

Mass Transport Release of Heavy Metal Oxyanions from Solidified/Stabilized Co-Disposed Flue Gas Desulfurization Brine and Coal Fly Ash Monoliths

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ABSTRACT

The United States (US) coal-fired power industry is facing increasing pressure to improve wastewater disposal practices. One of the most pressing waste disposal issues is the treatment of flue gas desulfurization (FGD) wastewater. Zero liquid discharge (ZLD) strategies are gaining significant interest in the industry and can include the coupling of a brine concentrator and solidification/stabilization (S/S) process. This current project evaluated the mass transport release of heavy metal oxyanions (As, Cr, and Se) from solids produced by this process utilizing a United States Environmental Protection Agency (USEPA) Method 1315 evaluation. Ferrous sulfate (FS) addition significantly decreased release of oxyanions As, Cr, and Se. The results indicate that FS addition could increase the likelihood of successful long-term disposal of S/S solids of concentrated FGD brines containing these heavy metal oxyanions.

1. INTRODUCTION

The United States (US) coal-fired power industry is facing increasing pressure to improve wastewater treatment and disposal practices. One of the industry's most important waste disposal issues concerns flue gas desulfurization (FGD) wastewater. The US Environmental Protection Agency (USEPA) recently released the proposed revision to the Steam Electric Power Effluent Limitation Guidelines (ELG) which regulate FGD wastewater treatment and includes limits for As, Hg, NO₂⁻/NO₃⁻, and Se.¹

FGD wastewater is a complex and difficult to treat water matrix with significant heavy metal content (As, Cd, Cr, Hg, and Se) and large salt content (Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, and Cl⁻).² Concern exists that currently proposed conventional treatment technologies

may not reliably meet the proposed ELG limits. Zero liquid discharge (ZLD) strategies are gaining significant interest due to the certainty of meeting ELG limits, elimination of an environmental wastewater discharge, and potential water reuse maximization in coal-fired power plants.

Any ZLD strategy for FGD wastewater will likely include volume reduction as a first step utilizing an advanced membrane or an evaporation process. The produced concentrated FGD brine will likely be solidified/stabilized (S/S). S/S consists of two processes: solidification (producing a solid product with improved physical properties) and stabilization (converting a contaminant to its less mobile and less toxic forms).³ S/S typically includes mixing of wastes (liquids, sludges, brines or solid waste) with Portland cement (PC), PC/coal fly ash (CFA), CaO/CFA, or Ca(OH)₂/CFA.³⁻⁸ The process “has been identified by the USEPA as the Best Demonstrated Available Technology for 57 regulated hazardous wastes.”³ Solidification improves the microstructure of a waste and decreases permeability which enhances flow of liquids around instead of through the material in a landfill thereby reducing leaching.³ It should be noted that although ZLD strategies have the advantage of producing no liquid discharge, this strategy greatly increases solid waste challenges as the FGD wastewater metals and salts must be successfully stabilized for the long term in an industry landfill.

We previously demonstrated the promising success of this ZLD strategy producing stabilized S/S solids with low heavy metal leaching potential.⁹ This work evaluated metal leaching through the toxicity characteristic leaching procedure (TCLP)¹⁰ and the USEPA Method 1313 (Liquid-Solid Partitioning as a Function of Extract pH Using a Parallel Batch Extraction Procedure).¹¹ Our previous work demonstrates that S/S using bituminous coal fly ash (BCFA) can achieve good retainment (68-90%) for As^V, Cd^{II}, Hg^{II} and Se^{IV}; however, good retainment for Cr^{VI} and Se^{VI} oxyanions requires addition of a reductant such as FeSO₄ (FS). A small addition of FS reduces Cr^{VI} to Cr^{III} and improves its retainment to greater than 99%. FS reduces Se^{VI} to Se^{IV}, which is immobilized by forming CaSeO₃ precipitate in the S/S solids; however, it's challenging to increase the retainment efficiency above 60% without a significant addition of FS (>2% by weight).⁹

The current study focuses on leaching of the major components and heavy metal oxyanions from the S/S solids utilizing the USEPA Method 1315 (Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure).¹² Unlike batch extraction methods (TCLP and USEPA Method 1313), USEPA Method 1315 can elucidate further understanding of contaminant release: (1) over a significant time period, and (2) “the result of diffusion through a tortuous pore network with aqueous partitioning at the solid–liquid interface.”^{13, 14} Leaching from solid monoliths rather than crushed solids are evaluated in this method which more closely resembles a leaching scenario for an actual S/S solid disposal process.¹² Deionized water is the leachate for this method which results in pH conditions closer to an actual S/S disposal scenario compared to the TCLP which is designed to replicate a municipal solid waste disposal scenario.¹³

The objective of this study was to evaluate the mass transport release of heavy metal oxyanions (As, Cr, and Se) utilizing the USEPA Method 1315. The impact of FS addition on the mass transport release of the elements was evaluated. To the best of our knowledge, few studies were found in the literature in evaluating the impact of a reductant on the mass transport release As, Cr, and Se from S/S solids.

The S/S solids were produced by mixing BCFA, PC, and simulated concentrated FGD brine with increasing amounts of FS. This scenario represents the most challenging FGD brine disposal scenario for power plants that utilize bituminous coal and have forced-oxidation scrubbers. Because bituminous coal contains more sulfur than sub-bituminous coal, power plants that use this coal generate a larger volume of FGD wastewater with higher concentrations of heavy metals and salts.² Approximately 48% of the coal produced in the US is bituminous and 44% is sub-bituminous, with 93% of the coal utilized for energy production.¹⁵ As the name implies, forced-oxidation FGD systems bubble air through the FGD slurry to oxidize CaSO_3 to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), a product with commercial value. This process can also oxidize heavy metals, including Se and Cr to their more mobile and toxic forms making the produced brine more difficult to treat or manage.³

2. EXPERIMENTAL SECTION

MATERIALS

CFA was obtained from a bituminous coal-fired power plant in the southeastern United States. PC was obtained from Home Depot (Cartersville, Georgia). Simulated concentrated FGD brine was obtained from a power company, and the composition is detailed in Table 1. The simulated brine was analyzed for metals utilizing inductively coupled plasma-mass spectrometry (ICP-MS) (Series 7700, Agilent Technologies, Santa Clara, California) through a combination of the USEPA Methods 200.8 and 6020a.^{16, 17} Liquid samples were digested by adding 5% HNO_3 /5% HCl and heating the sample for 1 h at approximately 95 °C. After cooling, the samples were analyzed utilizing ICP-MS. Anions were analyzed utilizing the USEPA Method 300.0 by ion chromatography (IC) (Dionex ICS-5000 DP, ThermoFisher, Waltham, Massachusetts).¹⁸ Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FS) was obtained from Fisher Scientific (Pittsburgh, PA).

SOLIDIFICATION/STABILIZATION

BCFA was mixed with the simulated brine and FS (if applicable) for 2 min in a benchtop mixer. Table 2 shows the formulations of the 4 mixtures in the project. After 2 min, PC was added to the mixture and the mixture was homogenized for an additional 18 min. The resulting cement slurry mixture was then poured into 7.62-cm diameter × 15.24-cm (cut to a height of 9.52-12.54 cm) plastic forms. The S/S solid was allowed to cure for 58-62 days. Table 3 shows the mass, surface area, and leachate interval volume for the monolith samples during the USEPA Method 1315 evaluation.

Table 1. Simulated FGD brine composition.

(a) Bulk Elements

Element	Concentration ($\mu\text{g/L}$)
Ca	33,664,945
Mg	3,312,244
Na	2,187,124
K	745,440
Si	110,445
Sr	195,860

(b) Trace Elements

Element	Concentration ($\mu\text{g/L}$)
Sb	101
As^V	1,916
Ba	2,872
B	4,676
Cd	9,163
Cr^{VI}	863
Cu	292
Fe	2,581
Pb	28
Hg	1,060
Mo	16
Se^{VI}	17,971
Ag	36
Ti	45

(c) Anions

Element	Concentration (mg/L)
Br⁻	1.3
Cl⁻	80,270
F⁻	< 0.5
NO₂⁻ (as N)	581
NO₃⁻ (as N)	50
SO₄²⁻	245
PO₄³⁻ (as P)	< 0.5

Table 2. S/S mixtures.

Mixture	Simulated Brine	BCFA	FS	PC
A	26.20%	63.8%	0.0%	10.0%
B	25.30%	62.9%	1.8%	10.0%
C	24.40%	62.0%	3.7%	10.0%
D	23.50%	61.0%	5.5%	10.0%

Table 3. S/S solid mass, surface area, and interval leachate volume.

Mixture	Mass (grams)	Surface Area (cm ²)	Leachate Volume (mL)	Leachate Volume/Surface Area (mL/cm ²)
A	717	319	3,190	10.0
B	860	342	3,420	10.0
C	812	384	3,830	10.0
D	834	391	3,910	10.0

USEPA METHOD 1315

Samples were placed in containers and on stands according to the requirements of the USEPA Method 1315.¹² The leachant was deionized water. The monolith surface area to leachant volume for all samples was approximately 10.0 mL/cm². The leachant was refreshed at cumulative leaching times of 0.08, 1.04, 2, 7, 14, 35, 49, 78, and 119 days except that leaching for Mixture B was stopped after 49 days due to loss of a sample. These leachate refreshment intervals differ somewhat from those suggested by the USEPA Method 1315. Leachate samples were taken at the end of each interval through filtration utilizing 0.45- μ m mixed cellulose ester (MCE) filters (Fisher Scientific). The conductivity, oxidation reduction potential (ORP), and pH of the leachate samples were immediately measured after filtration. The filtered leachate was also analyzed for metals utilizing a combination of the USEPA Methods 200.8 and 6020a with ICP-MS.^{16, 17} The leachate samples were analyzed for Cl⁻ and SO₄²⁻ utilizing the USEPA Method 300.0 with IC.¹⁸

3. RESULTS AND DISCUSSION**LEACHATE pH**

Figure 1 shows the leachate pH as a function of cumulative leaching time (t). The minimum pH measured for all Mixtures occurred at 0.08 days with values between 7.5 and 8.0. The pH increased with t to a maximum for most Mixtures at 35 days with values between 10.0 and 10.7. It is likely that the pH increased from 0.08 to 35 days due to increasing CaO dissolution.¹⁹ After 35 days, the pH decreased slightly with values of 10.0-10.6 at 119 days. This decrease was likely due to a decrease in available CaO content. The results indicate that an alkaline pH was maintained throughout the evaluation and FS addition did not appear to significantly impact leachate pH.

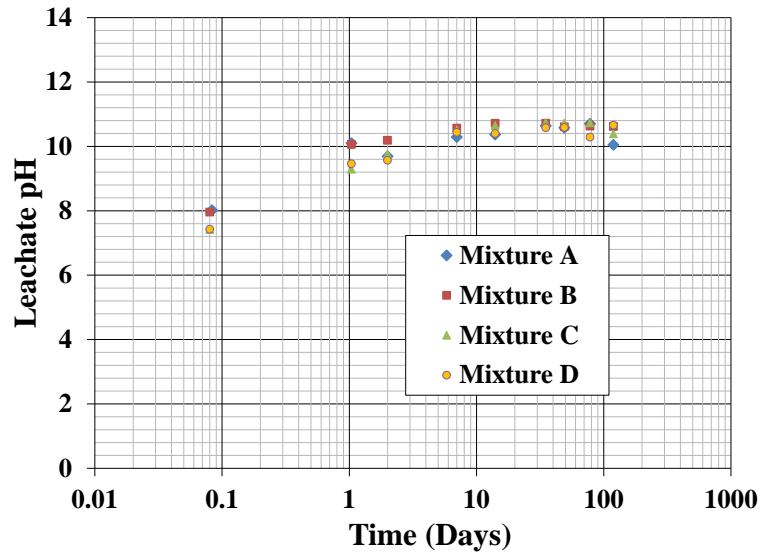


Figure 1. Leachate pH results.

Arsenic

Figure 2a-c shows the As flux, cumulative mass release, and D^{OBS} versus Fe^{II} addition at 1.04 and 49 days, respectively. The vast majority of As present in the S/S solids was expected to be As^V (AsO_4^{3-}) because only As^V was added to the simulated FGD brine and previous research has shown that As is present in CFA primarily as the oxyanion AsO_4^{3-} .²⁰⁻²² Previous research has shown that Ca- As^V complex precipitation is the likely dominant S/S immobilization mechanism as these complexes have low solubility at neutral and high pH with $NaCaAsO_4 \cdot 7.5H_2O$ being the expected dominant phase in S/S.²³⁻²⁶

Mass release through radial diffusion from cylinder in an infinite bath can be calculated by Equation 1.¹²

$$M \left(\frac{mg}{m^2} \right) = 2\rho C_o \left[\frac{D^{OBS} \cdot t}{\pi} \right]^{\frac{1}{2}} \quad (1)$$

M is the mass release during the interval; ρ is the density of the cylinder in kg/m^3 ; C_o is the available leaching content for the contaminant in mg/kg ; D^{OBS} is the observed diffusivity for the component in m^2/s ; and t is cumulative leaching time in seconds. For flux (F in $mg/m^2 \cdot s$), Equation 1 is divided by the interval t with the resulting Equation 2.¹².

$$F \left(\frac{mg}{m^2 \cdot s} \right) = 2\rho C_o \left[\frac{D^{OBS}}{\pi \cdot t} \right]^{\frac{1}{2}} \quad (2)$$

Elemental flux primarily controlled by diffusion will be proportional to the flux as calculated by Equation 2 for radial diffusion from a cylinder in an infinite bath and cumulative mass release will be proportional to mass release in Equation 1.¹² For all cumulative release

and flux graphs in this study, lines are shown on the graphs, labeled diffusion control, which represent graphs of Equations 1 and 2 for Mixture A. For this calculation, the D^{OBS} value was the highest value calculated for the element which always occurred at $t = 1.08$ labeled. D^{OBS} was calculated from Equation 1 for a known mass release.

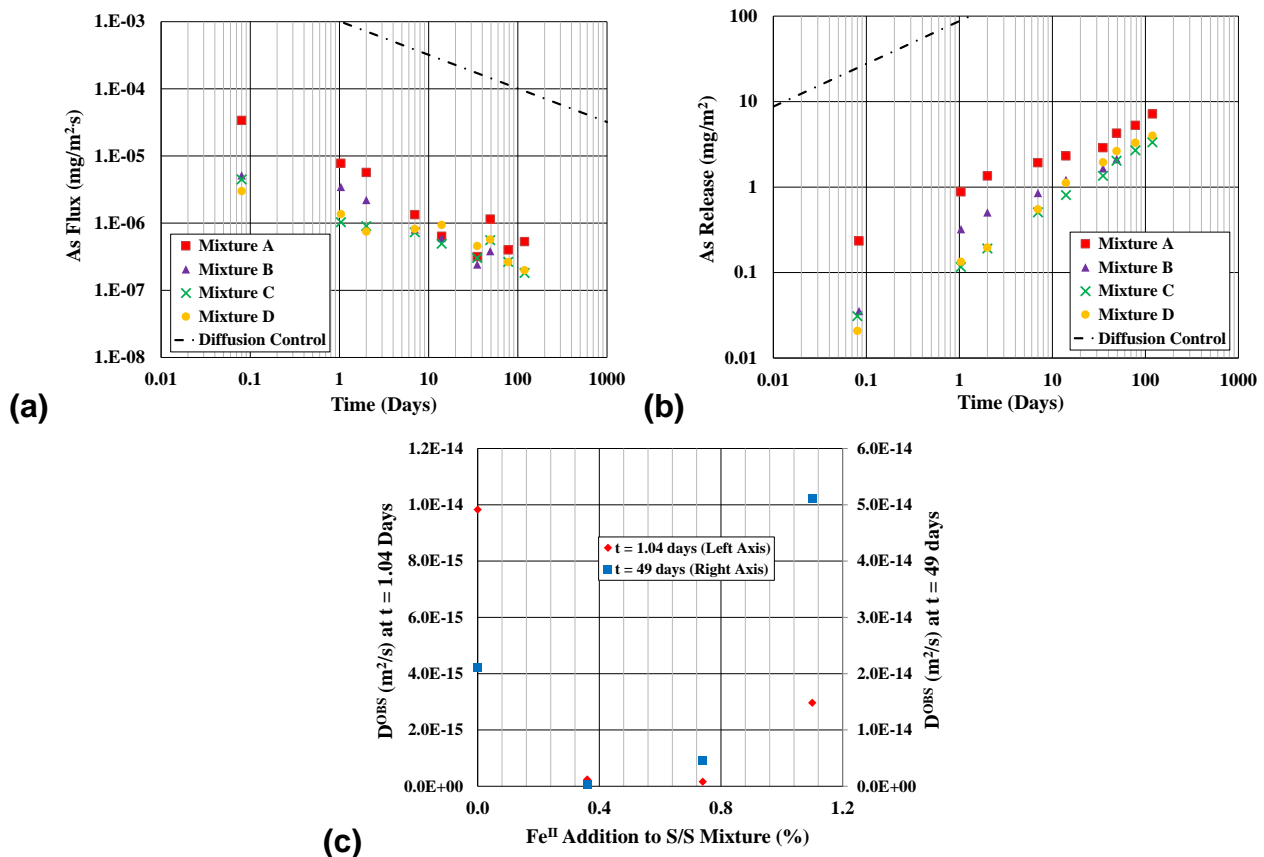


Figure 2. (a) As flux, (b) cumulative As release, and (c) As D^{OBS} versus Fe^{II} addition at 1.04 and 49 days.

Figure 2a shows that the As flux decreased over time from 3.4×10^{-5} - 3.2×10^{-7} , 5.1×10^{-6} - 2.4×10^{-7} , 4.5×10^{-6} - 1.8×10^{-7} , and 3.0×10^{-6} - 2.0×10^{-7} mg/m²s for Mixtures A-D, respectively. The As flux pattern slope for Mixture A was generally less than the diffusion control line which implies solubility controlled release. Figure 2b shows that cumulative release pattern also implies solubility controlled release as the slope of the cumulative release was generally less than the diffusion control line.

Figure 2a shows that the flux was lower for Mixtures with FS addition especially at shorter leaching times. The same trend was seen in the cumulative As release (Figure 2b) with lower cumulative release for Mixtures with FS addition. Although the likely primary As immobilization mechanism was likely Ca-As^V complex precipitation, FS addition likely enhanced As stabilization through sorption to produced hydrous Fe^{III} oxides. The addition of Fe^{II} and Fe^{III} has been shown to increase the As^V retainment in S/S solids.²⁷⁻²⁹ The

Dzombak and Morel model indicated that As^{V} sorbs readily to hydrous Fe^{III} oxides at a pH range in common with cement-based S/S.²⁵ Most of Fe^{II} from the added FS was likely quickly oxidized to Fe^{III} in the S/S matrix. The addition of FS could also have reduced some of the As^{V} to As^{III} ; however, As reduction was not expected to significantly impact the leaching results as As^{III} has been shown to sorb similarly or more strongly to hydrous Fe^{III} oxides than As^{V} at above neutral pH conditions.³⁰

As the leaching time increased the difference in the flux between the Mixtures with and without FS addition decreased. Figure 2c shows that the D^{OBS} decreased (9.8×10^{-15} - 1.6×10^{-16} m^2/s) with increasing Fe^{II} addition at $t=1.04$ days; however, this trend is reversed at $t=49$ days with D^{OBS} increasing (2.9×10^{-16} - 5.2×10^{-14} m^2/s) with increasing Fe^{II} addition. Hence, the impact of FS on As release decreased over time. For Mixtures with FS addition, the decrease in cumulative As release compared to Mixture A at $t=0.08$ days was 85-91% and at $t=49$ days was 38-50%. The reason that the difference in the As release for the different Mixtures decreased could be that the As sorbed to hydrous Fe^{III} oxides decreased significantly at longer leaching times and As release from all mixtures was dependent on the same phases.

Chromium

Figure 3a-c shows the Cr flux, cumulative mass release, and D^{OBS} versus Fe^{II} addition at 1.04 and 49 days, respectively. Cr^{VI} was added in the simulated brine in the experiments. Research has reported that the dominant Cr species in CFA is Cr^{III} , with Huffman et al. finding greater than 95% Cr^{III} in CFA samples.³¹ Cr^{VI} is much more mobile than Cr^{III} ; hence, the Cr^{VI} from the brine is likely to be much more mobile than Cr^{III} from the CFA.

Previous researchers demonstrated cement-based S/S to be effective in immobilizing Cr^{III} , but not Cr^{VI} .³²⁻³⁴ Cr^{III} has a lower solubility than Cr^{VI} under the high pH conditions expected in S/S.^{33, 35} In addition, Glasser noted that chemical incorporation of Cr^{III} in the Ca- Al^{III} -hydrate phase by replacing Al^{III} likely plays the most important role in Cr^{III} immobilization in Cr immobilization in S/S.³³

Figure 3a shows that the Cr flux decreased over time from values of 4.8×10^{-6} - 2.4×10^{-7} , 1.6×10^{-6} - 2.0×10^{-7} , 1.6×10^{-6} - 6.7×10^{-8} , and 1.6×10^{-6} - 7.4×10^{-8} $\text{mg}/\text{m}^2\text{-s}$ for Mixture A-D, respectively. Cr flux from Mixture A appeared to decrease essentially proportional to the diffusion control line. Figure 3b shows that cumulative release pattern increased essentially proportional to the diffusion control line.

Figure 3a shows that Cr flux was lower for Mixtures with FS addition. Unlike for As, the Cr fluxes for the Mixtures did not begin to converge at longer leaching times. Figure 3c shows that the D^{OBS} decreased with increasing Fe^{II} addition at $t=1.04$ days (2.5×10^{-16} - 9.2×10^{-19} m^2/s) and this trend continued at $t=49$ days with D^{OBS} decreasing (1.4×10^{-15} - 5.1×10^{-17} m^2/s) with increasing Fe^{II} addition. Figure 3b shows that the cumulative Cr release was also lower for the Mixtures with FS addition for all leaching times. Fe^{II} can reduce Cr^{VI} to Cr^{III} ^{34, 36}, and thus FS addition to S/S mixtures greatly decreased Cr^{VI} leaching in previous research.^{9, 34} The mechanism of Cr^{VI} reduction by FS to Cr^{III} is likely

responsible for the reduced flux and cumulative release for Mixtures B-D. The likely mechanism is: (i) Cr^{VI} in the S/S solid was reduced to Cr^{III} , which could be incorporated in the Ca- Al^{III} -hydrate phase, precipitated as $\text{Cr}(\text{OH})_3$, and/or adsorb to Fe^{III} oxides (existing and new); and (ii) some of the Cr^{III} originally from the BCFA and PC could also be incorporated in the Ca- Al^{III} -hydrate phase or adsorb to newly formed Fe^{III} oxides. FS addition shows significant promise for enhancing Cr stabilization in the S/S of concentrated FGD brines.

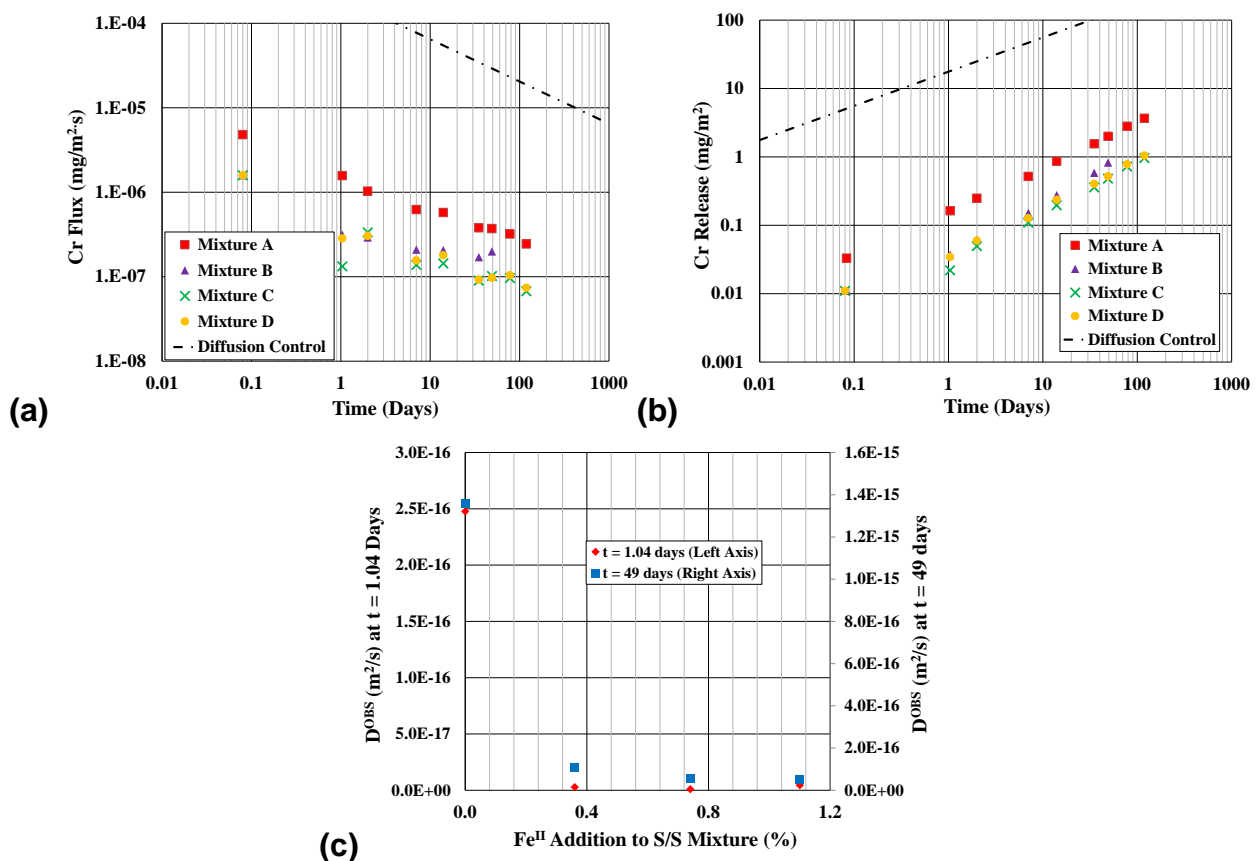


Figure 3. (a) Cr flux, (b) cumulative Cr release, and (c) Cr D^{OBS} versus Fe^{II} addition at 1.04 and 49 days.

Selenium

Figure 4a-c shows the Se flux, cumulative mass release, and D^{OBS} versus Fe^{II} addition at 1.04 and 49 days, respectively. Se^{VI} (as SeO_4^{2-}) was added in the simulated FGD brine in the experiments. Previous research indicates that Se^{IV} (versus Se^{VI}) is the dominant species present in CFA.^{22, 37, 38}

Se behaves differently based on oxidation state (Se^{IV} versus Se^{VI}) in S/S matrices. The likely dominant immobilization phase for Se^{IV} is CaSeO_3 in S/S matrices. Baur and Johnson hypothesized that CaSeO_3 controls Se^{IV} solubility in cement materials where Ca^{2+} concentrations are at the mM level.³⁹ Se^{VI} immobilization in S/S matrices is more complex. Baur and Johnson studied the sorption of Se^{VI} to the monosulfate (AFm-SO_4),

ettringite (AFt-SO₄) and observed only strong Se^{VI} sorption to AFm-SO₄ (Rd = 2.06).³⁹ However, our previous work did not detect AFm in S/S solids produced with bituminous CFA at significant quantities with XRD.⁹ Therefore, these two phases probably do not dominate Se^{VI} leaching in the S/S solids in this study. It could be that the more readily soluble CaSeO₄ (Log K_{sp} = 4.77) is the most important phase for Se^{VI} leaching.⁴⁰

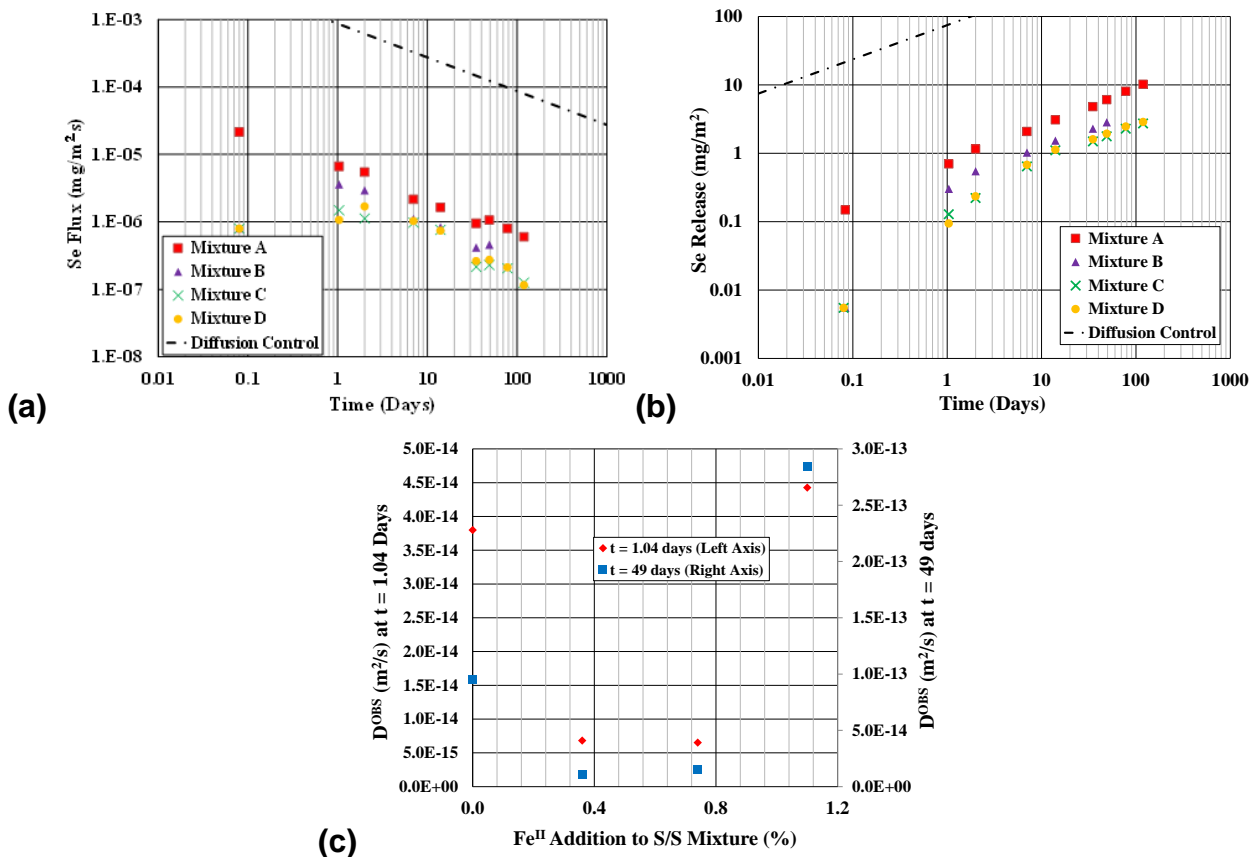


Figure 4. (a) Se flux, (b) cumulative Se release, and (c) Se D^{OBS} versus Fe^{II} addition at 1.04 and 49 days.

Figure 4a shows that the Se flux decreased from 2.2×10^{-5} - 6.0×10^{-7} , 8.0×10^{-7} - 4.6×10^{-7} , 7.9×10^{-7} - 1.3×10^{-7} , and 7.9×10^{-7} - 1.2×10^{-7} mg/m²s for Mixtures A-D, respectively. The Se flux pattern for Mixture A appeared to be proportional to the diffusion control line showing the characteristics of a highly soluble species as would be expected for the available Se^{VI}. Figure 4b shows that the cumulative Se release pattern for Mixture A increased proportionally to the diffusion control line, providing further evidence for diffusion-controlled Se^{VI} release and highly soluble species behavior.

The Se flux for Mixtures with FS addition were not proportional to the diffusion control line at $t < 10$ days and the flux actually increased $0.08 < t < 2.0$ days for Mixtures B, C, and D. The flux was less for Mixtures with FS addition likely due to the reduction of a portion of Se^{VI} to Se^{IV} followed by precipitation as CaSeO₃. As leaching time increased, the difference in the flux between Mixture A and the Mixtures with FS addition became less,

likely because the Se speciation differences between the Mixtures became less as the amount of available Se^{VI} was decreased. Figure 4c shows that D^{OBS} generally decreased with increasing Fe^{II} addition at $t=1.04$ days; however, at the highest Fe^{II} addition, the D^{OBS} was higher than with no addition. At $t=49$ days, D^{OBS} generally increased with increasing Fe^{II} addition. Figure 4b shows that the Se cumulative release was lower for the Mixtures with FS addition than Mixture A although the impact of FS addition decreased somewhat over time.

The results from this leaching experiment indicate that Se behaved as a highly soluble species and was readily released with diffusion as the primary limiting factor. FS addition decreased Se release from the S/S solids over the long term.

4. CONCLUSIONS

This study provided insight on the mass transport release of major components and heavy metal oxyanions from S/S solids of concentrated FGD brines through a USEPA Method 1315 evaluation. As^{V} demonstrated the characteristics of solubility-controlled release while Se^{VI} demonstrated the characteristics of high soluble species release. Diffusion appeared to control Cr^{VI} release, but only a small fraction of the available Cr was mobilized. FS addition significantly decreased oxyanion (As^{V} , Cr^{VI} , and Se^{VI}) release. FS addition can increase likelihood of successful long-term disposal of S/S solids containing significant concentrations of oxyanions including As^{V} , Cr^{VI} and Se^{VI} . The impact of FS did decrease somewhat at longer leaching times.

5. ACKNOWLEDGEMENTS

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