



## Performance of the Fluidized Bed Steam Reforming product under hydraulically unsaturated conditions



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### ABSTRACT

Several candidates for supplemental low-activity waste (LAW) immobilization at the Hanford site in Washington State, USA are being considered. One waste sequestering technology considered is Fluidized Bed Steam Reforming (FBSR). The granular product resulting from the FBSR process is composed primarily of an insoluble sodium aluminosilicate matrix with the dominant phases being feldspathoid minerals with a 1:1:1 molar ratio of Na, Al and Si. To demonstrate the durability of the product, which can be disposed of at the unsaturated Integrated Disposal Facility (IDF) at Hanford, a series of tests has been performed using the Pressurized Unsaturated Flow (PUF) system, which allows for the accelerated weathering of the solid materials. The system maintains hydraulically unsaturated conditions, thus mimicking the open-flow and transport properties that will be present at the IDF. Two materials were tested using the system: 1) the FBSR granular product and 2) the FBSR granular product encapsulated in a geopolymer to form a monolith. Results of the experiments show a trend of relatively constant effluent concentration of Na, Si, Al, and Cs as a function of time from both materials. The elements I and Re show a steady release throughout the yearlong test from the granular material but their concentrations seem to be increasing at one year from the monolith material. This result suggests that these two elements may be present in the sodalite cage structure rather than in the predominant nepheline phase because their release occurs at a different rate compared to nepheline phase. Also, these elements do not seem to reprecipitate when released from the starting material. Calculated one-year release rates for Si are on the order of  $10^{-6}$  g/(m<sup>2</sup> d) for the granular material and  $10^{-5}$  g/(m<sup>2</sup> d) for the monolith material while Re release is seen to be two orders of magnitude higher than Si release rates. SEM imaging and XRD analysis show how the alteration of the two materials is dependent on their depth in the column. This phenomenon is a result of depth-dependent solution concentrations giving rise chemical environments that may be supersaturated with respect to a number of mineral phases.

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### 1. Introduction

The U.S. DOE is constructing the Hanford Site Tank Waste Treatment and Immobilization Plant (WTP) to transform 56 million gallons of radioactive and chemically hazardous waste stored in Hanford's 177 underground storage tanks into stable glass for disposal. Within the WTP, the pretreatment facility will receive waste from the tank farms and separate it into high-level waste (HLW) and low-activity waste (LAW) process streams, which will be sent to their respective facilities for vitrification. Currently, the

design lacks the capacity to treat all of the LAW that is not encapsulated during initial vitrification at WTP thus supplemental solid waste form technologies are being considered to fill this gap. One of the potential waste forms to encapsulate the LAW, and other contaminants of concern (COCs) contained in the LAW waste stream, is the Fluidized Bed Steam Reformer (FBSR) sodium aluminosilicate granular mineral product. Once the LAW is encapsulated in the mineral, and after encapsulation in a binder material or placement in a high integrity container, the solid waste product will be permanently disposed at the Integrated Disposal Facility (IDF) located at the Hanford site. Encapsulation in a binder material is a necessary step to fulfill a required IDF compressive strength value of 3.4 MPa (500 psi).

The FBSR granular product is produced through the use of steam reforming based on the Thermal Organic Reduction (THOR<sup>®</sup>)

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process (Mason et al., 2003). The (Strachan and Babad, 1980) moderate-temperature process (700–750 °C) is capable of incorporating both acidic and basic liquids and solid low-level waste (LLW) or LAW into a mineral product. During the process organic species are converted to CO<sub>2</sub> and water and nitrates and nitrites are reduced to N<sub>2</sub> (Neeway et al., 2012b; Olson et al., 2005). The resulting mineral product is composed of sodium aluminosilicate (NAS) feldspathoid minerals, with a Na:Al:Si ratio of 1:1:1, including sodalite, nosean, and nepheline.

Feldspathoid minerals are generally characterized by an ordered framework of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra with alkali and alkaline earth cations present in the interstices. Nepheline, the most common mineral synthesized as a result of the FBSR process, has a theoretical formula of Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–2SiO<sub>2</sub>. If chloride is captured in the structure, the mineral sodalite forms with the theoretical formula 3Na<sub>2</sub>O–3Al<sub>2</sub>O<sub>3</sub>–6SiO<sub>2</sub>·2NaCl. The sodalite minerals is the first member of the group of sodalite minerals represented by the general formula R<sup>I</sup><sub>8</sub>(R<sup>II</sup>R<sup>IV</sup>O<sub>4</sub>)<sub>6</sub>A<sub>n</sub>. This group of minerals has the ability to accommodate a large range of chemistry within its structure (Brenchley and Weller, 1994; Lepry et al., 2013; Williams et al., 1968). For instance, a number of monovalent cations may substitute in the R<sup>I</sup> site (e.g. Cs<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>, and Tl<sup>+</sup>) while the tri- and tetravalent sites may be composed of various cations (e.g. Al<sup>3+</sup>, B<sup>3+</sup>, Ga<sup>3+</sup>, P<sup>3+</sup>, Ge<sup>4+</sup>, Si<sup>4+</sup>). The site of the anion, A<sub>n</sub>, can be occupied by monovalent species (e.g. Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, I<sup>-</sup>, OH<sup>-</sup>, MnO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, and SCN<sup>-</sup>) while the divalent site may be occupied by species (e.g. C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, or SO<sub>4</sub><sup>2-</sup>). The versatility of this mineral can be exploited in terms of the immobilization of complex wastes present at the Hanford site. For example, when this phase contains sulfates within the cage structure, the mineral nosean is formed with the formula 3Na<sub>2</sub>O–3Al<sub>2</sub>O<sub>3</sub>–6SiO<sub>2</sub>·Na<sub>2</sub>SO<sub>4</sub>. Theoretically, TcO<sub>4</sub><sup>-</sup> may be incorporated into the sodalite cage structure though this incorporation has only been shown unambiguously with ReO<sub>4</sub><sup>-</sup> (Mattigod et al., 2006). Iodine, on the other hand, has been shown to be encapsulated in the sodalite cage (Strachan and Babad, 1980). In order to determine the viability of the FBSR product as a waste form for LAW immobilization, the release extent and rate of various radionuclides and potential contaminants leaching from the FBSR material in an unsaturated environment must be determined in a system that simulates natural conditions. The PUF apparatus and the associated method are used to simulate this particular environment and produce credible estimates of radionuclide release rates. Importantly, the PUF method has the added advantage that neoformed and secondary alteration phases are likely to form as a result of accelerated weathering. These phases can then be identified through post-reaction solid state analyses such as XRD and SEM. Also, the evolution of solution chemistry as a result of water contact with the FBSR minerals can be followed. The objective of this investigation was to measure the extent and rate of radionuclide release from the granular form of the FBSR material, and from the monolith, which is a mixture of the granular material and an amorphous inorganic polymer known as a geopolymer also made of aluminosilicates. In this paper, we present results collected from two long-term (1 year) PUF experiments. The changes with time of various parameters (e.g. pH and electrical conductivity) were

followed along with the changes in solution concentrations of the primary feldspathoid elements (Na, Si, and Al), as well as Cs, I, and Re. The last three elements were selected since the radionuclides common in LAW are Cs, I, and Tc (where Re has been used as a non-radioactive surrogate for Tc (Jantzen et al., 2013; McKeown et al., 2007)).

## 2. Materials and methods

### 2.1. Production and preparation of FBSR products

Two different FBSR materials were tested and the initial elemental weight percentage of several elements is presented in Table 1. These values were obtained by adding 0.1 g of a ground sample in 9 mL of concentrated HNO<sub>3</sub>, 3 mL concentrated HF, and 2 mL of concentrated HCl. This acid cocktail was then digested at 210 °C for 30 min then, after cooling, 30 mL of a 5% boric acid was added, then the samples were digested again at 180 °C for 25 min. The resulting solutions were then analyzed by ICP-MS and ICP-OES.

The material was produced at THOR Treatment Technology's facility at Hazen Research Inc. (HRI) in Golden, Colorado, USA using the Engineering Scale Technology Demonstration (ESTD) pilot plant. The purpose of the pilot plant was to demonstrate the FBSR process mineralization as well as monitoring gaseous effluents created in the process to conform to environmental release standards (TTT, 2009). The waste stream used was based on the Rassat non-radioactive Hanford LAW simulant, which is a 68 tank blend waste composition (Lorier et al., 2005; Rassat et al., 2003). Several concentrations of elemental constituents were increased in an effort to make certain that FBSR off-gas and mineral were detected. The material is a mixture of 20% Product Receiver (PR) and 80% High-Temperature Filter (HTF) fines (TTT, 2009). The resulting material was generated from the DOE Advanced Remediation Technologies (ART) P1-B campaign and the granular material is herein referred to as P1BG, the "G" being used to identify the granular product. A second sample was fabricated by encapsulating the granular material in a geopolymer monolith to comply with compressive strength requirements of 500 psi (3.4 MPa) for waste forms at the Hanford site IDF. The encapsulating material used in these studies is made of a geopolymer, designated GEO-7, which contains amorphous to semi-crystalline inorganic polymers made from aluminosilicates cross-linked in a three-dimensional structure. This material has a similar mineralogy to the feldspathoid minerals produced during the FBSR process. The binder is mixed with the granular product at room temperature by mixing fly ash with a sodium hydroxide solution (Crawford and Jantzen, 2011). FBSR granular material loading in the geopolymer is 65.7% (Crawford and Jantzen, 2011). The monolith prepared with the P1-B material is referred to as P1BM. A detailed characterization of the products is also given elsewhere (Williams et al., 2013).

To prepare for the PUF tests, the fabricated monolith was first crushed and then sieved to obtain a –60 + 40 mesh size fraction (250–400 μm particles). The granular material was also sieved the same size fraction without additional crushing. These powder samples were washed through the sieves using ethanol to remove fines adhering to the particles of the desired size range. No further rinsing of the product was performed. The granular sample was also heated for 8 h at 525 °C to remove leftover carbon from the FBSR process.

### 2.2. X-ray diffraction

Samples for XRD analysis were taken at various column depths in the PUF column. The samples were ground along with a weighed quantity of standard rutile powder (ca. 10 wt%) in an agate mortar

**Table 1**  
Chemical composition in mass % of the two Hazen engineering-scale FBSR materials used in this study.

	Al	Na	Si	Re	I	Cs	S	Pb	Fe	Cr	Ba
P1BG, granular	16.8	14.1	18.0	0.02	0.06	0.13	0.43	0.21	1.7	0.08	0.15
P1BM, monolith	10.9	13.3	16.0	0.02	0.12	0.14	0.18	0.13	2.0	0.05	0.09

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