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MIXING OF ZEOLITE POWDERS AND MOLTEN SALT*

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ABSTRACT

Transuranics and fission products in a molten salt can be incorporated into zeolite A by an ion exchange process and by a batch mixing or blending process. The zeolite is then mixed with glass and consolidated into a monolithic waste form for geologic disposal. Both processes require mixing of zeolite powders with molten salt at elevated temperatures (>700 K). Complete occlusion of salt and a uniform distribution of chloride and fission products are desired for incorporation of the powders into the final waste form. The relative effectiveness of the blending process was studied over a series of temperature, time, and composition profiles. The major criteria for determining the effectiveness of the mixing operations were the level and uniformity of residual free salt in the mixtures. High operating temperatures (>775 K) improved salt occlusion. Reducing the chloride levels in the mixture to below 80% of the full salt capacity of the zeolite significantly reduced the free salt level in the final product.

INTRODUCTION

Methods are under investigation for disposal of the waste salt generated by electrometallurgical processing of spent nuclear fuel. Previous studies indicated that alkali, alkaline earth, and rare earth fission products, and transuranic ions present in a molten salt can be incorporated into zeolite A by ion exchange.[1] The zeolite has an open cage structure, which occludes anions in addition to the fission product cations.[2,3,4] The zeolite structure does not appear to be disrupted by the presence of the occluded chloride.[5] The occlusion is relatively irreversible at room temperature, as the chloride is not readily leached in the presence of water. Two occlusion operations are possible: (1) direct blending or (2) ion exchange. In the direct blending process, the salt is combined with enough zeolite to fully occlude the salt within the zeolite cage structure. The salt-loaded zeolite is then incorporated into a mineral waste form for geologic disposal.

In the ion exchange process, the molten salt is passed through a bed of zeolite. The fission products are concentrated in the zeolite; then the effluent salt, which is now devoid of fission products, is recycled. Since the salt is recycled, the total waste form volume is reduced. Because a substantial amount of salt adheres to the surface of the zeolite pellets in the column operation, the zeolite is blended with anhydrous zeolite at high temperature to fully sorb all of the residual surface chloride, as in the direct blending process. Once salt is fully occluded in the zeolite from either process, the salt-loaded zeolite powders are mixed with a glass and hot pressed to form a solid monolith intended for geological disposal.[6]

In the initial development of a glass-bonded waste form, salt-loaded zeolite powders are being prepared for hot pressing without an ion exchange step. As a result, all of the blending studies to date have been carried out by mixing anhydrous zeolite A powder with a simulated waste salt at high temperatures. When the factors that influence waste form performance become better understood, blending and other operations on zeolite pellets that have undergone ion exchange will be investigated. This initial study reports the effect of chloride loading, blending temperature, and rotation speed on the blending of zeolite powder and molten salts. Results indicate that the chloride can be essentially fully sorbed by the zeolite.

EXPERIMENTAL

Starting Materials

Zeolite 4A ($Na_{12}Al_{12}Si_{12}O_{48}$), 3A (partially potassium exchanged 4A) and 5 A (partially calcium exchanged 4A) were obtained in powder form from UOP (Des Plaines, IL); the reported mean particle size of the 4 A powder was ~3.5 µm. The powder was dehydrated in a step-wise fashion to 800 K under a nitrogen flow system and transferred directly to an inert-atmosphere glovebox.

The simulated waste salts were formed from reagent grade components (Johnson Matthey Co.), which were physically mixed, melted, filtered, and coarsely ground. The LiCl and KCl were obtained at the eutectic composition (42.5 wt% LiCl, melting point ~635 K) from APL Engineered Materials, Inc. The two compositions of the waste salt that were prepared for the blending tests are given in Table I.

High Temperature Blender

Two designs of high temperature blenders were used to mix the zeolite A powder and salt in order to fully occlude the salt within the zeolite structure. Both blenders were based on rotating double-cone designs, as shown in Fig. 1. Blender 1 rotates on an axis which runs along the basis of the two cones. Powder is lifted by two baffles located 180° apart, which bisect the cones. At the narrow end of one cone is a 8-in. (20-cm) conflat® flange with a 4-in. (10-cm) opening for loading and unloading the blender. The diameter at the center perpendicular to the axis of rotation of the blender is 8 in. (10 cm). The overall length is also 8 in. (10 cm). The mating flange contains a solid cone that prevents powder from packing on the edge of the inner flange.

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Table I. Salt Composition (wt%)

Component	Salt 1	Salt 2
KCl	45.3	49.7
LiCl	39.6	39.5
CsCl	3.7	2.3
$BaCl_2$	1.4	1.0
$SrCl_2$	0.6	0.4
$CeCl_3$	0.7	2.0
$LaCl_3$	1.1	0.6
$NdCl_3$	1.0	3.2
$PrCl_3$	0	0.8
YCl_3	0.1	0.1
NaCl	6.0	0
KI	0.4	0.3

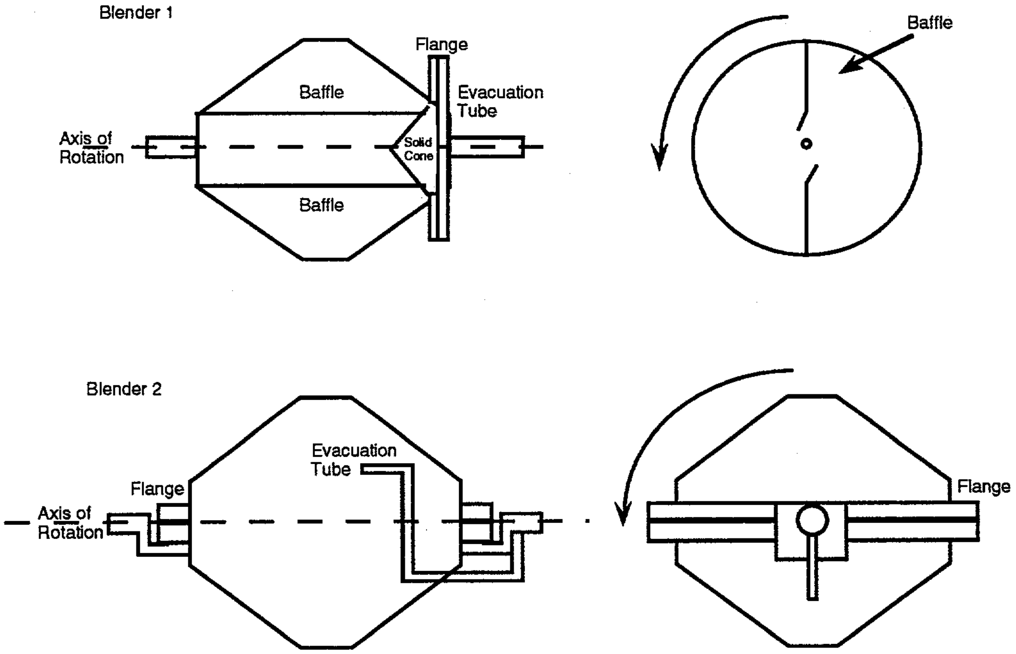

Fig. 1. Schematic of Two High Temperature Blenders

The axis of rotation of blender 2 is located at a 90° angle to that of the first. Unlike the first blender, the interior does not contain baffles. Loading and unloading are done through a 10-in. (25-cm) conflat® flange with an 8-in.

(10-cm) opening located in the center of the unit. The internal diameter of the blender at the flange is 8-in. (10-cm) and the overall length (perpendicular to the axis of rotation) is 9 in (23 cm). The maximum capacity is ~1.5 liters, approximately twice that of blender 1.

Loading and unloading of the blenders are done in an inert-atmosphere glovebox to prevent uptake of water by the hydrophilic, dehydrated zeolite. Copper gaskets are used to seal the blenders after loading. The blenders are evacuated prior to heating and rotation. Both blenders were designed to operate at temperatures as high as 825 K within a cylindrical furnace. The internal blender temperature was monitored with a thermocouple.

Surface Salt Determination

Surface salt content was used as a measure of blender success. One gram samples of the blended powders were shaken with 50 mL of deionized water at room temperature (300 K) for one minute and filtered. The chloride content of the filtrate was measured with a chloride ion selective electrode calibrated with NaCl solutions of known composition; the surface salt content of the blended mixture was calculated from the measured solution concentrations. The free chloride determined with the chloride selective electrode matched the mass lost by the washed sample to within ±5% after it had been dried at 385 K for 24 h.

The free salt was measured for identical samples of blended zeolite washed for 1, 5, 10, 20, and 60 minutes. Over time, the chloride content in the zeolite increased from 0.12 to 0.20 wt% of the sample (0.58 to 0.97% of total chloride), as shown in Fig. 2. Thus, longer washing times did not appreciably change the amount of salt removed from the sample. One would expect a much larger fraction of the chloride to be removed, on the order of several percent, if significantly more chloride was being removed from the interior of the crystals at the longer wash times.

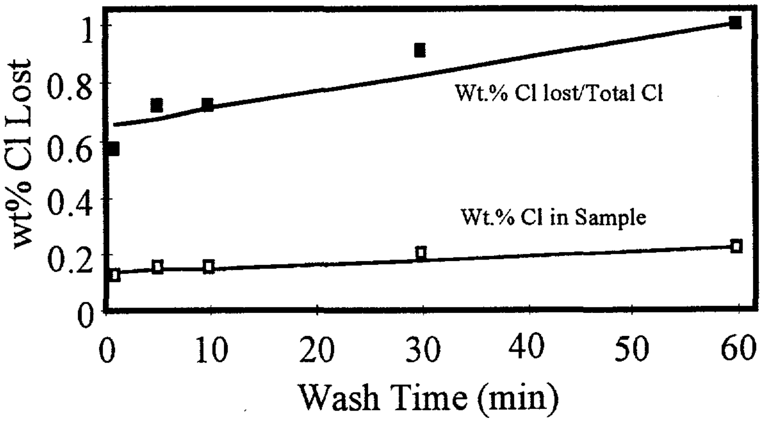

Fig. 2. Chloride Lost From Blended Zeolite and Salt Samples on Washing at 300 K

RESULTS

Blending of salt and zeolite at temperatures of 825 K for 20 h did not appear to destroy the crystal structure of the zeolite A. Figure 3 shows the X-ray diffraction patterns for dehydrated zeolite A and for a salt-loaded zeolite. Nearly all of the peaks observed in the pattern of the dehydrated zeolite are observed for the pattern of the salt-loaded zeolite. Generally, the peak intensities of the salt-loaded sample are lower, consistent with occlusion of salt in the zeolite structure. Relative peak intensities also differ, and some features have broadened. Some peaks shifted after blending, perhaps associated with a change in the zeolite unit cell due to the presence of a large amount of lithium.[7] Changes in the unit cell structure for salt-loaded zeolite A have been noted previously by neutron diffraction.[8] Peak splitting was observed in the patterns of several samples suggesting either incomplete or non-uniform occlusion of salt. Samples with low free chloride do not show this splitting. Salt features, when evident, are small and are consistent with NaCl (peak at 31° 2-Theta in Fig. 3b) rather than LiCl or KCl. Since the salt has relatively little sodium, this is consistent with occlusion and indicates ion exchange between the salt and the sodium initially present in the zeolite. There was no clear effect on the blender product attributable to the two different salt compositions.

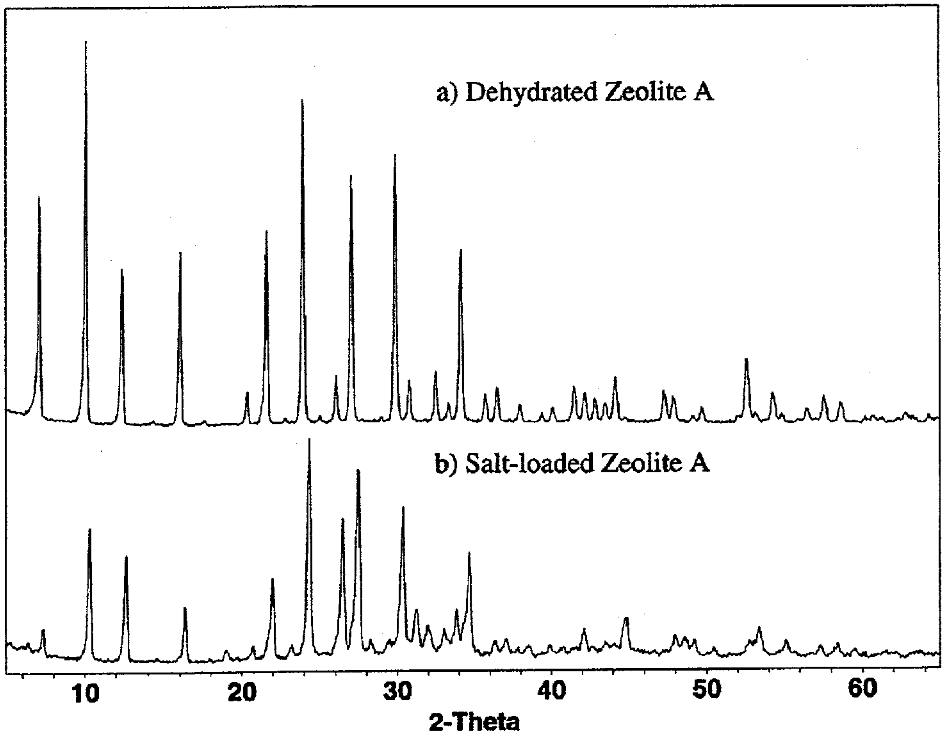

Fig. 3. X-ray Diffraction Patterns of Dehydrated and Salt-loaded Zeolite at 9.5 Chloride Ions Per Unit Cell Blended at 825 K for 20 h

Chloride Loading

There is a clear relationship between the capacity of the zeolite for chloride and the amount of free salt that remains in the hot blended sample. The capacity of the zeolite is approximately 12 chloride per unit cell ($Na_{12}Al_{12}Si_{12}O_{48}$). Chloride loadings between 4 and 11 ions per unit cell were investigated to determine the effect of loading on the amount of free chloride that remains after blending (and ultimately on waste form performance). Figure 4 shows the amount of residual free chloride in a zeolite blended at 825 K as a function of the chloride loading. There is a sharp upturn in free chloride above 9.5 chlorides per unit cell of zeolite A. This increase in free chloride is probably more indicative of incomplete blending than the limiting capacity of the zeolite for chloride.

Blending Temperature

The performance of blender 1 improved as temperature was increased. Figure 5 shows the effect of temperature on average free salt for tests conducted at a loading of 7.5 chlorides per unit cell of zeolite A. In Fig. 5 a clear improvement is observed as the blending temperature is increased from 725 to 775. A slight improvement in blender performance is observed as the operating temperature is increased further to 825 K. Since most of the initial tests were run at 725 K, part of the improvement might be due to changes in factors other than temperature, such as the rotation speed. However, a test run at 725 K implementing these changes had a free chloride loading of 0.7 wt%, significantly higher than similar samples blended at 825 K and similar to earlier tests at 725 K. The effect of temperature on Blender 2 has not yet been determined.

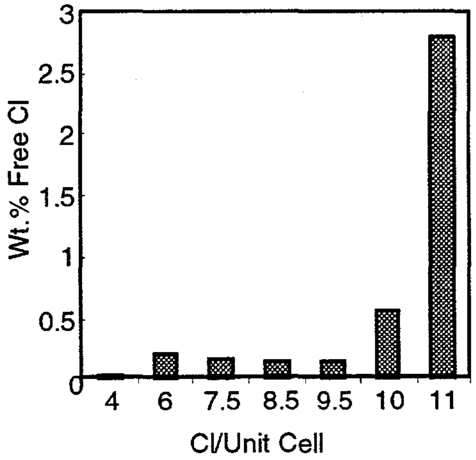

Fig. 4. Effect of Chloride Loading on Free Salt Content for Blending Temperatures of 825 K

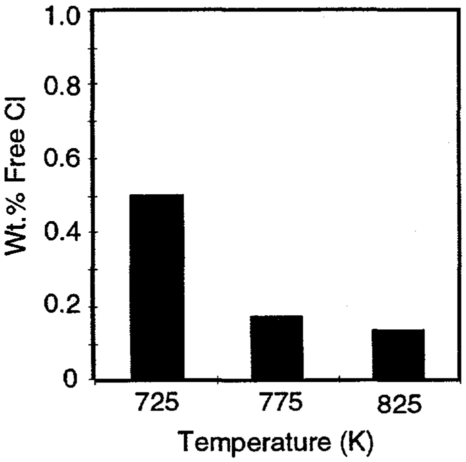

Fig. 5. Average Free Salt versus Temperature at 7.5 Chlorides per Unit Cell

Blender Operation

Rotation speed was found to be important in operation of blender 1. Speeds above 30 rpm or below 15 rpm were not as effective as ~20 rpm. At the highest speeds, the powder appears to be carried by the baffles as the unit rotates, so that it does not fall freely. At very low speeds, the rate of tumbling is reduced, yielding less efficient mixing

The free chloride content of the loose powders was generally very uniform; multiple samples taken from single blender tests did not show large variation in free chloride content, as is evident from the standard deviations calculated in Table II. Batch size, as shown in Table II, does not appear to strongly affect blender performance. One sample with a chloride loading of 8.5 per unit cell that was blended 825 K (550°C) had a free salt content of 1.5 wt%; this was the only sample at a loading level below 10 chloride per unit cell that had a very high free salt content and is not included in Table II.

Table II. Average Free Chloride in Series of Samples Mixed in Blender 1

Cl/UC[a]	Temp (K)	Batch Size (g)	Free Cl (wt%)	SD[b]
4.0	825	100	0.05	0.01
4.0	825	100	0.06	0.01
7.5	725	400	0.4	0.1
7.5	725	100	0.50	0.05
7.5	725	300	0.7	0.2
7.5	775	300	0.06	0.01
7.5	775	300	0.12	[c]
7.5	775	380	0.36	[c]
7.5	775	500	0.12	[c]
7.5	775	500	0.08	[c]
7.5	775	500	0.09	[c]
7.5	825	500	0.17	0.04
7.5	825	300	0.17	0.04
7.5	825	100	0.18	0.02
7.5	825	100	0.20	0.01
8.5	825	300	0.13	0.03
9.5	725	100	0.37	0.03
9.5	825	300	0.15	0.02
10.0	725	200	2.9	0.4
11.0	725	300	2.8	0.1

[a] Cl/UC = chlorides per unit cell of zeolite A ($Na_{12}Al_{12}Si_{12}O_{48}$).

[b] SD = Standard deviation.

[c] Only one measurement made.

In the earlier testing with blender 1, the zeolite-salt mixtures tended to become packed together in clumps. This packing was particularly notable at the point of intersection of the baffles with the walls and at the ledge formed where the outer flange mates with the inner flange containing the 4-in. (10-cm) diameter opening. The material on the baffles had a chloride content similar to the loose powders but was hard and presented a problem in removing material from the blender. The small amount of material on the edge of the flange generally had a higher free chloride content than the bulk material.

The tendency to pack was reduced by three methods. Firstly, cylindrical alumina beads with 0.75-in. (1.90-cm) diameter were added to the powder prior blending to break up any clumps that formed during a test. Secondly, the rotation direction of the blender 1 was changed periodically during a run. Finally, a solid cone was added to the outer flange (Fig. 1) to prevent packing of powders on the edge of the inner flange. The cone prevented powder from falling on the edge and directed the powder toward the center of the blender. The combination of these remedies reduced the tendency of the powders to pack in blender 1. The packing problem did not occur with blender 2 because it did not contain baffles or any flange edges.

Table III shows the results for samples mixed with blender 2. Results are generally superior to those of blender 1. The free salt content increases as the chloride content is raised. The initial zeolite composition does not affect performance greatly with the exception of potassium at 9.5 chlorides per unit cell. The poor result, in this case, may be related to a reduction in pore volume due to the larger ionic radius of potassium relative to sodium.

Table III. Free Chloride in Series of Samples Mixed in Blender 2 at 775 K

Cl/UC*	Batch Size (g)	Free Cl (wt%)	Zeolite
3.2	500	0.01	4A
4.0	500	0.02	4A
7.5	500	0.07	4A
9.5	500	0.04	4A
8	500	0.06	3A
9	500	0.09	3A
9.5	500	2.0	3A
7.5	200	0.03	5A

*Cl/UC = chlorides per unit cell of zeolite A ($Na_{12}Al_{12}Si_{12}O_{48}$).

DISCUSSION AND CONCLUSIONS

Blended zeolite was used for production of the starting materials required to fabricate zeolite-based mineral waste forms by hot isostatic pressing. The zeolites were produced over a range of chloride loadings to determine the effect of loading on the structural stability and leach performance of the hot-pressed material. The free salt content was used to assess the suitability of the blended zeolite for waste form production. The results reported here indicate that blended zeolite with low free chloride content has been produced routinely.

There are two main reasons for minimizing the free salt content of the blended powders to reduce the potential loss of fission products from the waste form. Firstly, any free salt, which may contain fission products, remaining in the waste form would likely be readily dissolved in groundwater if the waste form canister were breached. This free salt may migrate to the grain boundaries in the ceramic composite, making it more accessible to groundwater. Secondly, chloride greatly reduces the integrity of glasses. The chloride must be tied to the zeolite to ensure that as little salt as possible becomes dissolved in the glass phase of the waste form during fabrication. Consequently, elimination of free chloride was the initial determinant for blender performance. Results with the blender indicate that free salt may be essentially eliminated from the salt-loaded zeolite powders by high temperature blending

Chloride salt has been effectively occluded in the cage structure of zeolite A by high-temperature blending of molten salt and zeolite A powders. The zeolite A structure is maintained after blending, although some changes are observed in peak intensities and peak widths of the X-ray diffraction patterns. The free salt content in most samples may be reduced to below 0.1 wt% of the sample over a wide range of chloride loadings by blending at 825 K or higher, maintaining the chloride loading below 10 chloride ions per unit cell, and preventing the powders from packing. Although the blending process has not been optimized, general changes in performance due to temperature, time, chloride loading, and other factors have been determined. Further improvements in blender performance may be obtained as the effects of these parameters are better understood.

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