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J. S. Luo and W. L. Ebert
Chemical Technology Division
Argonne National Laboratory

American Ceramics Society
102nd Annual Meeting & Exposition
St. Louis, MO
4/30-5/3/00

This research was sponsored by the U.S. Department of Energy, Office of Environmental Management, under Contract W-31-109-ENG-38.
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MICROSTRUCTURAL CHARACTERIZATION OF HALITE INCLUSIONS IN A GLASS-BONDED CERAMIC WASTE FORM

J.S. Luo, V.N. Zyryanov, and W. L. Ebert
Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

A glass-bonded ceramic waste form is being developed to immobilize radioactively contaminated chloride waste salts generated during the conditioning of spent sodium-bonded nuclear fuel for disposal. The waste salt is first mixed with zeolite A to occlude the salt into cavities in the zeolite structure. The salt-loaded zeolite is then mixed with a borosilicate glass and consolidated by hot isostatic pressing. During this process, the zeolite converts to the mineral sodalite, which retains most of the waste salt, and small amounts of halite are generated. Halite inclusions have been observed within micron- to submicron-sized pores that form within the glass phase in the vicinity of the sodalite/glass interface. These inclusions are important because they may contain small amounts of radionuclide contaminants (e.g., $^{133}$Cs and $^{129}$I), and may affect the corrosion behavior of the waste form. Optical microscopy, scanning electron microscopy, and transmission electron microscopy were used to characterize the chemical nature and distribution of halite inclusions in the waste form.

INTRODUCTION

A glass-bonded ceramic waste form is being developed at Argonne National Laboratory (ANL) to immobilize high-level radioactive waste salts generated during the electrorefining of spent sodium-bonded nuclear fuel for disposal. The waste salt consists of potassium chloride/lithium chloride eutectic that becomes contaminated with actinides and fission products during electrorefining. This salt is blended with dehydrated zeolite to incorporate the salt into the zeolite cage structure. The salt-loaded zeolite is then mechanically mixed with a borosilicate glass and fused to produce the glass-bonded ceramic waste form. During this process, the zeolite converts to the mineral sodalite, and small amounts of nepheline and halite are generated. These phases are bound by the glass into a physically and chemically robust waste form. The formation of halite in the waste form is important because it likely contains small amounts of radionuclides, such as $^{133}$Cs and $^{129}$I. In this paper, we report the results of a detailed microstructural characterization of the halite inclusions that formed in a waste form made with nonradioactive surrogate salt. The waste form was examined with optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The information obtained from this work will be used to interpret the results of corrosion tests and develop a model for degradation of this ceramic waste form in a repository.
EXPERIMENTAL PROCEDURES

Samples of the glass-bonded ceramic waste form were produced by first mixing the surrogate salt (which included rare earth elements as surrogates for actinides and nonradioactive isotopes of key fission products) with zeolite, then mixing the salt-loaded zeolite with glass frit at a mass ratio of about 75% salt-loaded zeolite and 25% glass, and finally hot isostatically pressing the mixture at about 850°C. The details of waste form processing have been described elsewhere. The final sample consisted of approximately 75% sodalite and 25% glass by volume. Small amounts of nepheline and halite were also detected by x-ray diffraction.

Polished thin sections (approximately 30 μm thick) of the waste form were prepared and examined with a Zeiss optical microscope using transmitted light. Scanning electron microscopy was performed on the same sample using Topcon ABT-60 and Hitachi 3000 SEMs, both were equipped with back-scatter electron detectors and Noran Vantage DI x-ray microanalysis and digital imaging systems. Samples for TEM examination were prepared by ion-milling. Analyses were performed with a JEOL 2000FX unit operating at 200 kV and equipped with an IXRF ultra-thin window energy dispersive x-ray spectrometer (EDS) and a Gatan imaging filter system.

RESULTS AND DISCUSSION

Figure 1 shows transmission optical microscope images of the glass-bonded ceramic waste form. Transmission optical microscopy allows features beneath the sample surface to be examined. Three phases were observed by optical microscopy with different contrasts: dark gray sodalite granules, white (transparent) glass phase, and dark spherical pores (Fig. 1a). A higher magnification image (Fig. 1b) reveals an array of small pores in the glass phase near the sodalite/glass interface. It was determined under transmitted light that these pores were not empty. Examination with SEM/EDS indicated that the pores contained material having the halite composition, NaCl. Other inclusions were determined to be rare earth silicates, which were generally smaller than halite inclusions.

Figure 2 is a low-magnification TEM photomicrograph of the sodalite/glass boundary in the glass-bonded ceramic sample. The sodalite granule is clearly polycrystalline, composed of micrometer-sized sodalite crystallites. Two crystalline phases were distinguished on the glass side of the sodalite/glass interface: a spherical phase with light contrast and a much smaller phase with darker contrast (see Fig. 2). Sinkler et al. has characterized the dark contrast phase with TEM and found it to be comprised of rare earth silicates, including Ce₂Ti₂(Si₂O₇)O₄, Nd₄Si₄O₁₂, and Nd₂SiO₅.

The phase with the lighter contrast was identified as halite, which was easily recognizable based on its characteristic mottled appearance (Fig. 3a). Despite the absence of faceting, the halite inclusions were, in most cases, seen to be single crystal NaCl, as determined by electron diffraction and EDS. Figure 3b shows the electron diffraction pattern obtained from a typical inclusion; the diffraction matches that of NaCl. Analysis with EDS of the same area (Fig. 3c) indicates Na and Cl to be the dominant chemical components, consistent with the identification as halite.
Fig. 1. Transmission optical images of glass-bonded ceramic sample: (a) a low magnification view of the sample and (b) magnified view of a sodalite/glass interface (shown by box in Fig. 1a).
Figure 2. Transmission electron micrograph of the sodalite/glass interface. Halite and rare earth inclusions were observed within the glass phase near the interface.

Halite inclusions with various morphologies, with sizes ranging from 0.1 μm to over 1 μm were observed. Although halite particles typically had a mottled appearance and spherical morphology, other shapes were also detected. For example, Fig. 4a shows three halite crystals within a pore, and Fig. 4b a pore only partially filled with halite. Some pores were located near rare earth silicate inclusions, and in some instances, both halite and rare earth silicates appeared to occupy the same pore (see Figs. 4c and d).

Halite that is exposed at the surface of the waste form will dissolve immediately when contacted by water. The glass and sodalite phases will also dissolve when contacted by water, but at much lower rates than halite. Analyses of water used to remove fines from crushed and monolithic samples used in corrosion tests showed there to be nearly stoichiometric concentrations of Na and Cl, as expected for the dissolution of NaCl; the Cs and I concentrations indicate that similar fractions of the total amounts of Na and Cs and of Cl and I in the waste form are present in the halite inclusions. This suggests that some of the Cs and I from the waste salt may become incorporated as contaminants in the halite as the waste form is made, although these levels are below the detection levels of EDS.

In addition to the release of radionuclides present in the halite inclusions, dissolution of halite will increase the surface area of glass exposed to water. This
Figure 3. Halite inclusion as represented by (a) TEM photomicrograph, (b) electron diffraction pattern, and (c) EDS spectrum showing predominant Na and Cl peaks.

has been observed to result in preferential dissolution of glass near the sodalite in long-term corrosion tests. Figure 5 shows an SEM photomicrograph of the surface of a monolithic glass-bonded ceramic sample after it had been immersed in tuff ground water for 364 days at 90°C and an S/V ratio of about 10 m⁻¹. Work is in progress to address the impact of preferential dissolution and the role of halite inclusions on the release behavior of radionuclides from the glass-bonded ceramic waste form.

CONCLUSIONS

We have conducted a detailed microstructural characterization of halite inclusions in glass-bonded ceramic. Crystalline halite inclusions with various morphologies and sizes ranging from less than 0.1 μm to over 1 μm were detected in the glass phase near the sodalite/glass interface. Dissolution tests indicate that the halite inclusions contain trace concentrations of Cs and I, but these elements could not be detected in direct analysis of the halite crystals. Silicates and oxides containing rare earth elements, which are used as surrogates for fission products and actinides, were often present in the vicinity of the halite inclusions. The presence of halite may affect the behavior of these other inclusions as the waste form degrades.
Figure 4. Transmission electron photomicrographs of halite and rare earth silicate inclusions: (a) three halite crystals detected in a pore (grain boundaries are indicated by white arrows), (b) a pore partially filled with halite and the presence of rare earth silicates nearby, (c) rare earth silicates present in the vicinity of halite, and (d) rare earth silicate and halite apparently co-existing in a pore.

ACKNOWLEDGMENT

The authors thank M. Hash for preparing materials for examination and testing, and L. R. Morss, M. L. Lewis, and J. Harmon for their critical reading of the manuscript and editorial assistance. The work at ANL was sponsored by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under Contract W-31-109-ENG-38.
Figure 5. Scanning electron photomicrograph of the surface of glass-bonded ceramic being reacted in EJ-13 well water at 90°C for 364 days. A thin layer of material at the sodalite/glass interface has been preferentially removed, probably due to the prior dissolution of halite inclusions in that region.

REFERENCES


