



## Immobilization and exchange of perrhenate in sodalite and cancrinite

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## ABSTRACT

Highly alkaline nuclear tank wastes containing key anionic contaminants have leaked into the subsurface at the U.S. Department of Energy's Hanford Site. Laboratory studies showed that when simulated caustic tank wastes contact subsurface sediments, mineral dissolution and precipitation result in feldspathoid formation. Feldspathoids are environmentally important for waste management and disposal purposes because of their purported potential to sequester contaminants of interest (e.g.,  $^{99}\text{TcO}_4^-$ ,  $^{137}\text{Cs}^+$ ,  $^{90}\text{Sr}^{2+}$ ) into their structure. We investigated the incorporation of perrhenate ( $\text{ReO}_4^-$ ), a surrogate for  $\text{TcO}_4^-$ , in the presence of competing anions (X) including  $\text{OH}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  on feldspathoid formation and under conditions mimicking tank waste solution compositions. The resulting solids were characterized by their chemical composition, structure and morphology. Regardless of solution pH, sodalite formed in the presence of  $\text{Cl}^-$  and  $\text{NO}_2^-$  whereas  $\text{NO}_3^-$  promoted either cancrinite formation in 16-mol  $\text{OH}^-/\text{kg}$  (16 m) or mixed sodalite/cancrinite phases in 1-mol  $\text{OH}^-/\text{kg}$  (1 m) solutions. In the presence of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  less than 0.02 mol fraction of  $\text{ReO}_4^-$  was incorporated into the feldspathoid phase(s). Although, the  $\text{NO}_2^-$ -sodalite and mixed  $\text{NO}_3^-$ -cancrinite/sodalite phases incorporated significantly more  $\text{ReO}_4^-$  than  $\text{NO}_3^-$ -cancrinite or  $\text{Cl}^-$ -sodalite phases, the total  $\text{ReO}_4^-$  fraction was ~1% or less of the total sites. The  $\text{ReO}_4^-$  immobilized in  $\text{ReO}_4^-$ -sodalite,  $\text{NO}_2^-$ -sodalite, mixed  $\text{NO}_3^-$ -cancrinite/sodalite and  $\text{NO}_3^-$ -cancrinite was resistant to ion exchange with either  $\text{NO}_2^-$  or  $\text{NO}_3^-$ . The results imply that  $\text{ReO}_4^-$ , and thus by analogy  $^{99}\text{TcO}_4^-$ , does not compete well with smaller ions for incorporation into feldspathoids, but, once sequestered, is difficult to exchange.

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## 1. Introduction

At the U.S. Department of Energy's Hanford site in southeastern Washington, high-level radioactive waste (HLW) containing an estimated 1900 kg of  $^{99}\text{Tc}$  has leaked into the vadose zone underneath storage tanks [1,2]. The highly variable waste is characterized as a highly alkaline ( $\text{OH}^- = \sim 0.1\text{--}5.3$  mol/L), high ionic strength solution (up to  $I = 18$  M) with a density of  $2.09$  g/cm<sup>3</sup> and temperatures greater than  $100$  °C [3,4]. The tank waste contains radionuclides of concern such as  $^{137}\text{Cs}^+$ ,  $^{90}\text{Sr}^{2+}$ ,  $^{99}\text{TcO}_4^-$ ,  $^{129}\text{I}^-$ , soluble chemical processing by-products ( $\text{Na}^+$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Ni}^+$ ), and Al- and Fe-(hydr)oxide sludges [5,6]. Given the estimated inventory of  $^{99}\text{Tc}$  in the waste – 19,730 curies (Ci), the long half life of 211,000 years and the high subsurface mobility of the pertechnetate oxyanion ( $\text{TcO}_4^-$ ), which is the dominant  $^{99}\text{Tc}$  species under oxidizing conditions,  $^{99}\text{Tc}$  migration

into the vadose zone and groundwater poses a long-term environmental risk [7,8].

Previous investigations have shown that radionuclides, metals, and anions can be incorporated into feldspathoids (e.g., sodalite, cancrinite) that form when tank leachate reacts with native Hanford sediments at elevated temperature and hyper-alkalinity [9–11]. Mattigod et al. [12,13] indicated that perrhenate ( $\text{ReO}_4^-$ ), a nonradioactive surrogate for  $^{99}\text{TcO}_4^-$ , can be incorporated into sodalite. Recent work by Pierce et al. [14] suggests that  $\text{ReO}_4^-$  and  $\text{SO}_4^{2-}$  were simultaneously incorporated into mixed-anion sodalites. A mixed  $\text{ReO}_4^-/\text{TcO}_4^-$  sodalite has been reportedly synthesized in the same laboratory [15].

The open porous framework structure of cancrinite is made of layers of six-membered rings of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra stacked along the hexagonal c-axis direction in an AB–AB sequence (Fig. 1), resulting in the formation of the small  $\epsilon$ -cages, and a large 12-ring channel along the c-axis. While the 6.0 Å-wide channels can accommodate water, large extra-framework cations and anions, the 2.5 Å  $\epsilon$ -cages only house cations or water molecules, which can easily be substituted by other cations or small molecules in

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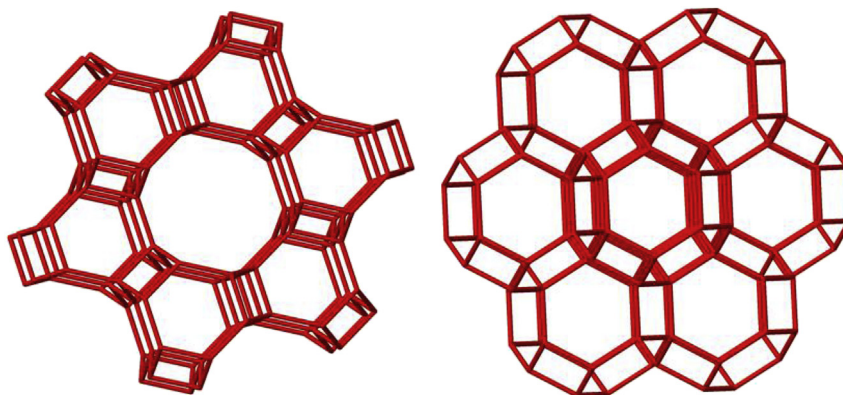


Fig. 1. The derived pore networks of cancrinite (left) and sodalite (right) [29]. For clarity cage oxygen, anions, and cations were omitted.

exchange experiments or during hydrothermal synthesis [16]. Sodalite consists of alternating  $\text{SiO}_4$  and  $\text{AlO}_4$  corner-sharing tetrahedra linked into four and six ring cages, which make up the sodalite  $\beta$ -cage (Fig. 1). These cages are  $\sim 6.5$  Å in diameter and are accessible through the 2.6 Å-wide six-membered rings that provide diffusion pathways for intra-framework ions [17]. The  $\beta$ -cage is occupied by four cations tetrahedrally associated with an anion at the center of the cage. Because of the similarity in structural framework of both feldspathoids, the characteristic XRD peaks used to distinguish cancrinite from sodalite are those of the 101 and 211 indices corresponding to d-spacings of  $\sim 4.67$  and 3.24 Å, respectively.

Although the effect of different anions on feldspathoid formation has been well studied [11,18], there is a lack of detailed information on anion selectivity in feldspathoids and the effect of this selectivity on  $\text{ReO}_4^-$  incorporation into these structures. Dickson et al. [19,20] showed that anion selectivity in mixed-anion sodalites was highly dependent on the size and, to a lesser extent, the charge of the competing anion. They reported that competitive incorporation of  $\text{ReO}_4^-$  into mixed-anion sodalites was enhanced by similarity in ionic radius and charge. There are few studies that address  $\text{ReO}_4^-$  incorporation into cancrinite, sodalite, and mixed cancrinite/sodalite phases such as those likely to form in caustic waste solutions. Thus, the objective of our study was to (1) determine the extent of  $\text{ReO}_4^-$  incorporation into sodalite and cancrinite, including a mixed phase and (2) determine the exchangeability of  $\text{ReO}_4^-$  with other anions from both minerals. We hypothesize that  $\text{ReO}_4^-$  incorporation will depend on the type of mineral(s) formed. We further hypothesize that the sequestered  $\text{ReO}_4^-$  will not appreciably exchange with other anions in an aqueous suspension.

## 2. Experimental methods

### 2.1. Mineral synthesis

Feldspathoids (sodalite and cancrinite) were synthesized in the laboratory according to procedures outlined by Deng et al. [10] by mixing solutions of NaOH (1 mol/kg or 16 mol/kg), 0.5 M  $\text{NaAlO}_2$ , 0.175 M  $\text{Na}_2\text{SiO}_3$ , 0.5 M NaCl, 0.5 M  $\text{NaNO}_2$  and 0.5 M  $\text{NaNO}_3$  with varying concentrations of  $\text{NaReO}_4$  (0.1 M or 0.5 M) in a 60-mL Teflon digestion bomb. The concentrations were based on concentrations reported for Hanford tank wastes and sediments [11,21,22]. All chemical reagents were used as received. The bombs were capped, agitated and heated at 80 °C in an oven for 4–16 weeks. The precipitates were washed three times with deionized water ( $0.054 \times 10^{-3}$  dSm $^{-1}$ ) by centrifugation at 17,000 rcf. The solids were dried at 70 °C for 24 h, weighed and subsamples dialyzed

against deionized water ( $0.054 \times 10^{-3}$  dSm $^{-1}$ ) until the electrolytic conductivity was  $\leq 0.01$  dSm $^{-1}$ . The solids were digested in 3% nitric acid and the  $\text{ReO}_4^-$  contents were measured by inductively coupled plasma mass spectrometry (Agilent 7700 ICP-MS, Santa Clara, CA). A summary of the synthesis condition is shown in Table 1.

### 2.2. Perrhenate exchange with $\text{NO}_2^-$ and $\text{NO}_3^-$

Ion exchange experiments were conducted at room temperature ( $23 \pm 2$  °C) in a stirred batch system using the following feldspathoids:  $\text{ReO}_4^-/\text{NO}_2^-$ -sodalite,  $\text{ReO}_4^-/\text{NO}_3^-$ -cancrinite/sodalite,  $\text{ReO}_4^-/\text{NO}_3^-$ -cancrinite, Cl-sodalite, and  $\text{ReO}_4^-$ -sodalite that were mixed with  $\text{NaNO}_2$  or  $\text{NaNO}_3$  aqueous solutions. The pure  $\text{ReO}_4^-$ -sodalite was synthesized from zeolite 4A using a method described by Liu and Navrotsky [23]. The particle size of the  $\text{ReO}_4^-$ -sodalite ranged from 0.34 to 16.83  $\mu\text{m}$ . For the ion exchange experiments 0.05 g of the listed feldspathoid phases were mixed with 10 mL of 0.1 M  $\text{NaNO}_2$  or  $\text{NaNO}_3$  in polypropylene bottles (liquid/solid ratio  $\sim 200:1$ ). The bottles were shaken on a reciprocal shaker at  $\approx 120$  rpm for 96 h. The suspensions were centrifuged at 17,000 rcf for 30 min and filtered with 0.45  $\mu\text{m}$  Acrodisc Syringe filters. Rhenium concentration in the supernatant solutions was determined by ICP-MS (Agilent 7700 ICP-MS, Santa Clara, CA) and concentration of  $\text{Cl}^-$  by ion chromatography (HPLC-10Ai, Shimadzu Inc., Canby, OR).

## 3. Characterization of solid phase(s)

### 3.1. Powder X-ray diffraction identification

X-ray diffraction (XRG-3100, Philips Analytical Inc., Mahwah, NJ) of powder samples was performed by scanning at 0.05° steps

Table 1  
Summarized conditions for the hydrothermal syntheses with 0.5 M counter anions (X).<sup>a</sup>

Sample ID	NaOH (m)	NaReO <sub>4</sub> (M)	Aging time (wk.)
Re:NO <sub>3</sub> -C + S-1	1	0.1	8
Re:NO <sub>3</sub> -C + S-2	1	0.5	8
Re:NO <sub>3</sub> -C-1	16	0.1	4
Re:NO <sub>3</sub> -C-2	16	0.5	4
Re:NO <sub>2</sub> -S-1	1	0.1	16
Re:NO <sub>2</sub> -S-2	1	0.5	16
Re:Cl-S-1	16	0.1	4

<sup>a</sup> X represents the different anions:  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{Cl}^-$ . C = cancrinite, S = sodalite.

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