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RELATING STRUCTURAL PARAMETERS TO LEACHABILITY IN A GLASS-BONDED CERAMIC WASTE FORM

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ABSTRACT

Lattice parameters for a crystalline material can be obtained by several methods, notably by analyzing x-ray powder diffraction patterns. By utilizing a computer program to fit a pattern, one can follow the evolution or subtle changes in a structure of a crystalline species in different environments. This work involves such a study for an essential component of the ceramic waste form that is under development at Argonne National Laboratory. Zeolite 4A and zeolite 5A are used to produce two different types of waste forms: a glass-bonded sodalite and a glass-bonded zeolite, respectively. Changes in structure during production of the waste forms are discussed. Specific salt-loadings in the sodalite waste form are related to relative peak intensities of certain reflections in the XRD patterns. Structural parameters for the final waste forms will also be given and related to leachability under standard conditions.

INTRODUCTION

Argonne National Laboratory is developing an electrometallurgical process for the treatment of metallic spent nuclear fuel to condition the material for disposal in a geologic repository. In this process, the spent fuel elements are lowered in a steel basket into a molten salt electrolyte and anodically dissolved from the cladding. Pure uranium is deposited on steel cathodes while the transuranic elements and fission products remain in the salt or with the cladding hulls. The transuranic elements and active fission products are left in the salt to be incorporated into a ceramic waste form. A metal waste form incorporates the fission products that are "noble" to the process and remain in the hull.

PRODUCTION OF THE CERAMIC WASTE FORM

The ceramic waste forms being studied incorporate a eutectic salt that contains surrogate fission products. Table I gives the general composition of the salt. The surrogate fission products are in these forms: KBr, RbCl, $SrCl_2$, YCl_3, KI, CsCl, $BaCl_2$, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, and $EuCl_3$. The surrogate fission products were not included in the structural model for lattice parameter determinations and computer simulations of XRD patterns. This assumption is justified because the elements Li, K, Na, and Cl account for 94.8 wt. % or 98.8 at. % of the salt.

Table I. Composition of salt

Compound	Wt. %
LiCl-KCl	85.4
NaCl	6.1
Surrogate fission products	8.5

Results are presented for two candidate waste forms: a glass-bonded zeolite and a glass-bonded sodalite. To produce the zeolite waste form, zeolite 5A, $Na48Ca_{24}Al96Si96O384$, is first dried until the water content is less than 0.5 wt. %. The zeolite powder is next hot mixed with the salt to obtain a salt loading of 60 Cl^- per unit cell (uc), or 21 wt. %. The blended zeolite is then mixed with glass in a 50:50 weight ratio and processed in a hot isostatic press (HIP) at about 823K and 155 MPa.[1] In the sodalite waste form, dried zeolite 4A is blended with salt to obtain three different salt-loadings: 25.6, 28.0, and 30.4 Cl^-/uc (approximately 10.5 wt. %). The zeolite and glass were then mixed so that the weight ratio of zeolite to glass is 75:25. This mixture was hot isostatic pressed (HIPed) at 1123K and 170 MPa.[1] Due to more aggressive processing conditions, the zeolite 4A transforms in-situ to sodalite. Each zeolite unit cell forms 16 sodalite unit cells so that the salt loadings for the sodalite unit cells are 1.6, 1.75, and 1.9 Cl^-/uc.

EXPERIMENTAL

X-ray diffraction patterns were obtained with a Scintag X1 diffractometer (Cupertino, CA), which utilizes Cu-K_α radiation and has a theta-theta goniometer configuration. Samples of the final waste forms were run with LaB_6 (NIST SRM 660) as an internal standard to check peak positions and profiles during structural refinement. Initial pattern matching routines were run using the Diffraction Management System Software by Scintag, Inc. Structure determination and refinement of lattice parameters were done using the General Structure Analysis sodalite waste forms with 1.6 Cl^-/uc of 1.75 Cl^-/uc, there may be a trace of halite but the evidence is inconclusive. The XRD patterns demonstrating this are shown in Figure 3. Nepheline, $NaAlSiO_4$, is also observed as a minor phase. The sodalite phase is described by the space group P43n, and the sodalite waste form with a salt-loading of 1.6 Cl^-/uc has a lattice parameter of 8.838 Å.

Different salt-loadings in the sodalite also affect the relative peak intensities in the XRD patterns. The values of relative peak intensities depend on atomic positioning and occupancy. Increased salt content in the sodalite unit cell reduces the intensity of the 100 reflection (I_{100}) relative to the intensity of the 211 reflection (I_{211}). Table II gives ratios for the peak intensities of these reflections for observed and computer-simulated patterns. The ratios for the computer-simulated pattern correspond very closely with those of the observed XRD patterns.

Table II. I_{100}/ I_{211} in the sodalite waste form.

XRD pattern	Salt-loading (Cl^- /uc)		
	1.6	1.75	1.9
Observed	0.55	0.49	0.44
Computer simulation	0.55	0.49	0.43

RESULTS OF LEACH TESTS

The waste forms were studied to establish a relationship between structure and behavior during leach tests under standard conditions. Table III lists normalized release rates of elements for the 28-day PCT. Rates are normalized for mass fraction. The zeolite waste form preferentially leached alkali cations and chloride ions. The normalized release rates of the sodalite waste form (1.6 Cl^-/uc) give evidence for congruent dissolution although the Li and K do not follow this proposed model.

A summary of the water content measurements for the zeolite waste form and the sodalite waste form (1.6 Cl^-/uc) is given in Table IV. The waste forms were prepared with material that had a water content of less than 0.5 wt. %. The zeolite waste form, upon sitting out in air has increased to 2.4 wt. %, and the leach test, not surprisingly, increases the water content even more. However, the water content of the sodalite waste form remains below 0.5 wt. %, even after a 28-day PCT.

Table III. Normalized release rates from 28-day PCT given in $g/m^2 \cdot d$

Element	Zeolite waste form	Sodalite waste form
Li	4.16E-01	1.34E-02
Na	4.38E-01	2.88E-03
K	3.90E-01	2.81E-06
Rb	4.20E-01	N/A
Cs	7.72E-02	1.14E-03
Ca	6.71E-03	N/A
B	1.18E-02	6.29E-03
Al	1.14E-03	2.89E-03
Si	4.33E-04	2.82E-03
Cl	8.28E-01	4.17E-03

Table IV. Water content in ceramic waste forms

Sample	Exposure	Water content (wt. %)
Zeolite waste form	Air	2.4
Zeolite waste form	28-day PCT	5.1
Sodalite waste form	Air	0.01
Sodalite waste form	28-day PCT	0.40

CONCLUSION

Salt-occlusion contracts the zeolite and sodalite unit cells. In the sodalite waste form, the change in salt-loading for a range of 1.6 Cl^-/uc to 1.9 Cl^-/uc is more evident in changes in relative peak intensities than in the lattice parameter. This was shown specifically for the 100 and 211 reflections of the sodalite waste form. Computer simulations of the salt-loadings were in good agreement with the observed data.

The performance of the waste forms has been given in terms of normalized release rates of important constituents. The degrees of hydration of the waste forms differ dramatically and will be the subject of further research. The sodalite waste form has a better retention of salt. The lower hydration in the sodalite waste form also suggests that the migration of water into the sodalite waste form is slower. This may be partly due to the smaller apertures in the framework of the sodalite, which are dependent upon the lattice parameter space group of the sodalite unit cell.

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Product consistency tests (PCT-B) were also performed according to ASTM C1285-94.[3] The samples were first crushed and sieved to obtain particle sizes between 75-150 μm. Then they were placed in deionized water at 90°C. The surface area-to-volume ratios were 2340 m^{-1} for the zeolite waste form and 2240 m^{-1} for the sodalite waste form. For the sodalite waste form with 1.6 Cl^-/uc and the zeolite waste form, tests were performed for a duration of 7, 14, and 28 days.

Upon completion of the PCT, several analyses were performed. Chloride concentrations and pH were measured with ion specific electrodes. Other elemental concentrations in the leachate were determined with inductively coupled plasma-atomic emission spectroscopy and atomic absorption spectroscopy. Water content of samples before and after the PCT was determined using the coulometric Karl-Fischer method.

STRUCTURE OF A CERAMIC WASTE FORM

XRD patterns illustrating the evolution of a zeolite waste form are shown in Figure 1. Dried zeolite 5A, in which Ca is exchanged for Na, has a cubic structure described by the space group Fm3c. During salt occlusion, the unit cell contracts, as evident by the shift in peak positions toward higher two-theta. In addition to reflections of the Fm3c space group, superlattice reflections for the space group F432 may be present and some examples are given in Figure 1. These space groups are in agreement with those found by Richardson.[4] The superlattice reflections become more distinct in the HIPed zeolite waste form, which may be described by space groups F432 and Fm3c with a lattice parameter of 24.32(5) Å.

In the HIPed product, minor phases of halite and microsommite are present. The halite phase may result from the ejection of some salt from the zeolite cages after processing in the HIP, and the microsommite may result from some phase transformation of zeolite. The peak positions of HIPed zeolite waste form appear slightly shifted from those of the salt-occluded zeolite 5A toward lower two-theta, which may be due to ejection of salt. Removal of salt would cause an expansion of the unit cell.

An illustration of the transformation to sodalite is given in Figure 2. Dried zeolite 4A, which contains only Na counter-ions, may be described with the space group Fm3c. The salt-loaded zeolite 4A also appears to show superlattice reflections of F432; an example of such a reflection is indicated in Figure 2. Richardson also determined that salt-occluded zeolite 5A may be described by the space groups of F432 and Fm3c.[4] A halite phase is observed after the HIP process for the sodalite waste form with a salt loading of 1.9 Cl^-/uc. In the

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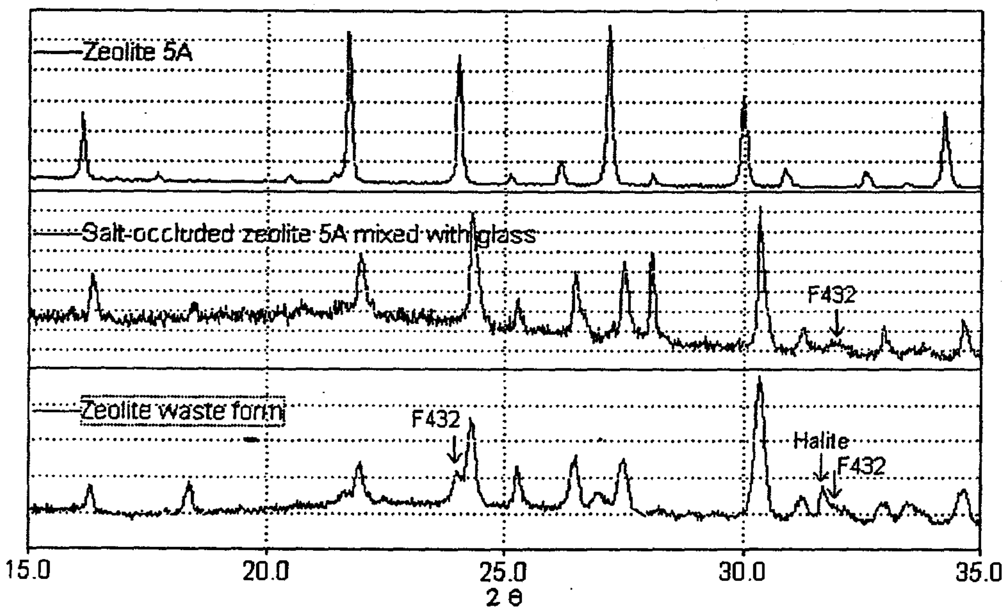

Figure 1. Evolution of a zeolite waste form.

Figure 2. Transformation to a sodalite waste form.

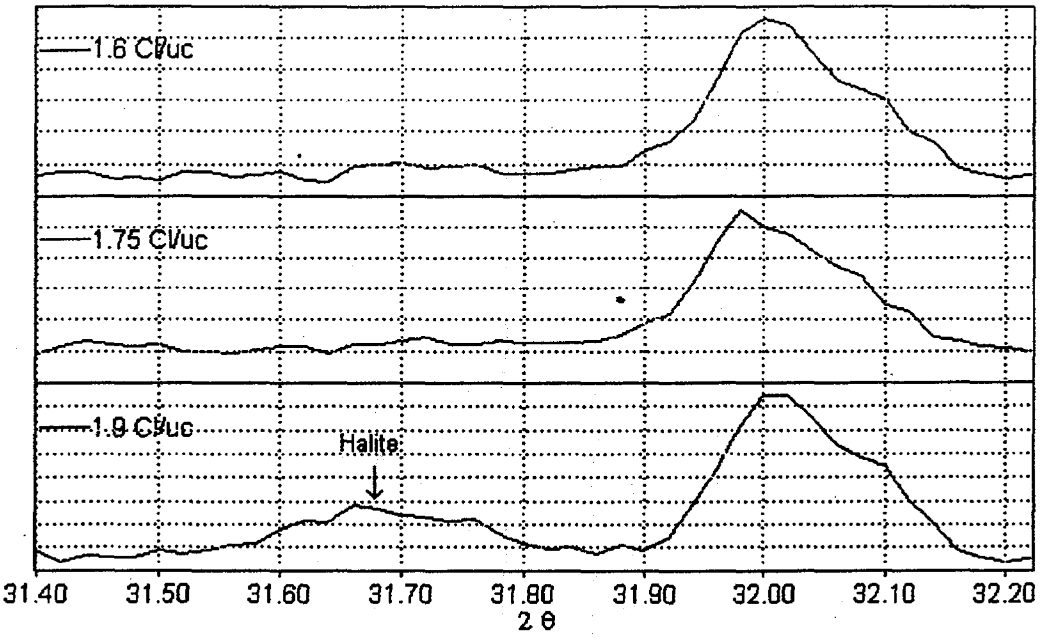

Figure 3. Halite presence in sodalite waste form with different salt loadings.