



# Reductive capacity measurement of waste forms for secondary radioactive wastes



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## H I G H L I G H T S

- Reduction capacities is important for redox sensitive radionuclide release.
- Correct measurement of reduction capacity is necessary for waste form capacity.
- Ce(IV) method should be used for total reduction capacity of waste form.
- Blast furnace slag is a major source of reduction in cementitious waste form.
- Additional getters can be used to increase reduction capacity in waste form.

## A R T I C L E I N F O

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## A B S T R A C T

The reductive capacities of dry ingredients and final solid waste forms were measured using both the Cr(VI) and Ce(IV) methods and the results were compared. Blast furnace slag (BFS), sodium sulfide, SnF<sub>2</sub>, and SnCl<sub>2</sub> used as dry ingredients to make various waste forms showed significantly higher reductive capacities compared to other ingredients regardless of which method was used. Although the BFS exhibits appreciable reductive capacity, it requires greater amounts of time to fully react. In almost all cases, the Ce(IV) method yielded larger reductive capacity values than those from the Cr(VI) method and can be used as an upper bound for the reductive capacity of the dry ingredients and waste forms, because the Ce(IV) method subjects the solids to a strong acid (low pH) condition that dissolves much more of the solids. Because the Cr(VI) method relies on a neutral pH condition, the Cr(VI) method can be used to estimate primarily the waste form surface-related and readily dissolvable reductive capacity. However, the Cr(VI) method does not measure the total reductive capacity of the waste form, the long-term reductive capacity afforded by very slowly dissolving solids, or the reductive capacity present in the interior pores and internal locations of the solids.

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## 1. Introduction

Large volumes of radioactive wastes were produced at the U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State during the Cold War era and most of the radioactive waste is presently stored in 177 underground Hanford storage tanks [1]. The radioactive waste generated at the Hanford Site is present in fuel reprocessing wastes, which are awaiting retrieval,

treatment, immobilization, and permanent disposal. After the wastes are retrieved from the storage tanks, current disposal plans call for separation of the waste into two fractions: a high-level waste (HLW) and a low-activity waste (LAW) stream, both which will be treated, vitrified, and disposed of separately. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is under construction to treat the radioactive wastes and immobilize them in a glass waste form. The HLW stream will be vitrified and stored at Hanford until a deep-geologic repository is built to receive this defense radioactive waste as well as commercial spent nuclear fuel. In addition, at least a portion of (~35%) the LAW stream will be converted into a borosilicate glass waste form, which will be

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disposed of in a shallow burial facility at the Hanford Site, the Integrated Disposal Facility (IDF) [2]. Even with careful engineering controls, a fraction of the volatile radionuclides ( $^{99}\text{Tc}$  and  $^{129}\text{I}$ ) during the vitrification of both the HLW and LAW streams is expected to escape. The volatilized radionuclides will be captured in melter off-gas scrubbers and returned to the melter. However, some of the volatile radionuclides are expected to be lost and become part of the secondary waste stream from the vitrification process [1]. A solidification treatment unit (STU) is being constructed at the effluent treatment facility (ETF) on the Hanford Site. The ETF processes low-level radioactive, mixed wastewaters, and secondary radioactive liquid wastes generated during various Hanford Site operations and in the future may process the secondary wastes from the WTP. Because of the cost considerations and volatility issues, the volatile secondary radioactive wastes need to be solidified in a low-temperature-based waste form [3–5].

Low-temperature waste solidification processes commonly use reductants that are inherently present in the dry blend or are added to improve the retention of redox-sensitive metal/metalloid and radioactive contaminants such as Cr, Se,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$ , and  $^{238}\text{U}$  in the solid waste forms. These redox-sensitive contaminants are generally much less soluble when present in their reduced valence states in solutions or solids. Their ability to adsorb or co-precipitate with solidification compounds and soils/sediments is much better in the reduced forms than in the oxidized forms. Thus, when chemically reduced, the mobility of these contaminants is significantly decreased even if disposed in subsurface environments. Therefore, measuring the reductive capacity of waste forms, as well as the dry ingredients used to make waste forms, is a key task needed to project the long-term performance of the waste forms after they are placed in the subsurface environment. Shallow land-burial repositories typically have partially water-saturated, mildly-oxidizing, and near-neutral pH conditions. The influx of  $\text{O}_2$ -saturated fresh pore waters and  $\text{O}_2$  in the air that partially fills the unsaturated pores will over time push the redox status of the repository toward oxidizing condition by consuming any reducing agents present in the waste forms and other repository materials. The weathering of the emplaced waste forms and the time required for the natural environmental oxidizing conditions to consume any reducing agents can be estimated by measuring the reducing capacity (i.e., meq of electrons/kg of material) of the emplaced materials.

At least two widely used measurement techniques have been described in the literature for determining reductive capacity in materials such as fly ash, blast furnace slag (BFS), and native sediments, etc. [6,7]. Simply stated, both procedures define reductive capacity as the amount of an oxidant that can be reduced by a testing material when sufficient time is given that the reaction proceeds to its maximum extent or equilibrium condition. The technique described by Angus and Glasser (1985) uses cerium (IV) as the oxidant, while the Lee and Batchelor (2003) method uses Cr(VI) as the oxidant. Because there are significant differences [a factor of ~22, with the Ce(IV)-based technique yielding the larger value [8] for material such as BFS which is a commonly used material in low-temperature cementitious waste forms], both procedures should be tested and the results need be compared to understand the range in reductive capacity for materials. The objectives of this study were to test these two methods and to measure the reductive capacity of several different waste forms and their dry ingredients as well as liquid simulants used to prepare different waste forms.

## 2. Materials and methods

Four different waste forms [Cast Stone, DuraLith, fluidized bed steam reformer (FBSR), and Ceramicrete] prepared with or

without  $^{99}\text{Tc}$  using different simulant compositions, as well as dry ingredients, were tested for reductive capacity measurements. More details for waste form preparation are found in previous reports [9,10].

### 2.1. Waste simulant and waste form details

Briefly speaking, Cast Stone is a cementitious waste form that was developed to solidify the low-activity and secondary waste that will be generated by the operation of the WTP at the Hanford Site [11,12]. Cast Stone consists of a mixture of Class-F fly ash, Grade-120 BFS, and Type-I/II Portland cement. For the Cast Stone waste form, eight different simulants were spiked with Tc or spiked with Re as a surrogate for Tc. The eight liquid simulants were the same simulants as used in the Cast Stone Phase-II tests (S1-2, -4, -6, -8, and -10 M Na; S2-2 M Na; S3-2 M Na; and S4-2 M Na), which are described in detail in Sundaram et al. (2011) [10]. Simulant S1 solutions with 4, 6, 8, and 10 M Na were prepared with increased amounts (multiplied by 2, 3, 4, and 5) of each constituent found in the S1-2 M Na simulant (Table 1) to make the target simulants. The other four simulant compositions (S1-2 M Na, S2-2 M Na, S3-2 M Na, and S4-2 M Na) are the same as simulants S1, S2, S3, and S4 described in Table 1. Phase I simulant used for screening test of Cast Stone [9] is also shown in Table 1. Both Tc-spiked and Re-spiked Cast Stone samples were prepared to measure reductive capacity.

Geopolymers, also known as alkali-activated aluminosilicate binders, form through the reaction of aluminosilicate materials, such as clay or fly ash, in a caustic solution. When the reactions proceed at near-ambient temperature, polymerization forms amorphous to semi-crystalline aluminosilicate networks [13]. A specific geopolymer known as “DuraLith” was included to test the reductive capacity measurement for Hanford WTP secondary wastes [14]. DuraLith is composed of three components—an activator, a binder, and an enhancer [3,9]. The activator is a solution of sodium hydroxide and/or potassium hydroxide with a rapidly dissolving form of silica, such as silica fume (also known as micro-silica) or fly ash. The binder is a mixture of meta-kaolinite, BFS, fly ash, or other additives. The binder and activator are the two main components that yield the geopolymer material. The enhancers are essentially getter material like  $\text{SnF}_2$ . Both Tc-free and Tc-spiked DuraLith waste forms were prepared with the four different simulants (S1, S2, S3, and S4) and measured for reductive capacity. Each of the dry ingredients used in preparing DuraLith (i.e., fumed silica, meta-kaolinite, river sand, silver zeolite, BFS, sodium sulfide hydrate [ $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ], and  $\text{SnF}_2$ ) were also analyzed to obtain their individual reductive capacities.

The two FBSR samples, namely FBSR granular product and FBSR encapsulated in Geo-7 geopolymer binder followed by milling to a powder, were tested for reductive capacity. The FBSR granules were prepared using a WTP secondary-waste simulant injected into a laboratory-scale steam reforming apparatus, and the reformer product was screened (<1.0 mm). The FBSR-GEO-7 monoliths (2-in.-diameter by 4-in.-long cylinders) also were prepared by mixing the FBSR solids with a geopolymer binder. The Geo-7 geopolymer was created by mixing fly ash with sodium silicate and sodium hydroxide with an FBSR product waste loading of 65.2%. More details regarding the two FBSR samples can be found in Pires et al. (2011) [15].

Ceramicrete is fabricated by an acid/base reaction of calcined magnesium oxide and mono potassium phosphate, which forms a slurry when mixed with water that sets into a hard ceramic in a few hours based on Eq. (1) [16,17].



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