

An evaluation of arsenic release from monolithic solids using a modified semi-dynamic leaching test

Dimitris Dermatas, Deok Hyun Moon*, Nektaria Menounou, Xiaoguang Meng, Richard Hires

W.M. Keck Geoenvironmental Laboratory, Center for Environmental Systems, Department of Civil, Environmental and Ocean Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, USA

Received 28 July 2003; accepted 21 April 2004
Available online 27 October 2004

Abstract

Quicklime and quicklime–fly ash-based stabilization/solidification (S/S) effectiveness was evaluated by performing semi-dynamic leaching tests (American Nuclear Society 16.1). Artificial soil samples, contaminated with arsenic trioxide (As_2O_3) as well as field soil samples contaminated with arsenic (As) were tested. The artificial soils were prepared by mixing amounts of kaolinite or montmorillonite with fine quartz sand. The S/S effectiveness was evaluated by measuring effective diffusion coefficients (D_e) and leachability indices (LX). Treatment was most effective in kaolinite-based artificial soils treated with quicklime and in quicklime–fly ash treated field soils. The experimental results indicate that D_e values were lowered as a result of S/S treatment. Upon treatment LX values were higher than 9, suggesting that S/S treated soils are acceptable for “controlled utilization”. Based on a model developed by de Groot and van der Sloot [G.J. de Groot, H.A. van der Sloot, in: T.M. Gilliam, C.C. Wiles (Eds.), *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, vol. 2, ASTM STP 1123, ASTM, PA, 1992, p. 149], the leaching mechanism for all of the treated soils was found to be controlled by diffusion. The effect of soluble silica (Si) on As leachability was also evaluated. When soluble Si concentration was less than 1 ppm, As leachability was the lowest. The controlling mechanism of As immobilization whether sorption, precipitation, or inclusion was also evaluated. It was determined that precipitation was the dominant mechanism.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Semi-dynamic leaching test; Stabilization/solidification (S/S); Quicklime; Arsenic (As); Leachability index (LX); Precipitation

1. Introduction

1.1. Background

Arsenic (As) is one of the most toxic elements. It occurs naturally in the environment by weathering and volcanism. In nature, As may exist in four different oxidation states: (–III), (0), (III) and (V) [1]. However, oxidized As(III) and As(V) are the most widespread forms in nature [1,2]. As_2O_3 is the form of As that is used in many industries such as agricultural pesticides, the glass industry, and the copper refining industry [3,4]. Therefore, arsenite, As(III), is expected to be the main

form of arsenic encountered in waste environments. Arsenite, is also known to be more toxic and mobile than arsenate, As(V) [5,6].

Even though industrial use of As has decreased in recent years, it remains a significant source for a number of human health problems [7]. Due to smelting of As-containing ores, and combustion of fossil fuels, As is still being introduced into soils, water, and the atmosphere [8]. Moreover, in the last several years the As threat to human health has received increased attention. The World Health Organization calls the drinking water related arsenic poisoning the largest human mass poisoning occurrence in history [9]. For all these reasons, in October 2001, the US Environmental Protection Agency (EPA) reduced the As standard for drinking water from 50 to 10 $\mu\text{g}/\text{l}$. This standard

* Corresponding author. Tel.: +1 201 216 8097; fax: +1 201 216 8212.
E-mail address: dmoon@stevens-tech.edu (D.H. Moon).

will be implemented by 2006 to better protect public health [10].

In the present study, the effectiveness of quicklime and fly ash stabilization/solidification (S/S) treatment to immobilize As in artificial soils was tested. Soils with an initial maximum As concentration of 124 mg/kg were remediated, in accordance with the sponsor's (US Department of Energy) request. Artificially contaminated soils, treated with quicklime or quicklime and fly ash, were subjected to semi-dynamic leaching in order to evaluate the effectiveness of the proposed treatment and the mechanisms responsible for As immobilization. In order to validate any observations from the artificial soils, field soil samples with higher As contamination were subjected to the same stabilization/solidification techniques.

1.2. State of the art

Stabilization/solidification is one of the most widely applied treatment processes for soils with heavy metal contamination [11]. The aim of this process is to transform hazardous waste into less hazardous or non-hazardous solids before landfill disposal [12].

Cement and hydrated lime ($\text{Ca}(\text{OH})_2$), sometimes combined with other pozzolanic materials such as fly ash, have been widely and successfully used as the main stabilizing agent for As immobilization by numerous researchers. Vandecasteele et al. [13] and Dutré et al. [14] studied As immobilization, using cement and hydrated lime. Côté et al. [15] used cement, fly ash–cement, soluble silicates–cement and fly ash–lime as stabilizing agents to evaluate arsenic leachability, whereas Sanchez et al. [16] used only cement.

Upon treatment with cement or lime, there are three possible mechanisms that may be responsible for the immobilization of As in soils:

- (a) Precipitation, during which least soluble calcium–arsenic (Ca–As) compounds are formed. Previous research by Dutré and Vandecasteele [6,14,17] demonstrated that the formations of $\text{Ca}_3(\text{AsO}_4)_2$ and CaHAsO_3 are responsible for the immobilization of As in contaminated soils that have been treated with cement, pozzolanic materials and lime.
- (b) Inclusion, which can be defined as either physical encapsulation or chemical inclusion [18]. Physical inclusion is achieved by creating a solidified monolith. During S/S As could also be incorporated into the newly formed pozzolanic products (chemical inclusion), such as calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) by isomorphic substitution. The formation of these calcium aluminosilicate hydrates occurs when pH increases to approximately 12.8 as a result of cement or lime addition. At this high pH the solubilities of silica and alumina present in fly ash and clay minerals are greatly increased and they become available for reaction with water and calcium derived from lime and/or fly ash to form a variety of pozzolanic products [19].
- (c) Sorption (including cation or anion exchange) on clays and pozzolanic reaction products [18,19].

Overall, the effectiveness of S/S treatment applications is evaluated using various leaching tests, depending on several factors. The researchers cited in the previous paragraphs all have used the American Nuclear Society 16.1 test [20], which is a semi-dynamic leaching test aimed at predominately evaluating the release of metals in diffusion-controlled environments. By applying this test we get the cumulative fraction of As leached versus time. It has already been reported that the leaching of contaminants out of a cement-based waste form is mostly a diffusion-controlled process [12,14,17]. ANS has standardized a Fick's-based mathematical diffusion model [20] based on Fick's second law which is used to evaluate the leaching rate with respect to time [15,21]. The leachability index (LX), which is a parameter directly derived from the ANS16.1 test results, is currently used by Environment Canada [22] as a performance criteria for utilization and disposal of treated waste. Treatment is considered effective in treated waste with LX values higher than 9.

In the present study quicklime (CaO) was used as the main S/S agent rather than using cement or hydrated lime for the following reasons: (a) there is a clear economic advantage in using quicklime because commercial quicklime is less expensive than hydrated lime and cement, (b) it accelerates the rate of reaction by its heat of hydration, thus reducing the time required for arsenic immobilization and (c) to advance the state-of-the-art on quicklime-based stabilization for As since there is only limited information available to date.

There are two ways of studying physicochemical behavior of soils; one is to look at natural soils and the other is to examine artificial soils. Most natural soil compositions are complex and contain several minerals or other constituents such as organic matter, oxygen, silica, alumina, iron, calcium, sodium, potassium, sulfate, magnesium, etc., all of which could participate in the immobilization reactions. Thus, the influence of any one of the natural soil constituents would be difficult to isolate [23]. Conversely, by using artificial soils the influence of individual components (especially clay minerals) on the leaching behavior can be determined with a high degree of confidence [23]. However, the leaching results obtained from artificial soils or field soils at a given site cannot be used to estimate As leachability at other sites. This is due to the chemical forms of As in the contaminated soil and the soil compositional characteristics, which are site-specific. Taking all this into account, in the present study, both artificial soils contaminated with chemical grade As, as well as As contaminated field soils were used. Artificial soils were used to isolate the clay mineral effects while field soils were used to validate the overall trends of the obtained results.

When preparing the artificial soils, clay–sand mixtures were used rather than pure clay in order to obtain specimens with gradation and mineralogy comparable to those of

naturally occurring soils. Clay–sand mixtures also provide materials that can be mixed and compacted more easily than pure clay.

1.3. Hypothesis

Treatment of As contaminated soils with quicklime and/or quicklime–fly ash mixtures will be effective (attain a leachability index (LX) higher than 9) in immobilizing As. A model introduced by de Groot and van der Sloot [24] will be applied to the results to predict the controlling leaching mechanisms such as initial wash-off, diffusion, and dissolution. The possible immobilization mechanisms considered will be precipitation, chemical inclusion, or sorption. Consequently, the effectiveness of this treatment will depend on surface area available, mineralogy and pore water chemistry as these will control the possible immobilization mechanisms. The presence of clays as well as the addition of fly ash in the quicklime treated soils will potentially enhance immobilization due to their high sorption capacity and their potential to form pozzolanic reaction products.

1.4. Objectives

The objectives of this study are the following:

- (1) To assess the effect of clay surface area and mineralogy on As leachability in artificial soil samples, both untreated as well as quicklime treated by:
 - a. testing two different clay minerals that represent the two extremes of clay behavior (kaolinite, montmorillonite);
 - b. testing the relative importance, if any, of the quantity of clays in the soil (15% versus 30%).
- (2) To evaluate the importance of fly ash addition in enhancing As immobilization. Fly ash contains silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃) and calcium oxide (CaO), which provide additional sources for the formation of pozzolanic reaction products, and in turn could immobilize As by sorption and/or chemical inclusion (fly ash addition in the untreated sample is also an indirect source of lime owing to its high CaO content).
- (3) To assess the long-term leaching behavior of As in quicklime treated soils, by determining diffusion coefficient values (D_e).
- (4) To evaluate the effectiveness of quicklime treatment based on leachability index values (LX > 9).
- (5) To determine the controlling As leaching mechanisms (diffusion vs. dissolution) in treated soils.
- (6) To evaluate the possible As immobilization mechanisms (precipitation versus chemical inclusion versus sorption) in treated soils.
- (7) To validate results derived from artificial soil samples, by applying quicklime and quicklime–fly ash S/S treatment to As contaminated field soil samples. The effectiveness of the S/S techniques is evaluated by determining the

LX. At the same time the controlling long-term leaching mechanisms are also determined.

2. Review of diffusion models

2.1. ANS model, diffusion coefficient D_e and leachability index LX

The long-term leachability of As from the quicklime treated soils was evaluated using the ANS method 16.1 [20]. By applying this method the cumulative fraction of As leached versus time is determined. It has been commonly reported that the leaching of contaminants out of cement-based waste forms is mostly a diffusion-controlled process [12,14,21]. Usually, a mathematical diffusion model based on Fick's second law is used to evaluate the leaching rate with respect to time [14,15,21]. ANS has standardized a Fick's law-based mathematical diffusion model [20] as follows:

$$\left(\frac{a_n}{A_0}\right) \left(\frac{V}{S}\right) \left(\frac{1}{\Delta t_n}\right) = \left(\frac{D_e}{\pi}\right)^{0.5} \left(\frac{1}{T_n^{0.5}}\right) \quad (1)$$

where a_n is the contaminant loss (mg) during the particular leaching period with index n , A_0 is the initial amount of contaminant present in the specimen (mg), V is the volume of specimen (cm³), S is the surface area of specimen (cm²), Δt_n is the duration of the leaching period in seconds, T_n is the elapsed time to the middle of the leaching period n in seconds and D_e is the effective diffusion coefficient (cm²/s). D_e values from Eq. (1) are termed "effective" because diffusion occurs in the liquid filling the interstitial space of a porous body. Therefore, the actual liquid path is longer than the one assumed by the model.

The exact solution of the diffusion equation depends on the initial and boundary conditions. The quicklime-based waste form was assumed to be a semi-infinite medium, just as the cement-based waste forms were in previous studies [14,15,21,25], due to the slow diffusion rate expected. This assumption implies that the release of contaminant from the waste form is insignificant as compared to its total mass in the waste form. Under this assumption, less than 20% of a leachable species can be leached out [14,15,21,25]. If the fraction leached is more than 20% of its initial concentration, the solution of the unsteady-state diffusion equation will be shape specific [20]. In this study, however, very low As release was expected from soils that have been treated with quicklime.

ANS 16.1 [20] is a standard method that provides diffusion rates that can be further applied to give parameters, which in turn, could be used to evaluate the effectiveness of an S/S treatment. One of these parameters proposed by ANS is the leachability index (LX). The LX is calculated using the diffusion coefficient found from Eq. (1). It is the average of the negative logarithm of the effective diffusivity terms (expressed in cm²/s). Therefore, the leachability index is defined

as follows [20]:

$$LX = \left(\frac{1}{m}\right) \sum_{n=1}^m (-\log(D_e))_n \quad (2)$$

where n is the number of the particular leaching period, and m is the total number of individual leaching periods.

The relative mobility of different contaminants can be evaluated by this index, which varies from 5 ($D_e = 10^{-5}$ cm²/s, very mobile) to 15 ($D_e = 10^{-15}$ cm²/s, immobile) [26]. According to Environment Canada [22], LX can be used as a performance criteria for the S/S wastes utilization and disposal. If the LX value is higher than 9, then the S/S wastes can be used in “controlled utilization”, providing that the information on the S/S wastes are acceptable for a specific utilization such as quarry rehabilitation, lagoon closure, road-base material and so on. If the S/S wastes have a LX value higher than 8, they can be disposed of in segregated or sanitary landfills. If the S/S wastes have a LX value lower than 8, they are not considered appropriate for disposal.

2.2. Determination of the controlling leaching mechanism

The type of leaching mechanism that controls the release of As can be determined based on the values of the slope of the logarithm of cumulative fraction release, $\log(B_t)$ versus the logarithm of time, $\log(t)$ line [24]. If diffusion is the dominant mechanism, then theory suggests the following relationship:

$$\log(B_t) = \frac{1}{2} \log(t) + \log\left(U_{\max} d \sqrt{\frac{D_e}{\pi}}\right) \quad (3)$$

where D_e is the effective diffusion coefficient in m²/s for component x (arsenic in this study), B_t is the cumulative maximum release of the component in mg/m², t is the contact time in seconds, U_{\max} is the maximum leachable quantity in mg/kg, d is the bulk density of the product in kg/m³.

According to de Groot and van der Sloot [24], if the slope of the curve from Eq. (3) is 0.5, the release of As will be slow and diffusion will be the controlling mechanism. When the slope is close to 1, the process is defined as dissolution. In that case, dissolution of material from the surface proceeds faster than diffusion through the pore space of the soil matrix [24]. During the dissolution process the materials will not be depleted until completion of the leaching experiment. Occasionally, a soluble layer exists on the surface of the material. During the initial phase of the leaching experiment, most of the soluble material in the soluble layer will be dissolved. This phenomenon is called surface wash-off, and the process typically results in a slope close to 0.

Typically, the long-term leaching characteristics of S/S treated wastes are controlled by diffusion. However, there are cases where the other processes, dissolution and wash-off may also occur [14,25,27]. It is important to determine the occurrence of dissolution and wash off because they may

lead to large amounts of the contaminant being released to the surrounding environment.

3. Experimental methodology

3.1. Description of the ANS16.1 test

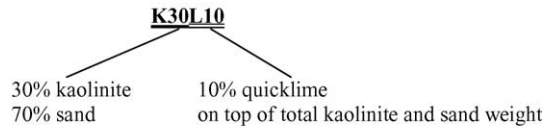
The long-term performance of S/S treatment has been difficult to predict in the past, since usually very little is known about the chemical species in the waste forms and their behaviors with respect to time. Semi-dynamic leaching tests are generally utilized to determine the leachability of contaminants from monolithic solidified waste forms and to evaluate the long-term behaviors of S/S wastes. “Semi-dynamic” describes the process where the leachant is replaced periodically after intervals of static leaching. Specifically, the ANS 16.1 test [20] was used to evaluate leachability of quicklime and fly ash treated samples. With the ANS 16.1 method [20], the diffusion controlled environment that is created when monolithic solids are soaking in water or other leachants for prolonged periods of time can be simulated. In nature, diffusion controlled environments can occur when a low permeability waste form lies below the groundwater table in a very low hydraulic gradient flow regime (aquicard scenario). ANS 16.1 [20] provides substantially more information regarding the “real time” rate at which heavy metals are released from the solidified product as compared to other leaching tests [28]. The leaching results extend over a 90-day period instead of a single result at the end of the test. Moreover, in the present study the artificial soil monoliths did attain low values of hydraulic conductivity indicating that a diffusion controlled environment would in effect simulate natural conditions more appropriately. Hydraulic conductivity was measured by conducting column percolation tests on specimens identical to the ones used in the present study and ranged between 2×10^{-6} and 5×10^{-10} cm/s [29].

Most previously reported semi-dynamic leaching studies on As immobilization were conducted using the standard ANS 16.1 method with distilled water as the leachant. In this study the existing method was modified and acetic acid at 0.014 N, pH 3.25 (similar to Toxicity Characteristic Leaching Procedure, pH 3) was used as the leachant. This modification was made in an effort to simulate possible “worst case” leaching conditions of S/S waste being disposed of in a landfill environment. With the present approach an attempt is made to simulate in a more realistic way the actual leaching conditions (landfill waste disposal area for a treated monolithic artificial soil following treatment with a high pH agent such as quicklime). That is, initially the conditions will be acidic and then gradually quicklime will overcome the buffering capacity of the liquid and the pH will be basic.

According to the ANS 16.1 method [20], the ratio of leachant volume to the specimen’s external geometric surface area (V_l/S) was maintained at 10 ± 0.2 cm. This ratio is usually sufficient to minimize leachant composition changes

Example 1: K30L10

- Letters in the name indicate chemicals: (K:kaolinite; M:montmorillonite; C:fly ash; L:quicklime)
- Numbers after the letters denote weight fraction of the chemicals.

**Example 2: M5C25L10**

5% montmorillonite, 25% fly ash C and 70% sand at 10% quicklime treatment level.

Fig. 1. A specimen designation guide.

as well as provide an ample concentration of extracted species for analysis [20]. The leachate was collected and replaced at designated time intervals (2, 7, 24, 48, 72, 96, 120, 456, 1128, and 2160 h) [20].

3.2. Sample preparation and analysis

During the present study soil mixtures of clay and sand were used. Kaolinite and montmorillonite were chosen because they represent the two extremes of physicochemical clay behavior, based on their surface area and cation exchange capacity (CEC). Hence, the effects on As immobilization of a relatively non-reactive clay (kaolinite) were compared to a highly reactive clay (montmorillonite). Additionally, the amount of clay present was varied to determine its relative contribution to As immobilization.

Field soil samples collected from two different As contaminated sites were also tested in this study. One came from the Anaconda site and the other from the Cataract Creek tailing facility, both located in Montana. Their total As concentrations were 820 and 3779 mg/kg, respectively.

A specimen designation guide is outlined in Fig. 1 to facilitate understanding of the nomenclature (artificial soils). Letters in the specimen designation show mineralogy or field sample origin, i.e., K: kaolinite, M: montmorillonite, S: Anaconda soil, T: Cataract Creek tailings, C: class C fly ash, and L: quicklime. Numbers following letters indicate the percent weight of the given attributes. For artificial soil samples, since the same type of fine quartz sand was added in all mixtures, complimentary to the clay or fly ash presence, sand was not included in the specimen designation. Sand content is always complimentary to the clay or fly ash content on a 100% weight basis. The content of fly ash was 25% on a weight basis (clay–sand–fly ash) for the artificial soils.

Also, upon quicklime treatment 10% of quicklime (L10) was added on a weight basis (clay–sand or clay–sand–fly ash). Similarly, 10% of quicklime (L10) was added on a weight basis to the field soils. However, the 25% fly ash was added by total weight of the respective soil sample.

Following preparation of all the different mixtures, samples were compacted in order to obtain monolithic solids.

Specifically, specimens with a 4.0 ± 0.4 cm height and a 4.70 ± 0.05 cm diameter were prepared by compaction at optimum water content. Optimum water content is the water content at which the maximum dry density is achieved for a given compactive effort. The specimen preparation for the optimum water content compaction experiment involved dry mixing of all constituents (clay, sand, quicklime, fly ash and arsenic) in designated percentages. Then, the optimum amount of distilled water was added to As contaminated clay–sand mixtures and they were allowed to mellow for a period of three days in order to attain a significant degree of arsenite operational equilibrium. Next, quicklime, fly ash or quicklime–fly ash, were added and the samples were compacted. The compaction was performed in accordance with ASTM D1557-91 [30] providing a compactive effort of 2700 kN m/m^3 ($56,000 \text{ ft lbf/ft}^3$). Samples were cured at 20°C in sealed sample bags for 28 days, and then subjected to the ANS16.1 leaching test [20]. Prior to ANS 16.1 test initiation, loose particles present on the solid's surface were rinsed out by immersing the solid in distilled water for 30 s. In order to suspend each specimen near the centroid of the acetic acid solution, a nylon mesh harness was used to support

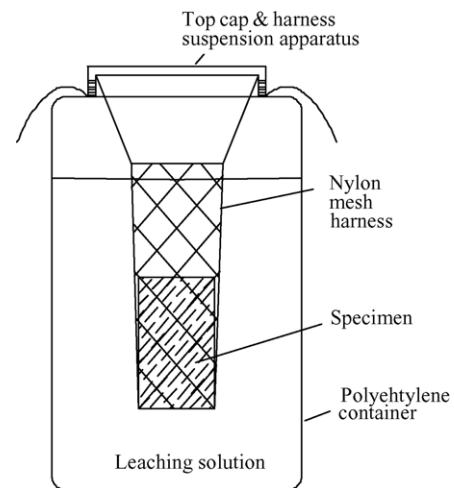


Fig. 2. Semi-dynamic leaching apparatus.

the specimen in a polyethylene container. Fig. 2 shows the semi-dynamic leaching apparatus.

Following test initiation, the leachate was filtered through a 0.4 μm pore-size membrane filter to separate the leachate and then analyzed at each designated time interval. The concentrations of soluble As were analyzed with a Zeeman Furnace Atomic Absorption Spectrometer (AAS) (Varian SpectrAA-400). During AAS analyses, 20 μl water samples and 5 μl palladium–citric acid modifier were injected in a partitioned graphite tube. The method detection limit was 0.7 $\mu\text{g/l}$ arsenic and the error range of the measurements was less than 10% when arsenic concentration in the sample was greater than 2 $\mu\text{g/l}$. The concentration of soluble silica was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Varian-Liberty). A number of blanks, replicates as well as spiked samples were prepared with each batch of samples for quality control purposes.

3.3. Materials

Kaolinite was provided by Dry Branch Company (Dry Branch, GA). Montmorillonite was provided by Kaopolite Inc. (Kaopolite, NJ). Chemical grade CaO (quicklime) powder was obtained by the Bellefonte Lime Company (Bellefonte, PA). Class C coal fly ash was provided by the American Fly Ash Company (Naperville, IL). According to the ASTM C618-91 standard [31], class C fly ash is derived from the combustion of sub-bituminous coal and has a high CaO content. The chemical properties and physical properties of kaolinite, montmorillonite, quicklime, and fly ash (Class C) are summarized in Table 1. Even though the actual field contamination might involve both As(III) and As(V) species,

arsenite, As(III) was used as the source of contamination for two reasons. First, based on numerous studies, As(III) is more soluble and hence more mobile than arsenate, As(V), in soils [5]. Moreover, As(III) is 25–60 times more toxic than As(V) and several hundred times more toxic than methylated As compounds [12]. Consequently, arsenic trioxide, As_2O_3 , was added to the clay–sand mixtures at contents based on the untreated weight of the soils (124 mg/kg).

In aqueous solutions and as a function of pH, arsenite occurs in different forms such as H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-} . At the high pH (>12) conditions induced by quicklime treatment, HAsO_3^{2-} , and AsO_3^{3-} are expected to be the dominant arsenite species [17].

Overall, the type of soil mixtures, the choice of additives and their respective levels were carefully selected to simulate closely the sponsor-provided actual field soil and existing contamination conditions.

4. Results and discussion

4.1. Cumulative release of As from artificial soils before and following S/S treatment

The cumulative fraction of As leached from untreated and treated samples was plotted on a semi-log graph in Figs. 3 and 4, respectively. The results are presented this way rather than using linear graphs since this was the best way to clearly show both high and low values of As leachability. Table 2 represents the ultimate cumulative fractions of As leached from the different samples upon test completion.

Table 1
Summary of material chemical and physical properties

	Percent content			
	Kaolinite	Montmorillonite	Quicklime	Class C fly ash
Chemical properties				
Material				
Silicon dioxide	45.70	67.20	1.20	34.2
Aluminum oxide	38.50	15.20	–	19.3
Iron oxide	0.40	1.87	–	5.64
Calcium oxide	0.20	1.92	95.40	25.8
Magnesium oxide	0.10	3.20	0.85	5.07
Sulfur trioxide	–	–	0.012 (as S)	2.2
Sodium oxide	0.04	2.58	–	2.04
Potassium oxide	0.10	0.96	–	0.52
Titanium dioxide	1.40	0.16	–	–
Reactivity: 30 s temperature rise ($^{\circ}\text{C}$)	–	–	38–41	–
Reactivity: 3 min temperature rise ($^{\circ}\text{C}$)	–	–	57–60	–
Physical properties				
No. 325 sieve residuals (%)	0.75	–	–	18.2
Particle size	55–65 (% <2 μm)	98 (% thru 100 mesh)	Available in all sizes	–
Specific gravity	–	–	–	2.77
Specific surface area (m^2/g)	66	760	40.0–41.5	31
pH	4.0–6.5	7	12.9	12.3
Moisture (% max)	3	10	–	–
CEC (meq./100 g)	4.5–5.5	80	–	–

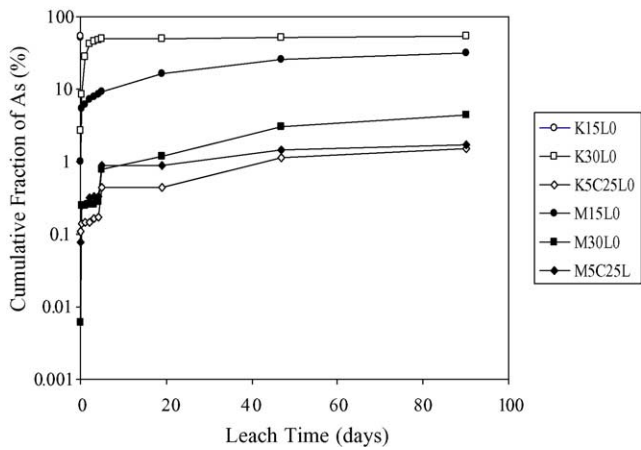


Fig. 3. Cumulative fraction of As (%) during the leaching time for untreated samples (K15L0 sample disintegrated after 7 h).

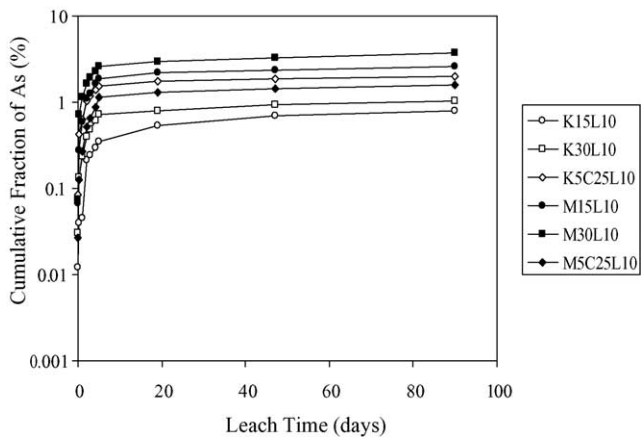


Fig. 4. Cumulative fraction of As (%) during the leaching time for treated samples.

In untreated samples, regardless of composition, an increase in the amount of clay led to a decrease in the amount of As leached (Table 2 and Fig. 3). More specifically, as shown in Fig. 3, even though the K15L0 sample disintegrated after 7 h of testing it was clear that a very high (more than 50% of the total) cumulative As fraction was leached out within this time period as compared to K30L0 (8.4% of the total). Sim-

ilarly, in montmorillonite–sand mixtures when the clay content increased from 15% to 30%, As leachability decreased significantly (Table 2 and Fig. 3). In the absence of treatment, and for the same percentage of clay, montmorillonite was significantly more effective in decreasing arsenic leaching than kaolinite. This is probably due to the larger surface area and cation exchange capacity of montmorillonite.

Upon addition of fly ash in untreated samples, the amount of As leached decreased even further (Fig. 3 and Table 2). Fly ash addition was also an indirect way of adding lime to the soils. Fly ash has a high percentage of CaO (Table 1) that provides the source for the formation of possible Ca–As precipitates.

Previous research has shown that Ca plays a role in the reduction of leachable As in wastes treated with cement and pozzolanic materials mainly through the formation of the compound CaHAsO_3 [17]. The Ca present in fly ash can also combine with water as well as alumina and silica derived from clay and/or fly ash dissolution to form a wide variety of pozzolanic reaction products such as CAH and CSH [19]. These pozzolanic products may contribute to As immobilization by sorption and/or chemical inclusion mechanisms.

The addition of 10% quicklime decreased As leachability in almost all of the samples as compared to their untreated state (Table 2 and Fig. 4). The As leachability differences amongst treated samples were small and were also obscured by the logarithmic nature of the plot (Fig. 4). The addition of 10% quicklime in the kaolinite–sand mixtures (K15L10 and K30L10) effectively reduced As release by more than 98%, as compared with the untreated sample results (Table 2). Arsenic release was also reduced by more than 91% in the M15L10 sample as compared to M15L0 sample (Table 2). However, the addition of quicklime in the M30L10 sample did not decrease As leachability further versus the M30L0 sample (Table 2). It appears that addition of quicklime in arsenic contaminated soils with low (15%) to high (30%) kaolinite content is necessary to significantly decrease As leachability. Conversely, in soils that have high montmorillonite content (30%) significant reduction of the amount of As released occurred without the need for quicklime treatment.

Similarly to M30L10, the quicklime–fly ash treated soils (K5C25L10 and M5C25L10) showed no significant As release differences when compared to their untreated state (K5C25L0 and M5C25L0). This indicates that As release

Table 2
Cumulative fraction As leached (%) following test completion

Artificial soils						
Untreated samples	K15L0	K30L0	K5C25L0	M15L0	M30L0	M5C25L0
Cumulative fraction of leached As (%)	53.71	54.15	1.52	31.15	4.47	1.718
Treated samples	K15L10	K30L10	K5C25L10	M15L10	M30L10	M5C25L10
Cumulative fraction of leached As (%)	0.80	1.04	1.97	2.56	3.73	1.59
Field soils						
Untreated samples	SL0	TL0				
Cumulative fraction of leached As (%)	2.21	11.67				
Treated samples	SL10	TL10	SC25L10	TC25L10		
Cumulative fraction of leached As (%)	0.83	0.57	0.35	0.15		

can be effectively reduced by the addition of fly ash alone and that concurrent addition of quicklime has no significant effect on As release.

Overall, the amount of As leached from the soil samples that have been treated with quicklime is much lower in the kaolinite–sand mixtures (<1%) than the montmorillonite–sand (<4%) and fly ash mixtures (<2%) (Table 2).

4.2. Cumulative release of As from field soil samples before and following S/S treatment

The results thus far clearly demonstrate that the quicklime-based treatment tested was effective in immobilizing As. However, as already discussed, artificial soil tests result can not be extended to actual field situations, mainly due to the site-specific nature of both the chemical form of As contamination and the soil compositional characteristics. Consequently, As contaminated field soil samples were also tested in order to validate the artificial soil results. These soils had As contents that were well above the content of As in the artificial soils, as mentioned in the sample preparation section. Yet significant amounts of clay minerals were not contained according to the data obtained by plastic limit tests and particle size distribution [28].

The cumulative As leachability for these contaminated field soil samples (Anaconda soil and Cataract Creek Tailing) was plotted on a semi-log graph and is shown in Fig. 5.

The As leachability results following test completion for field soil samples are also listed in Table 2. For the untreated Anaconda soil samples (SL0), only 2.2% of the total As release was observed following test completion. On the other hand, the release of As from the untreated tailing sample (TL0) was much higher at 12% of the total (Table 2). Upon quicklime treatment less than 1% As was released for all the treated field samples (Table 2). Arsenic leachability was even lower (less than 0.4%) when the samples were treated with quicklime–fly ash (Table 2).

Overall, quicklime and quicklime–fly ash treatment were both effective for the field soil samples, just as they were for

the artificial soil samples, even though the natural field soil samples had higher initial As concentrations. However, the untreated field soil samples, especially SL0, had a much lower As release than the release observed in the untreated artificial soil samples. This may be difficult to readily explain due to the degree of complexity of the natural field soil samples, which is obviously higher than the artificial soil samples. In nature there are many constituents that could participate in and influence As leachability [23]. Another factor that could possibly contribute to the low leachability of the untreated field soil samples is the form of As in the soils. Since As(III) is more mobile than As(V) the form of As in the field soils could be very important. It is possible that As is associated with mineral phases in the soil which are insoluble at the conditions of the modified ANS 16.1 test. Further research is required to obtain some of this information in order to evaluate the As speciation and subsequent release in these field soils.

4.3. Effectiveness of quicklime treatment and determination of the long-term controlling leaching mechanisms

The mean values of diffusion coefficients and leachability indices (LX) for all the field and artificial soil samples tested are shown in Table 3. The amount of As released during the ANS 16.1 tests [20] for some of the untreated samples far exceeded 20% of the total mass of the contaminant in the waste (Table 2 and Fig. 3), which is the upper limit for the diffusion model to be still applicable. Nevertheless, the amount of As leached from the untreated samples was determined in order to compare the changes in both the diffusion coefficients and the leachability indices following quicklime addition. As previously mentioned, the diffusion coefficients generally vary from 10^{-5} cm²/s (very mobile) to 10^{-15} cm²/s (immobile) [26].

The mean values of As diffusion coefficients for the untreated artificial soil samples ranged from 3.87×10^{-6} to 7.28×10^{-11} cm²/s. The samples where fly ash was added had the lowest D_e values. Upon addition of quicklime the mean values of As diffusion coefficients were significantly reduced (ranged from 6.93×10^{-10} to 1.48×10^{-11} cm²/s) as shown in Table 3. Specifically, there is a four and five orders of magnitude decrease in the As diffusion coefficients for the K30L10 and K15L10 samples respectively and a two orders of magnitude decrease in the diffusion coefficient of As for the M15L10 sample but no change for the M30L10 sample as compared to their untreated state (Table 3). There is a one order of magnitude increase in the diffusion coefficient of As for the K5C25L10 sample and no change for the M5C25L10 sample as compared to their untreated states (Table 3). Therefore, quicklime addition seems to have a more pronounced effect on kaolinite–sand mixtures as compared to montmorillonite–sand mixtures.

The mean values of As diffusion coefficients for all the field soil samples ranged from 2.75×10^{-8} to

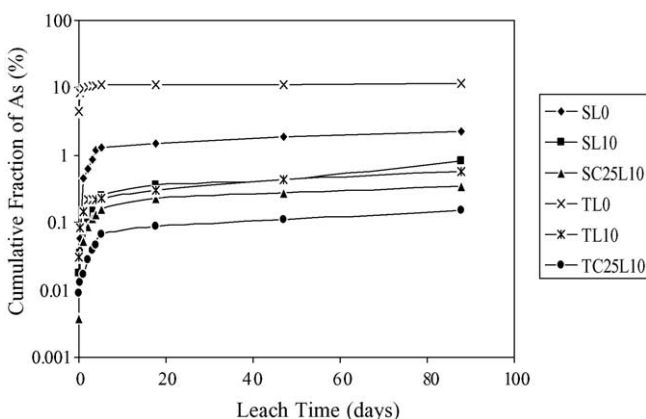


Fig. 5. Cumulative fraction of As (%) during the leaching time for field soil samples.

Table 3
Diffusion coefficients and LX values for As

Artificial soils			Field soils		
Sample	Mean D_e (cm ² /s)	Mean, LX	Sample	Mean, D_e (cm ² /s)	Mean, LX
K15L0	3.87E–06	5.41	SL0	1.66E–10	10.44
K30L0	1.51E–07	6.82	SL10	7.12E–12	11.38
K5C25L0	7.28E–11	10.14	SC25L10	2.81E–12	11.89
M15L0	1.11E–08	7.95	TL0	2.75E–08	9.37
M30L0	2.91E–10	9.54	TL10	5.84E–12	11.78
M5C25L0	2.64E–10	9.58	TC25L10	5.63E–13	12.66
K15L10	1.48E–11	10.83			
K30L10	3.83E–11	10.42			
K5C25L10	2.20E–10	9.66			
M15L10	3.22E–10	9.49			
M30L10	6.93E–10	9.16			
M5C25L10	1.42E–10	9.85			

5.63×10^{-13} cm²/s (Table 3). Overall, As diffusion coefficient values for the untreated samples (SL0 and TL0) are significantly higher than those for the treated samples (SL10, SC25L10, TL10, and TC25L10). More specifically, there is a two orders of magnitude decrease in the As diffusion coefficients for the SL10 and SC25L10 samples as compared to their respective untreated state and a four to five orders of magnitude decrease in the As diffusion coefficients for the TL10 and TC25L10 samples, compared also to their respective untreated state (Table 3). Therefore, quicklime and fly ash treatment resulted in an obvious reduction of As release.

Using the LX as a performance criteria for utilization and disposal of treated wastes, all the treated specimens tested for both artificial and field soils would be appropriate for a con-

trolled utilization, since they all had LX values for As release higher than 9 (Table 3). Even some of the untreated mixtures (M30L0, K5C25L0, M5C25L0, SL0) had LX values higher than 9.

Even though all the treated soils are categorized as soils that could be used in “controlled utilization” because of LX values higher than 9 (Table 3), when considering the As standard for drinking water (10 µg/l), a different picture can be drawn. That is, most of the treated samples leached As at concentrations well above the 10 µg/l limit (Table 4). This has implications regarding the safety of treated soils leaching in underground or surface water reservoirs and raises the question about the existent regulations for reusable treated wastes. When using acetic acid as the leachant, “worst case” condi-

Table 4
Arsenic concentration leached out from the treated samples based on each time interval

Time (days)	K15L10	K30L10	K5C25L10	M15L10	M30L10	M5C25L10
As (ppb) for artificial soils						
0.08	1.9	4.4	12.3	10.3	10.8	4.1
0.29	4.5	15.0	49.0	32.4	93.2	15.2
1	0.8	14.4	31.2	46.4	60.6	20.8
2	26.1	24.0	58.8	81.1	70.6	37.4
3	4.6	12.6	22.4	24.8	39.8	22.0
4	8.6	16.6	30.6	55.2	56.4	33.6
5	9.2	14.4	21.0	39.0	42.8	37.4
19	30.2	12.4	30.3	43.8	55.4	28.6
47	25.2	19.4	19.2	26.0	48.0	19.8
90	15.8	15.0	12.6	33.8	61.6	23.4
Time (days)	SL10	SC25L10	TL10	SC25L10		
As (ppb) for field soils						
0.08	20.0	4.0	119.8	32.0		
0.29	20.0	32.5	205.6	15.0		
1	42.0	21.0	235.8	15.0		
2	47.5	37.5	282.9	40.0		
3	53.0	30.0	12.7	35.0		
4	60.0	19.0	13.1	30.0		
5	42.0	28.0	44.5	70.0		
19	127.5	77.5	298.4	87.5		
47	78.0	48.0	501.9	75.0		
90	443.3	76.0	540.7	152.0		

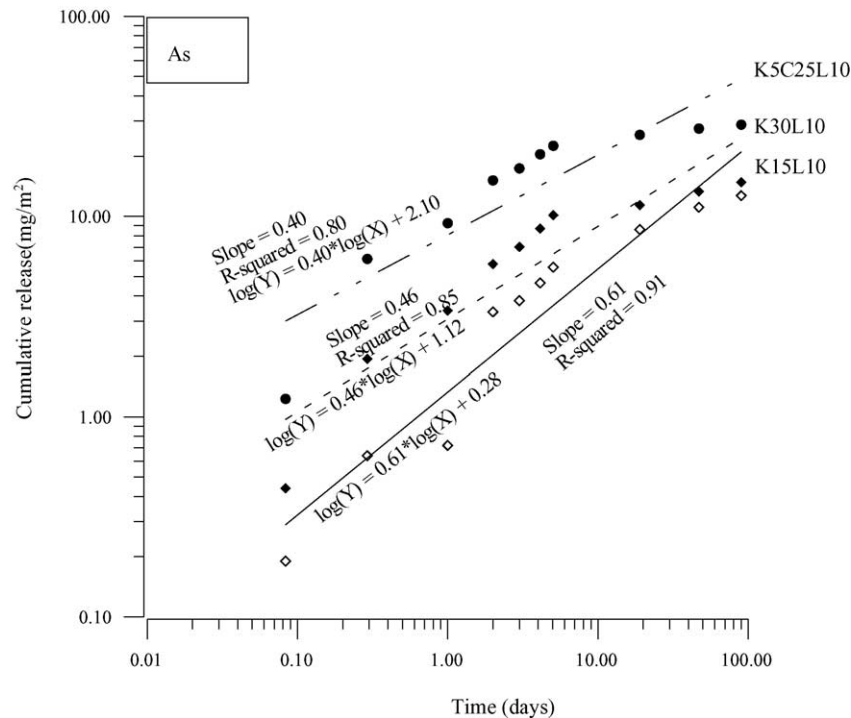


Fig. 6. Logarithm of the cumulative release of the As vs. the logarithm of time for kaolinite–sand mixtures upon quicklime treatment.

tions are being tested, whereas using deionized (DI) water would probably result in somewhat lower levels of release, especially during the first 5 days of testing. Following that period of time, the solution becomes Ca^{2+} and OH^- saturated, indicating that the results of the present study would not be significantly different if DI water was used as the leachant instead, since the buffering capacity of any leachant (be it DI or acetic acid) will be eventually exhausted and pH will be higher than 10.

All the As leachability results demonstrated that As release upon quicklime treatment was limited. The long-term leaching mechanisms were evaluated by the diffusion model developed by de Groot and van der Sloot [24]. The cumulative release of As from quicklime treated and quicklime–fly ash treated samples containing kaolinite were plotted versus time in Fig. 6. Similar results were obtained for the montmorillonite–sand and field samples and are presented in Table 5. The slopes for all the sample plots are summarized in Table 5.

From the untreated kaolinite samples only K5C25L0 had a slope close to 0.4 (Table 5), indicating the controlling leaching mechanism is diffusion. For the other kaolinite–sand samples, K15L0 and K30L0, leaching was controlled by wash-off (slopes are 0.01 and 0.24, respectively). Upon quicklime treatment the leaching mechanism was diffusion since the slope ranged from 0.4 to 0.61 for K15L10, K5C25L10 and K30L10. The montmorillonite–sand samples had slope values that ranged from 0.42 to 0.58 for their untreated samples and from 0.42 to 0.49 for their treated samples. These slopes indicate that As leachability is also

diffusion controlled with or without quicklime treatment. Arsenic release from the quicklime–fly ash treated samples is also diffusion controlled since the slope of K5C25L10 and M5C25L10 were 0.4 and 0.42, respectively. Similarly, As release from field soil samples upon quicklime and quicklime–fly ash treatment was also diffusion controlled since the slope of the curve representing the cumulative As versus time was close to 0.5. In their untreated states, As release was controlled by different mechanisms for the two field soils tested. For the Anaconda sample (SL0), which had a slope of 0.7, As release was controlled by dissolution. For the Cataract Tailing sample (TL0), the slope was low (0.11) and As release was therefore controlled by wash-off.

Table 5
Regression analyses results for As release

Artificial soils			Field soils		
Sample	Slope	R^2	Sample	Slope	R^2
K15L0	0.01	–	SL0	0.70	0.82
K30L0	0.24	0.6	SL10	0.54	0.97
K5C25L0	0.39	0.81	SC25L10	0.57	0.87
M15L0	0.42	0.91	TL0	0.11	0.65
M30L0	0.58	0.84	TL10	0.38	0.93
M5C25L0	0.42	0.91	TC25L10	0.43	0.97
K15L10	0.61	0.91			
K30L10	0.46	0.85			
K5C25L10	0.40	0.80			
M15L10	0.49	0.84			
M30L10	0.47	0.76			
M5C25L10	0.42	0.86			

4.4. The effect of Si and pH of the leachant on As leachability

The leachant pH was also monitored in this study. Table 6 shows the pH values of the leachant at designated time intervals as set by the ANS16.1 protocol. In the beginning of the test the leachant pH was low for all the samples (less than 4 for untreated and less than 5 for treated samples) and increased with time. At test completion (90 days) the leachant pH was around 8 for fly ash treated samples and around 12 for quicklime and quicklime–fly ash treated samples. In quicklime and quicklime–fly ash treated samples the pH changed drastically at 19 days because the leachant remained in contact with the solidified monolith for a longer time period (14 days) allowing for the buffering capacity of the liquid to be consumed and alkaline conditions to prevail. Overall, in all the clay–sand mixtures after quicklime and quicklime–fly ash treatment, when the leachate pH was higher than 10, As leachability was very low, generally less than 5% (Tables 2 and 6).

A dominant parameter in the soil mixtures studied here was silica (SiO_2), which was the single largest component in all the mixtures used. Silica is expected to participate in the immobilization process following quicklime and quicklime–fly ash treatment. Therefore soluble silica concentrations in the leachate were monitored for all treated artificial soil samples and the results are summarized in Table 7. The soluble silica results reflect the total amount of silica present in the mixtures. Montmorillonite has 67.2% and kaolinite has 45.7% of silicon dioxide (Table 1). Overall, soluble silica was higher in montmorillonite than in kaolinite soils (Table 7). Moreover, the amount of kaolinite and montmorillonite present (15% versus 30%) is reflected in the soluble silica concentrations. The K15L10 sample has almost half the amount of soluble silica present than the K30L10 sample (Table 7). Montmorillonite samples (M15L10 and M30L10) follow the same trend. Overall, As leachability results (Table 2) showed a drastic decrease (more than 98%) in As leachability when soluble silica concentrations were below 1 ppm in the leachate.

Table 6
pH data for untreated and treated samples

Time (days)	K15L0	K30L0	K5C25L0	M15L0	M30L0	M5C25L0
pH for artificial soils						
0.08	2.9	3.2	3.8	3.1	3.2	3.8
0.29	3.2	3.1	3.9	3.0	3.3	3.9
1.0	–	3.0	4.1	3.2	3.4	4.2
2.0	–	3.0	4.1	3.3	3.5	4.8
3.0	–	3.2	4.1	3.3	3.6	4.2
4.1	–	3.2	3.9	3.2	3.4	4.0
5.0	–	3.4	3.9	3.3	3.5	4.0
19.0	–	3.1	4.9	3.9	3.6	5.4
47.0	–	3.4	4.3	3.5	5.4	7.5
90.0	–	3.5	7.5	3.4	4.1	8.0
Time (days)	K15L10	K30L10	K5C25L10	M15L10	M30L10	M5C25L10
pH for artificial soils						
0.08	4.3	4.5	4.3	4.3	4.1	4.3
0.29	4.4	4.4	4.3	4.3	4.2	4.3
1.0	5.1	5.1	4.7	4.7	4.6	4.6
2.0	5.3	5.1	4.7	4.7	4.6	4.6
3.0	4.9	4.4	4.4	4.4	4.3	4.1
4.1	4.6	4.6	4.4	4.4	4.3	4.3
5.0	4.4	4.2	3.9	3.9	4.1	4.3
19.0	11.7	11.5	11.41	11.41	11.4	11.6
47.0	11.3	11.5	11.2	11.2	10.7	10.7
90.0	10.8	11.3	10.5	10.5	11.3	12.0
Time (days)	SL0	SL10	SC25L10	TL0	TL10	SC25L10
pH for field soils						
0.08	3.27	3.94	3.83	3.28	4.16	3.84
0.29	3.62	4.44	4.32	3.75	4.45	4.40
1.0	3.52	4.78	4.72	3.62	5.31	5.26
2.0	3.42	5.03	4.93	3.48	5.61	5.30
3.0	3.09	4.53	4.54	3.15	5.22	4.78
4.1	3.14	4.50	3.14	3.19	4.68	4.54
5.0	3.39	4.46	4.48	3.47	4.81	4.59
19.0	3.36	11.95	11.82	3.92	12.22	11.98
47.0	3.50	12.21	12.10	2.2	12.21	12.24
90.0	3.49	12.06	11.72	4.25	12.26	12.01

Table 7
Soluble silica concentrations for all treated artificial soils

Time (days)	K15L10	K30L10	K5C25L10	M15L10	M30L10	M5C25L10
Si (ppm)						
0.08	0.06	0.15	0.28	0.45	0.81	0.23
0.29	0.18	0.30	0.64	2.04	3.37	0.45
1	0.19	0.37	1.13	3.69	5.38	0.92
2	0.51	0.51	1.71	4.28	6.94	1.35
3	0.27	0.45	1.17	4.81	4.81	1.19
4	0.48	0.52	2.10	4.52	6.08	1.44
5	0.55	0.68	1.41	3.49	4.63	1.94
19	0.50	0.70	2.16	3.75	9.72	1.67
47	0.54	0.91	1.81	2.31	6.09	1.69
90	0.39	0.38	1.06	1.81	4.85	1.10

Meng et al. [32], in their study on As(III) removal by ferric chloride, also found that when Si was present in concentrations less than 1 ppm, soluble As concentrations were very low. Soluble As concentrations increased in solution when Si was higher than 1 ppm. The present findings seem to confirm this observation.

4.5. Mechanisms of As immobilization

Arsenic immobilization in soils subjected to S/S processes can be achieved by sorption, precipitation and/or inclusion. In this study, an attempt was made to determine the prevailing immobilization mechanism by evaluating the As leachability results.

Upon quicklime and quicklime–fly ash treatment As leachability from all the treated samples was found to be low (less than 4%), which indicates that the treatment was effective. The lowest As leachability was observed in the kaolinite–sand quicklime treated samples (K15L10 and K30L10). Also, the low clay content in the montmorillonite–sand mixtures (M15L10) showed significant reduction of As leachability compared to its untreated state. However, As leachability decreased insignificantly at the high clay content montmorillonite (M30L10) compared to treated kaolinite–sand samples (K15L10 and K30L10) and M15L10.

The role of sorption in the montmorillonite soils, once evident in M30L0 was no longer dominant following quicklime treatment since As leachability was similar in the samples with varied clay content. Moreover, As leachability was not altered by increasing the clay content in the kaolinite soils either. Additionally, the expected decrease in As concentrations (caused by sorption on the newly formed pozzolanic reaction products) in the leachate of treated montmorillonite–sand samples was not observed. As stated in the previous section, both the montmorillonite–sand mixtures and the fly ash treated soils would have much higher silica content than the kaolinite–sand mixtures and should therefore create more pozzolanic reaction products at a higher rate. At the same time immobilization of As by inclusion in the newly formed pozzolanic reaction products should have decreased leachability even more. So it seems that a

precipitation-based immobilization mechanism was in effect here.

This observation of precipitation-based immobilization was further reinforced by the reduction of As leachability in the field soil samples tested here upon quicklime-based treatment. Also soil mineralogy as evidenced by X-ray diffraction (XRD) analysis of the treated field soil samples (not shown here) support the findings in the artificial soils. All the field soils had very low clay content in their composition based on index property tests such as particle size distribution and plastic limit tests and XRD analyses data [28]. Because of the low clay content there was not enough silica present to produce pozzolanic reaction products that would support As immobilization by chemical inclusion and/or sorption in these formations. Therefore, the only way that As immobilization must be occurring would be through precipitation. Unfortunately, X-ray diffraction analysis showed no Ca–As precipitates or pozzolanic product formation. This is probably due to the limited amount of As present in the samples, which was always less than the detection limit of the instrument (5 wt.%). Therefore additional research is necessary, possibly with quicklime-treated soil samples that have a higher initial concentration of As.

5. Conclusions

Semi-dynamic leaching tests were performed to evaluate As leachability in quicklime-based S/S of field and artificial soil samples. The long term leaching mechanisms were identified along with the mechanisms responsible for As immobilization upon treatment. The use of artificial soils helped isolate the contributions of specific properties of clays, such as surface area and ion exchange capacity, in As leaching and immobilization following quicklime treatment. Fly ash was evaluated as a sole stabilizing agent in As contaminated soils.

Overall, it can be concluded that the quicklime-based treatment was effective in significantly reducing As leachability and that long-term As leaching was controlled by diffusion. The dominant immobilization mechanism appears to be precipitation.

The specific conclusions pertaining to the results presented herein, can be summarized as follows:

1. In all untreated samples, regardless of composition, As leachability was reduced with increasing amounts of clay. This reduction was more pronounced in the presence of high percentage montmorillonite which is the most active clay used in this study due to the larger surface area and the higher cation exchange capacity compared to kaolinite. The dominant mechanism of As immobilization in these soil samples appears to be sorption.
2. Addition of fly ash as a sole stabilizing agent in all the artificial soil samples studied here significantly reduced As leachability. Fly ash provided an indirect source of lime in the soils tested. The calcium oxide present reacted with As and formed insoluble Ca–As precipitates and/or participated in the reactions that lead to the formation of pozzolanic reaction products. The latter could immobilize As by sorption on their surface or by chemical inclusion.
3. Upon quicklime treatment As release was significantly reduced in almost all of the samples. Differences in As leachability that were related to the clays present as well as fly ash and were significant in untreated samples, were minimal upon treatment.
4. Of the differences observed before and following the treatment, the most pronounced are found in the artificial soils with kaolinite. Upon treatment As leachability was the lowest observed amongst all the soils tested. Low As leachability in these samples coincides with less than 1 ppm soluble silicate concentration. Samples that had higher soluble silica present in the leachate had also slightly higher As concentrations.
5. The reduced As leachability upon treatment when modeled versus time was found to be diffusion controlled. Therefore, only small amounts of As would be expected to leach in the environment. However, soluble As concentrations in the leachate were higher than the water drinking standard of 10 µg/l, suggesting caution should be taken for the disposal of treated wastes.
6. Upon quicklime treatment, the immobilization of As appeared to be controlled mainly by precipitation. This conclusion was based on several observations: (a) in the artificial soils the amount of clay did not influence As leachability, indicating that sorption was not the controlling immobilization mechanism; (b) also, samples with high silica content, such as montmorillonite or fly ash–clay soils which would be expected to form pozzolanic reaction products at higher rates and amounts, showed elevated As leachability levels compared to low silica samples (kaolinite soils). The pozzolanic reaction products could immobilize As by inclusion and/or sorption and reduce even more its leachability; (c) the natural field soil samples that had very low clay content showed significant reduction on As leachability upon quicklime treatment. In the absence of silicates, calcium that is abundantly available reacts with arsenic to

form Ca–As precipitates that efficiently immobilize the contaminant.

Acknowledgment

This work was made possible by a grant (Contract No. DE-AC21-92MC29117) from the US Department of Energy (US-DOE). The authors would like to thank Mohammed Sharaf and journal reviewers for critical comments and suggestions that improved the manuscript.

References

- [1] R.W. Boyle, I.R. Jonasson, *J. Geochem. Explor.* 2 (1973) 252.
- [2] J.A. Cherry, A.U. Shaikh, D.E. Tallman, R.V. Nicholson, *J. Hydrol.* 43 (1979) 373.
- [3] J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, NY, 1990.
- [4] V. Dutré, C. Vandecasteele, S. Opdenakker, *J. Hazard. Mater.* B68 (1999) 206.
- [5] M. Pansar-Kallio, P.K.G. Manninen, *Sci. Total Environ.* 204 (1997) 194.
- [6] S.A. Stronach, N.L. Walker, D.E. Macphee, F.P. Glasser, *Waste Manage.* 17 (1) (1997) 9.
- [7] M. Karim, *Water Res.* 34 (1) (2000) 304.
- [8] J.M. Azucue, S. Schiff, J.O. Nriagu, *Environ. Int.* 20 (3) (1994) 425.
- [9] R.L. Rawls, *C&EN Newsletter*, Available online at <http://pubs.acs.org/cen>, October 2002.
- [10] EPA Newsletter, Available online at <http://www.epa.gov/epahome/headline.110101.htm>, October 2002.
- [11] M.A. Yukselen, B. Alpaslan, *J. Hazard. Mater.* B87 (2001) 289.
- [12] V. Dutré, C. Vandecasteele, *Waste Manage.* 16 (7) (1996) 625.
- [13] C. Vandecasteele, V. Dutré, D. Geysen, G. Wasutens, *Waste Manage.* 22 (2002) 144.
- [14] V. Dutré, C. Kestens, J. Schaep, C. Vandecasteele, *Sci. Total Environ.* 220 (1998) 187.
- [15] P.L. Côté, T.W. Constable, A. Moreira, *Nucl. Chem. Waste Manage.* 17 (1987) 132.
- [16] F. Sanchez, C. Gervais, A.C. Garrabrants, R. Barna, D.S. Kosson, *Waste Manage.* 22 (2002) 249.
- [17] V. Dutré, C. Vandecasteele, *Waste Manage.* 15 (1) (1995) 56.
- [18] D. Dermatas, X. Meng, in: T.M., Gilliam, C.C., Wiles, (Eds.), *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, vol. 3, ASTM STP 1240, ASTM, PA, 1996, p. 501.
- [19] D. Dermatas, X. Meng, *Eng. Geol.* 2189 (2003) 2.
- [20] ANS, *Measurements of the Leachability of Solidified Low-Level Radioactive Wastes*, ANSI/ANS 16.1 American Nuclear Society, La Grange Park, IL, 1986.
- [21] H. Godbee, D. Joy, *Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory*, ORNL-TM-4333, Oak Ridge, Tennessee, 1974.
- [22] Environment Canada, *Proposed Evaluation Protocol for Cement-Based Solidified Wastes*, Environmental Protection Series, Report No. EPS 3/HA/9, 1991.
- [23] J.K. Mitchell, *Fundamentals of Soil Behavior*, John Wiley and Sons Inc., New York, NY, 1993, p. 172.
- [24] G.J. de Groot, H.A. van der Sloot, in: T.M. Gilliam, C.C. Wiles (Eds.), *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, vol. 2, ASTM STP 1123, ASTM, PA, 1992, p. 149.

- [25] A. Andrés, I. Ortíz, J.R. Viguri, A. Irabien, J. Hazard. Mater. 40 (1995) 32.
- [26] J.S. Nathwani, C.R. Phillips, Water Air Soil Pollut. 14 (1980) 389–402.
- [27] R. Ibáñez, A. Andrés, J.A. Irabien, I. Ortíz, J. Environ. Eng. 124 (1) (1998) 48.
- [28] M.R. Powell, R. Mahalingam, Environ. Sci. Technol. 26 (3) (1992) 508.
- [29] D. Dermatas, Stabilization and reuse of heavy metal contaminated soils by means of quicklime sulfate salt treatment, Final Topical Report, Phase I, submitted to the US Department of Energy, Report No. DE-AC21-92MC29117-FT, August 1995, 214 pp.
- [30] ASTM, The Test Method for Laboratory Compaction Characteristics of Soil Using Modified Effort, ASTM D1557-91, vol. 4.08, 1993, Section 4, pp. 227–234.
- [31] ASTM, Standard Speciation for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete, ASTM C618-91, vol. 4.02, 1991, pp. 303–305.
- [32] X. Meng, S. Bang, G. Korfiatis, Water Res. 34 (2000) 1255.