

## **Cesium and strontium incorporation into zeolite-type phases during homogeneous nucleation from caustic solutions**

**NELSON RIVERA,<sup>1,\*</sup> SUNKYUNG CHOI,<sup>2</sup> CALEB STREPKA,<sup>3</sup> KARL MUELLER,<sup>3</sup> NICOLAS PERDRIAL,<sup>4</sup> JON CHOROVER,<sup>4</sup> AND PEGGY A. O'DAY<sup>1</sup>**

<sup>1</sup>5200 North Lake Road, School of Natural Sciences, University of California, Merced, California 95343, U.S.A.

<sup>2</sup>U.S. Environmental Protection Agency, National Risk Management Research Lab, Ada, Oklahoma 74820, U.S.A.

<sup>3</sup>Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

<sup>4</sup>Department of Soil, Water and Environmental Science, University of Arizona, Tucson, Arizona 85721, U.S.A.

### **ABSTRACT**

Formation of faujasite- and sodalite/cancrinite-type phases associated with caustic waste reactions in the environment may structurally incorporate contaminant species such as radioactive Sr<sup>2+</sup> and Cs<sup>+</sup>, and thus provide a mechanism of attenuation. To investigate mineral evolution and structural incorporation of cations in simplified experiments, aluminosilicate solids were precipitated homogeneously at room temperature from batch solutions containing a 1:1 molal ratio of Si to Al and 10<sup>-3</sup> molal Sr and/or Cs, and aged for 30 or 548 days. Syntheses were done with solutions in equilibrium with atmospheric CO<sub>2</sub> and with gas-purged solutions. Experimental products were characterized by bulk chemical analyses, chemical extractions, XRD, SEM/TEM, TGA, solid-state <sup>27</sup>Al NMR, and Sr EXAFS. Chemical analysis showed that solids had a 1:1 Al:Si molar ratio, and that Sr was sequestered at higher amounts than Cs. After 30 days of aging in purged solutions, XRD showed that zeolite X (faujasite-type) was the only crystalline product. After aging 30 and 548 days in solutions equilibrated with atmospheric CO<sub>2</sub>, a mixture of sodalite, cancrinite, and minor zeolite X were produced. Surface areas of solids at 30 days were much lower than published values for zeolite phases synthesized at high temperature, although particle aging produced more crystalline and less aggregated phases with higher bulk surface areas. Characterization of products by <sup>27</sup>Al NMR indicated only tetrahedrally coordinated Al. Measured isotropic shifts of primary resonances did not change substantially with precipitate aging although the primary mineral phase changed from zeolite X to sodalite/cancrinite, indicating local ordering of Al-Si tetrahedra. Analysis of reaction products by Sr EXAFS suggested Sr bonding in hexagonal prisms and six-membered rings of the supercages of zeolite X that may be more site specific than those of monovalent cations. For samples aged for 548 days, interatomic distances from Sr-EXAFS are consistent with partial Sr dehydration and bonding to framework oxygen atoms in sodalite cages or in large channels in cancrinite. Incorporation of Sr into both faujasite and sodalite/cancrinite phases is favored over Cs during room-temperature synthesis, possibly because of increased cation site competition between Cs<sup>+</sup> and Na<sup>+</sup>. Results of this study help to constrain cation incorporation into sodalite/cancrinite mineral assemblages that form at caustic waste-impacted field sites and may aid in the predictive modeling of contaminant release.

**Keywords:** Zeolite X, sodalite, cancrinite, strontium, cesium