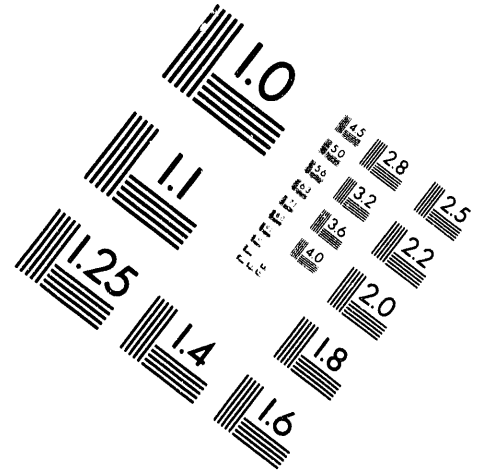
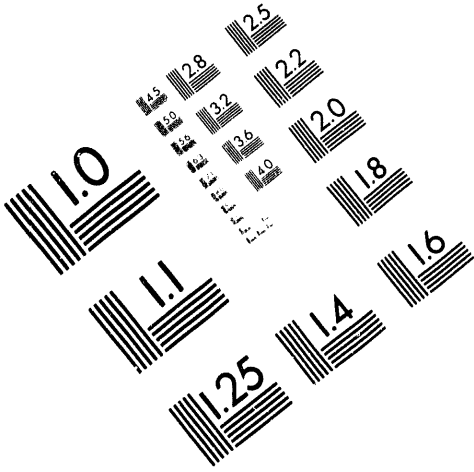




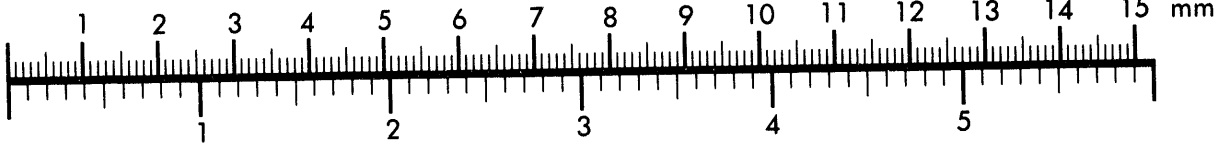
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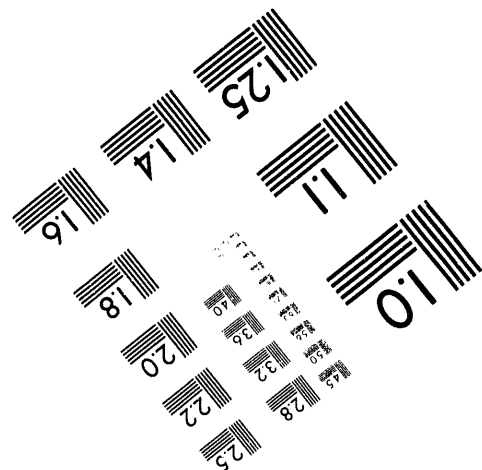
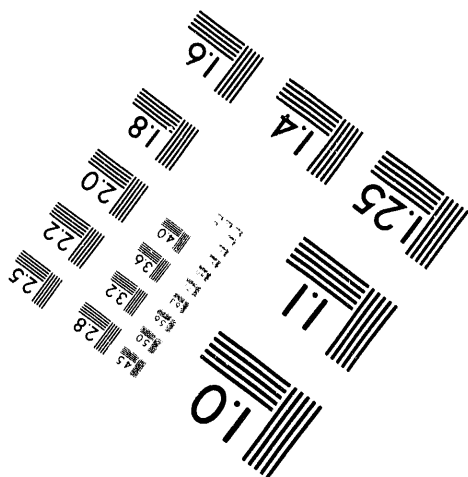
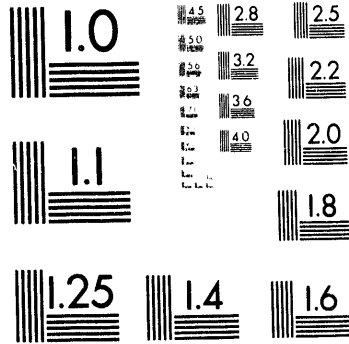
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Cation Segregation in Simulated Radioactive-Waste Zeolite-A Mixtures

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CATION SEGREGATION IN SIMULATED RADIOACTIVE-WASTE ZEOLITE-A MIXTURES

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1. ABSTRACT

Segregation of cations based on size is observed in samples of zeolite-A loaded with simulated radioactive-waste (~5 wt.% Li, K, Cs and Ba, 1 wt.% Sr and Y, <1 wt.% Na) prepared from chloride salts. In contrast to traditional Na zeolite-A, for which all 8-ring access super (α) cages are identical and situated on a simple face-centered-cubic lattice, these simulated rad-waste mixtures contain two types of α -cages situated on a NaCl-like lattice. The long range ordering of extra-framework ions is propagated by severe distortion of framework oxygens due to strong coordination with Li.

2. INTRODUCTION

The structure of zeolite-A is well known, with numerous crystallographic studies over the past few decades [1-8 and many more] detailing cation siting in synthetic Na zeolite-A and various ion-exchanged forms. From these studies a clear picture develops as to the traditional response of zeolite-A to the presence of cations, namely that structural units such as 6-rings and 8-rings will pucker slightly to accommodate close association with the cations. The degree of puckering varies roughly as the ratio of ionic charge to radius for the exchangeable cations [9]. In most cases, all super (α) cages are identical, i.e., there is no direct structural communication from any one cage to its neighbors. Furthermore, detailed studies to-date have been limited to consideration of single cation exchanges, where one to three different cation types are found in the product. Real world circumstances often deviate dramatically from these conditions.

This work is in support of the waste form development effort for Integral Fast Reactor (IFR) waste salt. The pyromechanical processing of spent fuel from the IFR results in a waste of LiCl-KCl-NaCl salt containing approximately 10 wt% fission products, primarily CsCl and

SrCl₂. For disposal, this waste must be immobilized in a form that is leach resistant. Zeolite-A has been identified [10] as a potential storage medium which provides leach resistance. When equilibrated with molten IFR waste salt, zeolite-A, forms an occluded salt compound which has favorable ion exchange properties for the fission products and barium. This study aims to identify sites within the zeolite where barium, cesium and strontium reside.

3. EXPERIMENTAL

A sample was prepared by complexing zeolite-A with a (LiCl-KCl-BaCl₂-CsCl-SrCl₂) salt mixture resulting in the composition given above. This sample and a sample of synthetic Na zeolite-A were transferred in a dry box to sealed vanadium canisters. Time-of-flight neutron powder diffraction data for the two samples were collected on the GPPD [11] diffractometer at the Intense Pulsed Neutron Source (IPNS). Refinement of the Na-A data produced the expected cubic (space group Fm3c) cell with Na⁺ cations sited preferentially opposite 6-rings and secondarily off-center in 8-rings. Preliminary interpretation of the mixture data showed, in addition to a sizable 1.5% contraction of the unit cell, the existence of new diffraction lines indicative of lower crystallographic symmetry (see Figure 1). More careful study revealed that the new reflections are of the (hhl): h, l = 2n+1 type and that the correct

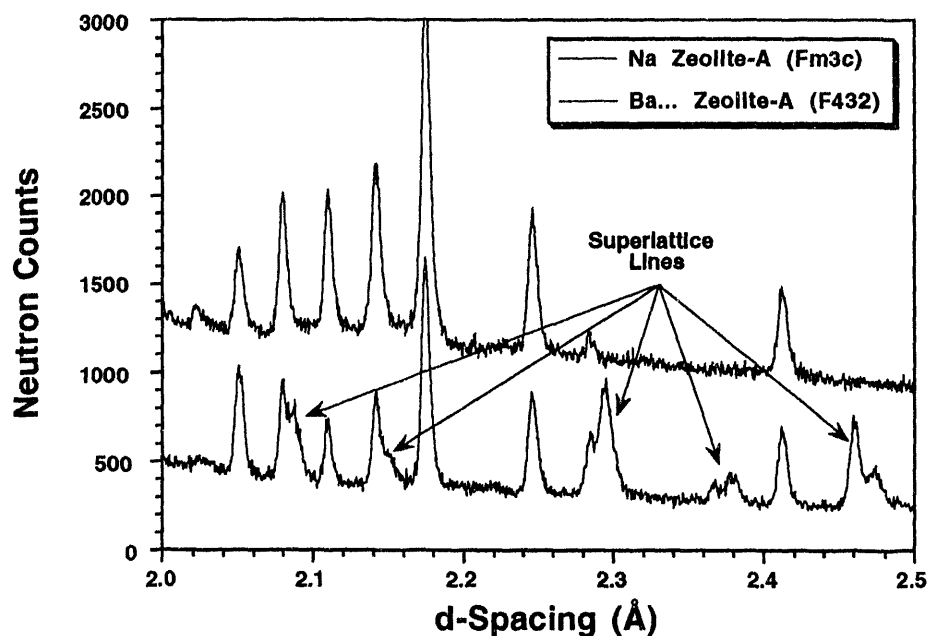


Figure 1. Comparison of small sections of the neutron diffraction patterns of Na zeolite-A and the simulated rad-waste zeolite complex.

space group is F432. This space group, a direct sub-group of Fm3c, allows differential siting of cations in neighboring α -cages.

Rietveld refinement [12], modified for time-of-flight neutron data [13], was performed to elucidate the details of the structure. It was immediately apparent that, indeed, the siting of extra-framework ions was quite different in the two crystallographically distinct cages. Based upon known parameters such as elemental scattering power and expected bond distances, and difference Fourier scattering density maps, a reasonable model for the chloride salt coordination in zeolite-A was developed.

4. RESULTS AND DISCUSSION

Neutron diffraction affords us some tremendous advantages. First, the negative scattering length of Li allows us to differentiate, for instance, between minor occupation of a heavy ion and maximal occupation of Li. Furthermore, the fact that oxygen is a strong scatterer allows us to observe the crystallographic ordering manifested in the varying degrees of puckering in opposing cages.

For the purpose of discussion, the two distinct α cages have been labeled α_1 and α_2 , and the single sodalite cage is labeled β . The predominant characteristics of the structural model are as follows: (1) Li^+ ions are strongly coordinated to all eight 6-rings of cage α_1 , (2) a complex $\text{Li}^+\text{-K}^+\text{-Cl}^-$ cluster "decorates" the α_1 cage surface, (3) 6-ring sites in the α_2 cage are alternately occupied by $\text{Ba}^{2+}/\text{Cs}^+$ and pairs of Li^+ ions, (4) Cl^- ions link the $\text{Ba}^{2+}/\text{Cs}^+$ and Li^+ ions, (5) Sr^{2+} is situated opposite a 6-ring, inside the β cage and (6) Li^+ ions are associated with 4-rings, in the β cage. Representative illustrations are given in Figure 2. In Figure 2a,

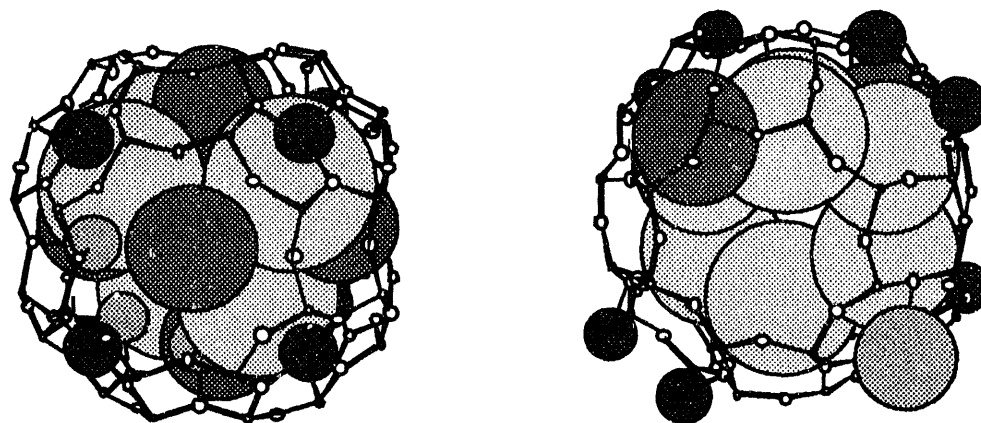


Figure 2. Illustrations of cation siting in (a) α_1 and (b) α_2 cages. Note the severe distortion of the 6-rings in α_1 .

from darkest to lightest, the large, extra-framework atoms are 8 Li⁺ in six-rings, 6 K⁺ near eight-rings, 6 Li⁺ near four-rings and 6 Cl⁻ bridging Li⁺'s and K⁺'s. Occupations are approximations from the refinements. In Figure 2b, darkest to lightest ions are Li⁺, Ba²⁺/Cs⁻, Sr²⁺ and Cl⁻.

When modelling the precise bonding structure of encapsulated atoms and molecules in zeolites, we must necessarily grapple with the realization that the local symmetry of encapsulated moieties may not obey the long-range symmetry of the zeolite. From experience [14, 15], we know that these moieties tend to adjust their shape and orientation to conform with a sub-set of the zeolite's full symmetry. For example, the center of the α_1 and α_2 cages in the rad-waste zeolite complex have 43 point symmetry. We might expect that clusters enclosed in these cages would have 3-fold or 4-fold point symmetry. As we will see, this is indeed what our data suggest.

In trying to fully detail the structure of the extra-framework atoms in the rad-waste mixture, we made extensive use of Fourier difference scattering density maps which provided starting coordinates for refineable atomic positions. Because the encapsulated materials need not obey the crystallographic symmetry, partial occupation is expected, so refinements for the extra-framework atoms included occupation factors as well as positional parameters.

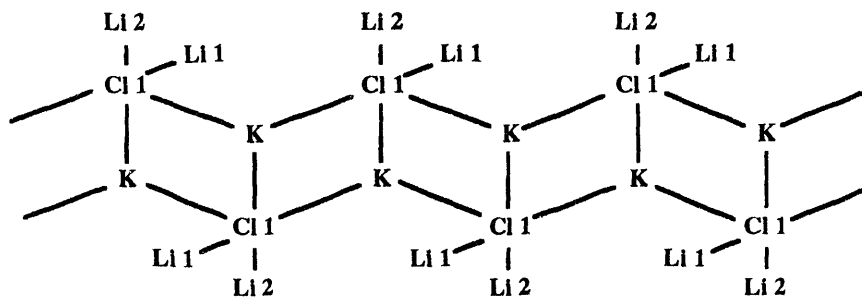


Figure 3. Idealized representation of Li⁺-K⁺-Cl⁻ cluster "decorating" the α_1 cage surface if all atoms were on high symmetry sites and attached to the framework. Rietveld refinement shows that this is not the situation. In this representation, end atoms are connected to atoms on opposing end.

α_1 -cage - The strong coordination of Li⁺ ions (labeled Li1a in figures) with 6-rings bounding the surface of this cage, illustrated in Figure 2a, does not deviate from the zeolite symmetry. Our interpretation of the remainder of the α_1 cage, however, reflects a competition between the energetic advantage of high cluster symmetry and the attraction of cations for framework oxygens. Our Rietveld refinements placed Li1a atoms on 3-fold axes in 6-rings,

Cl1a atoms near 3-fold axes, Li1b atoms on 2-fold axes near 4-rings and K atoms on 4-fold axes near 8-rings. Site occupancies suggested that all Li1a and K sites, 6 of 8 possible Cl1a sites and 4 of 12 Li1b sites are occupied. Figure 3 shows a logical arrangement of atoms which, when folded into a 3-dimensional $\text{Li}_{12}\text{K}_6\text{Cl}_6^{+12}$ cluster, roughly accounts for the observed data. This cluster has 6-bar symmetry. Although this arrangement looks good on paper, it has three major problems: (1) it requires that Cl1a atoms be on 3-fold axes which they clearly are not, (2) K-Cl distances are unreasonably long, and (3) this model precludes close association with the framework. Careful analysis of lower symmetry models which obey the constraints above led us to the model shown in Figure 4. This model represents a displacement of Li1b and Cl1a atoms and addition of 2 Cl1b atoms to accommodate proper bonding

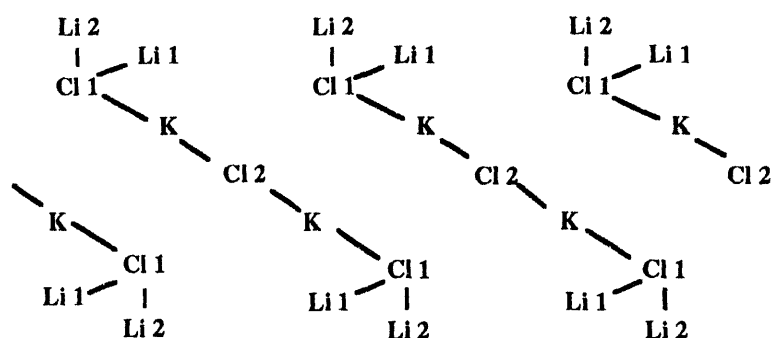


Figure 4. Model $\text{Li}^+\text{-K}^+\text{-Cl}^-$ cluster "decorating" α_1 cage, derived from Rietveld refinement results.

within the cluster and to the framework. Interatomic distances are tabulated in Table 1. Our proposed model in Figure 4, now a $\text{Li}_{12}\text{K}_6\text{Cl}_9^{+9}$ cluster, has 3-fold symmetry, as anticipated. As we will see, this ionic charge shortfall (the framework has a -12 charge per α -cage) is approximately made up by ions in the β cages. Because α_1 cages are separated from each other by α_2 cages, there is no reason to expect correlated orientations of clusters to produce long-range 3-fold (hexagonal) symmetry.

α_2 -cage - All of the large ions are collected in these cages. Scattering centers were found on 3-fold axes near 6-rings with distances to framework oxygens consistent with the average of Ba-O and Cs-O distances observed in Ba- and Cs-exchanged zeolites [6, 8]. Li^+ ions (Li2a) were found near 6-rings, not on the 3-fold axes. The severe distortion of 6-rings in the α_1 cages precludes such distortion in 6-rings of α_2 , forcing Li^+ ions to maximize their coordination by linking to 2 framework oxygens off center of the 3-fold axes. Site occupations suggest

Table 1

Representative bonding distances calculated from refined crystallographic model compared to values found in the literature for similar circumstances

Distances				
Atoms	Literature		Refined	Deviation
Li - O	1.97 Å [15]	Li1a - O	1.98(1) Å	0.01 Å
		Li1b - O	2.23(3)	0.26
		Li2a - O	1.98(5), 2.01(4)	0.01, 0.04
		Li3 - O	2.01(3), 2.08(1)	0.04, 0.11
Sr - O	2.46 [5]	Sr1b - O	2.78(1)	0.32
Ba - O	2.62 [6]	Ba,Cs - O	2.81(1)	0.00
Cs - O	2.99 [8]			
	Avg. 2.81			
Li - Cl	2.40 [16]	Li1a - Cl1a	2.49(2)	0.09
		Li1b - Cl1a	2.51(4)	0.11
K - Cl	3.18 [16]	K - Cl1a	3.25(2)	0.07
		K - Cl1b	3.17(1)	-0.01
Sr - Cl	2.99 [16]	Sr - Cl3	2.70(2)	-0.29
Ba - Cl	3.16 [16]	Ba,Cs - Cl2a	3.42(3)	-0.06
Cs - Cl	3.48 [16]			
	Avg. 3.32			

that 4 of 8 possible Ba²⁺/Cs⁺ and 8 of 12 Li⁺ sites are occupied. For this we postulate a 4-bar symmetric arrangement where Ba²⁺/Cs⁺ sites alternate with Li⁺. Chlorine atoms were found in sites which link cations. Interatomic distances, given in Table 1, indicate that Cl2a atoms are associated with Cs⁺ and that Cl2b atoms with Ba²⁺.

β-cages - The sodalite units of the rad-waste mixture have 23 local symmetry. Li⁺ ions (Li3) were found on 2-fold axes near 4-rings, atoms identified as Sr²⁺ were found roughly in the middle of α₂ 6-rings, and Cl⁻ ions (Cl3) were found in the center of the β-cage. Site occupations suggest that 2-3 of 12 Li⁺, 1-2 of 8 Sr²⁺, and 1-2 of 2 Cl⁻ sites are occupied. Li-O distances are as expected. Calculated Sr-O distances are longer and Sr-Cl distances shorter than found in the literature [16, 17], consistent with a suspicion that Sr²⁺ ions are actually slightly off the 3-fold axes.

5. CONCLUSIONS

Our interpretation of the intra-framework structure of this simulated rad-waste zeolite mixture is exceptionally detailed. Absolute details remain somewhat in doubt, but the refinements are quite stable and the analysis of models exhaustive. It is clear to the authors that this system is very favorable for the assembly of stable, highly symmetric complexes.

The discovery that strong segregation of fission product cations persists in radioactive-waste zeolite matrices may have far-reaching implications for the use of zeolites as nuclear waste storage media. Li^+ and K^+ may be viewed as pacifying ingredients which are preferentially intimately associated with the more toxic fission products. Further investigations with different mixtures may provide mechanisms for manipulating this cation association.

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