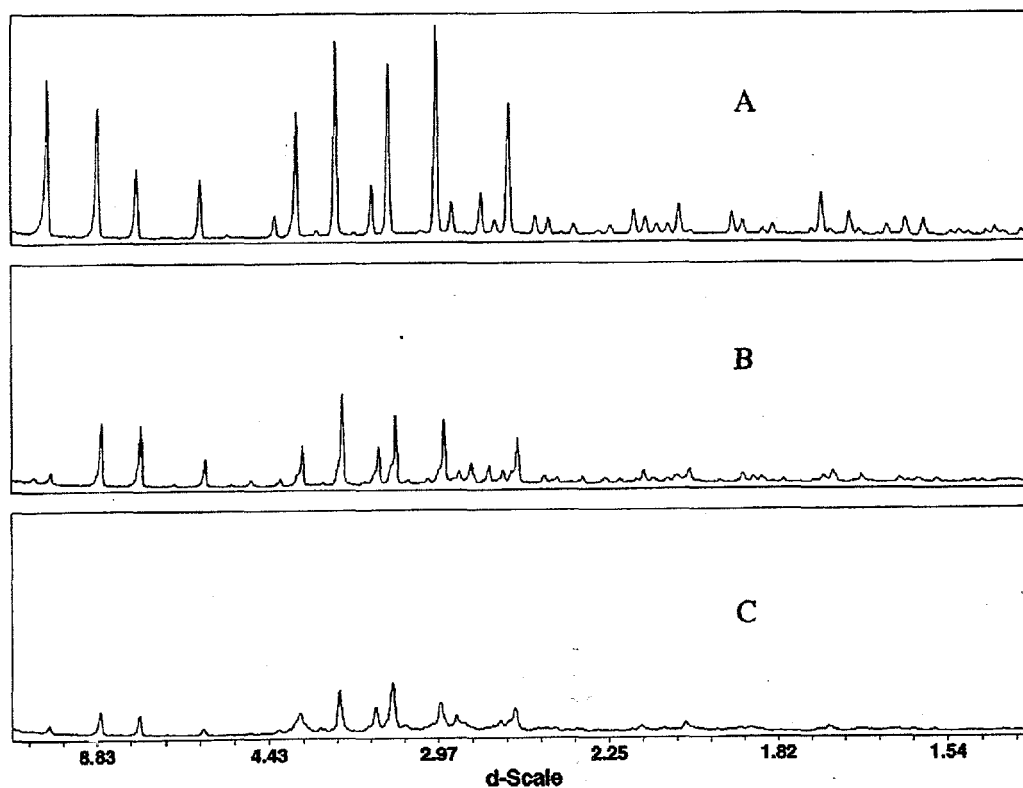


Fig. 1. A. XRD pattern of hydrated zeolite, sodium form.  
 B. XRD pattern of blended zeolite 7.5-775.  
 C. XRD pattern of blended zeolite after 23 h at 975 K.

Table II. Lines Used for Markers

Phase	Peak Position <sup>a</sup> for the Strongest Lines in the Region between d = 7.0 and 2.8 Å								
Blended Zeolite A	7.01 (44)		3.84 (3)	3.66 (100)	3.37 (38)	3.25 (77)		2.95 (77)	2.80 (20)
Carnegieite		4.16 (100)							
Nepheline		4.16 (80)	3.83 (100)			3.27 (70)	3.00 (100)		
Sodalite	6.2 (40)			3.62 (100)					
NaCl									2.82
KCl							3.15		

<sup>a</sup> Peak positions given in Å; normalized intensities given in parentheses.

## RESULTS AND DISCUSSION

### Effect of Temperature and Time

Samples of blended zeolite 7.5-825 were heated at 975 and 1025 K for 1 to 6 h. Each sample was examined with XRD. Table III shows the heating time and temperature for each sample along with the crystalline phases observed in its XRD spectrum. The phases are listed in order of decreasing intensity as measured by the peak height of their markers. These relative intensities are not related to the amount of the phase present in the sample, but are presented to demonstrate that the mix of crystalline phases changes with time. Temperature had a large effect on zeolite reactivity. The conversion rate was faster at 1025 K than at 975 K. At 1025 K, salt and nepheline were the major phases. Carnegieite was an intermediate phase because a strong peak was found at  $d = 4.16$  Å in the sample heated for 1 h and not in any of the others. Trace amounts of sodalite were formed after 6 h. At 975 K, damaged zeolite remained the major phase, although sodalite and nepheline were minor phases after 6 h. Because these results indicate that the zeolite was more reactive at 1025 K than at 975 K, the remaining experiments were done at 975 K. The heating times were adjusted so that the approximate lifetime of the zeolite structure could be determined and transitions of the zeolite to other phases could be monitored.

Table III. Phases<sup>a</sup> Formed by Heating Blended Zeolite 7.5-825 at 975 and 1025 K

Time (h)	Phases Formed at 975 K	Phases Formed at 1025 K
1	Zeolite, Salt <sup>b</sup>	Zeolite, Carnegieite, Salt
2	Damaged Zeolite, Salt	Salt, Nepheline
4	Damaged Zeolite, Salt	Salt, Nepheline
6	Damaged Zeolite, Sodalite, Nepheline, Salt	Salt, Nepheline, Sodalite

<sup>a</sup> Phases are listed according to descending intensities.

<sup>b</sup> Salt represents NaCl, KCl,  $\text{Na}_{0.8}\text{K}_{0.2}\text{Cl}$ , or mixture thereof.

## Effect of Different Salt Loadings

We studied the transitions that occur in blended zeolite at 975 K with three salt loadings, 4, 7.5, and 9.5 Cl/uc in five samples. We found that the conversion products depend on salt loading. The crystalline phases identified in blended zeolites heated for the specified time period are given in Table IV. The phases are listed in order of descending intensities, i.e., the strongest marker is listed first and the weakest marker last. Blended zeolite with 4 Cl/uc (4-825) is converted to various crystalline phases such as carnegieite, nepheline, free salt, and sodalite. The mix of these phases changes with time. Carnegieite and nepheline are the major phases at short times, while sodalite is the major phase at longer times. Another sample of blended zeolite with 4 Cl/uc gave the same products but reacted more slowly; this result will be discussed in more detail below. Blended zeolite containing 7.5 Cl/uc is converted either to damaged zeolite or to a mixture of damaged zeolite, sodalite, and nepheline. The markers for salt are weak in these patterns. Differences in conversion rate were also observed for the two samples; a possible reason is suggested below. Blended zeolite with 9.5 Cl/uc is converted to free salt, sodalite, and small amounts of nepheline. The markers for the salt are strong in the patterns. These data suggest that a salt loading of 7.5 Cl/uc may be preferred because the zeolite structure is retained longer, and because other crystalline phases such as carnegieite and free salt are less likely to form.

Table IV. Phases<sup>a</sup> Formed by Heating Blended Zeolite Containing 4, 7.5, or 9.5 Cl/uc at 975 K

Sample Type	Time at 975 K (h)	Phases in XRD Spectra
4-825	1	Zeolite
	2	Damaged Zeolite, Carnegieite
	4	Carnegieite, Nepheline, Sodalite, Salt
	6	Sodalite, Nepheline, Salt
	7-9	Sodalite, Nepheline, Salt
4-775	7	Zeolite, Salt
	24	Carnegieite, Nepheline, Zeolite, Salt, Sodalite
7.5-825	1, 2, 4	Damaged Zeolite, Salt
	6	Damaged Zeolite, Salt, Sodalite, Nepheline
7.5-775	1, 8	Zeolite
	14, 23	Damaged Zeolite, Salt
9.5-825	1, 4	Zeolite
	7	Zeolite, Salt, Sodalite, Nepheline
	9	Salt, Sodalite, Nepheline, Damaged Zeolite

<sup>a</sup> Phases are listed according to descending intensities.

<sup>b</sup> Salt represents NaCl, KCl, Na<sub>0.8</sub>K<sub>0.2</sub>Cl, or mixture thereof.

### Effect of Different Blended Zeolite Preparations

The blended zeolite's thermal reactivity also depended strongly on the procedure and temperature used in its preparation. Zeolite with 4 Cl/uc prepared at 825 K (4-825) was completely converted to other products within 4 h, while the sample prepared at 775 K (4-775) retained the blended zeolite XRD pattern for 7 h. The same trend was observed in the blended zeolite with 7.5 Cl/uc. Sample 7.5-825 was converted to a damaged zeolite within 1 h, while the sample 7.5-775 retained the blended zeolite XRD pattern for 8 h. A developmental procedure was used to blend the samples at 825 K. The results discussed above suggest that a blending temperature of 825 K was too high. How other changes in blending conditions affect the blended zeolite are discussed in another paper.[5] The procedure used to blend the zeolite and salt mixtures at 775 K has now been adopted as a standard procedure.

### Effect of Adding Glass

Equal amounts of blended zeolite and glass frit were heated to 975 K for up to 6 h and analyzed with XRD. Most of the experiments were done with blended zeolite 7.5-775 and 7.5-825, although a few were done with 4-775 and 9.5-825 for comparison. The results were as follows: (1) the blended zeolite was converted to sodalite or other crystalline phases more quickly when glass was present and (2) the differences in conversion rates of samples prepared at 775 and 825 K were negated by glass. Figure 2 shows the XRD spectra of mixtures of zeolite 7.5-775 and glass frit after 2, 4, and 6 h at 975 K. The blended zeolite was almost completely converted to other phases within 3 or 4 h, (i.e., the zeolite pattern was completely absent in these spectra). Sodalite was formed as the major phase. The markers for NaCl and nepheline were weak at 4 h and their intensity declined as heating time increased from 4 to 6 h. Similar spectra were obtained when blended zeolite 7.5-825 was substituted for 7.5-775. Since the results were comparable for both blended zeolites 7.5-775 and 7.5-825, differences in reactivity, discussed in the preceding section, are not as important when glass is present.

### Other Effects

Another result of the blended zeolite-glass studies was that salt loading influenced the new crystalline phases formed from the zeolite. Blended zeolite with 9.5 Cl/uc reacted with glass in the same manner as the blended zeolite with 7.5 Cl/uc. The blended zeolite 9.5-825 was converted to sodalite and NaCl very quickly, within 2 to 3 h. As heating time increased, the peak height of the NaCl markers decreased, while those for the sodalite marker increased. After 6 h at 975 K, sodalite was the major phase and NaCl, a very minor phase. The results were very different when blended zeolite 4-775 was used. They included a much slower conversion rate and different products. The zeolite phase remained for the entire 7 h heating period, although its intensity gradually decreased. Carnegieite first appeared after 3 h of heating, and the heights of the markers increased with heating time. The sodalite markers appeared at 4 h. The peak heights for the sodalite markers increased as those for the damaged zeolite's decreased. Free salt was not

observed in these spectra. Thus, blended zeolite containing 4 Cl/uc behaved very differently with glass than blended zeolites containing 7.5 and 9.5 Cl/uc.

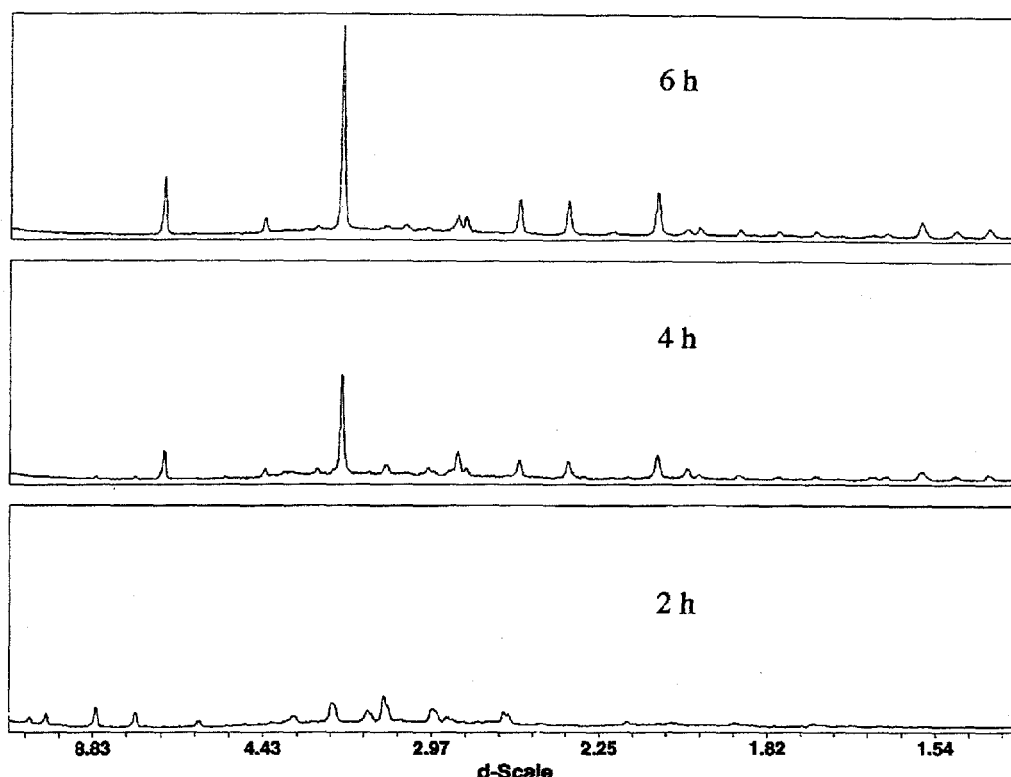


Fig. 2. XRD Spectra of Mixtures of Zeolite 7.5-775 and Glass Frit Heated for 2, 4, and 6 h at 975 K

A surprising result from the experiments that used glass and blended zeolites with 7.5 or 9.5 Cl/uc was that the peak area (measured by JADE) for the NaCl marker relative to that for the sodalite marker decreased with heating time [8]. The initial salt loading in these blended zeolites exceeded the capacity for sodalite. If all of the blended zeolite is completely converted to sodalite with no excess salt, the initial salt loading of the zeolite should be 4 Cl/uc or less. Blended zeolites with 7.5 and 9.5 Cl/uc should contain a large excess of salt if the zeolite is completely converted to sodalite, as suggested by the XRD data. The excess salt should be observable in the XRD spectra as free salt. The fact that the XRD patterns in Fig. 2 have a relatively weak NaCl marker suggests that other reactions are occurring. Salt volatilization was considered, but measurements of mass losses before and after heating showed that the salt could not have volatilized to the degree necessary. Another possible reaction is the conversion of glass to sodalite. Other mechanisms are also being considered, and new experiments are being planned to address this issue.

## CONCLUSIONS

The transitions that blended zeolites undergo vary with temperature, time, and salt loading. Phases such as nepheline were more likely to form when salt loadings were 4 Cl/uc and temperatures were greater than 975 K. Blended zeolite samples with 7.5 Cl/uc retained the zeolite crystalline structure longer than those with 4 or 9.5 Cl/uc. Transition rates to other crystalline phases were faster when the blended zeolite was prepared at 825 K than at 775 K. Zeolite reactivity was greater when glass was present. Glass enhanced the conversion to sodalite for zeolite loaded with 7.5 and 9.5 Cl/uc. The rate of sodalite formation was high, occurring within 3 to 4 h. Blended zeolite with 4 Cl/uc appears to be anomalous in that glass did not enhance its conversion to sodalite. Future work will focus on elucidating the reaction mechanism between the glass and the blended zeolite and determining how the glass affects the reactivity of the blended zeolite. The possible conversion of glass and salt into sodalite will also be investigated.

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