Immobilization and Exchange of Perrhenate in Sodalite and Cancrinite

Johnbull O. Dickson^{*1}, James B. Harsh¹, Markus Flury¹, and Eric M. Pierce²,

¹Department of Crop and Soil Sciences, Washington State University, P. O. Box 646420,

Pullman, WA 99164, USA

²Environmental Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge,

TN 37831.

*Corresponding Author: j.dickson@wsu.edu

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 (ReO_4^-), a surrogate for TcO_4^- , in the presence of competing anions (X) including OH^- , NO_2^- , NO_3^- and 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 Cl^- and NO_2^- whereas NO_3^- promoted either cancrinite formation in 16-mol OH^-/kg (16 *m*) or mixed sodalite/cancrinite phases in 1-mol OH^-/kg (1 *m*) solutions. In the presence of Cl^- , NO_2^- , and NO_3^- less than 0.02 mole fraction of ReO_4^- was incorporated into the feldspathoid phase(s). Although, the NO_2 -sodalite and mixed NO_3 -cancrinite/sodalite phases

incorporated significantly more ReO_4^- than NO_3^- -cancrinite or Cl-sodalite phases, the total ReO_4^- fraction was $\sim 1\%$ or less of the total sites. The ReO_4^- immobilized in ReO_4^- -sodalite, NO_2^- -sodalite, mixed NO_3^- -cancrinite/sodalite and NO_3^- -cancrinite was resistant to ion exchange with either NO_2^- or NO_3^- . The results imply that 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.

Keywords: Feldspathoids; Anion selectivity; Perrhenate; Technetium-99; Ion exchange.

Graphic Abstract.

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}Tc has leaked into the vadose zone underneath storage tanks [1, 2]. The highly variable waste is characterized as a highly alkaline ($\text{OH}^- = \sim 0.1$ to 5.3 mol/L), high ionic strength solution (up to $I = 18$ M) with a density of 2.09 g cm $^{-3}$ 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 (Na^+ , $\text{Al}(\text{OH})_4^-$, OH^- , NO_3^- , NO_2^- , CO_3^{2-} , Cl^- , SO_4^{2-} , PO_4^{3-} , Ni^+), and, Al- and Fe-(hydr)oxide sludges [5, 6]. Given the estimated inventory of ^{99}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 (TcO_4^-), which is the dominant ^{99}Tc species under oxidizing conditions, ^{99}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 (ReO_4^-), a nonradioactive surrogate for $^{99}\text{TcO}_4^-$, can be incorporated into sodalite. Recent work by Pierce et al. [14] suggests that ReO_4^- and 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 SiO_4 and AlO_4 tetrahedra stacked along the hexagonal c-axis direction in an AB–AB sequence (Fig. 1), resulting in the formation of the small ϵ -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 ϵ -cages only house cations or water molecules, which can easily be substituted by other cations or small molecules in exchange experiments or during hydrothermal synthesis [16]. Sodalite consists of alternating SiO_4 and AlO_4 corner-sharing tetrahedra linked into four and six ring cages, which make up the sodalite β -cage (Fig. 1). These cages are ~ 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 β -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 ~ 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 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 ReO_4^- into mixed-anion sodalites was enhanced by similarity in ionic radius and charge. There are few studies that address 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 ReO_4^- incorporation into sodalite and cancrinite, including a mixed phase and (2) determine the exchangeability of ReO_4^- with other anions from both minerals. We hypothesize that ReO_4^- incorporation will depend on the type of mineral(s) formed. We further hypothesize that the sequestered 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 NaAlO₂, 0.175 M Na₂SiO₃, 0.5 M NaCl, 0.5 M NaNO₂ and 0.5 M NaNO₃ with varying concentrations of NaReO₄ (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 to 16 weeks. The precipitates were washed three times with deionized water (0.054×10^{-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 (0.054×10^{-3} dSm⁻¹) until the electrolytic conductivity was ≤ 0.01 dSm⁻¹. The solids were digested in 3% nitric acid and the ReO₄⁻ 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 NO₂⁻ and NO₃⁻

Ion exchange experiments were conducted at room temperature (23 ± 2°C) in a stirred batch system using the following feldspathoids: ReO₄/NO₂-sodalite, ReO₄/NO₃-cancrinite/sodalite, ReO₄/NO₃-cancrinite, Cl-sodalite, and ReO₄-sodalite that were mixed with NaNO₂ or NaNO₃ aqueous solutions. The pure ReO₄-sodalite was synthesized from zeolite 4A using a method described by Liu and Navrotsky [23]. The particle size of the ReO₄-sodalite ranged from 0.34 to 16.83 µm. For the ion exchange experiments 0.05 g of the listed feldspathoid phases were mixed with 10 mL of 0.1 M NaNO₂ or NaNO₃ in polypropylene bottles (liquid/solid

ratio ~200:1). The bottles were shaken on a reciprocal shaker at ≈ 120 rpm for 96 h. The suspensions were centrifuged at 17,000 rcf for 30 min. and filtered with 0.45 μm Acrodisc Syringe filters. Rhenium concentration in the supernatant solutions was determined by ICP-MS (Agilent 7700 ICP-MS, Santa Clara, CA) and concentration of 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 with a 5 s dwell time over $2 - 50^\circ 2\theta$ using Ni-filtered $\text{CuK}\alpha$ radiation (35 keV, 30 mA, and $\lambda = 1.54050 \text{ \AA}$) and a graphite monochromator. Mineral identification was conducted by matching observed XRD peaks with published peaks for known minerals. Weight fractions of cancrinite and sodalite in the powder samples were determined from Rietveld refinements of crystallographic data using GSAS with EXPGUI interface [24] and reported structures of the following phases: $\text{Na}_8(\text{AlSiO}_4)_6(\text{NO}_2)_2$, $\text{Na}_8(\text{AlSiO}_4)_6(\text{Cl})_2$, and $\text{Na}_{7.6}(\text{AlSiO}_4)_6(\text{NO}_3)_{1.6}(\text{H}_2\text{O})_2$ [16, 25, 26]. During the Rietveld analysis the following crystallographic parameters were varied: atomic position, background, scale factor, zero error, unit cell, peak shape (5 parameters: U, V, W, and two peak shape parameters), isotropic thermal parameter (B), and preferred orientation.

3.2. Electron microscopy

Select samples were examined with a field emission scanning electron microscope (FESEM) with a field emission gun (FEI Quanta 200F, FEI Co., Hillsboro, OR) and Everhart-Thornley detector. The FESEM operates on an accelerating voltage of 30 keV with a resolution of 1 nm. Powder samples were mounted on carbon tabs and sputter-coated with platinum-

palladium for analysis on the FESEM. Particle size measurements were determined by dynamic light scattering (DelsaNano C Particle Analyzer, Beckman Coulter Inc., Brea, CA) equipped with a 633 nm Helium-Neon laser.

4. Results

4.1. Structures

Cancrinite was identified by the (101) and (211) Miller indices with corresponding d-spacings of ~ 4.64 and 3.24 Å, respectively, while the (211) and (330) Miller indices corresponding to d-spacings of ~ 3.64 and 2.10 Å were characteristic for sodalite. The refined powder XRD patterns (Fig. 2) showed that in the presence of Cl^- and NO_2^- sodalite was the dominant phase (100 wt.%) formed in the $1\text{ }m\text{ OH}^-$ and $16\text{ }m\text{ OH}^-$ solutions. The unit cell parameters (a) of these sodalites varied from 8.9345 to 8.9667 Å respectively (Table 2). Cancrinite was the only mineral identified by the refined XRD patterns in the $16\text{ }m\text{ OH}^-$ solutions containing NO_3^- while a mixed cancrinite/sodalite phase(s) (sodalite – 55-60%; cancrinite – 40-45 %) was observed in the $1\text{ }m\text{ OH}^-$ solutions containing NO_3^- . The observed cancrinite lattice parameters ($a = b$) and (c) ranged from 12.686 to 12.708 Å and 5.186 to 5.196 Å, for $1\text{ }m$ and $16\text{ }m\text{ OH}^-$, respectively. Aside from pure or mixed cancrinite and sodalite phase(s) no other minor phase(s) or inclusions were formed in the reacting solutions based on the observed XRD patterns. For full details of all refinement parameters, the reader is referred to the supplemental information available on the online version of this article.

4.2. Morphology

The SEM particle images are shown in Fig. 3. The ReO_4/NO_3 -cancrinite/sodalite formed in the $1\text{ }m\text{ OH}^-$ solution exhibited typical lepispheric (thin disc) morphology, while euhedral hexagonal crystallites characterized ReO_4/NO_3 -cancrinite formed in the $16\text{ }m\text{ OH}^-$ solutions. The

ReO₄/NO₂-sodalite occurred as wedge-shaped blade particles in the 1 *m* OH[−] solution whereas ReO₄/Cl-sodalite formed in the 16 *m* OH[−] solutions were predominantly hexagonal crystallites. The feldspathoid morphologies were similar to those reported by Deng et al. [11] for similar phases.

Increasing the solution alkalinity from 1 *m* OH[−] to 16 *m* OH[−] and reaction time from 4 to 8 weeks in the presence of NO₃[−] and ReO₄[−] changed the products from mixed sodalite/cancrinite phases to predominantly cancrinite (Fig. 3A-B). In the 16 *m* OH[−] solution aged for four weeks in the presence of NO₃[−] and ReO₄[−] only cancrinite was formed in the solution (Fig. 3B and Table 3); however, reducing the alkalinity to 1 *m* OH[−] coupled with an increased reaction time to 8 weeks resulted in the formation of mixed sodalite/cancrinite in which sodalite slightly dominates over cancrinite (Fig. 3A and Table 3).

The size of the feldspathoid crystallites increased with aging time. The wedge-shaped NO₂-sodalite crystallites observed in the 1 *m* OH[−] samples were generally larger than the lepispheric cancrinite/sodalite and the euhedral cancrinite particles formed in the 16 *m* OH[−] samples (Fig. 4).

4.3. Rhenium uptake

The ReO₄[−] uptake data are presented in Table 3. The sequestration of ReO₄[−] by sodalite formed in the 1 *m* OH[−] solution containing ReO₄[−] and NO₂[−] is ~1.5 – 10 times higher than that of the solutions containing Cl[−] and NO₃[−]. Approximately 0.1 – 0.5% of solution ReO₄[−] was incorporated into the ReO₄/NO₂-sodalite, whereas the uptake of ReO₄[−] by cancrinite from the 16 *m* OH[−] solutions ranged from 0.02 to 0.03%. The mixed cancrinite/sodalite phases sequestered ~0.05 – 0.1% of solution ReO₄[−]. Feldspathoids formed in the 1:1 molar ratio ReO₄[−]/X solution contained ~1.5 times higher ReO₄[−] concentrations than those solutions containing 0.2:1 ReO₄[−]/X

molar ratios. Feldspathoids aged for 16 weeks contained $\sim 2.3 - 4.7$ times more ReO_4^- than those aged for 4 and 8 weeks (Tables 1 and 3), however, this increase was still not proportional to the increase in ReO_4^- concentration in solution. Moreover, the amount of enclathrated ReO_4^- generally increased with particle size (Fig. 4 and Table 4).

4.4. ReO_4^- desorption from solids

After 96 h of reaction, the 0.1 *m* NO_2^- solution desorbed approximately 0.24% of the ReO_4^- from the ReO_4/NO_2 -sodalite cages, while the NO_3^- solution exchanged roughly 0.36% of the ReO_4^- from ReO_4/NO_3 -cancrinite, $\sim 0.29\%$ from ReO_4/NO_3 -cancrinite/sodalite, and 0.22% from the ReO_4 -sodalite (Table 4). The NO_3^- containing solution desorbed negligible Cl^- from the pure phase Cl-sodalite (data not shown).

5. Discussion

5.1. Feldspathoid formation as a function of solution composition

The alkalinity and type of anions present in the synthesis solution significantly affect the formation pathway and morphology of the feldspathoids for a given Si/Al molar ratio in solution. When ReO_4^- and NO_3^- anions were added concomitantly to the 1 *m* OH^- solution, a mixed cancrinite/sodalite was the dominant phase(s) (Fig. 3A), whereas the 16 *m* OH^- solution promoted the formation of pure cancrinite phase(s) (Fig. 3B). Deng et al. [11] found that NO_3^- promoted the formation of cancrinite at high pH whereas a mixed cancrinite/sodalite phase at low pH, but they argued a high Si/Al ratio (≥ 1.4) favored cancrinite formation. In our study, even though the Si/Al ratio was 4 – 10 times less, a mixed cancrinite/sodalite phase formed in the 1 *m* OH^- solution. On the other hand, NO_2^- and Cl^- in the presence of ReO_4^- favored the formation of pure sodalite regardless of the solution alkalinity (Fig. 3C-D). This implies that anions such as NO_2^- and Cl^- serve as suitable templates for sodalite formation regardless of solution alkalinity.

Deng et al. [11] reported similar findings in their study, where NO_2^- and Cl^- strongly favored the formation of sodalite over cancrinite.

Furthermore, the increased alkalinity resulted not only in the formation of different weight fractions of cancrinite and sodalite phase(s) but also different amounts of ReO_4^- sequestered. As the weight fraction (w/w) of the pure phase sodalite increased with a concomitant decrease of cancrinite, the concentration of ReO_4^- incorporated into the solids increased. This implies that monovalent anions favor sodalite nucleation. A similar observation was reported by Weller [27] where monovalent permanganate (MnO_4^-) fostered sodalite formation while divalent manganate (MnO_4^{2-}) promoted cancrinite formation.

5.2. The effect of feldspathoid phase formation on ReO_4^- incorporation

The amount of ReO_4^- sequestered in the feldspathoids depended on the type of feldspathoid (pure or mixed phase) and the ratio of ReO_4^-/X ($\text{X} = \text{NO}_3^-$, NO_2^- and Cl^-) in the 1 *m* OH^- and 16 *m* OH^- solutions (Fig. 5). As expected [20], the equimolar ReO_4^-/X solutions sequestered ReO_4^- at a higher amounts than the 0.2 ReO_4^-/X molar ratio solutions. The pure phase NO_2 -sodalite sequestered ReO_4^- at ~6 times higher rate than the pure NO_3 -cancrinite, whereas the mixed-phase NO_3 -cancrinite/sodalite incorporated ReO_4^- at 2.5 times higher rate than the pure NO_3 -cancrinite phase. The higher ReO_4^- content sequestered in the mixed-phase NO_3 -cancrinite/sodalite in comparison to the pure NO_3 -cancrinite was attributed to: (1) the suppression of ReO_4^- incorporation by the higher OH^- concentration (16×) in the 16 *m* OH^- solution and, (2) a greater resistance in cancrinite relative to sodalite to incorporating large anions such as ReO_4^- . Sodalite cages can host guest anions of varying size due to cooperative tilting and deformation of its frameworks and this is exemplified by the change in lattice parameter of NO_3 -sodalite (8.9762 Å) to that of ReO_4 -sodalite (9.1535 Å) [20]. In the presence

of more than one anion, sodalite shows a preference for the smaller ion, suggesting that the smaller cages are more stable (Fig. 5). In cancrinite, on the other hand, ReO_4^- incorporation is negligible. This suggests that the energetics of deformation in cancrinite needed to incorporate large anions such as ReO_4^- is less favorable as compared to that of sodalite.

Linear combination of the maximum ReO_4^- mole fractions in pure cancrinite and sodalite phases did not predict the amount of ReO_4^- sequestered in the mixed cancrinite/sodalite phase. The predicted values ranged from 0.011 to 0.013 ReO_4^- mole fractions in the 0.2 and 1:1 ReO_4^-/X molar ratio solutions respectively, which were 37 – 57% higher than actual measured ReO_4^- values. This suggests that ReO_4^- in the mixed system did not behave as two separate cancrinite and sodalite phases, at least when ReO_4^- incorporation is concerned. This is not surprising given that the morphology of the mixed system consists only of lepispheric particles (Fig. 3; [11]), which may behave differently than discrete cancrinite and sodalite phases.

5.3. Susceptibility of incorporated ReO_4^- to ion exchange

The NO_3^- -cancrinite released ~1.6 times more ReO_4^- than the pure phase ReO_4^- -sodalite, probably as a result of the more open cancrinite structure. In general, the feldspathoids released only trace amounts of ReO_4^- by ion exchange, supporting our hypothesis that the sodalite cages would effectively trap structural ReO_4^- . The resistance of the ReO_4^- enclathrated in the feldspathoid to ion exchange was attributed to the steric constraint imposed by the ion size relative to the cage's aperture diameter and the resulting high activation energy required for exchange to occur. Similarly, a negligible amount of Cl^- was desorbed by NO_3^- from a pure phase Cl^- -sodalite (Table 4). Mon et al. [28] showed that a relatively high activation energy was required for the release of Cs^+ from sodalite because a temperature increase from 23°C to 50°C had only a small effect on Cs^+ exchange. Furthermore, much larger amounts of the smaller Cs^+

ion were exchangeable from both sodalite (2.7 %) and cancrinite (31%) at 23°C in that study.

6. Conclusions and Implications

We synthesized ReO_4^-/X -bearing feldspathoids (cancrinite, sodalite and mixed cancrinite/sodalite). Alkalinity, solution compositions, anion size and extra-framework species selectivity determined the feldspathoid type and composition. Nitrite and Cl^- facilitated sodalite formation while NO_3^- in the 16 *m* OH^- solution favored cancrinite, and mixed cancrinite/sodalite formation in the 1 *m* OH^- solution. Perrhenate had little or no effect on the nature of the products because the feldspathoid minerals formed in this study are essentially the same as those reported by Deng et al. [11] where no ReO_4^- was used. Only the solid phases containing sodalite incorporated a significant amount of ReO_4^- , and this enclathrated ReO_4^- was not easily exchanged with NO_2^- or NO_3^- .

Because ReO_4^- is a suitable surrogate for $^{99}\text{TcO}_4^-$ under oxidizing conditions, our results suggest that sodalite can sequester ^{99}Tc as TcO_4^- , but the presence of smaller competing anions at similar or higher concentrations will preclude its incorporation during mineral formation. In an open system such as a waste stream that leaked into vadose zone sediments, other mineral phases such as zeolite, nosean, nepheline may form that have a higher affinity for larger anions. For example, Pierce et al. [14] showed that NO_3^- will incorporate into cancrinite and SO_4^{2-} into nosean; whereas Cl^- , NO_2^- and ReO_4^- will be intercalated into sodalite. In a dynamic, open system, TcO_4^- could be sequestered into the sodalite phases after other small competing anions have been selectively removed by earlier-forming phases, including sodalite. Additionally, a waste-reprocessing scheme (e.g., the fluidized bed steam reformer process) that reduces NO_3^- and NO_2^- could be used to enhance ReO_4^- (and ultimately TcO_4^-) sequestration into mixed-anion feldspathoids.

7. Acknowledgement

We thank the staff at the Franceschi Microscopy and Imaging Center at Washington State University for access to and assistance with the use of their SEM facilities. We also acknowledge the Mineralogical Society of America and the Bullitt Foundation for their support. This material is based upon work supported by the U.S. Department of Energy (DOE), Office of Science, Biological and Environmental Research, Subsurface Biogeochemical Research (SBR) Program, and was performed at Washington State University under contract No. DE-PS02-09ER65075 and at Oak Ridge National Laboratory under contract No. DE-AC05-00OR22725. The authors thank the two anonymous reviewers for their comments.

8. Supplemental Information

Full details of all refinement parameters are provided as supplemental material, and can be found in the online version of this article.

9. References

- [1] K.D. Crowley, Nuclear waste disposal: The technical challenges (vol 50, pg 32, 1997), *Physics Today*, 50 (1997) 85-85.
- [2] R.E. Gephart, R.E. Lundgren, *A Guide to understanding the Technical Issues*, 1998.
- [3] K. Pruess, S. Yabusaki, C. Steefel, P. Lichtner, Fluid Flow, Heat Transfer, and Solute Transport at Nuclear Waste Storage Tanks in the Hanford Vadose Zone, *Vadose Zone Journal*, 1 (2002) 68-88.
- [4] R.J. Serne, C.W. Lindenmeier, H.T. Schaef, Geochemical conditions in the vadose zone at leaking single-shell tanks in the B-BX-BY waste management area in Hanford's 200 E area, *Abstracts of Papers of the American Chemical Society*, 222 (2001) U492-U492.
- [5] D.I. Kaplan, R.J. Serne, Pertchnetate exclusion from sediments, *Radiochimica Acta*, 81 (1998) 117-124.
- [6] N.P. Qafoku, C.C. Ainsworth, J.E. Szecsody, D.L. Bish, J.S. Young, D.E. McCready, O.S. Qafoku, Aluminum effect on dissolution and precipitation under hyperalkaline conditions: II. Solid phase transformations, *Journal of Environmental Quality*, 32 (2003) 2364-2372.
- [7] S.F. Agnew, J. Boyer, C. R.A. T.B. Duran, J.R. FitzPatrick, K.A. Jurgensen, T.P. Ortiz, B.L. Young, Hanford chemical and radionuclide inventories: HDW Model, Los Alamos National Laboratory: Los Alamos, NM, 1997.
- [8] J.M. Zachara, J. Serne, M. Freshley, F. Mann, F. Anderson, M. Wood, T. Jones, D. Myers, Geochemical processes controlling migration of tank wastes in Hanford's vadose zone, *Vadose Zone Journal*, 6 (2007) 985-1003.
- [9] J. Chorover, S. Choi, P. Rotenberg, R.J. Serne, N. Rivera, C. Strepka, A. Thompson, K.T. Mueller, P.A. O'Day, Silicon control of strontium and cesium partitioning in hydroxide-weathered sediments, *Geochim Cosmochim Acta*, 72 (2008) 2024-2047.
- [10] Y.J. Deng, M. Flury, J.B. Harsh, A.R. Felmy, O. Qafoku, Cancrinite and sodalite formation in the presence of cesium, potassium, magnesium, calcium and strontium in Hanford tank waste simulants, *Appl Geochem*, 21 (2006) 2049-2063.
- [11] Y.J. Deng, J.B. Harsh, M. Flury, J.S. Young, J.S. Boyle, Mineral formation during simulated leaks of Hanford waste tanks, *Appl Geochem*, 21 (2006) 1392-1409.
- [12] S.V. Mattigod, J. Serne, B.P. McGrail, V.L. LeGore, Radionuclide Incorporation in Secondary Crystalline Minerals from Chemical Weathering of Waste Glasses. MRS Proceedings, 713, JJ5.1 in: B.P. McGrail, G.A. Cragnolino (Eds.) *Scientific basis for nuclear waste management XXV*, Material Research Society, Warrendale PA, Boston, MA, 2002.
- [13] S.V. Mattigod, B.P. McGrail, D.E. McCread, L.Q. Wang, K.E. Parker, J.S. Young, Synthesis and structure of perhenate sodalite, *Microporous Mesoporous Mater*, 91 (2006) 139-144.
- [14] E.M. Pierce, W.W. Lukens, J.P. Fitts, C.M. Jantzen, G. Tang, Experimental determination of the speciation, partitioning, and release of perhenate as a chemical surrogate for pertchnetate from a sodalite-bearing multiphase ceramic waste form, *Appl Geochem*, 42 (2014) 47-59.

- [15] E.M. Pierce, K. Lilova, W.W. Lukens, A. Navrotsky, J. Fritts, C. Rawn, C.M. Jantzen, D.M. Missimer, A. Huq, Structure and thermochemistry of perhenate sodalite and perhenate/pertechetate guest-guest sodalite, *Proceeding of the national Academy of Science* 2014, submitted.
- [16] J.C. Buhl, F. Stief, M. Fechtelkord, T.M. Gesing, U. Taphorn, C. Taake, Synthesis, X-ray diffraction and MAS NMR characteristics of nitrate cancrinite $\text{Na}_{7.6} [\text{AlSiO}_4]_6 (\text{NO}_3)_{1.6} (\text{H}_2\text{O})_2$, *J Alloys Compd*, 305 (2000) 93-102.
- [17] W. Depmeier, The sodalite family - A simple but versatile framework structure, in: G. Ferraris, S. Merlino (Eds.) *Micro- and Mesoporous Mineral Phases* 2005, pp. 203-240.
- [18] R.M. Barrer, J.F. Cole, Chemistry of soil minerals. Part VI. Salt entrainment by sodalite and cancrinite during their synthesis, *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, (1970) 1516.
- [19] J.O. Dickson, J.B. Harsh, W.W. Lukens, E.M. Pierce, Perrhenate incorporation into binary mixed sodalites: The role of anion size and implications for technetium-99 sequestration, *Chem Geol*, 395 (2015) 138-143.
- [20] J.O. Dickson, J.B. Harsh, M. Flury, W.W. Lukens, E.M. Pierce, Competitive incorporation of perhenate and nitrate into sodalite, *Environ Sci Technol*, 48 (2014) 12851-12857.
- [21] P.C. Lichtner, A.R. Felmy, Estimation of Hanford SX tank waste compositions from historically derived inventories, *Computers & Geosciences*, 29 (2003) 371-383.
- [22] N.P. Qafoku, C.C. Ainsworth, J.E. Szecsody, O.S. Qafoku, Transport-controlled kinetics of dissolution and precipitation in the sediments under alkaline and saline conditions, *Geochim Cosmochim Acta*, 68 (2004) 2981-2995.
- [23] Q. Liu, A. Navrotsky, Synthesis of nitrate sodalite: An in situ scanning calorimetric study, *Geochim Cosmochim Acta*, 71 (2007) 2072-2078.
- [24] B.H. Toby, EXPGUI, a graphical user interface for GSAS, *J Appl Crystallogr*, 34 (2001) 210-213.
- [25] J.C. Buhl, D. Reich, C. Mundus, W. MullerWarmuth, Si-29 MAS NMR investigations on the crystallization of nitrite-sodalite, *React Kinet Catal Lett*, 58 (1996) 13-18.
- [26] B. Beagley, C.M.B. Henderson, D. Taylor, The crystal structures of aluminosilicate sodalites - X-ray diffraction studies and computer modeling, *Mineralogical Magazine*, 46 (1982) 459-464.
- [27] M.T. Weller, Where zeolites and oxides merge: semi-condensed tetrahedral frameworks, *Journal of the Chemical Society-Dalton Transactions*, (2000) 4227-4240.
- [28] J. Mon, Y.J. Deng, M. Flury, J.B. Harsh, Cesium incorporation and diffusion in cancrinite, sodalite, zeolite, and allophane, *Microporous Mesoporous Mater*, 86 (2005) 277-286.
- [29] C. Baerlocher, L.B. McCusker, Database of zeolite structures, <http://www.iza-structure.org/databases>, 2014.

Table 1. Summarized conditions for the hydrothermal syntheses with 0.5 *M* counter anions (X)[†]

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

[†]X represents the different anions: NO₃[−], NO₂[−], and Cl[−]. C = cancrinite, S = sodalite.

Table 2. Unit cell and refinement parameters for mixed anion feldspathoids

Samples ID	__Sodalite__	____Cancrinite____		χ^2
	<i>a</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)	
Re:NO ₃ -C+S-1	8.9758(6) [†]	12.686(1)	5.186(1)	4.74
Re:NO ₃ -C+S-2	8.9886(9)	12.708(4)	5.196(3)	3.97
Re:NO ₃ -C-1	n/a	12.692(1)	5.190(1)	4.36
Re:NO ₃ -C-2	n/a	12.700(2)	5.194(1)	9.91
Re:NO ₂ -S-1	8.9498(9)	n/a	n/a	9.83
Re:NO ₂ -S-2	8.9667(4)	n/a	n/a	3.75
Re:Cl-S-1	8.9345(4)	n/a	n/a	3.61

a – unit cell parameter

[†]The number in parentheses is the estimated standard deviations (e.s.d.s) in the same decimal place as the digit preceding it.

χ^2 - weighted agreement factors

n/a – not applicable.

Table 3. Feldspathoid weight fraction and ReO_4^- /anion concentration

___Feldspathoid (wt%)___				
Sample ID	Sodalite	Cancrinite	$\text{X}^\dagger$ (mmol/kg)	ReO_4^- in solid (mmol/kg)
Re: NO_3^- -C+S-1	55	45	1632.24 ± 2.30	3.68 ± 0.05
Re: NO_3^- -C+S-2	60	40	1695.43 ± 26.13	6.91 ± 0.13
Re: NO_3^- -C-1	n/a	100	1630.64 ± 10.46	0.75 ± 0.02
Re: NO_3^- -C-2	n/a	100	1550.18 ± 30.37	2.81 ± 0.16
Re: NO_2^- -S-1	100	n/a	1646.90 ± 12.77	15.39 ± 0.07
Re: NO_2^- -S-2	100	n/a	1674.23 ± 27.37	16.67 ± 0.15
Re:Cl-S-1	100	n/a	1745.15 ± 6.95	1.62 ± 0.03

† X represents the different anions: NO_3^- , NO_2^- , and Cl^-

n/a – not applicable

Table 4. Solution ReO_4^- after aqueous exchange of feldspathoids with NO_2^- or NO_3^-

Feldspathoid type	ReO_4^- in feldspathoids (mmol/kg)	Solution ReO_4^- following 96 h of suspension (mmol/kg)	(%)
Re: NO_3^- -C-2 †	2.81 ± 0.16	0.01	0.36
Re: NO_3^- -C+S-2 †	6.91 ± 0.13	0.02	0.29
Re: NO_2^- -S-2*	16.67 ± 0.15	0.04	0.24
ReO_4^- -Sodalite †	1388.80 ± 17.72	3.05 ± 0.03	0.22

*exchange with 0.1 M NO_2^- solution

† exchange with 0.1 M NO_3^- solution

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

Fig. 2. Rietveld refinements of powder XRD data for mixed-anion feldspathoids (a), and mixed cancrinite/sodalite phase (b): In the lower diagram (Fig. 2b) the upper lines show the fit between the experimental (black) and calculated patterns (red), while the lower line displays the difference (blue) between these two patterns. (For additional details of all refined atomic parameters, the reader is referred to the supplemental information).

Re:X-SOD-1 sample contains 0.2 Re/X solution ratios; where “X” are anions (Cl^- , NO_2^- , and NO_3^-).

Fig. 3. The SEM micrographs of ReO₄/X-feldspathoids formed in either 1 *m* OH⁻ or 16 *m* OH⁻ solutions containing 0.2 – 1.0 ReO₄⁻/X ratios.

Fig. 4. Mixed-anion feldspathoid particles formed in either 1 *m* OH⁻ or 16 *m* OH⁻ solutions 0.2 – 1.0 ReO₄⁻/X ratios.

Blue bar is Re:NO₃-C-2; Red bar is Re:NO₃-C+S-2; Green bar is Re:NO₂-S-2.

C = Cancrinite; S = Sodalite

Fig. 5. Variation of ReO₄⁻ sequestered in feldspathoids with ReO₄⁻/X solution ratio