



## Assessment of cement kiln dust (CKD) for stabilization/solidification (S/S) of arsenic contaminated soils

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### ABSTRACT

A stabilization/solidification (S/S) process for arsenic (As) contaminated soils was evaluated using cement kiln dust (CKD). Laboratory-prepared slurries, made of either kaolinite or montmorillonite, and field soils spiked with either  $As^{3+}$  or  $As^{5+}$  were prepared and treated with CKD ranging from 10 to 25 wt%. Sodium arsenite and sodium arsenate at 0.1 wt% were used to simulate arsenite ( $As^{3+}$ ) and arsenate ( $As^{5+}$ ) source contamination in soils, respectively. The effectiveness of treatment was evaluated at curing periods of 1- and 7-days based on the toxicity characteristic leaching procedure (TCLP). As-CKD and As-clay-CKD slurries were also spiked at 10 wt% to evaluate As immobilization mechanism using X-ray powder diffraction (XRPD) analyses. Overall, the TCLP results showed that only the  $As^{5+}$  concentrations in kaolinite amended with 25 wt% CKD after 1 day of curing were less than the TCLP regulatory limit of 5 mg/L. Moreover, at 7 days of curing, all  $As^{3+}$  and  $As^{5+}$  concentrations obtained from kaolinite soils were less than the TCLP criteria. However, none of the CKD-amended montmorillonite samples satisfied the TCLP-As criteria at 7 days. Only field soil samples amended with 20 wt% CKD complied with the TCLP criteria within 1 day of curing, where the source contamination was  $As^{5+}$ . XRPD and scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX) results showed that Ca-As-O and NaCaAsO<sub>4</sub>·7.5H<sub>2</sub>O were the primary phases responsible for  $As^{3+}$  and  $As^{5+}$  immobilization in the soils, respectively.

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### 1. Introduction

Arsenic (As) naturally occurs in the environment through weathering and volcanism [1], and  $As^{3+}$  and  $As^{5+}$  are its most widespread forms. In addition, As has been widely used in industrial applications [2] such as tanning and wood preservation, and for pesticides and herbicides [3], as well as mining and smelting [4]. The major sources of As contamination to soils are pesticides, desiccants, and fertilizers [5]. Sodium arsenate (SA) has been historically used in agriculture, producing elevated As concentrations in soils above background levels [2].  $As^{3+}$  is reported to be more mobile than  $As^{5+}$ , and 25–60 times more toxic than  $As^{5+}$  [3,6–8]. Arsenic is listed as a class A carcinogen by the US Environmental Protection Agency (EPA) [9] with a LD<sub>50</sub> (lethal dose) of approximately 1–4 mg/kg for an adult [10]. Chronic exposure to As can cause cancer of the skin and organs, impair nerve functions, and inflict liver and kidney damage [11].

Stabilization/solidification (S/S) techniques are widely used for the treatment of hazardous wastes, beginning in the early 1970s [6]. S/S is one of the most common techniques applied in the US at Superfund sites, where about 24% of the sites between 1982 and 2002 used S/S processes [12]. Currently, cementitious S/S is recognized as the “best demonstrated available technology (BDAT)” by the USEPA for land disposal of most toxic elements [13]. The S/S application for heavy metal contaminated soils utilizing pozzolanic reagents has shown to be a cost-effective technique [6,14].

During stabilization, inorganic contaminants can be converted to forms which are much less mobile, soluble and toxic [6]. Solidification physically encapsulates the contaminants into a monolithic solid with a reduced surface area [15].

In this study, laboratory-prepared As-spiked soils were used to evaluate the effectiveness of cement kiln dust (CKD) as a potential stabilizing agent, and to determine if the minerals formed are consistent with the traditional S/S end products. CKD is a fine powdery material which is collected from kiln exhaust gases during the manufacture of Portland cement (PC) [16]. The generation of CKD is approximately 30 million tons world wide per year [17], with more than 4 million tons per year generated in the US [18]. The cost

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associated with CKD disposal is high, and the cement industry is interested in developing beneficial use applications for fresh CKD. As the price of CKD can be less than half the cost of PC depending on market conditions and regional availability, it becomes an attractive alternate to conventional pozzolans as long as CKD's efficacy in metals immobilization can be demonstrated.

In the past, S/S studies for As have used various combinations of stabilizing agents such as Type I PC, lime (L), Class C and Class F fly ashes, silica fume, iron (II) or (III), silicates and blast furnace slag [19–21]. However, S/S studies for As contaminated media using CKD could not be located by the authors.

It has been reported that As immobilization is associated with Ca–As precipitates formed during S/S treatment. Specifically, Akhter et al. [19] reported the formation of strätlingite ( $C_2ASH_8$ ) and  $NaCaAsO_4 \cdot 7.5H_2O$  in cement-fly ash samples containing  $As^{3+}$  and  $As^{5+}$ , respectively. That  $NaCaAsO_4 \cdot 7.5H_2O$  was observed in a cement-fly ash sample spiked with  $As^{3+}$  demonstrates the potential for the oxidation of As during S/S processes. Stronach et al. [22] reported that As solubility during S/S was limited by the formation of the sparingly soluble  $CaHAsO_3$  in the  $CaO-SiO_2-As_2O_3-H_2O$  system. Bothe and Brown [23] suggested that  $As^{5+}$  immobilization in arsenic-containing waste was achieved upon lime addition producing  $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ ,  $Ca_5(AsO_4)_3OH$  and  $Ca_3(AsO_4) \cdot 3(2/3)H_2O$ , depending on the molar Ca/As ratio. Based on S/S studies involving fly ash waste materials from the metallurgical industry treated with cement and lime, Vandecasteele et al. [24] reported that the leachable  $As^{3+}$  and  $As^{5+}$  concentrations were governed by the  $CaHAsO_3$  and  $Ca_3(AsO_4)_2$  phases, respectively. Moon et al. [21] reported that Ca–As–O and  $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$  were the main precipitates responsible for  $As^{3+}$  and  $As^{5+}$  immobilization in the lime–As slurries, respectively. In the lime– $As^{5+}$ –kaolinite slurries, Moon et al. [21] identified  $NaCaAsO_4 \cdot 7.5H_2O$  as being strongly associated with a significant decrease in the TCLP–As concentrations.

The purpose of this study was to evaluate the S/S treatment of As contaminated soils using CKD at dosage rates between 0 and 25 wt% (by dry weight). Kaolinite, montmorillonite and a field soil sample spiked with As ( $As^{3+}$  or  $As^{5+}$ ) were treated with CKD for curing periods up to 7 days. The toxicity characteristic leaching procedure (TCLP) for total As was used to evaluate the effectiveness of CKD treatment from a leaching perspective. Using As–CKD slurries, X-ray powder diffraction (XRPD) analyses were conducted to investigate the crystalline mineral formations associated with As immobilization at As concentrations of 100,000 mg/kg (10 wt%). Scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDX) were used to support XRPD results.

## 2. Experimental methodology

### 2.1. Soils and reagents

Kaolinite (K) and montmorillonite (M) (Clay Minerals Society, West Lafayette, IN) were used to evaluate the role of clay type on As leachability. Selected physicochemical properties of the clays are presented in Table 1. CKD (LaFarge North America, Whitehall, PA) having the physicochemical properties shown in Table 1 was used for this study.

Sodium arsenite ( $NaAsO_2$ ) and sodium arsenate ( $Na_2HAsO_4 \cdot 7H_2O$ ) (Fisher Scientific Co., Suwanee, GA) were selected as the  $As^{3+}$  and  $As^{5+}$  sources, respectively.

### 2.2. Laboratory-prepared slurries

Arsenic was first dissolved in deionized water as either  $As^{3+}$  (using  $NaAsO_2$ ) or  $As^{5+}$  (using  $Na_2HAsO_4 \cdot 7H_2O$ ). Briefly, soil slurry

**Table 1**  
Physicochemical properties of kaolinite, montmorillonite and CKD

	Kaolinite	Montmorillonite	Cement kiln dust (CKD)
Chemical analysis			
SiO <sub>2</sub>	43.9	62.9	19.04
Al <sub>2</sub> O <sub>3</sub>	38.5	19.6	6.12
TiO <sub>2</sub>	2.08	0.09	–
Fe <sub>2</sub> O <sub>3</sub>	0.98	3.35	2.68
FeO	0.15	0.32	–
MnO <sub>2</sub>	–	0.006	–
MgO	0.03	3.05	3.81
CaO	–	1.68	55.97
Na <sub>2</sub> O	<0.005	1.53	0.68
K <sub>2</sub> O	0.065	0.53	3.81
F	–	0.111	–
P <sub>2</sub> O <sub>5</sub>	0.045	0.049	–
S	0.02	0.05	–
SO <sub>3</sub>	–	–	8.96
LOI <sup>a</sup>	–	–	19.04
Free lime	–	–	8.28
Physical properties			
Surface area (m <sup>2</sup> /g)	23.5	31.82	–
pH (20% solids)	4.09	7.45	12.62
CEC (mequiv./100 g)	3.3	76.4	–

Note: Oxide values are expressed in percentages by mass.

<sup>a</sup> Loss on ignition.

samples were prepared by mixing 20 g of each clay with As at a liquid to solid ratio (L:S) of 10 to 1 resulting in an As concentration of 0.1 wt% (1,000 mg/kg). The As-spiked clays were mixed with CKD at doses between 10 and 25 wt% until they were visually homogeneous. A control sample without CKD was also prepared for each set of samples and cured up to 7 days. The specific test matrix of the treatment for laboratory-prepared slurries is presented in Table 2.

Prior to sub-sample collection for TCLP analyses, samples were aged using the following processes: the CKD-amended soil slurries were tumbled with the TCLP tumbler at 30 rpm for 24 h in order to accelerate the rate of reaction. After 24 h of tumbling, sub-samples were collected, air-dried, and designated as 1-day cured samples. The remaining soil slurries were thoroughly mixed on a daily basis. Additional sub-samples upon 7 days of curing were collected and air-dried. Cured samples and controls were subsequently subjected to TCLP tests.

### 2.3. Field soils

The field soil was collected from the Superfund site located in Tacoma, WA. Selected element compositions of the field soil analyzed by X-ray fluorescence (XRF), water content, and pH are presented in Table 3. The field soil was classified as “SP”, a poorly graded sand, with little or no fines according to the Unified Soil Classification Systems (USCS). Quartz, albite, cristobalite, anorthite, calcite and magnetite were identified based on XRPD analyses.

The field soil “as is” was treated with 5–10 wt% CKD due to the (low) initial As content of 178 mg/kg. The field soils were also spiked with either 0.1 wt%  $As^{3+}$  or  $As^{5+}$  for higher CKD dosages (20 and 25 wt%). All samples were cured for 1- and 7-days in sealed containers and the collected sub-samples were subjected to TCLP tests. The specific test matrix of the treatment for field soils is presented in Table 4.

### 2.4. As–CKD and As–clay–CKD slurries

The samples prepared in Sections 2.2 and 2.3 were used to simulate representative As leaching corresponding to a highly As contaminated site. However, to examine the relevant As mineralogy in S/S treated soils, a second set of CKD slurry samples was

**Table 2**  
Test matrix for laboratory-prepared soil slurries

Sample ID	Clay	CKD (wt%)	As <sup>3+</sup> (wt%)	L:S ratio	Sample ID	Clay	CKD (wt%)	As <sup>5+</sup> (wt%)	L:S ratio
S0	Kaolinite	0	0.1	10	S10	Kaolinite	0	0.1	10
S1	Kaolinite	10	0.1	10	S11	Kaolinite	10	0.1	10
S2	Kaolinite	15	0.1	10	S12	Kaolinite	15	0.1	10
S3	Kaolinite	20	0.1	10	S13	Kaolinite	20	0.1	10
S4	Kaolinite	25	0.1	10	S14	Kaolinite	25	0.1	10
S5	Montmorillonite	0	0.1	10	S15	Montmorillonite	0	0.1	10
S6	Montmorillonite	10	0.1	10	S16	Montmorillonite	10	0.1	10
S7	Montmorillonite	15	0.1	10	S17	Montmorillonite	15	0.1	10
S8	Montmorillonite	20	0.1	10	S18	Montmorillonite	20	0.1	10
S9	Montmorillonite	25	0.1	10	S19	Montmorillonite	25	0.1	10

**Table 3**  
Physicochemical properties of untreated field soil

Total content of element (mg kg <sup>-1</sup> )				Water content (wt%)	pH (1:1)
As	Fe	Mn	Zn		
178 ± 6	33271 ± 319	540 ± 47	4451 ± 52	11.76	10.63

**Table 4**  
Test matrix for field soil samples

Sample ID	Soil	CKD (wt%)	As <sup>3+</sup> (wt%)	As <sup>5+</sup> (wt%)	L:S ratio
S20	Field	5	–	–	0.1
S21	Field	10	–	–	0.1
S22	Field	20	0.1	–	0.1
S23	Field	25	0.1	–	0.1
S24	Field	20	–	0.1	0.1
S25	Field	25	–	0.1	0.1

**Table 5**  
Test matrix for As-CKD and As-Clay-CKD slurries

Sample ID	Clay	CKD	As <sup>3+</sup> (wt.%)	As <sup>5+</sup> (wt.%)	L:S ratio
S26	–	10 g	10	–	10
S27	–	10 g	–	10	10
S28	Kaolinite	25 wt%	10	–	10
S29	Kaolinite	25 wt%	–	10	10
S30	Montmorillonite	25 wt%	10	–	10
S31	Montmorillonite	25 wt%	–	10	10

prepared with 10 wt% As to enable the identification of As precipitates by XRPD (Table 5). The slurry samples were prepared and tumbled for 24 h by the process described in Section 2.2. The samples were then filtered using a 0.4- $\mu$ m pore-size membrane filter to separate the solids from the leachate. The filtrates were collected, air-dried and subjected to XRPD analyses (Section 2.6).

### 2.5. Toxicity characteristic leaching procedure (TCLP) tests

All of the samples prepared and aged by the processes described in Sections 2.2 and 2.3 were subjected to TCLP testing in accordance with US Environmental Protection Agency (USEPA) Method 1311 [25]. An acetic acid (pH 3 or 5 depending on soil pH) extraction solution was used to leach As from the controls and various As-spiked media, which were tumbled for 18 h at 30 rpm. Leachates were filtered through a 0.4- $\mu$ m pore-size membrane filter. The soluble As concentrations were measured from the leachate using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Varian Vista-MPX, Palo Alto, CA). Sample analyses were performed in duplicate and the averaged values were reported. For QA/QC purposes, two different quality control standards along with the method of standard addition (spiking) were used for every 10 samples.

### 2.6. X-ray powder diffraction analyses

The CKD-slurry samples prepared and aged by the process described in Section 2.4 were submitted for XRPD testing. The air-dried filtrates were hand-pulverized to pass through the #40 sieve and then were micromilled using a McCrone micronizing mill. Specifically, 1 g of the homogenized air-dried sample was pulverized for 5 min with 7 mL cyclohexane (Fisher, CAS 110-82-7), following the general rationale outlined by Dermatas et al. [26]. The resulting slurry was air-dried and then used for XRPD analyses. Step-scanned X-ray diffraction patterns were collected by a Rigaku DXR-3000 computer-automated diffractometer. XRPD analyses were conducted at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The XRPD patterns were collected in the  $2\theta$  range of 5–65° with a step size of 0.02° and a count time of 3 s per step. The qualitative analyses of the XRPD patterns were conducted using the Jade software Version 7.1 [27] and the PDF-2 reference database from the International Center for Diffraction Data database [28].

### 2.7. Scanning electron microscopy analyses

Select XRPD prepared samples were also evaluated by SEM–EDX analyses. Prior to SEM analyses, air dried sub-samples were 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 results of 0.1 wt% As-spiked soil slurries

The TCLP results obtained from the 0.1 wt% As-spiked kaolinite and montmorillonite samples with and without CKD treatments are presented in Figs. 1 and 2, respectively. The As<sup>3+</sup> and As<sup>5+</sup> concentrations of the kaolinite control samples were 22.9 and 20.88 mg/L after 7 days of curing, respectively. There was no significant difference in soluble As concentrations observed after 1 day of curing. However, the As<sup>3+</sup> and As<sup>5+</sup> concentrations from the montmorillonite control samples were higher (37.67 and 25.53 mg/L after 7 days of curing) than the kaolinite control samples. The kaolinite control exhibited a greater As adsorption capacity than montmorillonite, indicating that the clay-type plays a role in reducing the TCLP–As concentrations. It has been reported that  $\equiv$ Al–OH functional groups are more reactive toward As<sup>3+</sup> than SiO<sub>4</sub> tetrahedra,

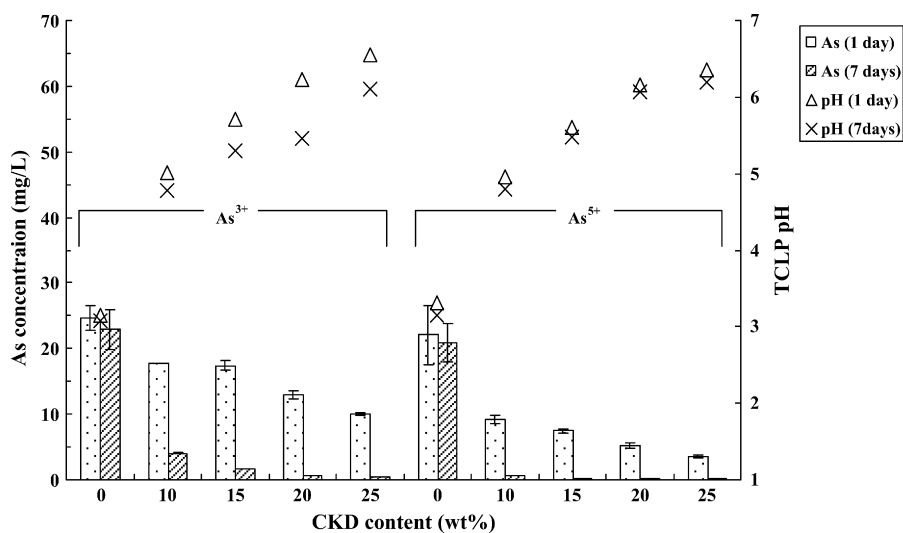


Fig. 1. TCLP–As concentrations along with TCLP pH in the presence of kaolinite upon CKD treatment after 1 and 7 days of curing.

the major surface components of phyllosilicates [29]. This indicates that kaolinite, with its lower Si:Al ratio (1:1) may have a greater adsorption capacity of  $As^{3+}$ . Manning and Goldberg [29] showed that  $As^{5+}$  extraction from kaolinite and montmorillonite at pH 7 were 66 and 80%, respectively, indicating the greater affinity of kaolinite for  $As^{5+}$  despite the greater specific surface of montmorillonite.

While adsorption processes may govern the fate and leaching of As in the controls, CKD treatment is expected to shift the As leaching and immobilization to precipitate-controlled mechanisms, as observed with traditional S/S processes. In CKD treatments, leachable  $As^{3+}$  and  $As^{5+}$  concentrations decreased with increasing CKD content for the kaolinite soils. The lowest TCLP– $As^{3+}$  concentration was approximately 10 mg/L at 1 day for the 25 wt% CKD dose (Fig. 1). At 7 days of curing, the TCLP– $As^{3+}$  concentrations from all kaolinite samples were less than the TCLP–As regulatory limit of 5 mg/L, at CKD doses as low as 10 wt%. For the TCLP– $As^{5+}$ , the treatment was even more effective owing to lower mobility and solubility of  $As^{5+}$ . At 25% CKD, the TCLP– $As^{5+}$  concentration (3.55 mg/L) satisfied the TCLP regulatory criteria at 1 day of curing. The TCLP– $As^{3+}$  concentrations from all kaolinite samples were less than 5 mg/L after 7 days of curing (Fig. 1).

Conversely, the TCLP–As leachability of CKD-amended montmorillonite soils was greater. The TCLP results showed that none of CKD treatments satisfied the TCLP regulatory limit at 7 days, regardless of As speciation. Specifically, about 62%  $As^{3+}$  and 42%  $As^{5+}$  reductions were achieved at 25 wt% CKD. Still, the TCLP–As concentrations were observed to decrease with increasing CKD dosage and curing. This suggests that longer curing periods may be required for regulatory compliance (<5 mg/L) if CKD is the pozzolan of choice. The pH values of the montmorillonite samples upon CKD treatment were slightly higher compared to those in kaolinite, likely due to the acidity of kaolinite. However, in both cases, the pH was high enough for the cement reactions to proceed (pH  $\approx$  12.5) and presumably dissolve the alumina and silica from both clays, albeit in different Si:Al proportions, which may have influenced the end product mineralogy.

It has been reported that As immobilization upon S/S treatment is mainly due to the formation of insoluble Ca–As precipitates [19,21–24]. This implies that while pozzolanic reaction products such as calcium silicate hydrate (CSH), calcium aluminum hydrate (CAH) and calcium aluminum silicate hydrate (CASH) can be produced at high rates in montmorillonite, they did not play a significant role in reducing the TCLP–As concentrations. This

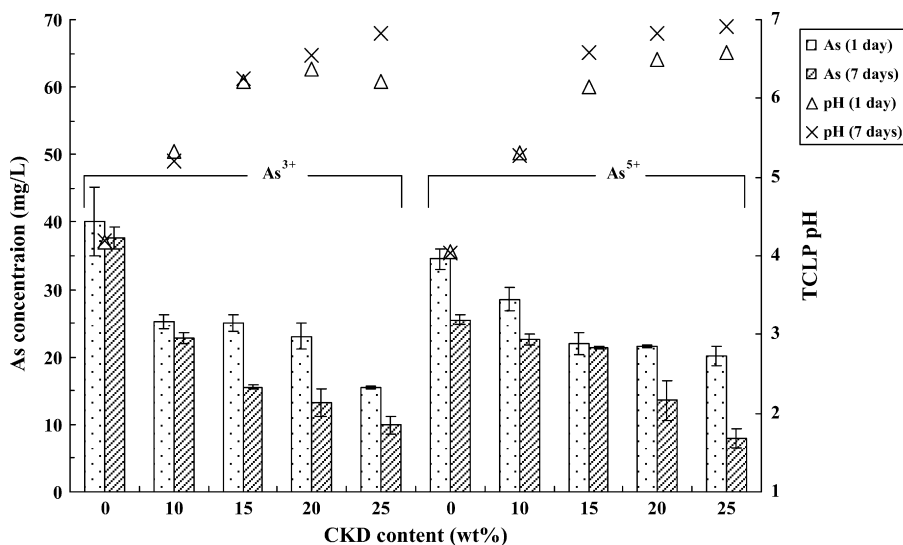


Fig. 2. TCLP–As concentrations along with TCLP pH in the presence of montmorillonite upon CKD treatment after 1 and 7 days of curing.

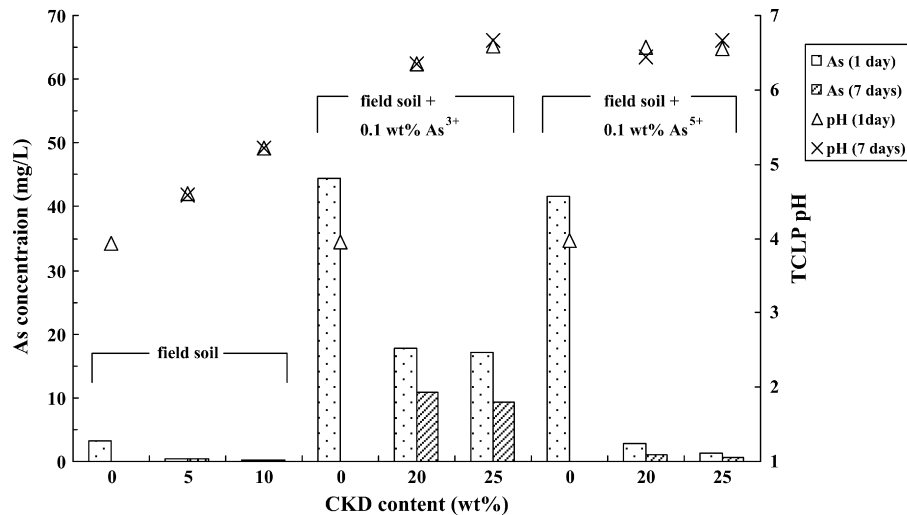


Fig. 3. TCLP-As concentrations along with TCLP pH in the field soils upon CKD treatment after 1 and 7 days of curing.

observation is consistent with a previous study where greater  $\text{As}^{3+}$  reductions were achieved using semi-dynamic leaching tests performed on lime-treated kaolinite samples [30]. Therefore, it was expected that As immobilization upon CKD treatment would most likely be associated with the formation of Ca-As precipitates.

### 3.2. TCLP results from field soils

The TCLP results of field soils are presented in Fig. 3. The TCLP-As concentration of the controls (unspiked soil) was approximately 3 mg/L. A CKD dose of 5 wt% was successful in reducing the TCLP-As concentration of the control below 0.5 mg/L after 1 day of curing. With the As spiking (0.1 wt%), the TCLP- $\text{As}^{3+}$  and TCLP- $\text{As}^{5+}$  concentrations from the untreated field soil were 44.45 and 41.51 mg/L, respectively. CKD treatment (>20 wt%) was only effective at meeting the  $\text{As}^{5+}$  TCLP regulatory limit of 5 mg/L after 1 day of curing. The TCLP  $\text{As}^{3+}$  concentrations exceeded the 5 mg/L limit even at 7 days curing, though they were gradually decreasing. The lowest TCLP  $\text{As}^{3+}$  concentration was approximately 9.3 mg/L at 25 wt% CKD. The results suggest that  $\text{As}^{3+}$  may be difficult to immobilize in a field setting, either requiring greater CKD amendment and/or longer curing times.

### 3.3. XRPD analyses of 10 wt% As-spiked CKD slurries

The XRPD patterns of the As-CKD and As-clay-CKD slurry samples for  $\text{As}^{3+}$  and  $\text{As}^{5+}$  are presented in Figs. 4 and 5, respectively. In the  $\text{As}^{3+}$ -kaolinite-CKD sample, kaolinite, calcite, quartz, and CAH were identified as major phases. In the  $\text{As}^{3+}$ -montmorillonite-CKD sample, montmorillonite, calcite, quartz, dolomite, CAH, and CASH were identified as major phases. In the  $\text{As}^{3+}$ -CKD sample, calcite, quartz, dolomite and ettringite were identified as major phases. Calcium arsenite (Ca-As-O, PDF# 001-0828) was identified as a very minor peak in all samples (Fig. 4), this compound also being reported during As immobilization in lime-treated soils [21]. The peak intensity of this phase in all samples was very low, but since no other Ca- $\text{As}^{3+}$  compounds were identified by XRPD analyses, Ca-As-O appears to be the crystalline phase most closely linked to  $\text{As}^{3+}$  immobilization. However, no correlation could be established between  $\text{As}^{3+}$  concentrations and clay-type due to very low peak intensities. Moreover, no crystalline Ca- $\text{As}^{5+}$  compounds were identified, indicating that no oxidation occurred during CKD-based S/S treatment. While pozzolanic reaction products strongly associated with heavy metals immobilization such as CASH [14] are known to form in montmorillonite, As immobilization was more pronounced in kaolinite, suggesting that CASH may not play

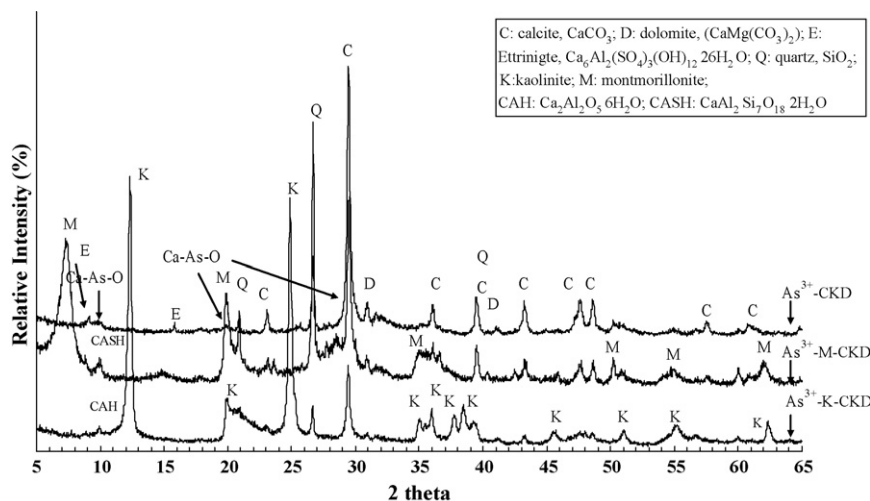


Fig. 4. XRPD patterns of the filtrates of  $\text{As}^{3+}$ -CKD and  $\text{As}^{3+}$ -clays-CKD samples.

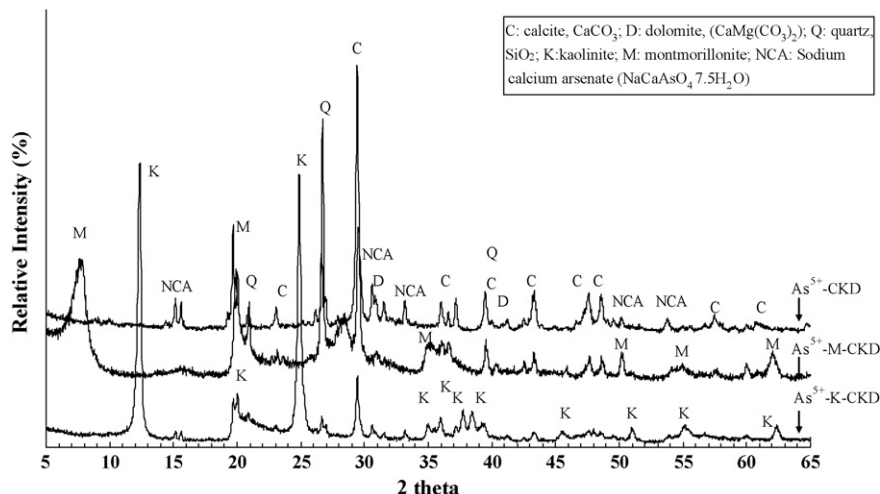


Fig. 5. XRPD patterns obtained from the filtrates of  $As^{5+}$ -CKD and  $As^{5+}$ -clays-CKD samples.

a role in  $As^{3+}$  immobilization by CKD. In other words, CASH is not as effective as Ca-As-O with respect to  $As^{3+}$  immobilization.

In the  $As^{5+}$ -kaolinite-CKD sample, kaolinite, calcite, quartz, dolomite, lime, and sodium calcium arsenate hydrate ( $NaCaAsO_4 \cdot 7.5H_2O$ , PDF# 025-1320) were identified as major phases. In the  $As^{5+}$ -montmorillonite-CKD sample, montmorillonite, calcite, quartz, and dolomite were observed as major phases. The formation of  $NaCaAsO_4 \cdot 7.5H_2O$  was not detected by XRPD in the montmorillonite samples although the hump at  $2\theta$

values of  $15.264^\circ$  and  $15.616^\circ$  may be obscuring trace quantities of  $NaCaAsO_4 \cdot 7.5H_2O$ . In the  $As^{5+}$ -CKD sample, calcite, quartz, dolomite and  $NaCaAsO_4 \cdot 7.5H_2O$  were clearly identified as major phases but no other Ca- $As^{5+}$  precipitates that control the immobilization of  $As^{5+}$  such as  $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ , Johnbaumite ( $Ca_5(AsO_4)_3(OH)$ ) and  $Ca_3(AsO_4)_2$  were detected [18,20,21,31]. Moreover, no Ca- $As^{3+}$  compounds were identified in the  $As^{5+}$  CKD slurries, indicating no As reduction occurred during CKD treatment. This suggests that  $NaCaAsO_4 \cdot 7.5H_2O$  is the main phase controlling  $As^{5+}$  solubility in CKD-treated soils. This compound

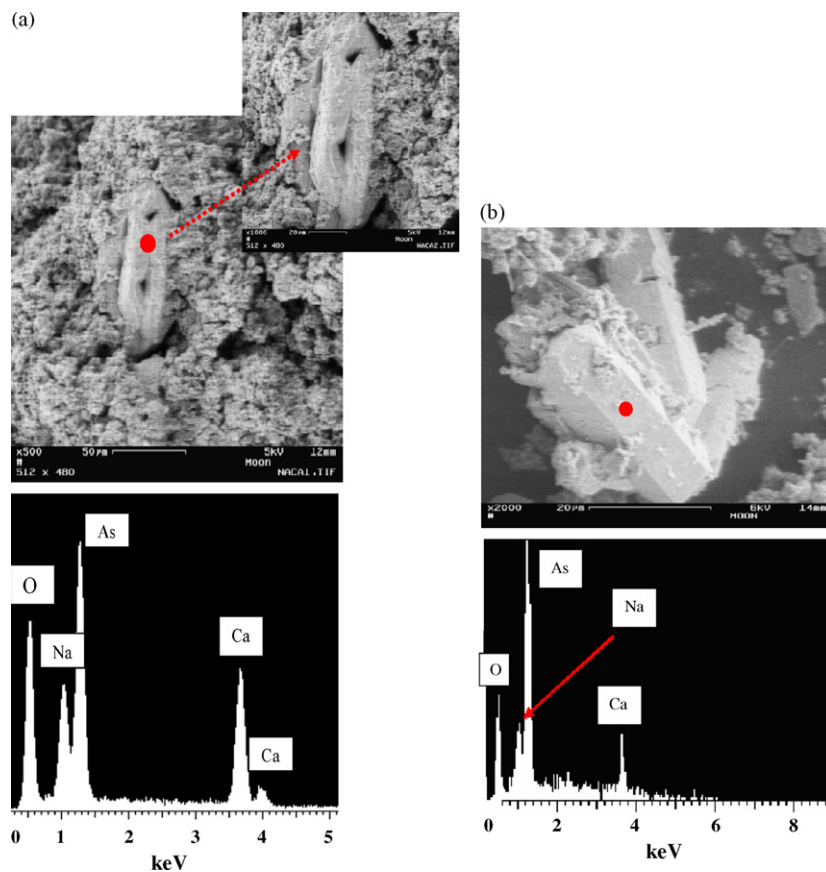


Fig. 6. (a) SEM analysis of synthesized  $NaCaAsO_4 \cdot 7.5H_2O$  and matching EDX data for point analysis and (b) SEM analysis of  $NaCaAsO_4 \cdot 7.5H_2O$  obtained in the residue of  $As^{5+}$ -CKD slurry and matching EDX data for point analysis.

has been previously detected as the phase responsible for  $\text{As}^{5+}$  immobilization in cement-fly ash samples spiked with  $\text{As}^{5+}$  [19] and lime- $\text{As}^{5+}$ -kaolinite slurries [21].

#### 3.4. SEM analyses

Akhter et al. [19] and Moon et al. [21] both detected  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  via XRPD analyses but no crystal images were provided as secondary evidence of mineral identification. Here,  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  was independently synthesized as a control slurry for XRPD and SEM-EDX analyses by mixing 0.5 g of sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) and 0.5 g of CaO in 20 mL of deionized water. This slurry was mixed for 1 h at 30 rpm using a TCLP tumbler and then filtered using a 0.4- $\mu\text{m}$  pore-size membrane filter. The filter residue was subsequently collected and analyzed by XRPD. The formation of  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  was identified along with  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  by XRPD (not shown here). Complementary SEM-EDX analyses confirmed the presence of  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  in the control slurry (Fig. 6a) and the previously described  $\text{As}^{5+}$ -CKD slurry sample (Fig. 6b). Comparison of Fig. 6a and b illustrates that the SEM-EDX results match in terms of morphology and relative elemental analysis, verifying the XRPD detection of  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  as the key crystalline phase linked to  $\text{As}^{5+}$  immobilization for CKD-based S/S treatment.

#### 4. Conclusions

S/S treatment of As contaminated soils was conducted using CKD. Laboratory-prepared slurries and field soils spiked with either 0.1 wt% (1,000 mg/kg)  $\text{As}^{3+}$  or  $\text{As}^{5+}$  were treated with up to 25 wt% CKD for curing times of 1- and 7-days. The treatments were evaluated for their leaching behavior by TCLP. A parallel study focused on the As immobilization mechanisms occurring in As-CKD, As-kaolinite-CKD, and As-montmorillonite-CKD slurries spiked with 10 wt%  $\text{As}^{3+}$  or  $\text{As}^{5+}$  via XRPD and SEM-EDX. The TCLP results of the laboratory-prepared soil slurry samples showed that upon 25 wt% CKD treatment, only the  $\text{As}^{5+}$  concentrations in the kaolinite soils were less than the TCLP criteria at 1 day of curing. All  $\text{As}^{3+}$ - and  $\text{As}^{5+}$ -spiked kaolinite soils treated with CKD (10–25 wt%) complied with the TCLP criteria at 7 days of curing. However, all As-spiked montmorillonite soils treated with CKD failed to meet the TCLP criteria after 7 days of curing. The TCLP results of field soil samples showed that only  $\text{As}^{5+}$  concentrations were less than the TCLP criteria within 1 day of curing at 20 wt% CKD. XRPD results revealed that Ca-As-O and  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  were primarily responsible for  $\text{As}^{3+}$  and  $\text{As}^{5+}$  immobilization in the CKD, respectively. The use of kaolinite and montmorillonite as surrogate soils has indicated that CKD has the ability to immobilize As. The formation of Ca-As-O and  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$  demonstrate that the immobilization of As is not attributed only to sorption or pH effects. Accordingly, it appears that CKD may hold promise for commercial S/S treatment pending more comprehensive evaluations with actual site soils. This would allow for the development of potentially more cost-effective S/S approaches while at the same time increasing the beneficial use of CKD.

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