

Lime based stabilization/solidification (S/S) of arsenic contaminated soils

Deok Hyun Moon¹

W. M. Keck Geoenvironmental Laboratory, Center for Environmental Systems,
Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, USA

Abstract

Lime based stabilization/solidification (S/S) can be an effective remediation alternative for the immobilization of arsenic (As) in contaminated soils and sludges. However, the exact immobilization mechanism has not been well established. Based on previous research, As immobilization could be attributed to sorption and/or inclusion in pozzolanic reaction products and/or the formation of calcium-arsenic (Ca-As) precipitates. In this study, suspensions of lime-As were studied in an attempt to elucidate the controlling mechanism of As immobilization in lime treated soils. Aqueous lime-As suspensions (slurries) with varying Ca/As molar ratios (1:1, 1.5:1, 2:1, 2.5:1 and 4:1) were prepared and soluble As concentrations were determined. X-ray diffraction (XRD) analyses were used to establish the resulting mineralogy of crystalline precipitate formation. Depending on the redox state of the As source, different As precipitates were identified. When As (III) was used, the main precipitate formation was Ca-As-O. With As(V) as the source, $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ formed at Ca/As molar ratios greater than 1:1. A significant increase in As (III) immobilization was observed at Ca/As molar ratios greater than 1:1. Similarly, a substantial increase in As (V) immobilization was noted at Ca/As molar ratios greater than or equal to 2.5:1. This observation was also confirmed by XRD. The effectiveness of both As (III) and As(V) immobilization in these slurries appeared to increase with increasing Ca/As molar ratios.

Keywords: XRD; arsenite; arsenate; lime; Ca-As-O; $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$

Corresponding author. Tel.: 201-216-8097; fax: 201-216-8212

E-mail address: dmoon@stevens-tech.edu (D. Moon)

Introduction

Arsenic (As) is known to be a very toxic element and a carcinogen to humans (Mollah et al., 1998). Even trace amounts of As can be harmful to human health (Karim, 2000). In nature, As is released in the environment through weathering and volcanism (Juillot et al., 1999). Arsenic is also released by anthropogenic activities. It was used extensively for agricultural applications such as herbicides and insecticides (Leist et al., 2000) and has thus created problems through leaching and infiltration to subsurface soils and ground water (Murphy and Aucott, 1998). Arsenic is also produced as a waste by-product from the mineral processing and smelting industries. As (III) and As (V) are the most widespread forms in nature (Boyle and Jonasson, 1973; Cherry et al., 1979), with As (III) being both more mobile and toxic (Pantsar-Kallio and Manninen, 1997; Boyle and Jonasson, 1973). More specifically, As (III) is 25 to 60 times more toxic than As (V) (Dutr  and Vandecasteele, 1995; Corwin et al., 1999). Stabilization/solidification (S/S) is one of the most effective methods to reduce the mobility of heavy metals (Yukselen and Alpaslan, 2001). Various combinations of type I portland cement (OPC), lime, type F fly ash, silica fumes, iron (II) or (III), silicates and blast furnace slag have been used in the treatment of soils contaminated with As (Akhter et al., 1997; Leist et al., 2000).

Several researchers have shown that As immobilization is mainly controlled by the formation of Ca-As precipitates. Dutr  and Vandecasteele (1995; 1998; 1999; 2002) demonstrated that the formation of $\text{Ca}_3(\text{AsO}_4)_2$ and CaHAsO_3 precipitates controls the immobilization of As in contaminated soils, which have been treated with cement, lime and pozzolanic material. At the high pH levels (12-13) induced by lime treatment, where a large fraction of As (III) occurs as HAsO_3^{2-} , the precipitation of CaHAsO_3 will take place. Within the same pH range, the formation of $\text{Ca}_3(\text{AsO}_4)_2$ occurs in the presence of As(V) ions. These precipitates were found to be responsible for the observed reduction in As leachability. Also, research by Bothe and Brown (1999) has suggested that lime addition reduces As mobility in contaminated slurries due to the formation of low solubility Ca-As precipitates such as $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ and johnbaumite, $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$.

Moreover, the reaction of alumino-silicious material, lime and water results in the formation of concrete-like products described as pozzolanic (LaGrega et al., 1994). Dermatas and Meng (2003) have demonstrated that in quicklime S/S applications, the formation of pozzolanic reaction products may be associated with heavy metal immobilization by sorption and inclusion in pozzolanic reaction products. Therefore, there seems to be three possible As

immobilization mechanisms to be considered. These are Ca-As precipitation, sorption or inclusion in pozzolanic reaction products. In this study, the prepared lime-As slurries were tested by X-ray diffraction (XRD) analyses and analyzed for soluble As in order to evaluate these mechanisms.

The objectives of this study are: 1) to investigate the formation of Ca-As precipitates in lime-As slurries prepared at different Ca/As molar ratios; 2) to then correlate soluble As concentrations with the type of crystalline phases as identified by XRD analyses; 4) to examine the possible oxidation of As(III) in contaminated soils as a result of lime treatment; and 5) to investigate the aging effect on Ca-As precipitates to evaluate whether the various phases formed persist or redissolve with time.

Experimental methodology

2.1. Reagents and materials

Three different commercially available As compounds were used as As contamination sources: arsenic oxide (As_2O_3), sodium arsenite (NaAsO_2) and sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$). The last two are very soluble and provide two different As oxidation states, As (III) and As(V). The As (III) source, As_2O_3 was chosen because of its low solubility (1.2-3.7 g/100ml at 20°C) (International Programme on Chemical Safety, 1997) compared to NaAsO_2 , which is highly soluble. This was done in order to evaluate the difference in solubility between various As(III) forms present in the soils. These chemicals were obtained from Fisher Scientific Company (Suwanee, Ga). Chemical grade hydrated lime ($\text{Ca}(\text{OH})_2$) powder was obtained from the Bellefonte Lime Company (Bellefonte, PA).

2.2. Slurry preparation and analysis

Lime-As slurries were prepared at five different Ca/As molar ratios (1:1, 1.5:1, 2:1, 2.5:1 and 4:1). This was done by using a liquid to solid (L:S) ratio of 10:1, by weight. Three separate sets of lime-As slurries were prepared by using three different As compounds as previously discussed. Likewise, Bothe and Brown (1999) evaluated the formation of Ca-As precipitates at Ca/As molar ratios that ranged from 1.5:1 to 2.5:1. The prepared slurry samples were then aged and periodically shaken at 20°C. After 4 days of continuous mixing using an Orbital incubator (Gallenkamp), a sub-sample was taken with a 5 mL pipette and filtered through a 47mm polycarbonate filter (pore size: 0.4 μm). The residue retained on the filter was air-dried

and characterized by XRD analysis. The filtrate was analyzed for soluble As concentration. All the experiments focused on 4-day test results, but the effect of aging was also considered. Time allowed for the aging experiments was 4 months for the lime-As₂O₃ (lime-As(III)) slurries. Initial results indicated no significant change in As concentrations between 4-month and 4-day samples. Thus, equilibrium was attained within 4 days. As a result, the time allowed for aging was shortened to 2 months for the lime-NaAsO₂ (lime-As(III)) and 40 days for the lime-Na₂HAsO₄·7H₂O (lime-As(V)) slurries. At the end of the aging experiments, the same procedure followed in the initial 4-day experiments was used with regards to XRD and soluble As concentration analyses. A number of blanks and check standards were prepared with each batch of samples for quality control purposes.

2.3. X-ray diffraction analyses

A Rigaku DXR 3000 computer-automated diffractometer was used. Step-scanned XRD data were collected using Bragg-Brentano geometry. Diffractometry was conducted at 40 kV and 30 mA using Cu radiation with a diffracted beam graphite-monochromator. The data were collected between 30 and 630 in 2 theta with a step size of 0.050 and a count time of 5 seconds per step. All the samples were pulverized and sieved through a 200-mesh sieve (0.074 mm diameter opening) prior to XRD analyses in order to obtain a uniform particle size distribution.

It is important to note that when a phase is not detected by XRD analyses, this does not mean that it is not there, but rather that it may be there only in quantities below the detection limit of XRD. As a general rule, the detection limit of the XRD analyses of crystalline phases is considered to be 5% of the total weight of the mixture. However, several factors do have a significant effect on the actual detection limit for any particular crystalline phase. These factors include: degree of crystallinity, hydration, surface texture of the sample, sample weight, particle orientation, mass absorption coefficients of different minerals, etc. (Mitchell, 1993). Any of these factors may have an influence on the resulting peak height and broadness, and thus the detection limit. Carter et al. (1987) established a 0.01% detection limit for quartz and a 0.03% limit for cristobalite. Conversely, pozzolanic mineral phases may very well be either poorly crystallized or amorphous, especially at the early stages of formation, which makes their detection by XRD more difficult.

Results and discussion

3.1. Formation of different phases in the lime-As slurries

Lime-As slurries produced Ca-As precipitates at all Ca/As molar ratios tested. The different phases identified by XRD and the corresponding soluble As results at 4-days of mixing and after aging are summarized in Tables 1 and 2, respectively. XRD patterns are presented in Figures 1 through 6 for all lime-As slurries.

In the lime-As₂O₃ (lime-As(III)) slurries, following 4 days of continuous shaking, three major phases were observed: portlandite (Ca(OH)₂), calcium arsenite (Ca-As-O), and calcite (CaCO₃) (Table 1 and Figure 1). Arsenolite (As₂O₃) was only identified at the lowest Ca/As molar ratio (1:1), due to its limited solubility, as shown in Figure 1 and Table 1. However, at Ca/As molar ratios greater than 1:1, the peaks of arsenolite disappeared (Figure 1). Also, following 4 months of aging, no arsenolite peaks could be identified for samples having a Ca/As molar ratio of 1:1 (Table 1 and Figure 2). Aside from the disappearance of arsenolite peaks, there were no significant differences in the observed XRD patterns between the sub-samples tested following 4 days and 4 months.

For the lime-NaAsO₂ (lime-As(III)) slurries, three major phases were identified by XRD: Ca(OH)₂, Ca-As-O, and CaCO₃ (Table 1 and Figure 3). No NaAsO₂ was identified due to its high solubility (Table 1 and Figure 3). No obvious differences were observed in the XRD patterns between the sub-samples tested at 4 days and 2 months (Figure 4). Overall, regardless of the arsenite source used, whether readily soluble NaAsO₂ or less soluble As₂O₃, the same Ca-As precipitate, Ca-As-O, was identified (Tables 1).

In lime-Na₂HAsO₄·7H₂O (lime-As(V)) slurries, five phases were identified (Table 1 and Figures 5). CaCO₃ and Ca(OH)₂ were identified at all Ca/As molar ratios. Due to its high solubility, no Na₂HAsO₄·7H₂O was identified (Table 1 and Figures 5). NaCaAsO₄·7.5H₂O was identified at Ca/As molar ratios up to 1.5:1. Johnbaumite, Ca₅(AsO₄)₃OH, was observed only at a Ca/As molar ratio of 1:1. Calcium arsenate hydroxide hydrate, Ca₄(OH)₂(AsO₄)₂·4H₂O, was observed at Ca/As molar ratios greater than 1:1 (Table 1 and Figures 5). Following 40 days of aging, NaCaAsO₄·7.5H₂O was no longer detected by XRD at Ca/As molar ratios greater than 1:1. Ca₄(OH)₂(AsO₄)₂·4H₂O and johnbaumite were still detected following 40 days of aging (Table 1 and Figure 6).

Bothe and Brown (1999) also found Ca₄(OH)₂(AsO₄)₂·4H₂O at Ca/As molar ratios between 2:1 and 2.5:1 as well as minor amounts of johnbaumite. According to their research, the

formation of johnbaumite was clearly observed in lime-As(V) slurries at Ca/As molar ratios between 1.7:1 and 1.9:1.

3.2. Soluble As concentration in lime-As slurries and the aging effect

Soluble As concentration results are summarized in Table 2 and presented in Figure 7.

In lime-As₂O₃ (lime-As(III)) slurries, the concentration of As in solution was 589 mg/L at a Ca/As molar ratio of 1:1 (Table 1). However, when the ratio was increased to 4:1, the As concentration decreased to 0.52 mg/L.

In lime-NaAsO₂ (lime-As(III)) slurries, the As concentration was high (2783 mg/L) at a Ca/As molar ratio of 1:1. The difference in soluble As concentrations, between lime-NaAsO₂ (lime-As(III)) and lime-As₂O₃ (lime-As(III)) slurries, can be readily explained by the solubility differences between the two As contamination sources. When the Ca/As molar ratio was increased to 4:1, the As concentration in the lime-NaAsO₂ slurries decreased to 3.6 mg/L. Overall, As (III) immobilization in lime-As₂O₃ (lime-As(III)) and lime-NaAsO₂ (lime-As(III)) slurries was more pronounced at Ca/As molar ratios greater than or equal to 1.5:1 (Figure 7).

In lime-Na₂HAsO₄·7H₂O (lime-As(V)) slurries, the soluble As concentration was very high (5165 mg/L) at a Ca/As molar ratio of 1:1, but decreased significantly to 1.5 mg/L at a Ca/As molar ratio of 4:1 (Table 2). Arsenic (V) immobilization was more pronounced at Ca/As molar ratios greater than or equal to 2.5:1.

Soluble As concentrations following the aging step are also summarized in Table 2 and plotted in Figure 7. After 4 months of aging, soluble As concentrations decreased with increasing Ca/As molar ratios for all slurries tested (Table 2) and was very low at a Ca/As molar ratio of 4:1.

The variable reaction time (aging) appeared to have an important effect on soluble As concentrations only in lime-As(V) slurries. In lime-As(III) slurries, no significant differences in soluble As concentrations were observed between the 4-day and 4-month results. This indicates that equilibrium was probably reached within the first 4 days (Figure 7). Conversely, As concentration in lime-As(V) slurries after aging, at Ca/As molar ratios up to 2.5:1, was significantly reduced when compared to 4-day results (Figure 7). However, no significant As concentration reduction was observed for a Ca/As molar ratio of 4:1. These results indicate that equilibrium was probably not reached in lime-As(V) slurries and that reactions were ongoing following 40 days of testing for all Ca/As molar ratios, except for a Ca/As molar

ratio of 4:1. This observation requires further investigation.

Even though the formation of Ca-As-O was observed in all lime-NaAsO₂ (lime-As(III)) and lime-As₂O₃ (lime-As(III)) slurries, significant As immobilization in the presence of this precipitate occurs only when Ca/As molar ratios are greater than or equal to 1.5:1 (Tables 1 and 2). At a Ca/As molar ratio of 1:1, Ca-As-O did form, but soluble As concentrations remained high (Figure 7). Therefore, it seems necessary to increase the amount of lime present in order to decrease As solubility. This finding could not be confirmed by XRD, since peak intensities of Ca-As-O (Figures 1, 2, 3, and 4) remained relatively unchanged at the various Ca/As molar ratios tested. This was probably due to peak overlapping between Ca-As-O, Ca(OH)₂ and CaCO₃, which obscured any relative changes in the peak intensities of Ca-As-O.

As already mentioned, several Ca-As precipitates formed in lime-As(V) slurries. However, As solubility remained high for Ca/As molar ratios up to 2:1 (Table 2 and Figure 5). Soluble As concentrations decreased drastically only when Ca/As molar ratios were greater than or equal to 2.5:1 (Table 2 and Figure 5). Bothe and Brown (1999) also reported that less than 0.5 mg/L of As was in solution when the Ca/As molar ratio in the slurries was between 2.2:1 and 2.5:1. The drastic decrease in As solubility at Ca/As molar ratios greater than or equal to 2.5:1 was also reflected in the XRD findings. Peak intensities for Ca₄(OH)₂(AsO₄)₂•4H₂O formation (Figure 5) increased as Ca/As molar ratios were increased from 1.5:1 to 2.5:1, whereas for Ca/As molar ratios greater than 2.5:1, peak intensities remained relatively unchanged. In order to account for peak intensity differences, changes in the largest (2 theta = 11.3) Ca₄(OH)₂(AsO₄)₂•4H₂O peak were monitored since no phase overlaps were associated with this peak.

Following 40 days of aging, the peaks for Ca₄(OH)₂(AsO₄)₂•4H₂O formation at ratios of 1.5:1, 2:1 and 2.5:1 increased, when compared to formation peaks at the same Ca/As molar ratios at 4 days. This observation correlates to As concentration results at the same molar ratios (Tables 1 and 2). This indicates that with elapsed time, more As reacts to form additional Ca₄(OH)₂(AsO₄)₂•4H₂O and soluble As concentration decreases. When the Ca/As molar ratio was 4:1 As concentration was low and did not change with time.

Overall, in the presence of As₂O₃ (As(III)) or NaAsO₂ (As(III)), the precipitation of Ca-As-O seems to control As immobilization. In the presence of Na₂HAsO₄•7H₂O (As(V)), Ca₄(OH)₂(AsO₄)₂•4H₂O formation was closely associated with a decrease in soluble As concentration. Consequently, As immobilization, in lime-As slurries, seems to be controlled by the precipi-

precipitation of Ca-As phases, whether As exists as As(III) or As(V).

Conclusions

Lime-As slurries prepared at different Ca/As molar ratios produced crystalline precipitate formations that were identified by XRD analyses. In all the slurries tested, the redox state of the As source used appeared to affect the resulting crystalline precipitate, i.e., slurries prepared with As (III) had different precipitates from the slurries prepared with As (V). Overall, the effectiveness of both As (III) and As (V) immobilization appeared to increase with increasing Ca/As molar ratios for all slurries tested.

For the first time, a Ca-As-O precipitate was identified by XRD. In lime-As slurries, when As (III) was used, the main precipitate formation was Ca-As-O, irrespective of the solubility of the As(III) source. Moreover, the oxidation of As(III) could not be confirmed in any of the precipitates identified. Aging had an important effect on soluble As concentrations only in lime-As(V) slurries with Ca/As molar ratios up to 2.5:1. Equilibrium was probably not reached in lime-As(V) slurries and reactions were ongoing following 40 days of aging for all Ca/As molar ratios, except for a Ca/As molar ratio of 4:1.

For the lime-As(V) slurries, the formation of $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ was closely associated with very low soluble As concentration. The formation of Ca-As-O found in lime-As slurries coincided with low soluble As concentrations. Therefore, it could be concluded that As (As (III) or As(V)), immobilization in lime stabilized soils is controlled by the precipitation of Ca-As phases.

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Table 1

Mineral formations in lime-As₂O₃, lime-NaAsO₂, and lime-Na₂HAsO₄•7H₂O slurries following 4 days of mixing and after aging

Phases following 4 days of mixing			
	lime-As ₂ O ₃ [As(III)]	lime-NaAsO ₂ [As(III)]	lime-Na ₂ HAsO ₄ • 7H ₂ O [As(V)]
Ca/As molar ratio	Phases	Phases	Phases
1	As ₂ O ₃ , Ca-As-O, CaCO ₃ , Ca(OH) ₂	Ca-As-O, CaCO ₃ , Ca(OH) ₂	NaCaAsO ₄ ? 5H ₂ O, Ca ₄ (AsO ₄) ₂ OH, CaCO ₃ , Ca(OH) ₂
1.5	Ca-As-O, CaCO ₃ , Ca(OH) ₂	>>	NaCaAsO ₄ ? 5H ₂ O, Ca ₄ (OH) ₂ (AsO ₄) ₂ ? H ₂ O, CaCO ₃ , Ca(OH) ₂
2	>>	>>	Ca ₄ (OH) ₂ (AsO ₄) ₂ ? H ₂ O, CaCO ₃ , Ca(OH) ₂
2.5	>>	>>	>>
4	>>	>>	>>
Phases after aging			
	lime-As ₂ O ₃ [As(III)]	lime-NaAsO ₂ [As(III)]	lime-Na ₂ HAsO ₄ • 7H ₂ O [As(V)]
Ca/As molar ratio	Phases	Phases	Phases
1	Ca-As-O, CaCO ₃ , Ca(OH) ₂	Ca-As-O, CaCO ₃ , Ca(OH) ₂	NaCaAsO ₄ ? 5H ₂ O, Ca ₄ (AsO ₄) ₂ OH, CaCO ₃ , Ca(OH) ₂
1.5	>>	>>	Ca ₄ (OH) ₂ (AsO ₄) ₂ ? H ₂ O, CaCO ₃ , Ca(OH) ₂
2	>>	>>	>>
2.5	>>	>>	>>
4	>>	>>	>>

Table 2

Soluble As concentrations in lime-As₂O₃, lime-NaAsO₂, and lime-Na₂HAsO₄•7H₂O slurries following 4 days of mixing and after aging.

Soluble As concentrations following 4 days of Mixing			
	lime-As ₂ O ₃ [As(III)]	lime-NaAsO ₂ [As(III)]	lime-Na ₂ HAsO ₄ • 7H ₂ O [As(V)]
Ca/As molar ratio	As conc. (mg/l)	As conc. (mg/l)	As conc. (mg/l)
1	589	2783	5165
1.5	2.5	40.8	3699
2	2.1	21.2	1739
2.5	0.9	16.6	6.8
4	0.5	3.6	1.5
Soluble As concentrations after aging			
	As conc. (mg/l)	As conc. (mg/l)	As conc. (mg/l)
Ca/As molar ratio	As conc. (mg/l)	As conc. (mg/l)	As conc. (mg/l)
1	489	2488	2278
1.5	ND	32.1	1979
2	ND	20.3	1077
2.5	ND	12.7	4.7
4	ND	3.4	1.8

Note-ND = not detectable

Figure 1. XRD patterns for lime-As₂O₃ slurries with different Ca/As molar ratios following 4 days of continuous mixing

Figure 2. XRD patterns for lime-As₂O₃ slurries with different Ca/As molar ratios following 4 months of aging

Figure 3. XRD patterns for lime-NaAsO₂ slurries with different Ca/As molar ratios following 4 days of continuous mixing.

Figure 4. XRD patterns for lime-NaAsO₂ slurries with different Ca/As molar ratios following 2 months of aging

Figure 5. XRD patterns for lime-Na₂HAsO₄•7H₂O slurries with different Ca/As molar ratios following 4 days of continuous mixing.

Figure 6. XRD patterns for lime-Na₂HAsO₄•7H₂O slurries with different Ca/As molar ratios following 40 days of aging.

Figure 7. Soluble As concentrations in lime-As slurries and aging effect

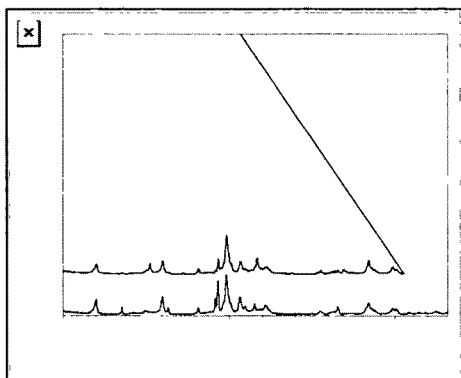


Figure 1. XRD patterns for lime-As₂O₃ slurries with different Ca/As molar ratios following 4 days of continuous mixing.

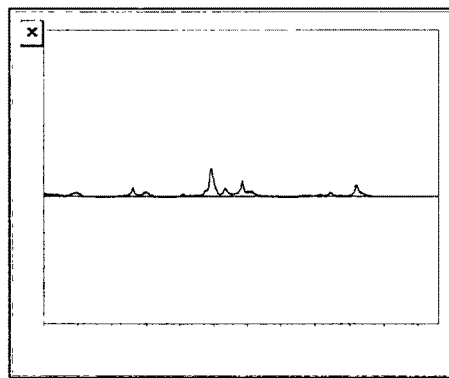


Figure 3. XRD patterns for lime-NaAsO₂ slurries with different Ca/As molar ratios following 4 days of continuous mixing.

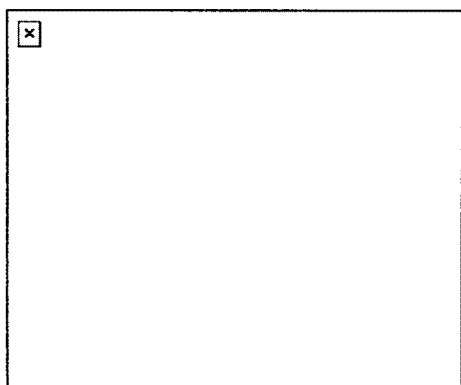


Figure 2. XRD patterns for lime-As₂O₃ slurries with different Ca/As molar ratios following 4 months of aging.

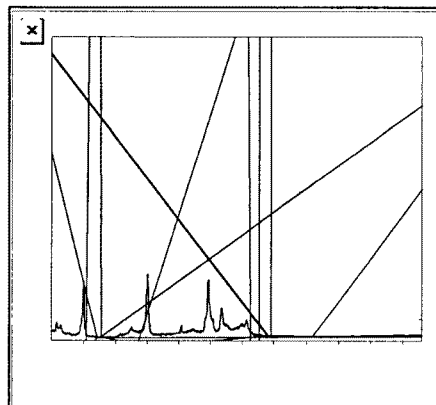


Figure 4. XRD patterns for lime-NaAsO₂ slurries with different Ca/As molar ratios following 2 months of aging

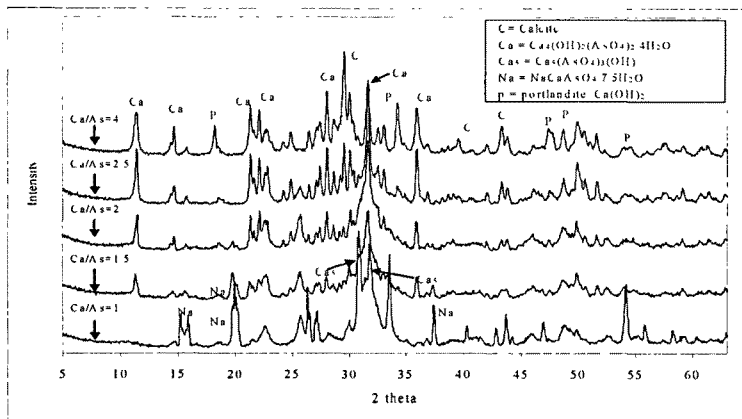


Figure 5. XRD patterns for lime- $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ slurries with different Ca/As molar ratios following 4 days of continuous mixing.

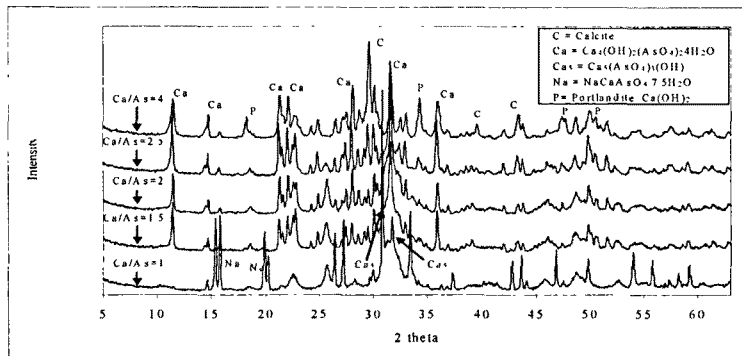


Figure 6. XRD patterns for lime- $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ slurries with different Ca/As molar ratios following 40 days of aging.

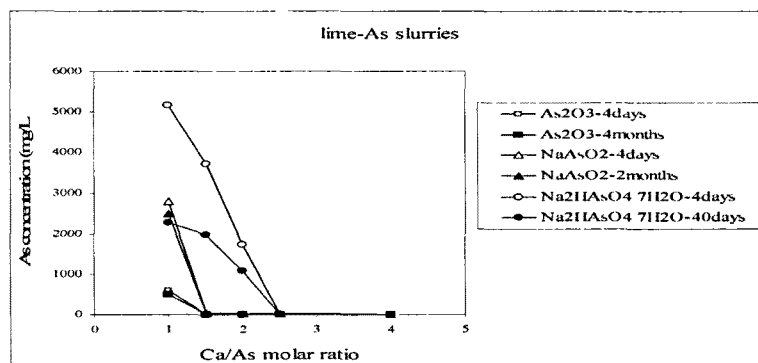


Figure 7. Soluble As concentrations in lime-As slurries and aging effect