



Stabilization/solidification of selenium-impacted soils using Portland cement and cement kiln dust

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ARTICLE INFO

Article history:

Received 9 October 2008

Received in revised form 22 February 2009

Accepted 23 February 2009

Available online 6 March 2009

Keywords:

Selenium

Stabilization/solidification

Toxicity characteristic leaching procedure

X-ray powder diffraction

Scanning electron microscopy

ABSTRACT

Stabilization/solidification (S/S) processes were utilized to immobilize selenium (Se) as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Artificially contaminated soils were prepared by individually spiking kaolinite, montmorillonite and dredged material (DM; an organic silt) with 1000 mg/kg of each selenium compound. After mellowing for 7 days, the Se-impacted soils were each stabilized with 5, 10 and 15% Type I/II Portland cement (P) and cement kiln dust (C) and then were cured for 7 and 28 days. The toxicity characteristic leaching procedure (TCLP) was used to evaluate the effectiveness of the S/S treatments. At 28 days curing, P doses of 10 and 15% produced five out of six TCLP-Se(IV) concentrations below 10 mg/L, whereas only the 15% C in DM had a TCLP-Se(IV) concentration <10 mg/L. Several treatments satisfied the USEPA TCLP best demonstrated available technology (BDAT) limits (5.7 mg/L) for selenium at pozzolan doses up to 10 times less than the treatments that established the BDAT. Neither pozzolan was capable of reducing the TCLP-Se(VI) concentrations below 25 mg/L. Se-soil-cement slurries aged for 30 days enabled the identification of Se precipitates by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX). XRD and SEM-EDX analyses of the Se(IV)- and Se(VI)-soil-cement slurries revealed that the key selenium bearing phases for all three soil-cement slurries were calcium selenite hydrate ($\text{CaSeO}_3 \cdot \text{H}_2\text{O}$) and selenate substituted ettringite ($\text{Ca}_6\text{Al}_2(\text{SeO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), respectively.

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1. Introduction

The main focus of this study was to conduct a treatability study using surrogate soils spiked with Se to benchmark the immobilization of Se in soft fine-grained media (clays and organic silts) that could be reasonably taken to model sediments and dredged material (DM). Selenium can be derived from many sources including igneous rocks, and silver, copper, lead, nickel and sulfide ores [1]. Industrial uses include rubber compounding, steel alloying, rectifiers, glass making, pigments (red) and photovoltaic and photoconductive applications, including solar cells. Se leaching from hard rock, coal mines (in mine water), runoff from tailings, coal and ash piles, and deposition of Se from other sources [2–11] invariably result in Se accumulation in river sediments and DM taken from navigational channels and private berths in major port cities. Se occurs in four oxidation states: selenide ($2-$); selenium (0);

selenite ($4+$); and selenate ($6+$); the reduced forms being principally associated with mined ores and engineered uses, whereas the oxidized forms represent the most mobile, toxic and accumulative species in soil systems. In soil environments, Se is stable as selenate [Se(VI)] over the entire range of pH, whereas selenite [Se(IV)] occurs as HSeO_3^- and SeO_3^{2-} under acidic and alkaline conditions, respectively, [2,3].

Exceeding the upper intake level of Se at 400 $\mu\text{g}/\text{day}$ may lead to selenosis, and includes such acute and chronic symptoms as gastrointestinal disorders, skin and tooth discoloration, hair loss, sloughing of nails, fatigue, cardiovascular and neurological damage, and cirrhosis of the liver [1]. These health concerns have resulted in the establishment of low regulatory criteria for Se compared to other metals such as arsenic, chromium(VI) and lead which gain much more attention. The US National Fresh Water Quality Standard is for Se is 0.005 mg/L [4]. The USEPA maximum contaminant level for drinking water for Se is 0.05 mg/L [12]. The toxicity characteristic leaching procedure (TCLP) limit has been established as 1 mg/L [13].

As an oxyanion, Se has been difficult to remove from several non-water wastes (e.g., soils, residues, mine tailings, filter cakes, etc.) which has resulted in a stabilization/solidification (S/S) based best

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demonstrated available technology (BDAT) for Se bearing wastes (D010 wastes) of 5.7 mg/L [14]. The main challenge is that for multiple metal bearing wastes, the minimum solubility range for Se ($\sim 6.5 < \text{pH} < 7.5$) does not coincide with most other metals also requiring immobilization [15]. The TCLP BDAT limit was established based on a S/S treatability study using D010 mineral processing wastes with approximately 700 mg/kg total Se and an untreated TCLP-Se concentration of 3.74 mg/L. The treated residuals contained between 0.154 and 1.8 mg/L for the S/S BDAT study, which used pozzolan to waste ratios between 1.3 and 2.8 (130–280% added). However, variances even to the TCLP BDAT limit have been granted for very high Se bearing wastes (up to 1024 mg/L TCLP for untreated waste) such as those from the glass industry, allowing up to 25 and 51 mg/L TCLP Se, depending on the industrial source [15,16]. To achieve these levels prior to ultimate disposal in a landfill, pozzolan to waste ratios of 1.8–2.7:1 (to achieve 25 mg/L) and 2.7:1 (to achieve 51 mg/L) were identified as effective by USEPA, versus higher doses (up to 5:1) which began to resemble pure dilution (at a very high cost).

For this treatability study, an upper concentration of Se was adopted on the order of the BDAT studies (~ 1000 mg/L Se) to bracket a worst case scenario for hotspots, though it is recognized that the expected concentrations in real sediments will typically be on the order of 200 mg/L or less. For example, the San Luis Drain, in the central valley of California, is reported to contain aqueous and sediment Se concentrations on the order of 0.6 mg/L and 38–83 mg/kg, respectively [17–19]. Concentrations as high as 183 mg/kg Se have been detected [19]. The costs for the removal and disposal of the San Luis Drain sediments were estimated to be on the order of $\$11\text{--}34/\text{m}^3$ ($14\text{--}45/\text{yd}^3$) [17].

The federal TCLP limit is not the only trigger for managing Se-impacted media—local soil cleanup criteria and/or permits for contaminated soils often regulate on total concentrations, which vary from state to state. An example directly illustrating this involves the recent removal of dewatered DM ($403,000 \text{ m}^3$; $530,000 \text{ yd}^3$) from an existing US Army Corps of Engineers (USACE) confined disposal facility for mine reclamation. Approximately 10% of the environmentally delineated DM (or $38,200 \text{ m}^3$; $50,000 \text{ yd}^3$) above the contract volume was found to contain B, As and Se concentrations exceeding the regulated fill standards in Pennsylvania (PA), which for Se is limited to 26 mg/kg [20]. There were two choices—leave the Se-impacted DM in place, or adhere to a beneficial use permit (several possible), which required either pozzolanic treatment, blending, engineering controls, and/or deed restrictions, etc., all of which add significantly to the cost of removal.

This recent project experience was the direct motivation for undertaking this study, since no Se-impacted DM treatability studies were readily available. The main concern for S/S processes was that the USEPA BDAT TCLP studies involved extremely high pozzolan doses ($>1:1$) compared to conventional DM treatment ($\ll 1:1$). Due to their large volumes, the management of Se-impacted contaminated sediments cannot support even a 1:1 pozzolan to waste dose (at 1:1, the raw pozzolan cost is $\sim \$65/\text{m}^3$). This begs the question, with the typical dosing of pozzolanic products to the sediments removed from the Port of New York and New Jersey (conducts most DM treatment in USA) which is on the order of 8–12% Portland cement ($\sim \$6.5/\text{m}^3$), what Se treatment can be achieved by the existing dosing scheme, an accepted practice by several neighboring states.

Accordingly, artificially Se-contaminated soils were prepared using montmorillonite, kaolinite and DM to evaluate the effectiveness of two pozzolans to immobilize Se for various fine-grained media. Commercially available montmorillonite and kaolinite were chosen due to the need to simplify, isolate and identify key Se immobilization mechanisms. The inclusion of actual DM makes S/S

somewhat more challenging than for ordinary soils, owing to its organic matter content and other constituents that may interfere with the cement reactions. Each soil was independently spiked with Se(IV) and Se(VI) to achieve 1000 mg/kg Se prior to treatment. Type I/II Portland cement and cement kiln dust from the same plant were applied to all soils at doses ranging from 5 to 15%. Cement kiln dust offers a potentially more cost effective solution than Portland cement (up to 50% less), depending on the treatment volumes required. Treatment efficiency was evaluated using the TCLP test, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM)—energy dispersive X-ray spectroscopy (EDX) to identify the key mineral phases associated with Se(IV) and Se(VI) immobilization.

2. Materials and methods

2.1. Experimental matrix and nomenclature

The experimental design of the S/S study and the nomenclature used to refer to samples (excluding dose and curing time) are presented in Table 1. Twelve samples and six control samples were prepared, varying the type of soils and stabilizing agents and their doses. To assess the leachability of Se(IV) and Se(VI) in the treated soils, TCLP tests were conducted in duplicate.

The sample nomenclature used in the TCLP study reflects five parameters: (1) clay type; (2) selenium type; (3) pozzolan; (4) pozzolan dose; (5) curing time. The three soils were montmorillonite (M), kaolinite (K) and dredged material (DM). Selenium is referenced using its oxidation state, either Se(IV) or Se(VI). Portland cement and cement kiln dust are denoted as P and C, respectively. The curing time in days is indicated after the hyphen. An example ID nomenclature breakdown for sample DMSe(IV)C15–28 is as follows: DM spiked with selenite and treated with 15% C and cured for 28 days.

2.2. Materials

Montmorillonite, kaolinite and dredged material were used to simulate artificially contaminated soils to investigate the immobilization of Se as a function of soil physicochemical properties with respect to cation exchange capacity (CEC), surface area, and the ability to provide the necessary silica and alumina to facilitate the pozzolanic reactions. Kaolinite and montmorillonite were selected because they bracket low and high plasticity clays, thus covering a range of behavior with respect to their surface area, ion exchange and CEC. DM was chosen to simulate Se contamination in natural sediments.

Kaolinite (Hydrated Aluminum Silicate 35, Huber Engineered Materials, Georgia, USA) and bentonite, a sodium montmorillonite (The American Colloid Company, Illinois, USA), were commercially obtained in milled powder form. The DM was obtained from the USACE Craney Island confined disposal facility in Hampton Roads, VA [21]. The DM was classified as an inorganic clays or high plasticity fat clay (CH) in accordance with the Unified Soil Classification System with a gravimetric moisture content of approximately 130%, however, this was adjusted to 70% by air drying for use in this study. Selected chemical and physical properties of M, K and DM are provided in Table 2.

The Portland cement and cement kiln dust used in this study were provided by Lafarge North America, (Whitehall, PA). The Type I/II Portland cement and cement kiln dust both originated from the Lafarge Ravena (NY) plant. A summary of the bulk chemistry (by XRF) of these stabilizing agents is presented in Table 2.

Table 1
Treatability matrix for selenium stabilization/solidification (S/S) study.

Sample	Soils			Contaminant		Stabilizing agent	
	Montmorillonite	Kaolinite	Dredged material	Se(IV)	Se(VI)	PC	CKD
MSe(IV)	✓			✓			
MSe(IV)P	✓			✓		✓	
MSe(IV)C	✓			✓			✓
KSe(IV)		✓		✓			
KSe(IV)P		✓		✓		✓	
KSe(IV)C		✓		✓			✓
DMSe(IV)			✓	✓			
DMSe(IV)P			✓	✓		✓	
DMSe(IV)C			✓	✓			✓
MSe(VI)	✓				✓		
MSe(VI)P	✓				✓	✓	
MSe(VI)C	✓				✓		✓
KSe(VI)		✓			✓		
KSe(VI)P		✓			✓	✓	
KSe(VI)C		✓			✓		✓
DMSe(VI)			✓		✓		
DMSe(VI)P			✓		✓	✓	
DMSe(VI)C			✓		✓		✓

Table 2
Physicochemical properties for montmorillonite, kaolinite, dredged material, Type I/II Portland cement and cement kiln dust.

Parameter	M (wt%)	K (wt%)	DM (wt%)	Type I/II P (wt%)	C (wt%)
Silicon dioxide (SiO ₂)	65.15	45.82	58.01	20.15	14.02
Aluminum oxide (Al ₂ O ₃)	17.68	38.34	12.95	4.76	3.21
Iron oxide (Fe ₂ O ₃)	4.22	0.14	6.14	3.11	2.02
Calcium oxide (CaO)	0.97	<0.01	4.01	62.54	45.33
Sodium oxide (Na ₂ O)	2.58	0.15	1.82	0.29	0.61
Potassium oxide (K ₂ O)	0.85	0.11	2.46	0.55	2.12
Magnesium oxide (MgO)	1.86	0.03	1.77	3.80	2.83
Sulfur trioxide (SO ₃)	0.49	<0.01	1.82	3.05	6.61
Titanium dioxide (TiO ₂)	0.22	0.61	0.78		
Loss on ignition (LOI)	4.68	13.86	10.01	1.06	21.82
Moisture content			130		0.30
pH (L:S, 1:1)	7.00	4.0–6.5	7.47	12.24	12.73
pH (L:S, 20:1)				11.25	12.14

2.3. Se-spiked soils

Each soil was spiked with sodium selenite (Na₂SeO₃) and sodium selenate (Na₂SeO₄) (99% and 98% purity, respectively, Aldrich) at 0.1 wt% (1000 mg/kg) to simulate Se(IV) and Se(VI) source contamination. Specifically, either sodium selenite or sodium selenate was first dissolved in deionized water and then mixed with clay. Fifty percent water content based on the total weight of clay was used. After being thoroughly homogenized, the samples were placed in sealed 500-L high-density polyethylene (HDPE) containers and were left to mellow for a period of 7 days.

After the mellowing period was complete, the soils were mixed with Portland cement and cement kiln dust at dosages of 5, 10 and 15 wt% (expressed as grams of stabilizing agent/100 g dry soil). Specifically, 30 g of each soil was placed in a stainless steel mixing bowl and was manually homogenized with the respective

Table 3
TCLP Se(IV) and Se(VI) concentrations and TCLP pH in the soil controls.

Species	Control					
	Montmorillonite		Kaolinite		Dredged material	
	Se (mg/L)	pH	Se (mg/L)	pH	Se (mg/L)	pH
Se(IV)	53.8	5.04	51.1	4.84	33.7	6.18
Se(VI)	63.8	5.03	53.5	4.84	63.1	6.14

dose of each stabilizing agent. Water was added at the 10% level based on total sample weight. An additional 20% water was added to the montmorillonite samples to promote full hydration. Ultimately, two sub-samples for each of the eighteen samples were created. After mixing, the amended soils were stored in sealed 125-mL HDPE bottles at room temperature and cured for 7 and 28 days.

2.4. Preparation of soil–cement slurries for XRD

The 0.1 wt% Se spiking levels used in the TCLP extraction studies were too low to enable accurate identification of the Se minerals by XRD. Accordingly, Se-soil–P slurries were prepared using a 10 wt% Se(IV) or Se(VI) dose (100,000 mg/kg) to enable the identification of Se precipitates by XRD (Se detection limit is ≤5 wt%) and SEM–EDX. Specifically, selenium was first dissolved in deionized water as either Se(IV) (using Na₂SeO₃) or Se(VI) (using Na₂SeO₄), and then thoroughly mixed with either K, M and DM. Slurry samples were prepared by mixing 10 g of each soil with Se at a L:S of 10:1 resulting in a Se concentration of 10 wt%. The Se-spiked soils were then mixed with 15 wt% P until they were visually homogeneous. The slurry samples were then rotated in the TCLP tumbler at 30 rpm for 30 days to promote equilibrium. The samples were then filtered using a 0.4 μm pore-size membrane filter to separate the solids from the leachate. The remaining solids were collected, air-dried, sieved using #200 mesh (75 μm) and subjected to XRD analyses.

2.5. TCLP tests

The TCLP tests were conducted in accordance with EPA Method 1311 [22] to evaluate the leachability of Se(IV) and Se(VI) from the Se-spiked soil (Section 2.3). All samples were passed through a No. 10 sieve (2 mm) prior to the TCLP tests. Specifically, 2 g of soil was placed in 40-mL high-density polyethylene (HDPE) bottles and mixed with a designated 40 mL of TCLP extraction fluid. The leaching fluids were selected based on the pH and buffering capacity of the soil as specified in the procedure. All samples were tumbled at 30 rpm in a TCLP tumbler (Millipore) for 18 h in accordance with the TCLP method. The pH (Denver Instrument UB-10) was measured and the leachate was filtered through a 0.45- μm pore-size membrane filter prior to an inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Varian Vista-MPX, Varian, Palo Alto, CA) for Se(IV) and Se(VI) analysis. Sample analyses were performed in duplicate and averaged values were reported. For QA/QC purposes, two different quality control standards along with the method of standard addition (spiking) were used every 10 samples. Moreover, if the two analyses of the same standard differed by more than 10%, a new calibration curve was constructed and the samples reanalyzed.

2.6. X-ray diffraction (XRD) analyses

XRD was used to investigate the crystalline mineral phases responsible for Se(IV) and Se(VI) immobilization in the soil–cement slurry samples (Section 2.4). Representative samples were air dried for 24 h and then were pulverized to pass through a US standard No. 200 sieve (75 μm). Step-scanned X-ray diffraction data was collected with a Rigaku Ultima IV. The XRD analyses were conducted at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The data were collected over the range from 5° to 65° 2θ with a step size of 0.02° and a count time of 3 s per step. XRD patterns were qualitatively analyzed using Jade software version 7.1 [23] and reference to the patterns of the International Centre for Diffraction Data database [24].

2.7. Scanning electron microscopy (SEM) analyses

Prior to SEM analyses, representative samples were air-dried and prepared using double-sided carbon tape. SEM analyses were performed using a LEO-810 Zeiss microscope equipped with an energy dispersive X-ray spectroscopy (EDX), ISIS-LINK system.

3. Results and discussion

3.1. TCLP

Due to the L:S ratio of the TCLP test (20:1) and the Se spiking levels involved, the theoretical maxima for dissolved Se, assuming complete anion exclusion in each soil would be 50 mg/L for the soil controls. For the pozzolan amended systems, in which the dosages are additive (above 100%), the dilution represented by the 5, 10 and 15% doses correspond to the maximum soluble concentrations of total Se of 47.62, 45.45 and 43.48 mg/L, respectively. Thus, these concentrations are the benchmarks for evaluating reduced leaching (enhanced immobilization).

Under TCLP extraction conditions, the imparted acidity translates to most sorbed cations being forced into solution, generally leaving low(er) cation (and counter ion) coverage on the clay surfaces. Unless co-precipitated or scavenged by other species, this would mean that Se(IV) and Se(VI), modeled as strongly binding inner- and loosely binding outer-sphere species [25], would be very affected and relatively unaffected by pH dependant phenomenon at water-solid interfaces, respectively. Moreover, Johnson et al. [26]

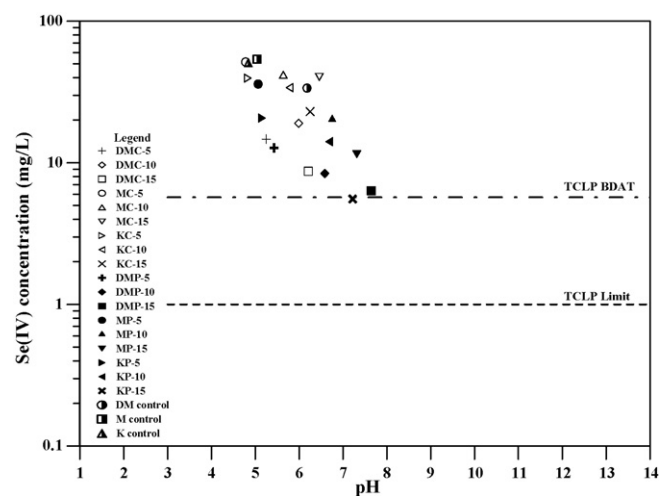


Fig. 1. Se(IV) TCLP concentrations for Portland cement (P) and cement kiln dust (C) treated soils at 7 days.

demonstrated the irreversible sorption of selenite in batch experiments using 27 combinations of Type V Portland cement, silica fume and clay. Accordingly, all things considered equal and if Se sorbed to the control soils, the measured Se(IV) concentrations should be less than the corresponding Se(VI) concentrations under the same TCLP conditions, as suggested by their inner and outer sphere binding behavior, respectively. The data in Table 3 supports this generalized trend.

The controls for the M and K soils are close to, and somewhat above, the theoretical concentrations for both Se(IV) and Se(VI), the Se(IV) concentrations being significantly lower (~20%). For the DM, the lower Se(IV) concentrations suggests a possible sorption mechanism that may be related to its organic matter content. However, organo-selenium species were not explicitly evaluated in this study.

3.1.1. Se(IV)-spiked media

The TCLP-Se(IV) results obtained from the three soils (M, K, DM) individually stabilized with P and C at doses of 5, 10–15% are shown as a function of the TCLP-pH in Figs. 1 and 2 for curing times of 7 and 28 days, respectively. The TCLP-Se(IV) results for the controls are presented to illustrate the relative reductions (or lack thereof) in Se(IV) leaching associated with the P and C treatments. Also shown

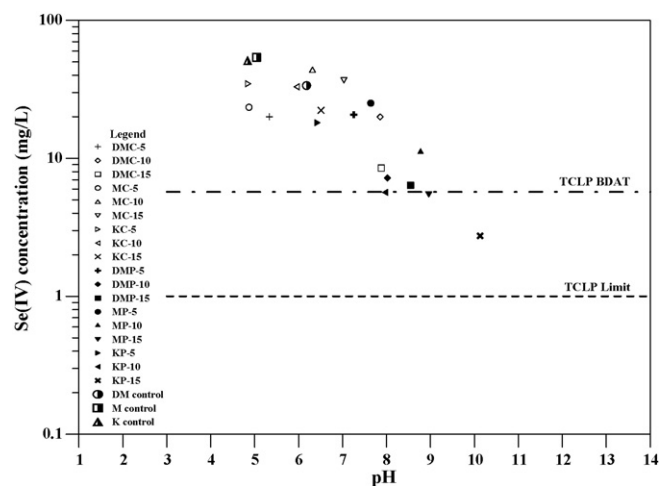


Fig. 2. Se(IV) TCLP concentrations for Portland cement (P) and cement kiln dust (C) treated soils at 28 days.

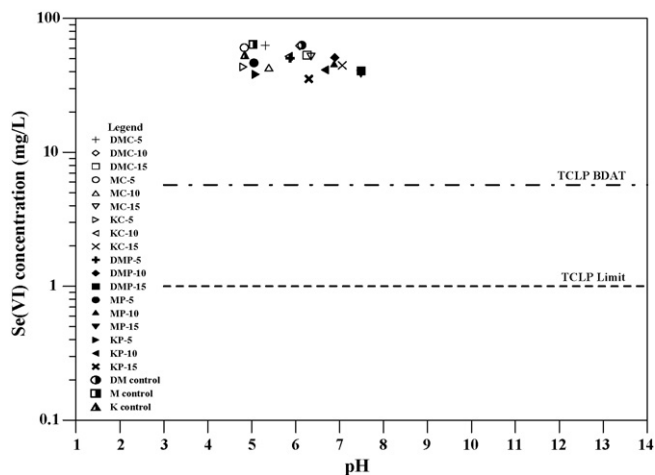


Fig. 3. Se(VI) TCLP concentrations for Portland cement (P) and cement kiln dust (C) treated soils at 7 days.

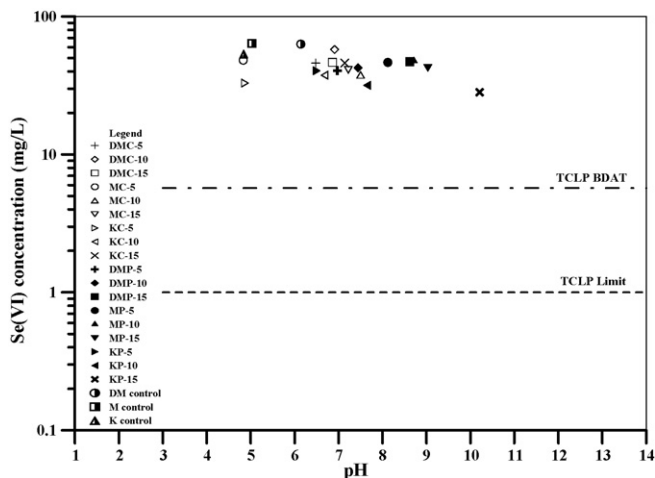


Fig. 4. Se(VI) TCLP concentrations for Portland cement (P) and cement kiln dust (C) treated soils at 28 days.

in Figs. 1 and 2 for comparison purposes are the TCLP BDAT limit (5.7 mg/L) and the TCLP toxicity criterion (1 mg/L). All treatments failed the TCLP criterion, one treatment satisfied the TCLP BDAT at 7 days, and three treatments satisfied the TCLP BDAT at 28 days with three other treatments <10 mg/L. As the pozzolan dose and curing time increased, the leachable Se(IV) concentration typically decreased, sometimes significantly.

At 7 days, only the 15% P dose to the DM soil satisfied the TCLP BDAT. The clustering of the data by dose indicates that 10 and 15% P were able to more strongly buffer the TCLP extractant than the 15% C, producing pH values generally between 6 and 8, where Se is at its minimum [22]. The spiked DM soils routinely had the lowest Se concentrations and the C-treated DM outperformed the corresponding P-treated M soil at all dosing levels.

At 28 days, the most effective stabilizing agent on Se(IV) leachability was P. The lowest TCLP Se concentration of 2.7 mg/L was observed in the sample KSe(IV)P15–28. In general, with increased curing time, most treatments resulted in greater pH buffering of the TCLP solution but did not necessarily correlate to substantially lower Se(IV) concentrations. This was certainly the case with C which had difficulty immobilizing Se(IV) in the K and M soils. As before, 5% C was not able to elevate the pH substantially above the M and K controls, and the DMSe(IV)C5–7 sample was actually more acidic than the DM control. The corresponding P pairs had pH values that were 2–3 units higher. Ten and fifteen percent P were generally able to produce Se(IV) concentrations below or near the TCLP BDAT level. The lowest average Se(IV) concentrations were measured in the K soil, followed by the DM and M soils. However, the average concentration of the C-treated DM was almost the same as the P-treated M soil, perhaps due to the natural pH of the DM.

3.1.2. Se(VI)-spiked media

The TCLP results obtained from the Se(VI) samples are presented in Figs. 3 and 4 using the same presentation format as the TCLP-Se(IV) results. The pH buffering offered by the P was again evident as the P-stabilized soils tended to be the least acidic. However, for both 7- and 28-day curing, the reduction of the TCLP-Se(VI) concentrations for all samples was not significant; the lowest achievable TCLP-Se(VI) concentration was 28.3 mg/L (KSe(VI)P15–28 sample). Regardless of the type of S/S agent, the lowest Se(VI) leaching levels were associated with the K soil. Nevertheless, many of the Se(VI) concentrations were close to the values associated with the anion-excluded Se concentrations (43–47 mg/L), corresponding to

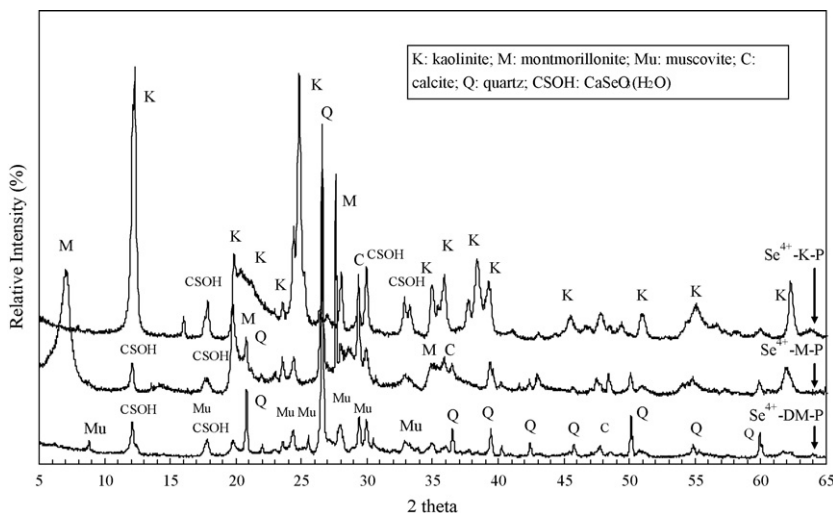


Fig. 5. X-ray diffractograms of the filtrates from Se(IV)-soil-P slurries tumbled for 30 days.

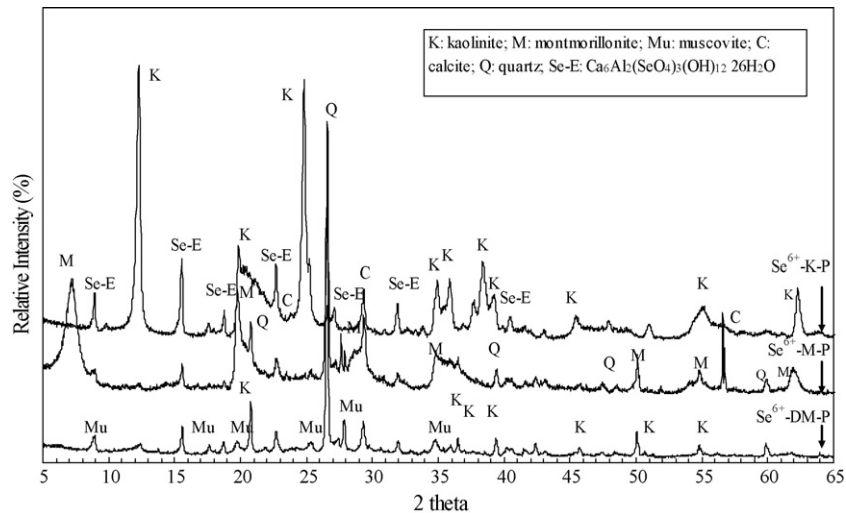


Fig. 6. X-ray diffractograms of the filtrates from Se(VI)-soil-P slurries tumbled for 30 days.

the mere dilution offered by the pozzolans themselves. This was especially the case for the DM soils.

3.2. XRD

The qualitative XRD results for the Se(IV) and Se(VI) spiked soil-cement slurries are presented in Figs. 5 and 6, respectively. The X-ray diffractograms for the K, M and DM soil-cement slurry samples are arranged vertically, top to bottom, in each figure. Based on the work of Baur and coauthors [27–29], attempts were made in the Se(IV) and Se(VI) systems to verify the presence of CaSeO_3 , and Se(VI)-substituted ettringite (AFt) and monosulfate (AFm) phases, respectively.

In each of the diffractograms in Fig. 5, the predominant Se(IV) mineral detected was calcium selenite hydrate ($\text{CaSeO}_3 \cdot \text{H}_2\text{O}$), having primary reflections at 17.971° , 30.029° , 12.232° and 27.158° 2θ degrees based on the powder diffraction file (PDF) #97-003-3955 in the ICDD [24]. In the Se(IV)-K-P slurry, the third peak (12.232°) is obscured by a strong kaolinite reflection, but all other peaks are clearly recognizable. Specifically, the Se(IV)-K-P slurry contained kaolinite, calcite and $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ as major phases. Aside from the difference in the base soils, the Se(IV)-M-P slurry also showed peaks of quartz, whereas the Se(IV)-DM-P slurry additionally contained muscovite.

The formation of calcium selenite, CaSeO_3 , (PDF #35-0884, 35-0885) was not identified in any of the samples tested. Specifically, no major peaks were observed based on 2θ values of 38.100° , 29.063° and 49.786° (PDF #35-0884), or 30.378° , 28.037° and 33.797° (PDF #35-0885). This is in contrast to Ghosh-Dastidar et al. [30] who found that the sorption of $\text{SeO}_2(\text{g})$ on hydrated lime at elevated temperatures resulted in the formation of CaSeO_3 under $\text{SO}_2(\text{g})$ deficient conditions, as confirmed by XRD. Likewise, Baur and Johnson [27,28] generated CaSeO_3 , but used neat aqueous experiments and synthetically generated monosulfate, ettringite and calcium silicate hydrate (CSH) phases. While they explicitly sought $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ in XRD spectra, no agreement could be attained for either the available PDF files with their measured XRD spectra (8° , 16° and 24° 2θ), or the experimentally determined solubility product data, leading Baur and Johnson [27] to ultimately conclude that SeO_3^{2-} was incorporated into AFm phases at high Se concentrations. In both cases [27,28,30], these prior studies did not actually involve pozzolanically stabilized soils.

Fig. 6 shows select diffractograms for the P-stabilized Se(VI) spiked soils. In the Se(VI)-K-P slurry, kaolinite, calcite and

Se-ettringite ($\text{Ca}_6[\text{Al}_2(\text{OH})_6]_2(\text{SeO}_4)_3 \cdot 26\text{H}_2\text{O}$) were identified. In the Se(VI)-M-P slurry, montmorillonite, quartz, calcite and Se-ettringite were identified. In the Se(VI)-DM-P slurry sample, Se-ettringite was the only detectable Se-bearing phase.

Several researchers have reported on the substitution of numerous oxyanions in ettringite and monosulfate ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4) \cdot 12\text{H}_2\text{O}$) phases [27–29,31–34]. Comparison of ettringite with Se(VI)-ettringite for the XRD spectra shown in

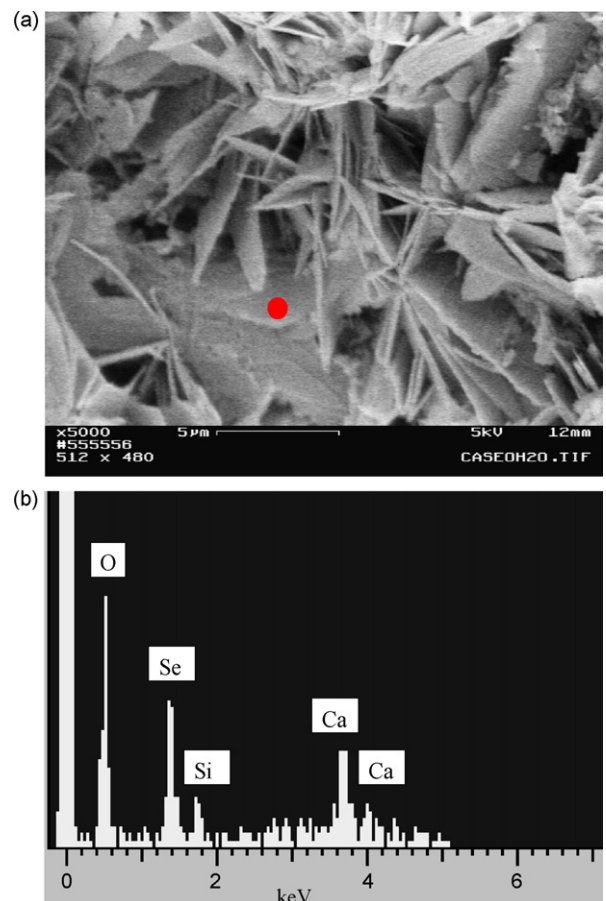


Fig. 7. SEM image of Se(IV)-kaolinite-P slurry sample showing monoclinic $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ (a), and its empirically-derived composition by EDX (b).

Fig. 6 indicated the presence of Se(VI)-ettringite in all soil–cement slurries. Specifically, the primary peak reflections of ettringite (9.091° , 15.784° and 22.944° 2θ ; PDF #00-041-1451) did not match the measured diffractograms, whereas the four primary reflections (15.561° , 22.753° , 8.980° and 18.821° 2θ ; PDF #00-042-0224) of Se(VI)-ettringite were well defined. The main difference between ettringite and Se(VI)-ettringite are the ordering of the primary peak reflections (9.091° vs 15.561° 2θ), and the emergence of a strong tertiary reflection (18.821° 2θ) for Se(VI)-ettringite.

The only difference between the soil–cement samples (Section 2.3) and slurries (Section 2.4) was the selenium dose. The detection of calcite in all slurry samples clearly indicates that calcium was not mass limiting in terms of Se binding. Thus, the formation of $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ and $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SeO}_4)_3 \cdot 26\text{H}_2\text{O}$ are very important in terms of Se immobilization. Since no other crystalline Se compounds were detected in the slurry samples (including selenate Afm), and since Se appears to be mass limiting for both sets of samples, it is reasonable to conclude that calcium selenite hydrate and Se(VI)-ettringite were likely the solubility controlling crystalline phases in the more dilute soil samples.

The K_{sp} value of $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ has been estimated to be $10^{-6.84}$ to $10^{-7.27}$ at 25°C and for a pH value of 9 for synthetically generated calcium selenate hydrate from aqueous suspensions [27]. Other sources [35,36] report K_{sp} values on the order of $10^{-7.65}$ to $10^{-7.76}$. These values are relatively high, but illustrate that Se-precipitates are predicted at elevated pH.

The base homologue for selenate ettringite is (sulfate) ettringite or $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$, which has a reported K_{sp} value of $10^{-44.8}$ between 5 and 75°C and at pH between 10.5 and 13, as determined from aqueous dissolution and precipitation experiments [37]. Macphree and Barnett [38] report a similar range of K_{sp} values ($10^{-44.43}$ to $10^{-45.09}$) for their ettringite precipitation experiments conducted between 5 and 30°C . At 25°C , the estimated K_{sp} value for Se(VI)-ettringite, $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SeO}_4)_3 \cdot 26\text{H}_2\text{O}$ is $10^{-40.7}$, whereas under Al and Se mass limiting conditions, the possibility exists for the formation of selenate Afm or $\text{Ca}_4\text{Al}_2\text{O}_6\text{SeO}_4 \cdot x\text{H}_2\text{O}$ with a K_{sp} of approximately $10^{-28.59}$ [28,33]. The latter, however, was not observed in the slurry samples (thus Al was not mass limiting). The very low K_{sp} values for Se(VI)-ettringite suggest that the compound will control the solubility of selenium to very low levels while remaining very stable under alkaline conditions in the long term. Decomposition of ettringite, however, is known to occur due to carbonation reactions, and conversion to gypsum prevails when the pH drops below approximately 10.5, though some researchers have still observed ettringite at pH as low as 9.5 [39].

3.3. SEM–EDX

SEM–EDX results obtained from the Se(IV)-kaolinite–P slurry are presented in Fig. 7. The results showed that platy crystals were formed upon P treatment (Fig. 7a). The analyzed crystals contain O, Se, Ca, and Si elements based on the EDX analyses (Fig. 7b). Since the Se peak was distinct at 1.42 keV ($L\alpha$), these compounds appear to be calcium selenite hydrate ($\text{CaSeO}_3 \cdot \text{H}_2\text{O}$) with minor impurities of Si, consistent with the XRD analyses (Fig. 5).

The SEM–EDX results obtained from the Se(VI)-kaolinite–P slurry are presented in Fig. 8. In this sample, Se-rich needle-like crystals were formed upon P treatment (Fig. 8a). Based on the EDX analysis, O, Al, Se, Ca and Si elements were observed in the crystal, again suggesting trace silica as an impurity. More specifically, Se ($K\alpha = 11.207$ keV) was observed in the structure, not S ($K\alpha = 2.307$ keV). This indicates that the needle-like structure is mostly likely Se(VI)-ettringite, or $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SeO}_4)_3 \cdot 26\text{H}_2\text{O}$, as confirmed by XRD analysis (Fig. 6).

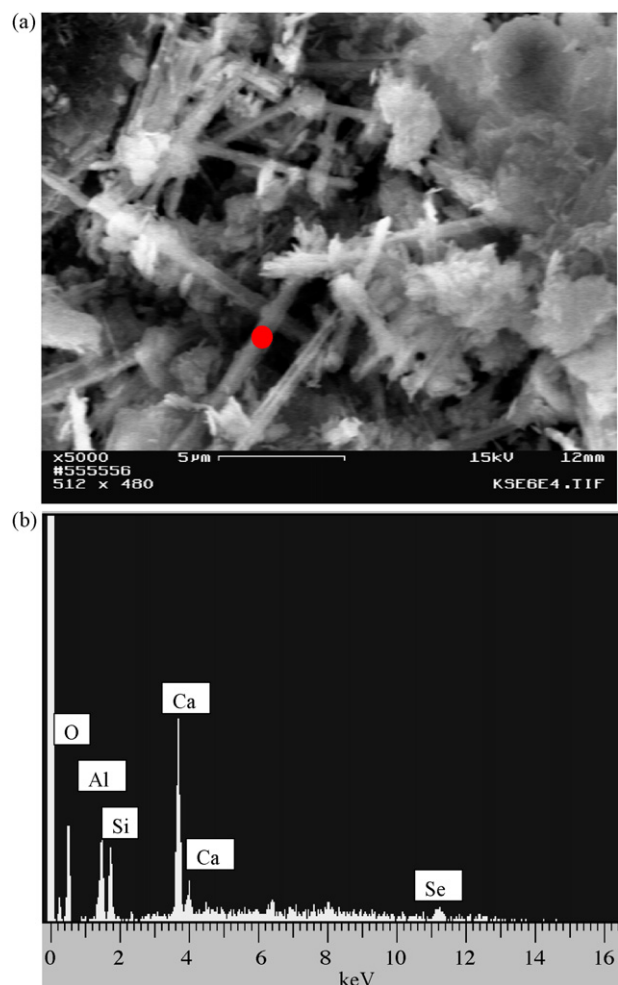


Fig. 8. SEM image of Se(VI)-kaolinite–P slurry sample showing needle-like Se-substituted ettringite [$\text{Ca}_6\text{Al}_2(\text{SeO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$] (a), and its empirically derived composition by EDX (b).

4. Conclusions

In this study, S/S processes were applied to two high water content clays and dredged material (DM) each individually spiked with 1000 mg/kg Se(IV) and Se(VI) to simulate very high sediment contamination. The dosing amounts of Portland cement (P) and cement kiln dust (C) were taken to be consistent with those ranges (up to 15%) used in commercial stabilization approaches for DM.

TCLP tests performed on the stabilized soils indicated that the P treatment was more effective than the C treatment in reducing both Se(IV) and Se(VI) concentrations. The lowest Se(IV) and Se(VI) concentrations were both observed upon P-treated kaolinitic soils, after 28 days of curing. All treatments failed to meet the TCLP–Se criteria (1 mg/L), but several Se(IV) stabilized soils passed the TCLP–BDAT standard (5.7 mg/L). The important accomplishment here is that the doses used in this study for high water content materials (up to 15 wt% pozzolan) are substantially less than those used in the TCLP BDAT compliance studies (up to 280 wt%) for similar levels of Se contamination. Our treatability study data suggests that for real sediments containing Se(IV) at observed levels up to 200 mg/L, the maximum doses used in this study will likely be successful under real (more dilute) conditions. This is an important cap to allow for future optimization.

To gain insight into the solubility controlling phases for the selenium in the pozzolanically treated soils, soil–P slurries were prepared using 100,000 mg/kg Se and 15% P to enable the identification

of Se precipitates by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM)–energy dispersive X-ray spectroscopy (EDX). The key selenium bearing phases found in all Se(IV)- and Se(VI)-soil–P slurries were calcium selenite hydrate ($\text{CaSeO}_3 \cdot \text{H}_2\text{O}$) and Se(VI)-ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SeO}_4)_3 \cdot 26\text{H}_2\text{O}$), respectively, as confirmed by XRD and SEM–EDX analyses. These compounds have not been previously identified in soil–cement systems.

These phases were likely to control Se solubility in the more dilute soil–cement systems that were exposed to the TCLP extraction solutions. However, the TCLP–pH data for all experiments (Figs. 1–4) suggest that the calcium selenite hydrate and Se(VI)-ettringite may have been attacked or dissolved entirely. While more success was clearly achieved with Se(IV), it appears that it will be very difficult to maintain the immobilization of Se(VI) under TCLP conditions as the TCLP–pH data for up to 15% P equilibrated and persisted below the minimum pH to ensure the stability of ettringite ($\text{pH} > 10.5$), as shown in Figs. 3 and 4. However, as most stabilized DM is placed in controlled fills at brownfields, mine restoration and other upland sites, it should remain strongly buffered (alkaline) under outdoor environmental conditions. Thus, the real threat of Se leaching will likely be substantially less than that implied by the TCLP test.

Acknowledgements

The Portland cement and cement kiln dust for this study were provided by Lafarge North America (Mr. Jeff Fair).

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