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PRODUCTION OF SODALITE WASTE FORMS BY ADDITION OF GLASS

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Spent nuclear fuel can be treated in a molten salt electrorefiner for conversion into metal and mineral waste forms for geologic disposal. Sodalite is one of the mineral waste forms under study. Fission products in the molten salt are ion-exchanged into zeolite A, which is converted to sodalite and consolidated. Sodalite can be formed directly from mixtures of salt and zeolite A at temperatures above 975 K; however, nepheline is usually produced as a secondary phase. Addition of small amounts of glass frit to the mixture reduced nepheline formation significantly. Loss of fission products was not observed for reaction below 1000 K. Hot-pressing of the sodalite powders yielded dense pellets (~2.3 g/cm^3) without any loss of fission product species. Normalized release rates were below 1 g/m^2-day for pre-washed samples in 28-day leach tests based on standard MCC-1 tests but increased with the presence of free salt on the sodalite.

INTRODUCTION

In the electrorefining of spent nuclear fuel, rare earth and active metal fission products are retained in a molten chloride salt.[1] The salt is processed by direct ion exchange with a column of zeolite A. The fission products are retained by the zeolite, and the clean salt is recycled. After ion exchange chloride ions are also retained within the cages of the zeolite A and must be incorporated into the waste form. In one of the two mineral waste forms currently under study, this zeolite is combined with a glass and hot pressed to form a solid monolith. In the second waste form scheme, the salt-loaded zeolite is converted to sodalite and consolidated by hot pressing.

Sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) is one of the few natural minerals that contains insoluble chloride. This characteristic indicates that this mineral has potential for good leach resistance for chloride. Because of its compact structure (pore diameters are < 2.5 Å) ion exchange in sodalite is limited to small ions and is slow.[2] Conversion of mixtures of zeolite A and halide salts to sodalite at elevated temperatures has been reported.[3] Sodalite can be synthesized from mixtures of zeolite A and salt, it may be synthesized directly from the ion exchange column packing, with appropriate pre-treatment of the zeolite to adjust the chloride content. The Si:Al ratio of natural sodalite is similar to that of zeolite A, and both structures are based on an arrangement of truncated octahedral units commonly called "beta" or "sodalite" cages.[4] The more compact cage structure of sodalite, compared to zeolite A, reduces the chloride capacity by a third.

Because of its potential in retaining chloride and other potential advantages over the alternative waste form, glass-bonded zeolite A, sodalite was examined as a possible mineral waste form for the electrorefining of spent nuclear fuel. Manufacture of sodalite is currently achieved routinely from mixtures of simulated waste salts and zeolite A. However, the retention

of salt in the final product is highly dependent on the purity of the sodalite. Secondary phases, such as nepheline, result in production of free chloride. The results discussed here indicate that a phase-pure sodalite product, that apparently is necessary for chloride retention in the mineral waste form, can be synthesized readily when a small amount of glass frit is added to the mixture. Composition and synthesis conditions are possible over a relatively wide range. Leach resistance, product density, and fission product loading all indicate that sodalite is a viable potential waste form for molten salt streams containing fission products.

EXPERIMENTAL

Sources

Sodalite powders were synthesized from mixtures of ground zeolite A pellets or powders, chloride salts, and glass frit. Commercial grade zeolite 4A ($Na_{12}Al_{12}Si_{12}O_{48}$) powders were obtained from UOP Corp. Clay-bound pellets, 1/16" and 1/8", were obtained from Union Carbide and Johnson Matthey, respectively. The zeolites were dehydrated to 625-725 K in a nitrogen gas flow, and transferred directly to an inert atmosphere facility.

The mixed chloride salts had compositions similar to those expected for the salt waste stream coming from the electrorefining process; a typical composition is given in Table 1. The LiCl and KCl were obtained at the eutectic composition (~42 wt % LiCl, melting point, ~635 K) from Lithcoa Co. The remaining salts were of high purity, 99.99 % or greater, and ultra-dry. They were purchased from APL Engineered Materials. All components were used as-received without further pre-treatment. None of the salt components was radioactive. To make up the mixed salt simulating the waste stream, the salts were physically mixed, melted, filtered, and coarsely ground. In some cases, the eutectic salt was used as the chloride source without additives. The glasses were obtained from Miles Laboratories in powder form.

Table I. Typical Salt Composition Used in Sodalite Synthesis

Salt	Mole %
KI	0.11
$NdCl_3$	0.25
$LaCl_3$	0.26
$CeCl_3$	0.18
YCl_3	0.04
$SrCl_2$	0.22
$BaCl_2$	0.41
LiCl	55.15
KCl	35.96
CsCl	1.32
NaCl	6.10

Zeolite A was loaded with salt by one of two methods. In the first, the zeolite was physically mixed with the salt at the desired final chloride concentration, 4-8 wt % chloride. In the second method, the zeolite was pre-loaded with LiCl-KCl eutectic salt by contacting the dehydrated zeolite, either pellets or powders, with a large amount of the molten salt. Residual free salt was removed by application of argon pressure at 700 K. The salt-loaded zeolite was subsequently contacted with a large amount of molten simulated waste salt in a batch process. A salt:zeolite mass ratio of 4.5 was used in the two contact steps. Application of argon was again used to remove residual free salt. The latter method resulted in samples with higher fission

product loadings than the former because the fission product concentration was increased by ion exchange between the zeolite and the waste salt. In all cases the zeolite is in contact with the salt at 700 K for a minimum of 24 hours under an inert atmosphere.

Sodalite Synthesis: Fully salt-loaded zeolite A contains approximately 28 wt % chloride salt by weight, in addition to the residual free salt located on the surface. Even after application of argon gas pressure, the free salt on the crystal surfaces may make up as much as 50 wt % of the salt-zeolite mixture. Sodalite, fully loaded, can accommodate only 12 wt % chloride. For non-aqueous conversion to sodalite, the salt content of the zeolite was reduced by adding fresh dehydrated zeolite 4A to the salt-loaded zeolite. Next, dehydrated glass frit equivalent to 3 to 10 wt % of the zeolite and salt mixture was added. This mixture was placed in an alumina crucible and heated to 1000 K in an inert atmosphere box. This heating step was carried out in air for some samples. When the sodalite was prepared from a mixture of zeolite A, salt, and glass, the mixture was simply heated without any pre-treatment.

Hot pressing: Sodalite powders were uniaxially hot pressed into solid monolithic pellets. In several cases, the powders were washed prior to pressing to remove residual free salt. From 2 to 4 g of sodalite powder was loaded into a graphite die having a 1-in. (2.54 cm) diameter bore. The powder was then cold pressed to 30 MPa prior to hot pressing. The hot pressing was conducted with the sample under a nitrogen atmosphere. The sample was first heated rapidly to 675 K. At this temperature, a mechanical pressure of 28 MPa was applied to the powder sample. The temperature was then increased at 20 K/min to the final temperature and maintained for up to 30 min before the cooling cycle was initiated.

Leach testing: Pelletized samples were tested to determine their ability to retain fission product cations and chloride. These tests were all conducted with deionized water in Teflon vessels at 363 K for 28-day periods. A leachant volume to surface area ratio of 10 mL/cm^2 was used. The Normalized Release rate (NRR) was calculated using the formula:

$$NRR = c_i V / f_i A d$$

where c_i is the concentration of the ion in leachant (g/mL), V is the volume of leachant (mL), A is the surface area of the solid (m^2), f_i is the fraction of the ion in the solid, and d is the experiment length in days. Pellets were tested for 28 days.

RESULTS

Synthesis

Phase-pure sodalite was consistently synthesized from mixtures of zeolite A, glass frit, and mixed chloride salts having compositions similar to those generated in the electrorefining of spent nuclear fuel. Sodalite was successfully synthesized both in air and under an argon atmosphere. The X-ray diffraction patterns were consistent with published data for mineral sodalite.[5] The synthesized sodalite showed a shift in the diffraction peaks to smaller d-spacings, consistent with a shrinkage of the unit cell caused by incorporation of lithium into the structure. The major sodalite peak at d=3.62 was generally shifted to 3.56 ± 0.04. The peak at d=2.09 was shifted to 2.05 ± 0.02. The other peaks showed similar behavior. These shifts correspond to a sodalite unit cell size parameter of 8.9 ± 0.2 Å.

Because sodalite fully accommodates, at most, only 1/3 as much halide as zeolite A, much of the salt occluded within the zeolite A structure during ion exchange and all of the free

salt on the crystal surfaces had to be removed. The chloride content was reduced to between 1 and 2 atoms per sodalite unit cell. Conversion of salt-occluded zeolite A to sodalite did not require extensive mixing or preheating to redistribute the salt in the zeolite. A rapid heat-up of the zeolite was apparently sufficient to distribute the salt.

For the salt compositions used in the synthesis, the formation of sodalite does not appear to be affected by the fission product content. Elemental analysis indicated no changes in composition with conversion of the salt-loaded zeolite to sodalite at 1000 K. Complete volatilization of cesium (perhaps as CsCl) was observed at 1150 K.

Heating of mixtures of zeolite A and salt without addition of the glass produced inconsistent synthesis results. Though sodalite was usually the predominant product, secondary nepheline phases and salt features were typically observed in the diffraction patterns. In many cases, nepheline and salt were predominant. The nepheline X-ray diffraction peak intensities appeared to follow those of the chlorides when both were present, indicating a correspondence.

Consolidation

When sodalite samples were uniaxially hot pressed, the white powders were transformed into gray-black solid pellets. The resulting samples were hard and polishable, but brittle. Densities between 2.1 and 2.4 g/cm^3, near the theoretical value for sodalite of 2.31 g/cm^3,[6] were obtained routinely. The sodalite diffraction patterns were unchanged by hot pressing. Chemical analysis of the sodalite powders showed compositions similar to the resulting pellets, as in shown Table II.

Table II: Composition of Powder and Pellet Samples*

	Al	Li	K	Na	Sr	Ba	Cs	Nd
Powd1	14.4	0.84	3.62	12.4	0.81	0.16	0.31	0.08
Pellet1	14.9	0.89	3.52	12.3	0.64	0.16	0.33	0.08
Powd2	15.5	0.68	2.46	13.1	0.47	0.13	0.19	0.07
Pellet2	15.9	0.69	2.48	12.3	0.48	0.15	0.18	0.08
Powd3	15.3	0.71	2.59	14.7	0.04	0.12	0.27	0.09
Pellet3	15.1	0.63	2.48	13.6	0.05	0.12	0.31	0.07

* Analysis by inductively-coupled plasma/atomic emission spectroscopy; cesium by flame emission.

Normalized Release Rates

The need for phase-pure sodalite is shown by a comparison of 7-day leach tests for a hot-pressed sodalite pellet (synthesized without addition of a glass) and a similar hot-pressed pellet that reacted to nepheline. A large reduction in release rates was observed when secondary phases and the associated free salt were minimized. In Table III, the normalized release rates for the nepheline sample are much greater for all elements that are exchangable. The mass loss observed for the nepheline pellet after the 7-day test is an order of magnitude greater than for sodalite. This is likely associated with loss of salt, because the framework species, Al and Si, are released to a lesser extent in the nepheline sample. Simple water washing showed loss of 35 to 50 % of the chloride from the nepheline sample and 5 to 10 % loss from the sodalite.

Table III: 7-Day Leach Test* Results for Sodalite and Nepheline Samples

Element	Sodalite	Nepheline
Cs	1.2	132
Ba	<0.01	25
Na	0.4	6
K	1.6	9.4
Sr	0.01	3.3
Li	2.3	6.7
Al	0.8	0.3
Si	0.7	0.04
% Mass Loss	0.1	1.1

*7-day tests in deionized water at 363 K.

Average normalized release rates (NRRs) are given below in Table IV for 28-day tests in deionized water at 363 K. Samples that were washed with deionized water prior to hot pressing to remove any residual free salt generally had release rates below the 1 g/(m^2·day) developmental goal. The samples that were not washed, however, all show very high release rates for chloride, the alkali metals, and strontium. These high release rates may therefore be directly attributed to dissolution of residual free salt. The strontium release rates are higher than those seen in tests conducted with samples in which glass was not added to the powders prior to synthesis. The high strontium values may be partially attributed to the presence of strontium in the glass frit.

Table IV: Average Normalized Release Rates

	Washed		Unwashed	
	NRR*	S.D.†	NRR*	S.D.
Cl	0.17	0.08	13	11
Al	0.22	0.03	0.21	0.07
Si	0.2	0.03	0.17	0.03
Na	0.24	0.09	1	1
Li	0.5	0.3	6	4
K	0.7	0.4	27	5
Ba	0.2	0.1	-	-
Sr	0.6	0.3	5.4	0.7
Cs	1.0	0.9	18	12

*Units of g/(m^2·day) †Standard Deviation

DISCUSSION

Sodalite Synthesis

Sodalite can be synthesized by a solid-state reaction directly from mixtures having zeolite A and chloride salts of compositions expected from the electrorefining of spent nuclear fuel. Because zeolite A is used as the ion exchanger in removing the fission products from salt, this method offers a promising alternative to glass-bonded zeolite without adding significantly more steps to the process.

The one clear advantage of sodalite over glass-bonded zeolite A is greater thermal stability. Sodalite is thermally stable to at least 1150 K, and this greater thermal stability allows

higher loadings of heat-producing fission products. It is also possible to consolidate sodalite without addition of large quantities of glass to act as a binder, which increase the waste form volume. For zeolite A, a binder is necessary because a lower temperature is used in the hot pressing step.[7]

A disadvantage is that for ion exchange with zeolite A in molten salt systems, the anions occluded within the zeolite structure are located primarily in the alpha cages of zeolite A.[8] In the molten chloride system, the zeolite can occlude between 10 and 12 Cl per unit cell.[9] In the more compact sodalite structure, alpha cages are absent, and all of the chloride, as well as the cations, must reside in beta cages. In fully loaded sodalite, one chloride is present in each beta cage, effectively reducing the chloride capacity by two thirds.[10] It appears that most of the salt occluded in the zeolite A is retained within the beta cages on conversion of salt-loaded zeolite A to sodalite.

The sodalite that was synthesized with LiCl-KCl-based salts was highly crystalline and structurally identical to the mineral sodalite. However, shifts in the diffraction peaks indicate a smaller unit cell size, apparently due to occupation by lithium of sites normally occupied by sodium. A sample of mineral sodalite, $Na_{7.5}Al_6Si_6O_{24}Cl_{1.5}$, which was heated in a molten mixed chloride salt, showed a nearly identical shrinkage in the unit cell volume to that observed for sodalite that was synthesized from zeolite A and salt. Elemental analysis showed partial exchange of sodium for lithium.

Sodalite formation may have been enhanced by addition of dehydrated zeolite A in the sodium form, 4A, to the salt loaded zeolite to reduce overall lithium concentration. Addition of dehydrated zeolite A in the lithium form resulted in partial or complete reaction to $LiAlSiO_4$ rather than sodalite. If the salt concentration was not diluted by addition of dehydrated zeolite, reaction to $LiAlSiO_4$ was again observed. It appears that reducing the lithium content of the zeolite is desirable for sodalite formation. When the additional dehydrated zeolite is in the potassium or calcium exchanged forms (3A and 5A respectively), sodalite was also produced.

Sodalite Performance

The sodalite materials synthesized thus far do not show leach resistance consistently below 1 g/(m^2·day). The two elements showing the highest release rates were Li and Cs. The release rates for these two elements tended to be inversely related. Samples that showed good retention of cesium tended to lose lithium, while those that retained cesium tended to lose lithium. This may indicate a relationship between the sites occupied by the two cations within the sodalite structure, even though lithium is present in much greater quantity than cesium.

The consolidated samples had gross densities approaching the theoretical maximum for the mineral sodalite. Hot pressing of powders is a viable method for consolidating sodalite into a monolithic waste form. The pellets were hard but brittle. Large cracks were observed on the surface of the pellets with a light microscope. This brittleness was not quantified, but it may be possible to improve toughness by introducing a binder, perhaps additional glass, into the mixture. A binder should also reduce the cracking of the pellet surfaces.

Residual free salt appears to be a major problem for use of sodalite as a waste form. It may be possible to thoroughly distribute the salt evenly throughout the zeolite at a concentration somewhat below 4 Cl per unit cell (2 Cl per unit cell of sodalite), but the time required may preclude use of such a mixing step in an actual high throughput operation. In addition, an examination of the relationship between the chloride concentration and the free salt content in the powders showed no direct correlation. Pre-heating the zeolite to 775 K to distribute the salt more evenly throughout the zeolite powder prior to conversion to sodalite at 1000 K did not reduce the amount of residual free salt in the sodalite product. A method for reducing the amount of residual free salt must be developed if the performance of sodalite as a waste form is to be improved further.

CONCLUSIONS

Because of the greater thermal stability of sodalite compared to zeolite A, conversion of zeolite A to sodalite produces a more robust waste form, though it adds extra steps to the waste form process. To gauge the ultimate effectiveness of sodalite as a waste form, sodalite with few secondary phases and minimal free salt must be synthesized consistently. It appears that addition of a small amount of glass frit to the salt-loaded zeolite A prior to heating has solved the former problem. The latter factor may continue to be the source of the relatively high normalized release rates observed in several samples. Minimization of the free salt requires study if sodalite is to be used as a mineral waste form. Sodalite continues to be a possible candidate for a mineral based waste form to retain fission products in a molten chloride salt.

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