



# Reductive capacity measurement of waste forms for secondary radioactive wastes



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## HIGHLIGHTS

- 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.

## ARTICLE INFO

### Article history:

Received 12 August 2015

Received in revised form

21 September 2015

Accepted 23 September 2015

Available online 28 September 2015

### Keywords:

Reductive capacity

Waste form

Blast furnace slag

Cast stone

Geopolymer

Ceramicrete

## ABSTRACT

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.

Published by Elsevier B.V.

## 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].



**Table 1**  
Composition of WTP secondary waste simulants.

Element (mole/liter)	S1 caustic scrubber median	S2 statistical – cluster 1 3/16/2038	S3 statistical – cluster 2 05/28/2024	S4 caustic scrubber/10% of SBS blend	Phase I simulant
Na	2	2	2	2	2
Al(OH) <sub>3</sub>	1.88E-01	2.28E-01	1.84E-01	8.48E-02	0.23
Si	3.76E-03	4.08E-03	1.55E-03	2.78E-02	–
K	1.16E-03	1.30E-03	4.36E-03	5.74E-02	–
NH <sub>4</sub> <sup>+</sup> (total)	–	–	–	8.82E-01	–
OH <sup>-</sup>	7.96E-01	8.70E-01	4.90E-01	2.04E-08	1.2
NO <sub>3</sub> <sup>-</sup>	6.56E-01	3.80E-01	7.94E-01	2.26E + 00	0.69
CO <sub>3</sub> <sup>2-</sup>	4.56E-02	9.32E-02	7.88E-02	2.08E-02	1.5E-6
Cl <sup>-</sup>	4.50E-02	4.34E-02	5.82E-02	2.08E-02	–
NO <sub>2</sub> <sup>-</sup>	2.40E-02	2.10E-02	7.66E-02	8.62E-02	–
PO <sub>4</sub> <sup>3-</sup>	1.37E-02	9.70E-03	1.21E-02	1.02E-02	1.7E-2
SO <sub>4</sub> <sup>2-</sup>	8.82E-03	1.16E-02	1.03E-02	8.72E-02	9.7E-3
F <sup>-</sup>	1.11E-03	7.50E-04	8.84E-04	2.04E-08	–
Cr	4.06E-04	4.06E-04	4.06E-04	2.18E-03	8.43E-3 (1×)
Ag	1.25E-05	1.25E-05	1.25E-05	4.70E-05	2.5E-4 (100×) <sup>a</sup>
As	6.96E-05	6.96E-05	6.96E-05	3.22E-05	–
Cd	3.14E-06	3.14E-06	3.14E-06	4.32E-05	5.0E-5 (100×)
Hg	2.26E-05	2.26E-05	1.13E-05	1.06E-05	3.3E-5 (1×)
Pb	1.80E-05	1.80E-05	1.80E-05	1.66E-05	7.9E-4 (100×)
Tc	3.62E-05	3.62E-05	3.62E-05	1.12E-03	–
<sup>99</sup> Tc (Ci/Liter)	6.05E-05	6.10E-05	6.10E-05	1.88E-03	1.3E-5 Ci/L
I	9.24E-06	9.24E-06	9.24E-06	1.26E-04	2.9E-6
<sup>129</sup> I (Ci/Liter)	1.91E-07	1.91E-07	1.91E-07	2.60E-06	–
TOC <sup>b</sup> (as oxalate)	1.88E-01	2.28E-01	1.84E-01	8.48E-02	0.23

<sup>a</sup> Numbers in parentheses denote spiking proportions of contaminants of concern.

<sup>b</sup> Total organic carbon.

The process is simple and quite similar to the Cast Stone mixing process. For the Ceramicrete waste form, only S1 simulant spiked with Tc was prepared. This Ceramicrete final waste form and all its dry ingredients (SnCl<sub>2</sub>, fly ash [Type C], silver zeolite, MgO, and KH<sub>2</sub>PO<sub>4</sub>) were also analyzed for reductive capacity.

## 2.2. Particle size analysis

The measurement of the reductive capacity of the dry materials and final waste forms is sensitive to their grain-size distribution, because particle size affects the rate at which the redox reactions occur in the test solutions. Therefore, all the dry materials and final waste forms were ground to less than a 1.0-mm size fraction and sieved before reductive capacity measurements. Particle-size characterization was also done with a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, Massachusetts) particle-size analyzer with a Hydro G wet dispersion accessory (equipped with a continuously variable and independent pump, stirrer, and ultrasound). The Mastersizer has a nominal size measurement range of 0.02 μm–2000 μm. The actual range is dependent on the accessory used as well as the properties of the solids being analyzed. When coupled with the Hydro G wet dispersion accessory, the nominal measuring range is 0.02 μm–2000 μm dependent on material density. A performance check of the particle-size analyzer was performed with a particle-size standard traceable to the National Institute of Standards and Technology before any particle-size analysis was undertaken. Small aliquots of the samples (~0.2–1 g for dry powders) were diluted in degassed DIW in the Hydro G dispersion unit with the pump and stirrer speeds set at 2500 rpm and 1000 rpm, respectively, for 60 s before making the particle-size measurements. The total volume of the dispersion unit was ~800 mL. Appropriate dilutions were determined by the amount of light passing through the diluted material (obscurant), which was measured by the particle-size analyzer. Samples were analyzed, initially without sonication and then during sonication (100%, 20 W) after an initial sonication period of 60 s. Duplicate samples

were measured to confirm the mixing and sub-sampling technique to make sure that a representative particle-size distribution (PSD) of the material could be obtained.

## 2.3. Reductive capacity measurement

The Ce(IV) method for measuring reductive capacity described by Kaplan et al. (2005) and Augus and Glasser (1985) [6,8] was slightly modified. Generally, two different concentrations of Ce(IV) stock solution (10 mM and 40 mM) were prepared in 10% H<sub>2</sub>SO<sub>4</sub> solution using (NH<sub>4</sub>)<sub>4</sub>Ce(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O (Sigma–Aldrich). Based on results of preliminary tests, if the reductive capacity of the sample was higher than 100 meq/kg, the 40-mM Ce(IV) stock solution was used. For samples with less than 100 meq/kg reductive capacity, the 10-mM Ce(IV) stock solution was used. The procedure then used 0.5 g of testing sample (<1 mm size fraction) mixed with 15 mL of the appropriate Ce(IV) stock solution in a 20-mL vial. Immediately after mixing, the vial was tightly capped and placed on a platform shaker to mix completely at room temperature (23 ± 2 °C) for 1 day. To determine the effect of mixing time, the reaction time also was varied between 1 h and 7 days for certain samples (BFS and Cast Stone) to test for kinetic effects before measuring the reduction capacity of other materials. The solution was then filtered with a 0.45-μm syringe filter (Whatman) after the target reaction time. Then 0.05 mL of Ferroine solution [0.025M Fe(o-phenanthroline)<sub>2</sub><sup>3+</sup>, Fluka] was mixed with 5 mL of the filtrate, and the final solution was titrated using a Metrohm titrator that dispensed 20 mM of ammonium ferrous sulfate prepared in 4% H<sub>2</sub>SO<sub>4</sub> solution until the solution developed and retained a lilac color. Before the measurement of reductive capacities, the concentration of ammonium ferrous sulfate solution was initially calibrated with standard Ce(IV) solution (1 M, Sigma–Aldrich). The reductive capacity was calculated by determining the difference between the oxidizing equivalents in Ce(IV) solution [meq Ce(IV)] and the reducing equivalents of Fe(II) needed to neutralize excess Ce(IV) after reaction with the sample [meq Fe(II)]. The final reductive capacity per gram was calculated by

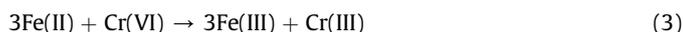
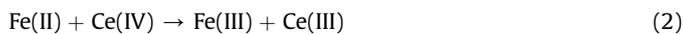
dividing the reductive capacity (meq) by the mass of sample (g).

The Cr(VI) reduction capacity procedure developed by Lee and Batchelor (2003) [7] was also modified. The Cr(VI) stock solutions (10 mM or 30 mM) were prepared with  $K_2CrO_4$  (Sigma–Aldrich) in 10-mM  $NaHCO_3$  solution. The Cr(VI) solutions were then purged with  $N_2$  gas for 2 h, and the stock solution was introduced into an anoxic chamber (Coy Laboratory Products Inc.) containing a mixed gas atmosphere (4%  $H_2$  and 96%  $N_2$ ). One-gram samples of the waste form or dry ingredients were placed in 20-mL quartz vials and then introduced into the anoxic chamber. The sample vial and Cr(VI) stock solution were kept in the anoxic chamber for 2 days to allow any air present in the containers to diffuse out before use. After the 2-day air-purging period, 10 mL of the Cr(VI) stock solution was mixed into the sample vial, and the pH of the suspension was adjusted to  $7 \pm 1$  by adding a 1-M NaOH or 1-M  $H_2SO_4$  solution. The vials were tightly capped, removed from the chamber, placed on a platform shaker, and allowed to mix at room temperature ( $23 \pm 2$  °C) for 7 days. To determine the effect of shaking time, some of the test vials with BFS and Cast Stone samples were allowed to shake for varying times, ranging from 1 h to 7 days. After mixing, the vial was transferred back into the anoxic chamber, and 0.142 g of sodium sulfate was added. The vials were re-sealed, removed from the chamber, and shaken on the platform shaker for one more day. This was done to remove any potentially adsorbed Cr(VI) from the materials being tested so that the final Cr measurement in solution truly reflected all the Cr(VI) that was reduced and precipitated as Cr(III). The final supernatant was filtered with a 0.45- $\mu m$  syringe filter, and the concentration of Cr(VI) in the final filtrate was determined by a titration method. One mL of the filtrate was mixed with 1 mL of the  $H_2SO_4$  solution (1:1 ratio) and 0.05 mL of Ferroine solution, as used for Ce(IV) method. The resultant solution was titrated with 20 mM or 10 mM ammonium ferrous sulfate solution, which was prepared in 4%  $H_2SO_4$  solution, until the solution became and remained lilac in color. The final reductive capacity was calculated by determining the difference between the oxidizing equivalents in Cr(VI) and the reducing equivalents of Fe(II) as described above in Ce(IV) method.

### 3. Results and discussion

#### 3.1. Particle size analysis

The reductive capacities of the waste forms and their individual dry ingredients were measured separately by using both redox pairs, Ce(IV)/Ce(III) or Cr(VI)/Cr(III), with back titration of excess oxidant with Fe(II). In both the Ce(IV) and Cr(VI) methods, the test materials reach an end point based on the following reactions:



The amounts of Ce(IV) and Cr(VI) consumed by the solid materials are used to quantify the reductive capacities. Measuring the reductive capacity of porous materials involves diffusion of oxidants [Ce(IV) or Cr(VI)] into the pores present in the sample materials. In the Ce(IV) method, a strong acid (10% sulfuric acid) is used to facilitate the dissolution of the solid materials so that the oxidant can easily contact the smaller dissolving particles or the reduced solutes generated from the dissolution process. However, in the Cr(VI) method, because 10-mM carbonate buffer solution is used to adjust the pH to around 7.0, there is little solid dissolution, and the particle-size reduction and the contact between the Cr(VI) oxidant and reduced species within the solids may not be complete. In this case, the PSD of the porous material is also a sensitive factor in

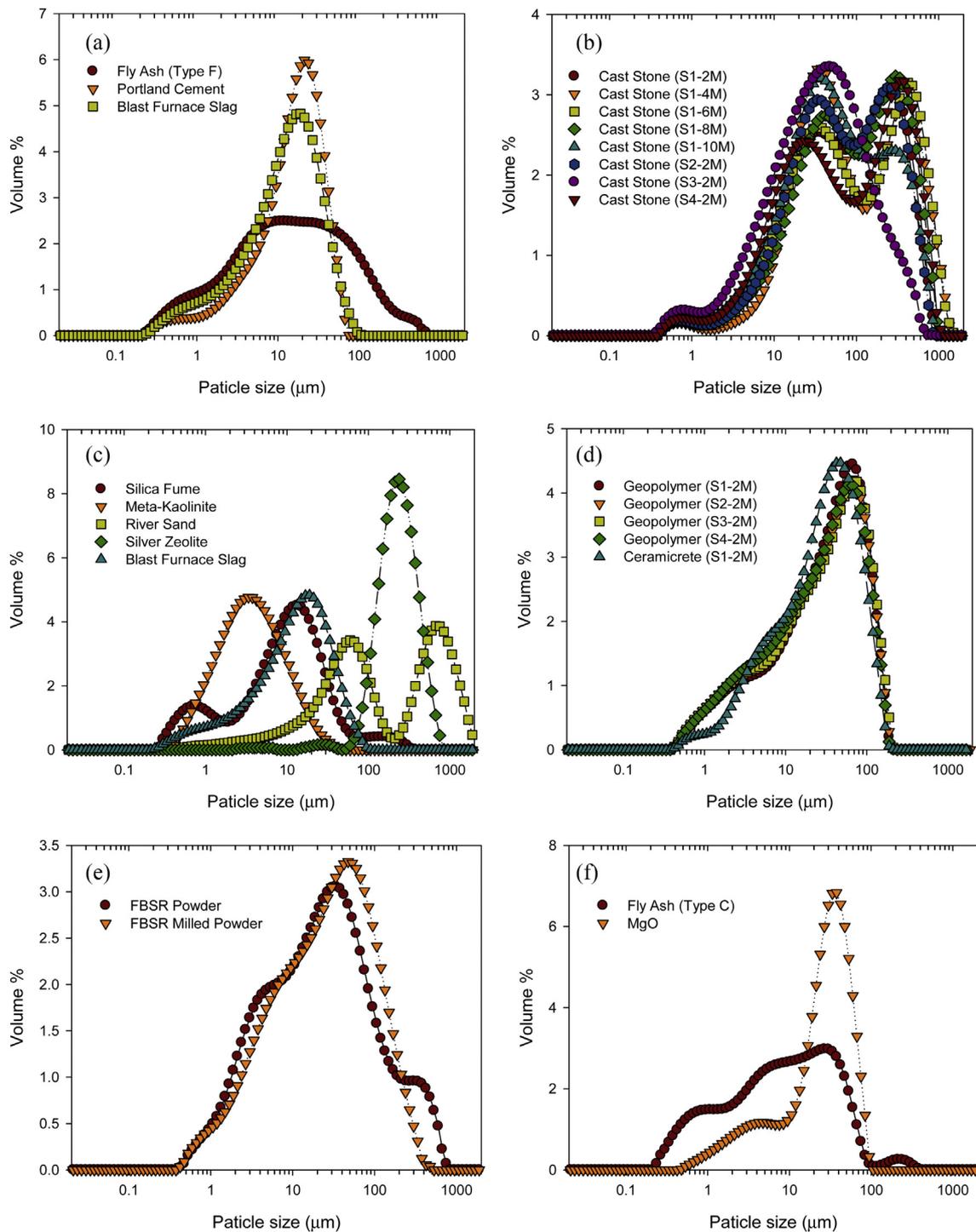
measuring reductive capacity.

The measured PSDs of the crushed waste forms and their individual ingredients used in the reductive capacity analyses are shown in Fig. 1. The PSD of fly ash (Type F) was a little bit wider than those of the cement and BFS samples, which both had a narrow range centered around 20  $\mu m$  (Fig. 1a). The Cast Stone samples showed a bimodal PSD around 40  $\mu m$  and 400  $\mu m$ , except for the Cast Stone prepared with S1-2M simulant (Fig. 1b). The PSDs of the Duralith(Geopolymer) dry ingredients and the Duralith waste form prepared with the four different simulants are shown in Fig. 1c and d, respectively. Metakaolinite, fumed silica, and BFS have narrow PSDs with an average particle size less than 20  $\mu m$ , while river sand has a wide PSD with a bimodal distribution between 60 and 1100  $\mu m$  (Fig. 1c). Silver zeolite has a narrow PSD and larger average particle size (257  $\mu m$ ). However, because zeolite is a highly porous material with varying sizes of internal pores, the diffusion of oxidants, Ce(IV) or Cr(VI) inside these pores might be limited. The Duralith and Ceramicrete waste form samples also show a narrow and unimodal PSD (Fig. 1d). The PSDs of Duralith samples made with the four simulants were similar to each other. The PSDs of the two FBSR samples and the dry ingredients used to prepare Ceramicrete are shown in Fig. 1e and 1f, respectively. The two FBSR samples show very similar PSD results with an average size between 50  $\mu m$  and 70  $\mu m$ . Type-C fly ash showed a wider PSD range than MnO, but the PSD of Type-C fly ash, which ranged from 0.2  $\mu m$  to 100  $\mu m$  (Fig. 1f), is narrower than that of Type-F fly ash used in Cast Stone formulation, which ranged from 0.1  $\mu m$  to 1000  $\mu m$  (Fig. 1a).

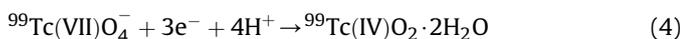
#### 3.2. Kinetic effects on the measured reductive capacity

The effects of contact time between the oxidizing reagent and sample solids were evaluated for BFS and Cast Stone samples using both the Ce(IV) and Cr(VI) methods to determine the optimal reaction time for measuring reductive capacity, and the results are given in Fig. 2. Augus and Glasser [6] and Kaplan et al. [8] used only an 1-h reaction time to measure the reductive capacity of BFS using the Ce(IV) method. However, as shown in Fig. 2, it took at least 1 or 2 days to reach reductive capacity steady state using the Ce(IV) method in our tests for the BFS and Cast Stone. Roberts and Kaplan [18] also mentioned that an hour of mixing the Ce(IV) solution with solid samples is sufficient time to allow Ce(IV) to diffuse completely using the Augus and Glasser [6] method. However, according to our results, at least a 1- or 2-day reaction time is needed to measure complete reductive capacity of all the solid materials using the Ce(IV) method.

Using the Cr(VI) method, it took at least 4 days for the measured reductive capacity values to reach steady state values. Because the Ce(IV) method uses 10% sulfuric acid, and the pH in Ce(IV) stock solution is between 0 and 1, the Ce(IV) method measures almost total reductive capacity of the solid sample that can be dissolved within a relatively short reaction period (i.e., 1–2 days). However, because the Cr(VI) method uses 10-mM  $NaHCO_3$  solution, and the pH is adjusted to around 7.0, the Cr(VI) method measures primarily the surface and an unknown portion of the internal particles' reductive capacity of the sample, over 4 days needed to reach steady state (i.e., attain a constant value for the reductive capacity). These kinetic effects and the potentially limited accessibility of the internal reductants within the solid particles to reaction with the oxidizing reagent in the Cr(VI) method lead to differences between the reductive capacities measured using these two methods. In secondary waste forms, because  $^{99}Tc$  is considered to be uniformly distributed and can react with reductants present in each waste form following by the reaction,



**Fig. 1.** Measured particle size distributions (PSDs) of dry ingredients used for making Cast Stone (a), Cast Stones (b), dry Ingredients of Duralith (c), Geopolymers (d), FBSR Waste Forms (e), and dry Ingredients used for Ceramicrete (f).



the reductive capacity measured by the Ce(IV) method is expected to be more useful for estimating total reductive capacity of waste forms and predicting the long-term leaching of Tc from secondary waste forms.

### 3.3. Reductive capacity measurements

The reductive capacities of different secondary waste forms

prepared without  ${}^{99}\text{Tc}$  and their dry ingredients were measured using two methods, and the results are given in Table 2. Different waste forms with  ${}^{99}\text{Tc}$ -spiked simulants were also used to test the reductive capacity, and the results are shown in Table 3. The dry blend ingredients with the largest reductive capacity are BFS, tin chloride, tin fluoride, and sodium sulfide. The reductive capacity of the particular BFS used in forming the Cast Stone waste forms was 799 meq/kg when the Ce(IV) method was used. This value is slightly lower than the reported value of 820 meq/kg by Lukens et al. [18] and Roberts and Kaplan [19] for the BFS used at Savannah River to produce Saltstone.

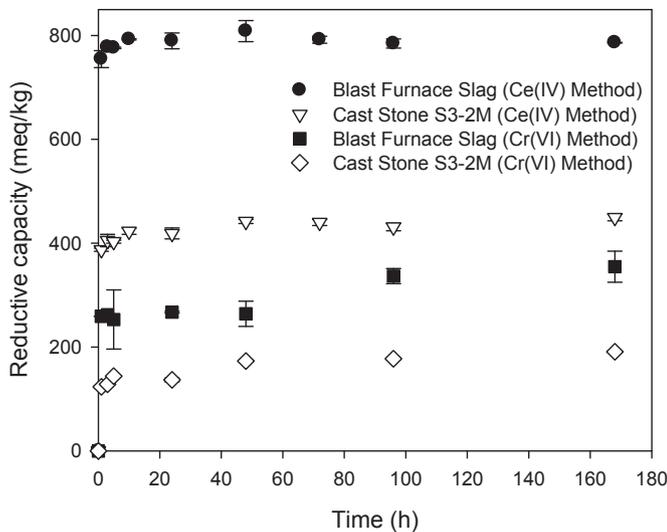


Fig. 2. Effect of reaction time for the measurement of reductive capacity.

The reductive capacity of the BFS used to make Cast Stone as measured with the Cr(VI) method was 346 meq/kg, which is noticeably lower than the 799 meq/kg value determined with the Ce(IV) method. However, the different values from these two

methods are readily explained by the kinetic effects of contact time and the effects of different solid dissolution rates at different pH conditions as mentioned previously. The BFS contains both ferrous ion and sulfides that are strong reductants for  $^{99}\text{Tc}$  to enhance immobilization of  $^{99}\text{Tc}$  inside waste forms. Both Fe(II) and S(II) become reactive reductants once they dissolve, and they can effectively reduce contaminants such as  $^{99}\text{Tc}$  that may be present in the pore water within the waste form to form more stable species such as reduced Tc(IV) in the secondary waste form. However, based on the measurement condition, only ferrous-iron oxides present in the BFS surfaces can be measured by the Cr(VI) method, while all reducing materials, including sulfur compounds and the ferrous iron oxides in the BFS can be measured when the Ce(IV) method is used.

Both tin fluoride and tin chloride, used for making DuraLith and Ceramicrete waste forms, respectively, show very high reductive capacities. The measured reductive capacity (8700 to 12,000 meq/kg) for tin compounds using the two methods was similar to their theoretically calculated reductive capacities, 10,549 and 12,764 meq/kg for tin fluoride and tin chloride, respectively. Tin chloride, an ingredient of Ceramicrete, and tin fluoride, an ingredient of DuraLith, are strong reducing agents that have a standard reduction potential,  $E_0$ ,  $[\text{Sn(IV)/Sn(II)}] = +0.15 \text{ V}$  [20]. The tin (II) solids can readily oxidize to Sn(IV) upon contact with oxygen or redox-sensitive constituents. When alkaline pH conditions are maintained and the Sn(II) solution is added, Sn(II) oxide ( $\text{SnO} \cdot \text{H}_2\text{O}$ )

Table 2

Reductive capacities of secondary waste forms without Tc and their ingredients.

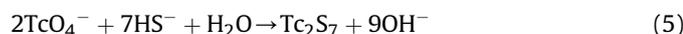
Materials	Simulants	Reductive capacity (Ce(IV) method) (meq/kg)	Reductive capacity (Cr(VI) method) (meq/kg)
<b>Cast stone ingredients</b>			
Blast furnace slag		798.7 ± 14.2	345.6 ± 21.9
Fly ash (Type F)		77.3 ± 1.3	2.0 ± 0.4
Portland cement		79.0 ± 33.0	35.2 ± 2.9
<b>Cast stone variants</b>			
Cast stone S1-2M	S1 (2-M Na)	398.7 ± 3.2	185.4 ± 7.6
Cast stone S1-4M	S1 (4-M Na)	442.0 ± 3.4	181.9 ± 8.2
Cast stone S1-6M	S1 (6-M Na)	485.3 ± 5.7	192.8 ± 1.7
Cast stone S1-8M	S1 (8-M Na)	540.0 ± 1.9	189.1 ± 1.4
Cast stone S1-10M	S1 (10-M Na)	595.6 ± 2.0	179.0 ± 2.8
Cast stone S2-2M	S2 (2-M Na)	401.7 ± 4.6	184.4 ± 3.9
Cast stone S3-2M	S3 (2-M Na)	449.6 ± 1.4	199.8 ± 7.3
Cast stone S4-2M	S4 (2-M Na)	461.1 ± 12.6	212.4 ± 2.0
<b>DuraLith ingredients</b>			
Silica fume		300.6 ± 6.7	22.5 ± 2.6
Meta-kaolinite		0.4 ± 0.0	0.3 ± 0.2
River sand		1.6 ± 1.2	1.0 ± 0.8
Silver zeolite		47.7 ± 6.2	1129.0 ± 52.4
Blast furnace slag		798.7 ± 14.2	435.9 ± 8.1
Sodium sulfide hydrate		8210.8 ± 287.9	31,049.9 ± 1158.
Tin fluoride		12,194.3 ± 120.3	8652.1 ± 715.5
<b>DuraLith geopolymer</b>			
DuraLith S1-2M	S1 (2M Na)	456.9 ± 3.1	128.2 ± 2.4
DuraLith S2-2M	S2 (2M Na)	458.2 ± 3.1	114.3 ± 0.7
DuraLith S3-2M	S3 (2M Na)	464.9 ± 2.9	134.4 ± 2.5
DuraLith S4-2M	S4 (2M Na)	411.7 ± 2.6	115.6 ± 0.6
<b>Ceramicrete ingredients</b>			
Tin chloride		10,038.8 ± 98.3	11,315.2 ± 613.2
Fly ash (Type C)		84.1 ± 4.1	27.0 ± 1.7
Silver zeolite		47.7 ± 6.2	1129.0 ± 52.4
MgO		281.6 ± 0.0	199.5 ± 12.2
KH <sub>2</sub> PO <sub>4</sub>		18.1 ± 0.7	10.6 ± 0.7
<b>FBSR</b>			
FBSR powder		2823.2 ± 45.0	21.7 ± 2.5
FBSR milled powder		914.9 ± 8.1	16.4 ± 5.4
<b>Simulants</b>			
Simulant 1	S1 (2M Na)	366.4 ± 19.8	218.2 ± 6.0
Simulant 2	S2 (2M Na)	450.0 ± 1.2	229.5 ± 3.3
Simulant 3	S3 (2M Na)	441.9 ± 8.1	325.6 ± 13.4
Simulant 4	S4 (2M Na)	281.1 ± 2.3	289.8 ± 4.3

**Table 3**  
Reductive capacities of  $^{99}\text{Tc}$  loaded secondary waste forms.

Materials	Simulants	Reductive capacity (Ce(IV) method) (meq/kg)	Reductive capacity (Cr(VI) method) (meq/kg)
<b><math>^{99}\text{Tc}</math>-loaded cast stone</b>			
$^{99}\text{Tc}$ -loaded cast stone S1-2M	S1 (2-M Na)	379.4 ± 5.6	212.5 ± 7.7
$^{99}\text{Tc}$ -loaded cast stone S1-4M	S1 (4-M Na)	445.3 ± 13.0	209.6 ± 6.5
$^{99}\text{Tc}$ -loaded cast stone S1-6M	S1 (6-M Na)	495.6 ± 2.0	215.7 ± 13.1
$^{99}\text{Tc}$ -loaded cast stone S1-8M	S1 (8-M Na)	556.7 ± 3.2	219.3 ± 9.9
$^{99}\text{Tc}$ -loaded cast stone S1-10M	S1 (10-M Na)	528.3 ± 2.6	205.0 ± 14.8
$^{99}\text{Tc}$ -loaded cast stone S2-2M	S2 (2-M Na)	402.5 ± 3.3	203.7 ± 25.1
$^{99}\text{Tc}$ -loaded cast stone S3-2M	S3 (2-M Na)	500.4 ± 5.2	211.1 ± 13.6
$^{99}\text{Tc}$ -loaded cast stone S4-2M	S4 (2-M Na)	423.7 ± 8.6	204.0 ± 7.3
<b><math>^{99}\text{Tc}</math>-loaded DuraLith</b>			
$^{99}\text{Tc}$ -loaded DuraLith S1-2M	S1 (2-M Na)	581.9 ± 10.5	116.9 ± 12.9
$^{99}\text{Tc}$ -loaded DuraLith S2-2M	S2 (2-M Na)	536.6 ± 8.9	105.1 ± 7.6
$^{99}\text{Tc}$ -loaded DuraLith S3-2M	S3 (2-M Na)	561.9 ± 17.9	131.2 ± 5.7
$^{99}\text{Tc}$ -loaded DuraLith S4-2M	S4 (2-M Na)	540.0 ± 18.1	126.5 ± 5.2
<b><math>^{99}\text{Tc}</math>-loaded ceramicrete</b>			
$^{99}\text{Tc}$ -loaded ceramicrete S1-2M	S1 (2-M Na)	943.5 ± 2.4	167.6 ± 2.8

precipitates and then dissolves to form stannite salt  $[\text{NaSn}(\text{OH})_3]$  with excess base. Most of the secondary waste forms considered in this study use large amounts of caustic ingredients so that  $\text{Sn}(\text{II})$  solutions can convert to the stannite salt, which serves as a continuous source of reducing agent in the final solid waste form and thus can behave as getter material to enhance immobilization of redox sensitive contaminants in waste forms [21,22].

Sodium sulfide, an ingredient of DuraLith, can produce  $\text{HS}^-$  when dissolved in water, which promotes the formation of many metal sulfide precipitates. Liu et al. [23,24] also reported that the reaction between sulfide and  $\text{TcO}_4^-$  in pH 9 aqueous solution under anoxic conditions produces  $\text{Tc}_2\text{S}_7$  precipitate according to the reaction



Note that the sulfur in this compound ( $\text{Tc}_2\text{S}_7$ ) is a mixture of polysulfides such that each sulfur is not  $-2$  charged. Also,  $\text{Na}_2\text{S}$  can oxidize to  $\text{Na}_2\text{S}_2\text{O}_3$ , which can react with  $\text{TcO}_4^-$  and reduce the  $\text{Tc}(\text{VII})$  to form  $\text{TcO}_2$  such as the suggested reaction [19].



In addition,  $^{99}\text{Tc}$  sequestration kinetics are faster with increasing  $\text{S}/\text{Fe}(\text{II})$  ratios between 0 and 0.056, and confirmed the importance of  $\text{FeS}$  in  $^{99}\text{Tc}$  sequestration [25]. Therefore,  $\text{Na}_2\text{S}$  can be used as an oxygen scavenger to make an anoxic condition in the secondary waste form for improving  $^{99}\text{Tc}$  retention as reduced  $\text{Tc}(\text{IV})$  species. The measured reductive capacities of  $\text{Na}_2\text{S}$  varied significantly from 8200 meq/kg to 31,000 meq/kg, depending on the method used. Higher reductive capacities were found for  $\text{Na}_2\text{S}$  and  $\text{SnF}_2/\text{SnCl}_2$ . The higher reductive capacities for these reagents are consistent with  $^{99}\text{Tc}$  speciation results reported by Um et al. [3], which shows higher percentages of reduced  $^{99}\text{Tc}(\text{IV})$  species in DuraLith and Ceramicrete waste forms based on  $^{99}\text{Tc}$  XANES analysis, even though their curing (aging) times after preparation were relatively short compared to the curing times used for Cast Stone. Even though the BFS used to make Cast Stone also showed significant reductive capacity, the magnitude of the reductive capacity of the BFS material is not as large as the reductive capacity for  $\text{Na}_2\text{S}$  and  $\text{SnF}_2/\text{SnCl}_2$  on a mass basis.

Other dry ingredients had reductive capacities less than 100 meq/kg, except silver zeolite [i.e., 1100 meq/kg using the  $\text{Cr}(\text{VI})$  method] and fumed silica [i.e., 300 meq/kg using the  $\text{Ce}(\text{IV})$  method]. However, the silica fume (or fumed silica) used in our work has a minor fraction of elemental silicon that can produce

$\text{H}_2(\text{g})$  when it dissolves. Upon dissolution, it forms silicate ions at the low pH value used in the  $\text{Ce}(\text{IV})$  method, and the  $\text{H}_2(\text{g})$  oxidizes to water and consumes some of the oxidant,  $\text{Ce}(\text{IV})$ . The low reductive capacity for fumed silica, 23 meq/kg measured with the  $\text{Cr}(\text{VI})$  method, occurs because the  $\text{Cr}(\text{VI})$  method is performed at a pH of 7, and very little silicon is dissolved to generate  $\text{H}_2(\text{g})$ . The measured reductive capacity values usually showed higher values for the  $\text{Ce}(\text{IV})$  method than for the  $\text{Cr}(\text{VI})$  method, except for three samples, sodium sulfide, silver zeolite, and tin chloride. The reason for the higher measured reductive capacity for the  $\text{Cr}(\text{VI})$  method is not clearly understood now. However, some interaction or chemical reaction between  $\text{Ag}$  and  $\text{Cr}(\text{VI})$  may be possible to form very stable silver chromate ( $\text{Ag}_2\text{CrO}_4$  with very low solubility of  $1.2 \times 10^{-12}$  mol/mL in  $\text{H}_2\text{O}$ ), which removes all the excess unused  $\text{Cr}(\text{VI})$ , thus leading to inflated reductive capacity values upon back titration.

The measured reductive capacity values of the four different liquid waste simulants (see Table 1) were similar, ranging from 220 to 450 meq/kg (Table 3). Simulant 4 (S4) does have a slightly lower reductive capacity from the  $\text{Ce}(\text{IV})$  method, which agrees well with the Eh results for different simulants shown in Um et al. [3]. The highest Eh value was found in the S4 simulant ( $E_{\text{h, corrected}} = 304.7$  mV) compared to others (S1 = 142.6 mV, S2 = 153.6 mV, and S3 = 161.4 mV), which is indicative of a lower reductive capacity.

The results of measured reductive capacities for Cast Stone samples made with different simulants with or without  $^{99}\text{Tc}$  spikes are shown in Fig. 3. When  $\text{Cr}(\text{VI})$  was used as an oxidant, the reductive capacity of the Cast Stone without  $^{99}\text{Tc}$  was first measured in both oxic and anoxic environments, and the results were very similar regardless of simulant types used or the oxygen conditions. Effects of oxygen (an additional but uncontrolled oxidizing reagent) during the measurement of the reductive capacity using the  $\text{Cr}(\text{VI})$  method were negligible. Therefore, Cast Stone samples with  $^{99}\text{Tc}$ -spiked simulants were measured without using the anoxic chamber. The results showed slightly higher values than those of Cast Stone samples prepared without  $^{99}\text{Tc}$  and measured in either oxic (no chamber used) or anoxic (chamber was used) environments. However, the differences in reductive capacity values among the three Cast Stone samples are within their error ranges, indicating that the reductive capacities can be considered to be the same. The measured reductive capacities of Cast Stone samples from the  $\text{Ce}(\text{IV})$  method also showed similar results, irrespective of different simulant types used (S1, S2, S3, and S4). However, higher reductive capacity values were found as the concentration of S1 (from S1-2M to S1-10M) was used to

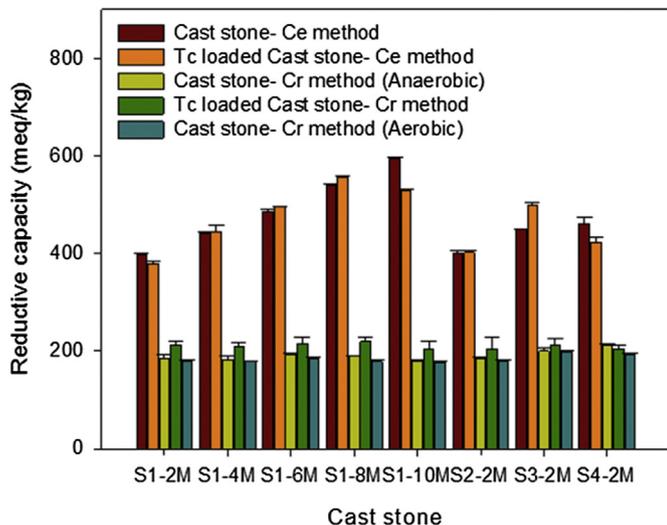


Fig. 3. Measured reductive capacity of Cast Stone samples without  $^{99}\text{Tc}$  and  $^{99}\text{Tc}$ -loaded Cast Stone samples using the Ce(IV) and Cr(VI) methods. For the Cr(VI) method, the reductive capacity was measured under both anoxic and oxic environments for Cast Stone samples prepared without  $^{99}\text{Tc}$ . Other reductive capacities were conducted only in an aerobic environment.

prepare the Cast Stone samples. The increasing reductive capacity measured in Cast Stone containing the increasing simulant concentrations might be related to the reactions that occur in the Cast Stone as it hydrates and transforms from slurry to a hardened paste. Also, increasing nitrite concentration with increasing simulant concentration could increase the reductive capacity in Cast Stone prepared with increasing simulant concentrations. The progressively higher salt and alkaline concentrations in the S1 simulant solution as it was concentrated from 2-M to 10-M Na normalized may dissolve more reducing materials present in Cast Stone dry ingredients, especially the BFS. The higher amount of dissolved reducing agents in the evolving Cast Stone pore water is then readily titrated by the acidic Ce(IV) oxidizing reagents, thus leading to the larger reduction capacity value. A similar increase in reductive capacity in the Cast Stone solids made with varying concentrations of the S1 simulant was not observed when using the Cr(VI) method. This perhaps is caused by the fact that the Cr(VI) method is performed at pH values near 7.0, and fewer of the dry ingredients with reductive capacity are dissolved or reacted during the hydration process.

The two FBSR solids also showed high reductive capacities when measured with the Ce(IV) method (900 meq/kg to 2800 meq/kg). The reductive capacities of granular FBSR and crushed FBSR with Geo-7 binder by the Ce(IV) method were much higher than the reductive capacities measured by the Cr(VI) method (16 meq/kg to 22 meq/kg), most probably because of the nature of the FBSR compounds and the different pH conditions between the two reducing capacity measurements. The FBSR process involves slowly adding and atomizing liquid waste in a bed of particles in an upward-flowing reducing-gas mixture that destroys nitrate and nitrite present in the waste feed under the highly reducing environment [25]. Carbonaceous reductants, such as sugar and CO, are introduced into the reducing-gas reactor as a reformer to create the reducing conditions. Therefore, reduced materials, such as coal, sulfide-containing secondary minerals, etc., are present in the FBSR product. Major mineral phases in the FBSR product are nosean, nepheline, sodalite, and corundum [26,27]. Some of these minerals can accommodate sulfate or sulfide, depending on the redox environment in the steam reforming process [26]. Organic substances in the FBSR product generate low reductive capacity values

when measured with the Cr(VI) method because the dissolution rate of these organics is very slow in the neutral pH conditions used in the Cr(VI) method [7]. With 10% sulfuric acid used in the Ce(IV) method, most of the organic and inorganic materials present in FBSR are completely dissolved. Also, the FBSR major minerals are feldspathoids and zeolite minerals, which have highly porous cage structures. At neutral pH conditions, these minerals are considered to be stable so that there is little reaction when the Cr(VI) method is used to measure their reductive capacities. In the Ce(IV) method performed at very low pH levels, these zeolite minerals were partially dissolved and could be inflating the measured reductive capacities. Finally, DuraLith and Ceramicrete waste form samples showed higher reductive capacities than the Cast Stone samples because of the higher masses of highly reactive reductants used to prepare these waste forms.

### 3.4. Prediction of Cast Stone reductive capacity

The measured reductive capacities of Cast Stone samples prepared without  $^{99}\text{Tc}$  were compared with the reductive capacities estimated by summing values of the independently measured reductive capacity for each dry ingredient multiplied by its weight percent in the Cast Stone formulation. The comparison is shown in Fig. 4, where a little bit higher reductive capacity is measured in the cured Cast Stone solids than is calculated from the sum of the reductive capacities of the individual dry ingredients, which suggests that increase in the reductive capacity originated from the curing (or aging) process in Cast Stone. The time-dependent nature of the Cast Stone reductive capacity could be the cause of the varying contributions of Tc(IV)/Tc(VII) species as a function of different aging times (e.g., contribution of Tc(IV) increased in the Cast Stone as the aging process increased) observed and discussed in Um et al. [3]. However, the relationship shown in Fig. 4 can be useful to estimate at least the initial reductive capacity of various waste forms based on the measured reductive capacities of their individual dry ingredients.

## 4. Conclusions

Our main goal was to evaluate the methods, compare the results, and discuss reasons for observed differences in measured

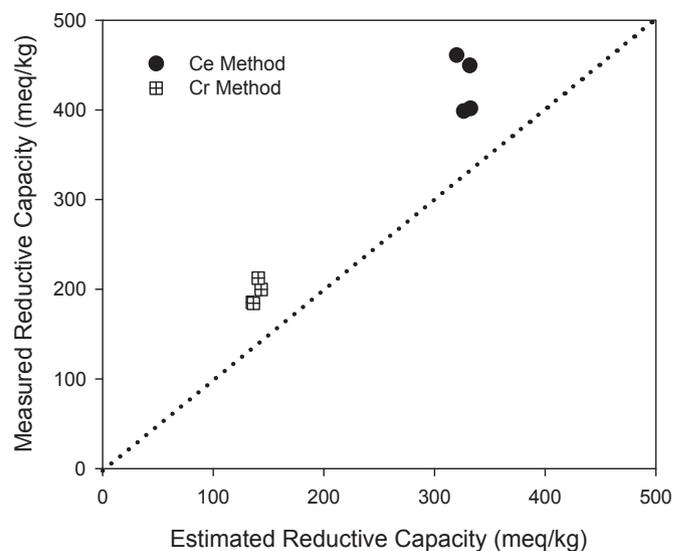


Fig. 4. Relationship between estimated and measured Cast Stone reductive capacities. The measured values are the symbols, and the dotted line indicates a 1:1 correlation between measured and calculated reductive capacity values.

reductive capacities. The reductive capacities of dry ingredients used to prepare each waste form and the four waste forms—Cast Stone, Duralith, FBSR, and Ceramicrete—prepared using different liquid waste simulants with or without  $^{99}\text{Tc}$  were measured with two methods that use different oxidants [i.e., Ce(IV) and Cr(VI)]. The measured reductive capacity values were generally higher when using the Ce(IV) method compared to those obtained when the Cr(VI) method was used. The difference is probably caused by the different pH conditions used in these two methods. The materials with the highest measured reductive capacities are BFS, sodium sulfide, and  $\text{SnF}_2/\text{SnCl}_2$  used as starting ingredients to make various waste forms. Sodium sulfide and  $\text{SnF}_2/\text{SnCl}_2$  exhibit significantly higher reductive capacities per gram of sample compared to all other ingredients. The reductive capacities for the four different simulants at 2-M Na concentrations were similar, but again, the values differed depending on method used. The simulant S4 did exhibit a slightly lower reductive capacity value compared to the other three simulants (S1, S2, and S3). However, the minor differences in reductive capacity for the various 2M Na simulants did not contribute any significant differences in the overall reductive capacity measured in the final waste forms because the volume or weight percent of the 2M Na simulants was not high (<10 wt%) in the final waste forms. The overall reductive capacities of the different waste forms were also not influenced by whether the simulant did or did not contain  $^{99}\text{Tc}$  as would be expected given the low Tc concentration ( $\sim 1 \times 10^{-3}$  to  $< 8 \times 10^{-6}$  M depending on simulant). The granular FBSR sample exhibited a larger reductive capacity than the FBSR-Geo-7 waste form. This finding suggests that the Geo-7 binder itself does not have significant reductive properties and simply diluted the reductive properties of the granular FBSR product, or alternatively the Geo-7 coating over the FBSR grains partially protected the grains long enough in the acidic Ce(IV) slurry that the total reductive capacity of the FBSR product was not measured. The Duralith and Ceramicrete waste forms showed significantly larger reductive capacities than Cast Stone because of the large amounts of the strong reductants, sodium sulfide and  $\text{SnF}_2/\text{SnCl}_2$  used in preparing these two waste forms. Based on the measured reductive capacity values for most of the materials investigated, including individual dry ingredients and final waste forms using the two different methods, the reaction time and the solution pH condition are the critical parameters that influence the measured reductive capacity values.

### Acknowledgments

The authors acknowledge Washington River Protection Solutions, LLC, Richland, Washington for the project funding and programmatic guidance. We also acknowledge Steven Baum, Keith

Geiszler, Cristian Iovin, Igor Kutnyakov, and Dennese Smith in the Geosciences group at PNNL for their analytical and laboratory support. Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

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