



Experimental determination of the speciation, partitioning, and release of perrhenate as a chemical surrogate for pertechnetate from a sodalite-bearing multiphase ceramic waste form



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ABSTRACT

A key component to closing the nuclear fuel cycle is the storage and disposition of nuclear waste in geologic systems. Multiphase ceramic waste forms have been studied extensively as a potential host matrix for nuclear waste. Understanding the speciation, partitioning, and release behavior of radionuclides immobilized in multiphase ceramic waste forms is a critical aspect of developing the scientific and technical basis for nuclear waste management. In this study, we evaluated a sodalite-bearing multiphase ceramic waste form (i.e., fluidized-bed steam reform sodium aluminosilicate [FBSR NAS] product) as a potential host matrix for long-lived radionuclides, such as technetium (⁹⁹Tc). The FBSR NAS material consists primarily of nepheline (ideally NaAlSiO₄), anion-bearing sodalites (ideally M₈[Al₆Si₆O₂₄]X₂, where M refers to alkali and alkaline earth cations and X refers to monovalent anions), and nosean (ideally Na₈[AlSiO₄]₆SO₄). Bulk X-ray absorption fine structure analysis of the multiphase ceramic waste form, suggest rhenium (Re) is in the Re(VII) oxidation state and has partitioned to a Re-bearing sodalite phase (most likely a perrhenate sodalite Na₈[Al₆Si₆O₂₄](ReO₄)₂). Rhenium was added as a chemical surrogate for ⁹⁹Tc during the FBSR NAS synthesis process. The weathering behavior of the FBSR NAS material was evaluated under hydraulically unsaturated conditions with deionized water at 90 °C. The steady-state Al, Na, and Si concentrations suggests the weathering mechanisms are consistent with what has been observed for other aluminosilicate minerals and include a combination of ion exchange, network hydrolysis, and the formation of an enriched-silica surface layer or phase. The steady-state S and Re concentrations are within an order of magnitude of the nosean and perrhenate sodalite solubility, respectively. The order of magnitude difference between the observed and predicted concentration for Re and S may be associated with the fact that the anion-bearing sodalites contained in the multiphase ceramic matrix are present as mixed-anion sodalite phases. These results suggest the multiphase FBSR NAS material may be a viable host matrix for long-lived, highly mobile radionuclides which is a critical aspect in the management of nuclear waste.

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1. Introduction

Nuclear power represents one solution to the looming energy crisis (Ewing, 2006; Marris, 2006). Currently, nuclear energy represents an important portion of the net electricity generation in the US, especially given the projected increase in total primary energy consumption and the desire to reduce CO₂ emission from fossil fuels (e.g., coal). However, for the US to realize a nuclear power

renaissance will require closure of the nuclear fuel cycle. A key aspect to closing the nuclear fuel cycle is the storage and disposition of nuclear waste in geologic systems. For example, the ability to predict the behavior of waste forms (e.g., mineral and glass) over geological time scales constitutes one of the main scientific challenges for evaluating the long-term impacts of nuclear waste storage on public health and environmental resources (Gin et al., 2013; NRC, 2011).

Multiphase ceramic waste forms have been studied extensively as a potential host matrix for radionuclides (Lumpkin, 2006; Stefanovsky et al., 2004). Some of the most studied multiphase waste forms include the multiple versions of SYNthetic ROCK

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(SYNROC) (Ringwood et al., 1978), tailored ceramics (Harker, 1988), pyrochlore (Icenhower et al., 2006; Weber et al., 1986), zirconolite (Clinard et al., 1984a,b), and glass–ceramics (O'Holloran et al., 1997). For an overview of the state-of-the-science on the afore-mentioned multiphase waste forms see the reviews by Lutze and Ewing (1988), Lee et al. (2006), Caurant et al. (2009), and NRC (2011). Improving the scientific and technical basis for using multiphase ceramic waste forms in nuclear waste management requires an understanding of the speciation, partitioning, and the release behavior of radionuclides immobilized in the multiphase matrix. In this study, we evaluate the potential for a sodalite-bearing multiphase ceramic waste form to resist aqueous corrosion and retain key long-lived risk driving radionuclides (e.g., technetium-99 [^{99}Tc]).

Feldspathoids and zeolites, such as sodalite (general formula of $M_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{X}_2$, where M is an alkali cation—such as Cs, K, and Na—and X is a monovalent anion, such as Br^- , Cl^- , I^- , and TCO_4^- , ReO_4^- , SO_4^{2-}), are a large and diverse class of minerals characterized by a crystalline framework of tetrahedral Al and Si with a three-dimensional pore system that can accommodate a variety of anions (Brenchley and Weller, 1994; Buhl et al., 1989, 2001; Campbell et al., 2000; Deer et al., 1963; Fechtelkord, 2000; Gesing and Buhl, 1998; Johnson et al., 2000; Mattigod et al., 2006; Shannon et al., 2000; Srdanov et al., 1994; Zhao et al., 2004). The common theme in sodalite group minerals is the flexible framework structure that can expand to trap various guest anions by cooperative changes in the Al–O–Si bond angle (Pauling, 1930). Because of the flexible framework, sodalite group minerals have been studied by a number of investigators as a potential host media for the immobilization of defense high-level waste (HLW), commercial nuclear waste, and transactinide elements, such as plutonium, in multiphase ceramic waste forms (Barney, 1974; Fanning et al., 2003; Hatch, 1953; Hench et al., 1981, 1986; Moschetti et al., 2000; Sinkler et al., 2000). For example, a glass-bonded sodalite has been considered as a host matrix for the disposal of electrorefiner wastes from sodium-bonded metallic spent nuclear fuel removed from the EBR II fast breeder reactor (Fanning et al., 2003; Moschetti et al., 2000; Sinkler et al., 2000). In addition to the nuclear waste management application, sodalite group minerals have been postulated to form in the environment at locations where the unintentional release of caustic, high ionic strength, Al-rich waste solutions that exceed 60 °C have reacted with subsurface sediments; which consist mainly of quartz, feldspar, hornblende, mica, chlorite, illite, kaolinite, smectite, and calcite (Serne et al., 1998), at the Hanford site in Richland, WA (Bickmore et al., 2001; Chorover et al., 2003; Deng et al., 2006a,b; Mashal et al., 2004; Moner et al., 2005; Qafoku et al., 2003a,b; Rivera et al., 2011; Zachara et al., 2007; Zhao et al., 2004).

In this study, we evaluate the fluidized-bed steam reformer sodium aluminosilicate (FBSR NAS) multiphase ceramic waste form for Hanford low-activity waste (LAW) immobilization by providing insight into the speciation, partitioning and release behavior of Re. The FBSR NAS ceramic matrix is primarily composed of nepheline (ideally $\text{NaAlSi}_3\text{O}_8$), anion-bearing sodalites (ideally $M_8[\text{AlSiO}_4]_6\text{X}_2$), and nosean (ideally $\text{Na}_8[\text{AlSiO}_4]_6\text{SO}_4$). The perchrenate (ReO_4^-) ion was added to the LAW simulant as a chemical analogue for the perchrenate (TcO_4^-) ion during the synthesis of the FBSR NAS granular product. The volume of LAW planned for immobilization at Hanford is the largest in the DOE complex and is one of the largest inventories (approximately 8.9×10^{14} Bq total activity) of long-lived radionuclides, principally ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$), planned for disposal in a near-surface burial facility (Mann et al., 2003). Vitrification at the Hanford Waste Treatment and Immobilization Plant (WTP) represents the baseline treatment approach for the LAW stream (ORP, 2011). However, the treatment capacity at WTP is not sufficient for the estimated volume of LAW and it is anticipated

that a supplemental technology, such as the FBSR NAS waste form or an equivalent material, will be required to meet project goals (DOE, 2012; ORP, 2011).

The objective of the experiments discussed in this manuscript was to determine for the first time the oxidation state, speciation, and mineral association for the rhenium (Re) in the FBSR NAS waste form matrix. In addition to determining the Re speciation in the FBSR NAS waste form, a 2.5-year long weathering experiment was conducted under hydraulically unsaturated conditions with the goal of determining (1) the alteration phase or phases that form as a result of long-term weathering, (2) the evolution in the solution chemistry that occurs during the multiphase wasteform-water interaction, and (3) to gain insight into the ReO_4^- release mechanism, as a chemical analogue to TcO_4^- .

2. Material production and characterization

2.1. Description of the fluidized-bed steam reformer production process

The Thermal Organic Reduction (THORSM) Treatment Technology (TTT) Fluidized-Bed Steam Reformation (FBSR) process operates by introducing high sodium nitrate content tank wastes into a moderate temperature (650–800 °C) fluidized bed. The tank waste is reacted with carbon and iron-based reductants to convert nitrates and nitrites directly to nitrogen gas. Radionuclides, alkali metals, sulfate, chloride, fluoride, and non-volatile heavy metals in the waste stream are reacted with clay (kaolinite) or other inorganic materials to produce a polycrystalline mineral product. For additional details on THOR-TTT FBSR process see Jantzen (2002), Olson et al. (2004), Soelberg et al. (2004), or visit the THORSM-TTT website (www.thortt.com).

2.2. Synthesis and composition

A pilot-scale test of THOR Treatment Technology mineralized FBSR process technology was conducted at the SAIC STAR facility at INEEL. The results of the pilot-scale tests conducted with the externally heated 6-in. reformer system is described in Olson et al. (2004). The pilot-scale run was terminated on August 5, 2004, and resulted in a continuous operating time (COT) of 68 h and 26 min with a LAW slurry feed rate that ranged from 3 to 5.5-kg/h. The FBSR LAW 1104/1123 sample used to produce the test results discussed below represents a sample of the bed product removed at 55:30 h of the COT cycle. The FBSR LAW 1125 filter fines were also removed during this time period and represent the final filter fines. The additives used to produce the mineralized product include the Hanford LAW simulant, starting bed media, carbon reductive additive, and mineralized additive. The Hanford LAW simulant, which primarily consist of sodium and potassium salts, used in this pilot-scale test was a six-tank composite sample designed to represent dissolved radioactive saltcake (Mahoney and Rassat, 2003; Olson et al., 2004). The purpose of the starting bed material was to facilitate heat transfer to the atomized feed and prevent over-quenching in the feed zone. A wood-based carbon received from Berger Brothers of Chicago was used as the reductive additive in this test. Carbon was added to the system to provide heat input to the bed and to form reducing conditions for nitrogen oxides destruction. The mineralized clay additive used was OptiK-asT clay, which consists mainly of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with a minor amount of muscovite [$(\text{K},\text{Na})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si}_{3.1}\text{Al}_{0.9})\text{O}_{10}(\text{OH})_2$]. The kaolin clay was added to provide sufficient reactive Al and Si to combine with alkali elements in the feed to produce nepheline and other aluminosilicate mineral phases in the reformer. The raw materials used to prepare the FBSR waste forms were

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