

Immobilization and leaching characteristics of arsenic from cement and/or lime solidified/stabilized spent adsorbent containing arsenic

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Received 12 October 2006; received in revised form 26 August 2007; accepted 27 August 2007

Available online 31 August 2007

Abstract

Solidification/stabilization (S/S) of hazardous iron oxide coated cement (IOCC) spent adsorbent containing arsenic (As(III)) was investigated in the present study. Cement and lime-based S/S effectiveness was evaluated by performing semi-dynamic leach tests. The S/S effectiveness was evaluated by measuring effective diffusion coefficients (D_e) and leachability indices (LX). It was found that though cement or lime alone were efficient in preventing arsenic leaching (D_e being in range of 10^{-10} to 10^{-12} for all the matrices) from the solidified matrices, the best combination for arsenic containment in the matrix was obtained when a mixture of cement and lime was used. The LX values for all the matrices were higher than 10, suggesting that the S/S treated arsenic sludge are acceptable for “controlled utilization”. Calcite formation along with precipitation and conversion into non-soluble forms (calcium arsenite, calcium hydrogen arsenate hydrates, calcium hydrogen arsenates, etc.) were found to be the responsible mechanism for low leaching of arsenic from the solidified/stabilized samples. A linear relationship between cumulative fraction (CFR) of arsenic leached and square root of leach time (R^2 ranging from 0.90 to 0.94) suggested that the diffusion is the responsible mechanism for arsenic leaching. Thus, cement and lime show effective containment of the As(III) within the matrix thus indicating S/S by cement and lime, which is also a low-cost option, as a suitable management option for the toxic As(III) sludge.

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Keywords: Solidification/stabilization; Arsenic sludge; Cement; Lime; Iron oxide coated cement (IOCC)

1. Introduction

The global epidemic of arsenic poisoning, especially from potable groundwater, has become a matter of grave environmental concern in recent years. Therefore, the research on improving the established or on developing novel treatment technologies for removing arsenic from contaminated ground waters is an emerging issue. New cost-effective technologies applicable at small scales remain in demand since majority of people affected worldwide live in small communities. As a result, for such small scale treatment systems, packed bed methods, such as ion exchange and adsorption, are gaining immense popularity especially in countries like Bangladesh where the water system is not centralized and individual households or small groups are served by their own wells [1].

Arsenic can be sorbed onto various adsorbents. Among these, iron oxide coated cement (IOCC) has been found to be a very promising adsorbent in the removal of arsenic from the aqueous environment [2–7]. However, after the adsorbent medium is completely exhausted, the disposal of the spent medium is a major consideration, since it contains toxic levels of arsenic which may leach out into the environment and thus has to be disposed of safely according to the prevailing environmental regulations. Otherwise it runs the risk of groundwater as well as surface water contamination with the leachate (arsenic) from the exhausted bed.

Waste immobilization techniques, such as portland cement processes, lime-based technology, bituminization, emulsified asphalt processes, polyethylene extrusion and vitrification, [8–14] are the recent technologies that are widely used to prevent the free movements of the contaminants in waste and surrounding media. Currently, cementitious solidification/stabilization (S/S) is recognized as the “best demonstrated available technology (BDAT)” by the US Environmental Protection Agency (USEPA) for the land disposal of most toxic elements. Because

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of this, they are the most widely used of all hazardous waste management alternatives.

Most hazardous wastes can be incorporated into a waste cement system. The suspended pollutants would be incorporated into the final hardened concrete. During this solidification process, the concrete formation binds and strengthens the mass, coats and incorporates some contaminant molecules in the siliceous solids, and block pathways between pores. Thus, this process is highly effective for waste components with high levels of toxic metals [15,16]. In addition to this, alkaline matrices such as $\text{Ca}(\text{OH})_2$ and cement are commonly used in waste conditioning because they are inexpensive, readily incorporate wet wastes and their alkalinity reduces the solubility of many inorganic toxic or hazardous metals.

Cement and hydrated lime ($\text{Ca}(\text{OH})_2$) have an extensively documented history of use in the stabilization of arsenic [12,13,17–23]. The leaching of calcium was linked with the leaching of arsenic for all S/S formulations. With the increase in the calcium leachate concentration from the cement, immediate decrease in the arsenic concentrations has been found to occur [18,20].

The major objective of this study was to develop an effective method, based on the S/S technique, to treat the toxic arsenic rich spent adsorbent for its safe disposal. This spent adsorbent is the product obtained by the removal of arsenic from the aqueous environment by adsorption using iron oxide coated cement as adsorbent media [2,4,5,7].

2. Theory

An appropriate way to examine the effectiveness of the immobilization of the contaminants is to perform leaching tests [18]. Leach tests can be used to evaluate the effectiveness of solidification/stabilization process. The laboratory leaching data can simulate the behavior of waste forms under ideal, static or worst case field condition.

A semi-dynamic leaching test was performed on different solidified samples (monolithic matrices) to characterize leaching behavior of the waste material. For this leaching test, a monolith of regular geometry and known surface area is immersed in a definite volume of leachant solution. The leachant is replaced at regular intervals with fresh solution. This test is a rapid and inexpensive way to evaluate the leaching rate of species from cement-stabilized waste [24].

The leaching of contaminants from the solidified/stabilized waste materials treated by semi-dynamic leach test was then evaluated using the ANS 16.1 model (ANS, 1986) and penetration theory.

2.1. Diffusion coefficient D_e and leachability index L (ANS method)

Various reports have shown that the leaching of contaminants from the cement-based waste forms is mostly a diffusion-controlled process [20,25]. Hence, the ANS model which was established based on Fick's diffusion theory and standardized by ANS [26] was used. The cumulative fraction of the con-

taminant leached against time can be determined using this model.

In order to assess the leaching behavior of arsenic in the cement and/or lime treated wastes, the effective diffusivity (D_e) of the leached samples were determined by the ANS standardized Fick's law-based mathematical diffusion model as follows:

$$D_e = \left(\frac{a_n/A_0}{\Delta t_n} \right)^2 \left(\frac{V}{S} \right) T \quad (1)$$

where V is the volume of specimen (cm^3), S the geometric surface area of specimen (cm^2), $(\Delta t)_n$ the duration of n th leaching interval (s) and a_n, A_0 are the concentrations of solidified species at n th leaching time and at the beginning. The D_e values from Eq. (1) are termed "effective" because diffusion occurs.

The effectiveness of S/S by various stabilizing agents can be assessed by determining the leachability index (L). According to Environment Canada (1991) [27], L can be used as a performance criterion for the utilization and disposal of S/S waste. To evaluate the leachability of a diffusing species, leachability index is calculated as:

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

where $b = 1 \text{ cm}^2 \text{ s}^{-1}$,

$$L = \left(\frac{1}{m} \right) \sum_{n=1}^m (-\log(D_e))_n \quad (3)$$

where n is the number of the particular leaching period and m is the total number of individual leaching period [25]. This leachability index can be used to compare the relative mobility of solidified species on a uniform scale, which varies from 5 ($D_e = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ very mobile) to 15 ($D_e = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ immobile) [28]. 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 [29].

2.2. Effective diffusion coefficient (penetration theory)

Diffusion is the mainly responsible mechanism for leaching of contaminants from S/S matrices. According to the penetration theory, the diffusion flux (J) across the solid/solution interface of a semi-infinite medium, assuming a constant diffusion coefficient, has been given as [11,20]:

$$J = \sqrt{\frac{D_e}{\pi t}} C_0 \quad (4)$$

where C_0 is the initial concentration of the leaching substance in the S/S waste specimen (mg cm^{-3}), D_e the effective diffusion

coefficient ($\text{cm}^2 \text{s}^{-1}$) and t is the leach time (s). The total amount of contaminant leached that has diffused out of the medium surface at time t , M_t can be derived from Eq. (4) by integration over time and surface area, and is given as [18]:

$$M_t = 2M \frac{S}{V} \sqrt{\frac{D_e t}{\pi}} \quad (5)$$

where M , S and V are the total initial amount of contaminant in the S/S waste specimen (mg), surface area of specimen (cm^2) and volume of specimen (cm^3), respectively.

Assuming a constant diffusion coefficient for each S/S matrix, cumulative fraction of a substance (CFR) can be defined as a ratio of M_t to M and is given by:

$$\text{CFR} = \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{D_e t} \quad (6)$$

3. Materials and methods

All the experiments were carried out using double distilled water. The sludge (S) generated from the As(III) and As(V) adsorption processes by IOCC (results presented elsewhere [2,30]) containing very high levels of arsenic was used as the waste material for this study. The binder materials used for the S/S studies are:

- Ordinary portland cement (OPC) (of 43 grade as per IS 8112-1989) [brand: ACC limited]
- Hydrated lime $\text{Ca}(\text{OH})_2$ [brand: Merck, India]

3.1. Extraction test

To determine the hazardous nature of the arsenic sludge, the leachability of arsenic ions from the exhausted IOCC sludge was examined by individually subjecting the As(III) and As(V) wastes to the extraction test. The extraction test DIN 38 414 S4 (DIN, 1984), used in this study, is a German standard method for the ‘determination of the leachability of sludge and sediments by water’. In this agitated extraction test, 1 l of distilled water was added to 100 g of the dried exhausted adsorbent (grain size < 10 mm) and mechanically shaken for a period of 24 h at room temperature.

3.2. Preparation of monolithic matrices

The binder materials (cement (C) and lime (L)) were mixed with the hazardous arsenic sludge in a definite ratio as given in Table 1. Five different solidified waste matrices were prepared by mixing different compositions of binder materials to investigate the composition which gives the optimum immobilization for the arsenic present in the sludge. Water was added in a proportion to make slurry of these binders and arsenic rich waste materials.

PVC pipes of diameter 1.5 cm and length 6 cm, to give a length to diameter ratio of 4.0 as per the ANSI/ANS standards, were used as moulds for the preparation of solid matrices. One end of the empty pipe was blocked with a flat glass plate and the arsenic sludge along with the binder materials (C and L) in

Table 1
Composition of different solidified/stabilized (S/S) matrices

Matrices composition	Ratio (w/w)	Notations
IOCC + cement	3:1	S3C1
IOCC + cement + $\text{Ca}(\text{OH})_2$	3:1:0.5	S3C1L0.5
IOCC + cement + $\text{Ca}(\text{OH})_2$	3:0.5:0.5	S3C0.5L0.5
IOCC + $\text{Ca}(\text{OH})_2$	3:1	S3L1
IOCC + cement + $\text{Ca}(\text{OH})_2$	3:0.5:1	S3C0.5L1

desired compositions were added to the pipe from the other end. These PVC moulds were kept at a temperature of $303 \pm 2 \text{ K}$ for 24 h for curing and setting of the matrices. Ratio of leachant volume to volume of specimen was kept as 1:10 (v/v) as per ANSI standard method [26].

A total of five monolithic matrices were prepared having five different compositions as described in Table 1.

3.3. Semi-dynamic leach test

To determine the effectiveness of immobilization of arsenic after solidification and the mechanism of leaching of contaminants from the monolithic solidified waste forms, semi-dynamic leach tests were performed. In ‘semi-dynamic’ leach tests, the leachant is replaced periodically after intervals of static leaching. Formation of precipitate during the periods of static leaching may influence the concentration of the contaminants in the leachate. Therefore, it is best to avoid precipitation and, if precipitation is unavoidable, the precipitate has to be analysed together with the species in solution. In this study, the leachate is therefore acidified before analysis.

In this study, the solidified/stabilized waste samples were leached in a closed vessel without agitation using distilled water at a leachant to solid mass ratio of 10:1 (Fig. 1). The leachates were collected after a fixed duration of 2, 7, 24, 48, 72, 96, 120, 168, 336, 456 and 672 h (28 days) as per ANSI/ANS 16.1 standard [18,20,26,31]. Over the 28 day duration of the experiment, 11 renewals were performed.

The results were reported with 95% confidence limit. The D_e and L values reported are mean values of 11 leaching intervals.

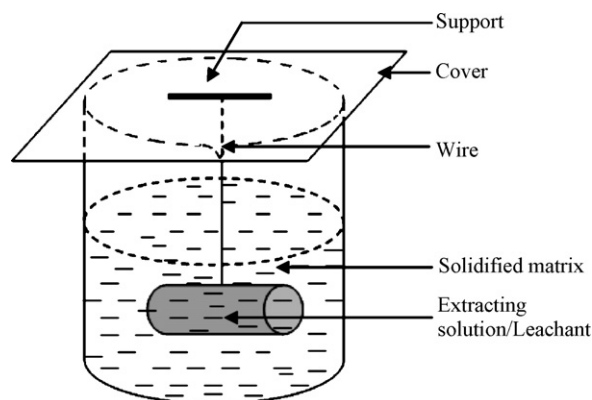


Fig. 1. Experimental setup for the semi-dynamic leaching test for S/S of arsenic sludge.

3.4. Characterization of the mould

To ascertain the mechanism of arsenic leaching and other micro structural properties, X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were performed on the prepared monolithic matrices of 28 days of age. The monolithic matrices were crushed and dried, ground to powder and then subjected to XRD and SEM analyses. For the XRD analysis of the adsorbent, Miniflex diffractometer 30 kV, 10 Maq; Rigaku Corp., Tokyo, Japan with Cu K α source was used. The diffractograms were recorded between angles $2\theta = 10^\circ$ and 70° with a scan rate of $2^\circ/\text{min}$ at room temperature. SEM photographs of the samples were carried out on a JEOL JSEM-5800 at an acceleration voltage of 20 kV.

3.5. Arsenic determination

Quantitative determination of arsenic was done with the help of UV–vis spectrophotometer (Thermospectronic, Model no. UV-1, UK) at a wavelength of 535 nm, by the silver dithiodiethylcarbamate method (minimum detectable quantity: $1 \mu\text{g As}$), commonly known as the SDDC method [32].

4. Results and discussion

Prior to the chemical treatment experiments for the prevention of arsenic leaching, solubility of arsenic from the untreated sludge was estimated. The analysis of the leachate has shown that not all arsenic present in the waste enters the aqueous phase, possibly due to the existence of poorly soluble complexes with the ions present in the adsorbent surface.

4.1. Leaching of arsenic from the spent adsorbent

The raw As(III) containing sludge was classified as a hazardous waste due to the fact that arsenic concentration in the leachate according to the extraction test was 2.87 mg l^{-1} , higher than the acceptable limit according to the newly revised maximum contaminant level (MCL) of the United States, which is 1 mg l^{-1} [33].

The As(V) concentration in the leachate from the As(V) containing sludge was 0.34 mg l^{-1} , much below the MCL, and thus did not require any treatment.

When the untreated wastes were leached in distilled water, the pH of the leachates varied between 12.5 and 13, indicating the alkaline nature of the waste.

4.2. Semi-dynamic leaching

The five different S/S monolithic matrices were subjected to the semi-dynamic leach test. The cumulative As(III) leachability values from different solidified waste specimens subjected to the semi-dynamic extraction test are plotted as a function of time in Fig. 2. It is essential for the semi-dynamic leach tests that no equilibrium should be reached during any period of static leaching. Highest leaching of As(III) was observed from the matrix having the composition of S3L1. The lowest leaching

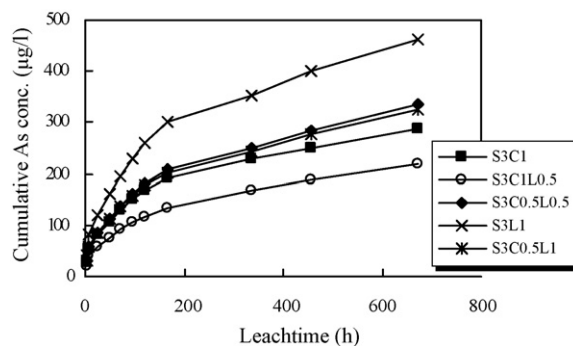


Fig. 2. Cumulative concentration of As(III) leached from the S/S wastes as a function of time.

was observed for the S3C1L0.5 matrix. The initial part of the plots show a sharp rise in As(III) concentration leached from the monolithic solidified/stabilized (S/S) samples. This may be attributed to the mass transfer controlled processes in the initial stages whereas diffusion becomes predominant at the later stages.

4.2.1. Diffusion coefficient

It is believed that leaching of contaminants out of the cement-based waste-form is mostly a diffusion-controlled process [20,34]. The fractions of arsenic released over the different (static) leach periods were summed to calculate the CFR value and plotted versus the square root of the leach time. The plot of CFR versus square root of time exhibited a good linear relationship, as can be seen from Fig. 3, suggesting a diffusion-based leaching mechanism for the arsenic contained in the sludge. Effective diffusion coefficients (D_e) were thus calculated from the slopes of these plots and also confirmed with ANSI/ANS 16.1 (ANS, 1986).

Diffusion coefficients computed as per the ANS method as well as the penetration theory are listed in Table 2. The mean values of the As(III) diffusion coefficients for the different matrices ranged from 2.9×10^{-12} to $1.07 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ as per the ANS method and 2.8×10^{-12} to $1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ as per the penetration theory. The matrix having the composi-

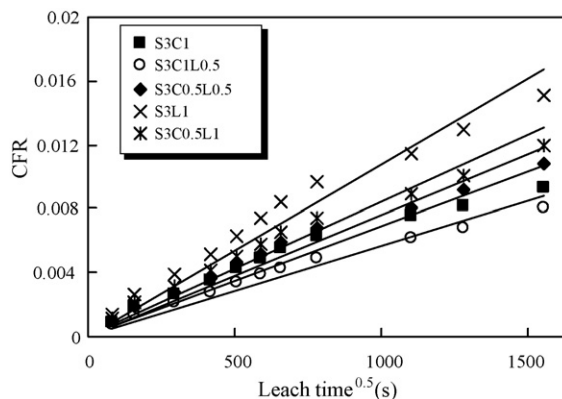


Fig. 3. Plot of cumulative fraction of arsenic released from the S/S waste as a function of square root of leach time for the semi-dynamic leach test.

Table 2
Comparative studies of effective diffusion coefficients and leachability index

Composition	Effective diffusion coefficient D_e (10^{-11}) ($\text{cm}^2 \text{s}^{-1}$)			Leachability index (L)	
	ANSI	Penetration theory	R^2	ANSI	Penetration theory
S3C1	0.46	0.41	0.90	11.57	11.39
S3C1L0.5	0.29	0.28	0.95	11.72	11.56
S3C0.5L0.5	0.54	0.50	0.95	11.45	11.29
S3L1	1.07	1.00	0.94	11.15	10.99
S3L1C0.5	0.65	0.61	0.94	11.36	11.21

tion S3C1L0.5, with both cement and lime as binder materials, had the lowest D_e values compared to the other solidified samples. Dutré and Vandecasteele [18,20] reported diffusion coefficients in the order of 10^{-10} to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$, as per the penetration theory, for arsenic solidified sample having cement and lime. These findings are well comparable with the results obtained in the present study. According to Dutré et al. [11], for arsenic, the best combination is obtained when a mixture of cement and lime is used. Fig. 4 shows a comparison of diffusion coefficients obtained from ANSI and penetration theory.

4.2.2. Leachability index

The leachability indices for all the S/S matrices are shown in Table 2. Minimum amount of leaching ($L = 11.72$) was observed in the case of mould containing sludge, cement and $\text{Ca}(\text{OH})_2$ in the weight ratio 3:1:0.5. However, as is evident from the results that the leachability indices of all the treated samples were higher than nine, and hence, all the samples can be considered acceptable for “controlled utilization”. Therefore, the treatment of arsenic (As(III)/As(V)) containing spent adsorbent with cement and/or lime mixtures is effective in immobilizing arsenic. Fig. 5 shows the variability of the leachability indices with leach time for the different S/S samples with time.

Upon treatment with cement and lime, the possible mechanisms that may be responsible for the immobilization of arsenic are precipitation, chemical inclusion, or sorption [29].

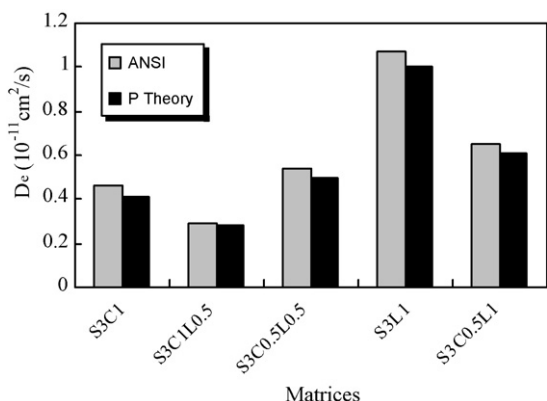


Fig. 4. Comparison of diffusion coefficients for the different matrices containing arsenic.

- Precipitation occurs with the formation of least soluble calcium–arsenic (Ca–As) compounds. Previous researches [11,18,35] have demonstrated that the formations of $\text{Ca}_3(\text{AsO}_4)_2$ and CaHAsO_3 are responsible for the immobilization of arsenic in wastes/soils that have been treated with cement, pozzolanic materials and lime.
- Inclusion may be either physical encapsulation or chemical inclusion [36]. Physical inclusion is achieved by creating a solidified monolith. Chemical inclusion may occur during S/S when arsenic is incorporated into the newly formed pozzolanic products (chemical inclusion), such as calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) by isomorphous 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 cement are greatly increased and they become available for reaction with water and calcium derived from lime to form a variety of pozzolanic products [31].
- Sorption (including cation or anion exchange) of the arsenic onto the pozzolanic reaction products may also be responsible for the immobilization [31,36].

XRD and SEM studies of the matrices were done in order to estimate the microscopic structures and morphology of surfaces.

Fig. 6(a)–(e) shows the morphology of the different S/S matrices of As(III) at 28 days of age. All the pictures represent a highly porous system which is very helpful for the entrapment of arsenic. No formation of ettringite crystals were observed in

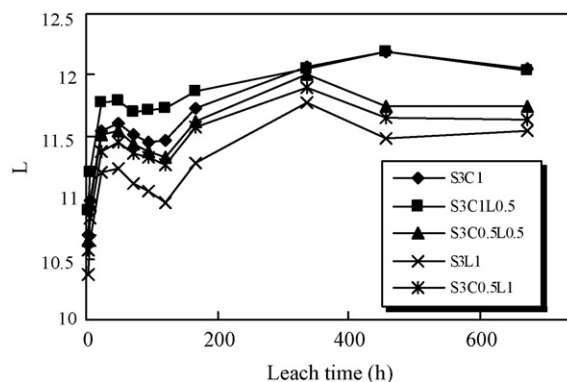


Fig. 5. Variation in the leachability indices with leach time for the different S/S samples (ANSI method).

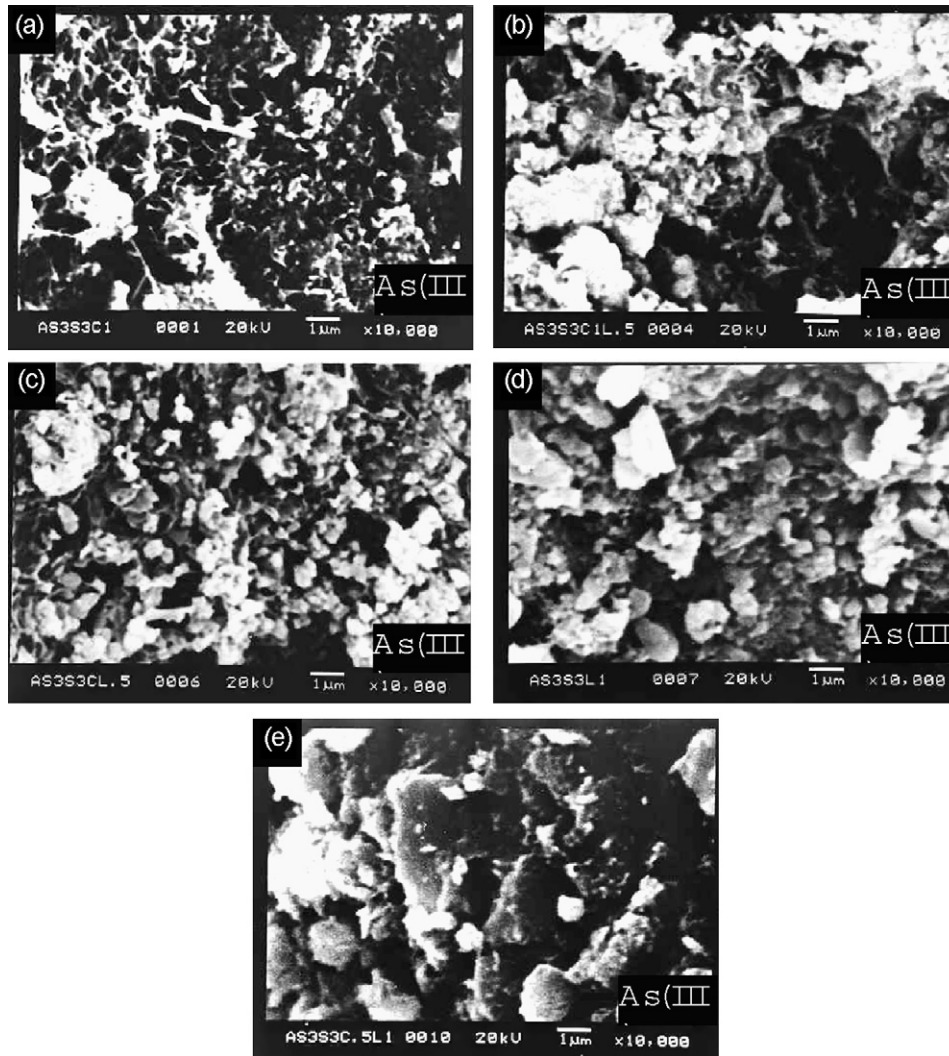


Fig. 6. SEM photographs of different solidified/stabilized (S/S) matrices: (a) S3C1; (b) S3C1L0.5; (c) S3C0.5L0.5; (d) S3L1 and (e) S3C0.5L1.

any of the matrices as is evident from the figures, in contrast to the results of earlier studies on S/S with cement and fly ash [14,31]. Ettringite is responsible for swelling and deterioration of the S/S matrices, which increases matrix porosity and consequently leaching of arsenic and hence is undesirable. Absence of ettringite could be one of the causes that led to very low arsenic leaching from all the matrices. As literature confirms, ettringite formation is the result of the addition of sulfate either through ferrous sulfate or some other form of sulfate. In the present study, no such salt was added which contained appreciable amount of sulfate. Hence, no ettringite formation was observed as a result of lack of sulfate.

Fig. 7(a)–(e) shows the XRD patterns of the five S/S matrices of As(III). As is evident from the figure, the XRD patterns for all the five samples are nearly similar and each indicate common peaks of calcite, $\text{Ca}(\text{OH})_2$, calcium arsenite (Ca-As-O), calcium arsenates (CaAs_2O_6 , $\text{Ca}_2\text{As}_2\text{O}_7$, $\text{CaO-As}_2\text{O}_5$), calcium hydrogen arsenate hydrates ($\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$, $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$), calcium hydroxide arsenate hydrate ($\text{CaAsO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$) and calcium hydro-

gen arsenates (CaHAsO_4 , $\text{CaH}_4(\text{AsO}_4)_2$, $\text{Ca}(\text{H}_2\text{AsO}_4)_2$). Table 3 shows the observed d -values for these various compounds formed in comparison with the literature values.

Calcite formed during carbonation reaction seal the pores in the cement matrix, which hinder the penetration of contaminant from the matrix as well as passage of atmospheric CO_2 into the interior of the mould. This process may also be responsible for the reduction in leaching from the matrix having cement as well as $\text{Ca}(\text{OH})_2$ [28]. The formation of the non-soluble calcium arsenite, calcium hydrogen arsenate hydrates, calcium hydrogen arsenates and sparingly soluble calcium arsenates also contributed towards the significant reduction of arsenic mobility [23,35,37,38]. The presence of CaHAsO_4 and $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ may account for the negligible amount of arsenic that leached out from the matrices [38]. From these findings, it may be rightly stated that formation of Ca-As precipitates is one of the predominant mechanism responsible for As(III) immobilization in the sludge for the present study as also found by various researchers [11,18,35,39,40].

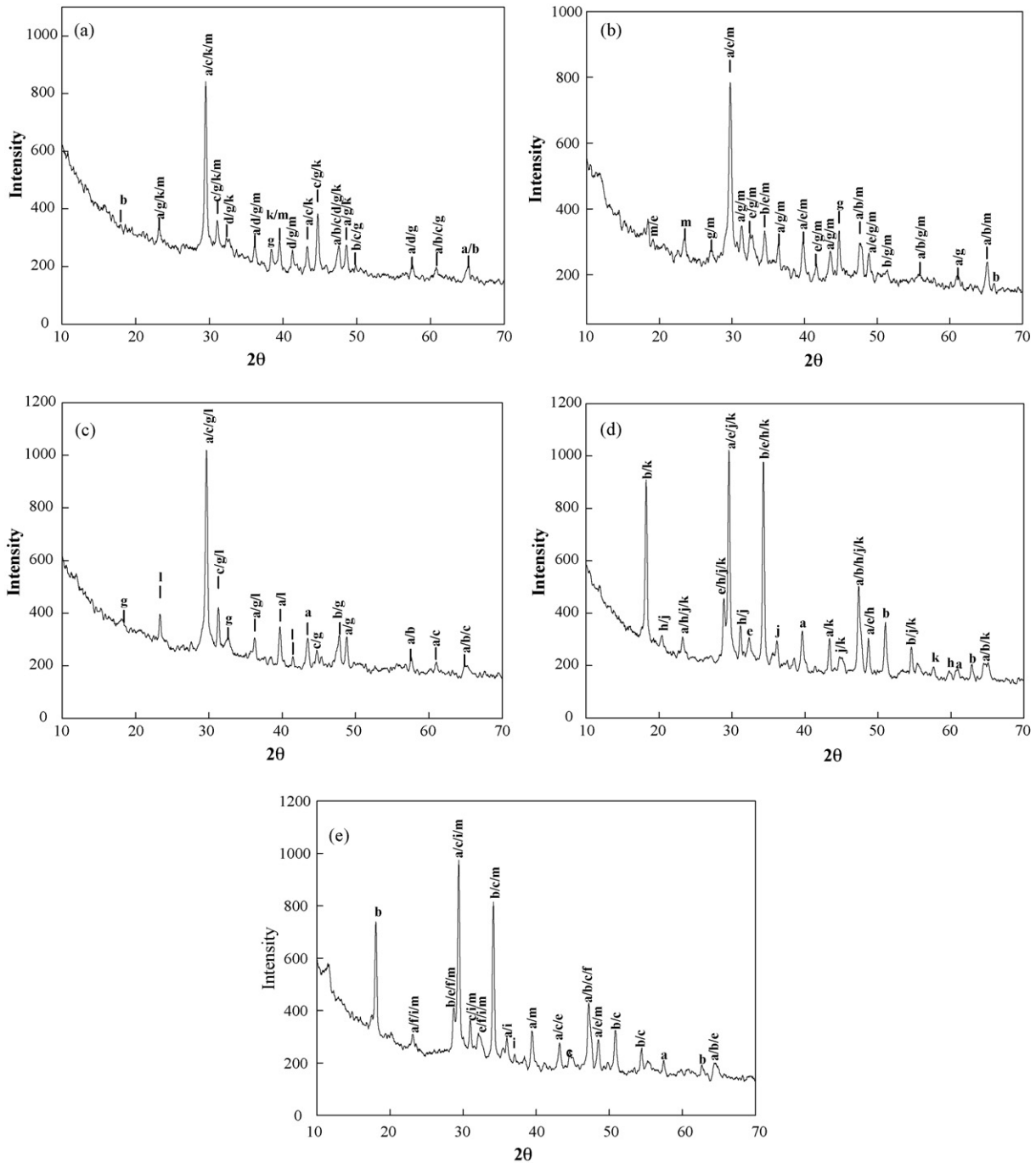


Fig. 7. XRD patterns of the S/S matrices of As(III): (a) S3C1; (b) S3C1L0.5; (c) S3C0.5L0.5; (d) S3L1 and (e) S3C0.5L1 [a: calcite; b: $\text{Ca}(\text{OH})_2$; c: calcium arsenite (Ca-As-O); d: calcium arsenate (CaAs_2O_6); e: calcium arsenate ($\text{Ca}_2\text{As}_2\text{O}_7$); f: calcium arsenate ($\text{CaO-As}_2\text{O}_5$); g: calcium hydrogen arsenate hydrate ($\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$); h: calcium hydrogen arsenate hydrate ($\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$); i: calcium hydrogen arsenate hydrate ($\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 5\text{H}_2\text{O}$); j: calcium hydroxide arsenate hydrate ($\text{CaAsO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$); k: calcium hydrogen arsenate (CaHAsO_4); l: calcium hydrogen arsenate ($\text{CaH}_4(\text{AsO}_4)_2$) and m: calcium hydrogen arsenate ($\text{Ca}(\text{H}_2\text{AsO}_4)_2$)].

One of the main reasons of better arsenic immobilization in the cement-based S/S matrices could be due to the alkaline nature and buffering capacity provided by calcium hydroxide and the calcium silicate hydrates [41]. The best performance by the S3C1L0.5 matrix may also be attributed to the formation of $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ which gave some intense peaks as shown in Fig. 7(b).

Samples S3L1 and S3C0.5L1 (Fig. 7(d) and (e)) exhibit almost the same XRD patterns with high portlandite peak intensity. This may be due to the addition of excess lime to the samples which in turn remained unreacted in the waste. The presence of this excess lime may be the reason behind the worst performance of these two samples as compared to the other samples.

Table 3
X-ray diffraction data of compounds in the S/S As(III) sludge

Compounds	JCPDS number	Observed <i>d</i> -value	Standard <i>d</i> -value
Calcite	72-1650	3.833	3.85 (0 1 2)
		3.028	3.024 (1 0 4)
		2.484	2.496 (1 1 0)
		2.279	2.282 (1 1 3)
		2.09	2.094 (2 0 2)
		1.911	1.899 (0 1 8)
		1.873	1.869 (1 1 6)
Ca(OH) ₂	84-1264	4.901	4.901 (0 0 1)
		2.625	2.623 (0 1 1)
		1.927	1.923 (0 1 2)
		1.796	1.793 (1 1 0)
		1.688	1.684 (1 1 1)
		1.484	1.480 (2 0 1)
		1.442	1.446 (1 0 3)
Calcium arsenite (Ca–As–O)	01-0828	3.037	3.05
		2.884	2.85
		2.625	2.65
		2.094	2.09
		2.032	2.01
		1.927	1.94
		1.796	1.81
Calcium arsenate (CaAs ₂ O ₆)	17-0443	1.688	1.69
		1.911	1.91
		2.767	2.76
		2.484	2.45
		1.603	1.617
Calcium arsenate (Ca ₂ As ₂ O ₇)	17-0444	2.165	2.14
		3.002	3.01
		2.759	2.78
		2.599	2.59
		2.262	2.26
Calcium arsenate (CaO–As ₂ O ₅)	29-0294	2.15	2.13
		1.866	1.857
		3.852	3.89
		3.114	3.11
		2.793	2.80
Calcium hydrogen arsenate hydrate (Ca ₅ H ₂ (AsO ₄) ₄ ·9H ₂ O)	26-1055	1.927	1.95
		4.822	4.84 (2 1 2)
		3.013	3.01 (5 1 2)
		2.877	2.90 (3 2 1)
		2.747	2.75 (5 1 4)
		2.468	2.44 (4 2 4)
		2.026	2.01 (7 2 1)
Calcium hydrogen arsenate hydrate (CaHAsO ₄ ·2H ₂ O)	13-0583	1.901	1.905 (2 0 1 2)
		1.866	1.869 (1 1 1 2)
		4.332	4.32 (1 2 1)
		3.83	3.85 (0 3 1)
		3.088	3.09 (1 1 2)
		2.874	2.87 (0 0 2)
		2.608	2.60 (0 6 0)
Calcium hydrogen arsenate hydrate (Ca ₅ H ₂ (AsO ₄) ₄ ·5H ₂ O)	17-0162	1.919	1.922 (0 6 2)
		1.87	1.877 (2 4 1)
		1.55	1.571 (3 5 0)
		3.038	3.04 (1 2 5)
		2.885	2.87 (1 3 2)
Calcium hydrogen arsenate hydrate (Ca ₅ H ₂ (AsO ₄) ₄ ·5H ₂ O)	17-0162	2.793	2.79 (1 3 2)
		2.493	2.48 (0 4 2)
		2.426	2.45 (2 0 4)
		2.426	2.45 (2 0 4)

Table 3 (Continued)

Compounds	JCPDS number	Observed <i>d</i> -value	Standard <i>d</i> -value
Calcium hydroxide arsenate hydrate (CaAsO ₃ (OH)·2H ₂ O)	25-0138	3.826	3.84 (0 4 0)
		3.088	3.08 (1 4 1)
		3.018	3.02 (1 2 1)
		2.483	2.48 (1 4 1)
		2.022	2.00 (2 1 3)
		1.919	1.92 (3 1 2)
		1.661	1.668 (2 0 2)
Calcium hydrogen arsenate (CaHAsO ₄)	72-0641	4.861	4.864 (1 1 0)
		3.826	3.827 (1 1 1)
		3.088	3.069 (1 2 0)
		3.02	3.046 (1 2 0)
		2.608	2.608 (1 2 1)
		2.273	2.277 (0 3 0)
		2.085	2.085 (1 3 1)
		2.023	2.02 (1 3 2)
		1.919	1.914 (1 1 3)
Calcium hydrogen arsenate (CaH ₄ (AsO ₄) ₂)	16-0691	3.809	3.81
		3.013	3.00
		2.858	2.86
		2.478	2.46
		2.267	2.28
		2.178	2.17
Calcium hydrogen arsenate (Ca(H ₂ AsO ₄) ₂)	44-0279	3.114	3.10 (1 2 1)
		3.038	3.04 (2 1 1)
		2.885	2.879 (2 1 0)
		2.793	2.806 (3 1 1)
		2.63	2.642 (0 1 2)
		2.284	2.285 (1 2 2)
	1.877	1.872 (1 3 2)	

5. Conclusions

Semi-dynamic leach tests were performed to evaluate the leachability of arsenic from cement and/or lime stabilized arsenic sludge. From the results, it is evident that the solidification with only cement or lime or with both cement and lime is a very suitable technique to reduce the leachability of arsenic from the arsenic rich hazardous waste. The addition of lime lowered the diffusion coefficient further. The reduction in the arsenic leachability was due to the formation of calcite which seals the pore of the cement matrix. The formation of precipitates and other insoluble Ca–As compounds as calcium arsenates, calcium arsenite, calcium hydrogen arsenate hydrates and calcium hydrogen arsenates also helped in reducing arsenic leaching. XRD and SEM analyses confirmed the formation of calcite along with other compounds and the other experimental observations. The reduced arsenic leachability upon treatment when modeled versus time was found to be diffusion-controlled. Therefore, only small amounts of arsenic would be expected to leach into the environment. A comparison between the diffusion coefficients and leachability indices as obtained from both penetration theory and ANSI showed a very good agreement with each other.

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