

Solidification/stabilization of arsenic salts: Effects of long cure times

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Abstract

Leachability of As^{III} and As^V from various solidification–stabilization (S/S) binders has been studied over a period of four years. Type I portland cement (OPC), both alone and mixed with a number of additives, results in toxicity characteristic leaching procedure (TCLP) leachabilities of $\leq 3 \text{ mg l}^{-1}$ for arsenite and $\leq 2 \text{ mg l}^{-1}$ for arsenate. There is no appreciable change in leachability after 3 years of cure, compared with 28 days of cure. The combination of OPC and Class F fly ash as a binder results in substantially degraded performance, as measured by TCLP leachability. Furthermore, the OPC–FA–As mixtures show increasing leachability with time. These solidified products have been studied using powder X-ray diffraction (XRD), derivative thermal gravimetry (DTG) and solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS–NMR). The As^V salt, NaCaAsO₄ · 7.5H₂O, is identifiable by XRD in many of these samples, particularly when sodium arsenate is the model As waste, but even when sodium arsenite is the original form of As. The OPC–FA mixtures show substantial respeciation during long curing times. There is evidence for formation of strätlingite from XRD, and there is substantial conversion of octahedrally coordinated aluminum, which is the predominant form at 28 days, to tetrahedrally coordinated aluminum at longer cure times, as shown by NMR. These matrix changes are correlated with increased leachability, although direct cause and effect cannot be established. These results emphasize the importance of long-term testing to identify specific combinations of S/S binders and wastes that are prone to undergo respeciation, and consequent leachability changes, after long cure times. © 1997 Elsevier Science B.V.

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1. Introduction

Solidification/stabilization (S/S), also known as chemical fixation or encapsulation, is widely applied to waste streams and contaminated soils. The most common form of the technology uses a cement or pozzolanic binder to convert the waste to a solid (if necessary) and, depending on the constituents of the waste stream and the binder, the treatment may reduce toxicity and/or water solubility of hazardous materials and may create a monolithic waste form that limits contaminant mobility due to its low permeability and small surface area. The process is most commonly applied in cases where the contaminants of concern are heavy metals in cationic forms, e.g., Cd^{2+} , Cr^{3+} , Pb^{2+} . However, applicability to a wide variety of waste materials, including As wastes, has been proposed.

Arsenic wastes are grouped together for discussion of treatment standards in the land disposal regulations promulgated by the US EPA [1]. Considerable discussion is allocated to S/S, since it was considered by EPA to be a “potentially applicable technology”. However, S/S is not currently considered BDAT for any arsenic waste or wastewater. The following quote indicates the reasons. “EPA has relatively inconclusive performance data for stabilization of arsenic in three different wastes using nine different binders. Analysis of these data indicates that the effectiveness of any particular stabilization binder appears to be highly dependent upon the waste types. This result is what might be expected giving (sic) the chemical nature of arsenic and the relative sensitivity of the effectiveness of stabilization processes with respect to the presence of organics and organo-metallics.” Treatment standards include the following: for non-wastewaters: 5.6 or 5.0 mg l^{-1} in EP (or TCLP) leachates; for wastewaters: 5.0 or 0.79 mg l^{-1} in total composition. It seems clear from the discussion that EPA would like to establish the 0.79 mg l^{-1} standard for all As wastewaters, but received many comments that such a stringent standard was not always attainable.

In specific language, EPA does not preclude the use of S/S for treatment of As (particularly inorganic As) wastes, but recommends that its use be determined on a case-by-case basis. Given the wide range of chemical characteristics of As wastes, such a position is quite reasonable. Nevertheless, as a result of these misgivings, there has not been (at least to the authors’ knowledge) a large scale demonstration or remediation in which As concentrations in the wastes have been high. Treatment of As-containing wastes by S/S techniques for disposal in controlled landfill environments is being practiced [2], and general interest in the technology as applied to As is high, as evidenced by presentations and discussion at a recent USEPA workshop [3].

Inorganic arsenic wastes are those that have been most seriously studied. The chemistry of arsenic as it applies to S/S, particularly including an extensive discussion of the solubilities of arsenic salts, has been reviewed in a recent report by Taylor and Fuessle [4]. A common strategy employed to optimize S/S is to identify the toxic species of greatest interest in the material, then arrange for the presence of appropriate counterions in the stabilized product that will minimize the solubility of the toxic species. Arsenic, of course, does not form an insoluble hydroxide, and hence the mechanism that operates during S/S of many heavy metal cations does not apply for As. As^{III} and As^{V} are commonly observed in solution as AsO_3^{3-} and AsO_4^{3-} , respec-

tively, and protonated forms of these oxo-anions depending on pH [5]. The oxo-anions form a wide variety of water soluble salts. Nevertheless, many insoluble metal arsenates are well known, and it is easy to oxidize As^{III} to As^{V} , even at appreciable rates with air alone. Since arsenic is a common impurity in metal ores, considerable attention has been devoted to removing As from process waters to produce tailings that contain insoluble As [6]. As^{III} is commonly precipitated as a sulfide which is insoluble at low pH, but more soluble under strongly basic conditions. As^{V} may be precipitated with lime to produce $\text{Ca}_3(\text{AsO}_4)_2$, which has very low water solubility. Unfortunately, the calcium arsenate is not stable with respect to reaction with atmospheric CO_2 , which produces CaCO_3 and releases soluble arsenate. There is a very insoluble ferric arsenate, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, but the crystalline form of this mineral, scorodite, is much more soluble under basic conditions than under acidic conditions. Precipitation of arsenate with Fe^{III} also occurs under basic conditions to produce ‘basic ferric arsenate,’ but the identity and stability of this species are controversial. A variety of other insoluble metal arsenates are known, but not thoroughly investigated, particularly with respect to stability as a function of pH. Arsenic sulfides are also commonly encountered in wastes, and, as noted above, these may also have significant solubilities under the basic conditions typical of S–S.

The leachate results from a variety of As-containing wastes subjected to S–S with a number of binders have been summarized by Conner [7]. When the As concentrations in the waste are high ($> 635 \text{ mg kg}^{-1}$), leachate concentrations often can be brought below 5 mg l^{-1} , but usually not below 0.79 mg l^{-1} . Treatment sometimes actually increases the leachability, presumably because of different speciation under basic conditions. Similar results have been reported for other TCLP leaching studies, and column and long-term equilibrium batch leaching experiments indicate that As leaches at an elevated rate compared to most heavy metal cations [8–11]. We are not aware of published studies attempting to determine the speciation of arsenic compounds under the conditions of cementitious S–S.

2. Experimental

2.1. Materials and sample preparation

Type I portland cement (OPC) (20.6% SiO_2 , 5.2% Al_2O_3 , 2.4% Fe_2O_3 , 64.9% CaO , 3.3% MgO , 2.9% SO_3 , 0.07% Na_2O , 0.56% K_2O) manufactured by River Cement Company, St. Louis, MO was used to prepare samples containing OPC. River Cement Company also supplied the OPC without gypsum and a Type 1A cement containing air-entraining agent. The white (low iron content) cement was obtained from Lehigh Cement, Waco, TX. The fly ash was Class F power plant ash. Lumnite and Refcon are high alumina refractory cements. The sodium silicate was Type N from PQ Corporation, Valley Forge, PA. Reagent grade NaAsO_2 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ were the salts used. The arsenic salt was added to the binder mixture in 20 ml borosilicate glass vials so that the ratio of As to binder was 0.10 by weight. A ratio of water to binder of 0.5 was used to prepare all samples. The samples were mixed by hand with a glass stirring rod. The

Table 1

Arsenic concentrations in TCLP leachates from samples containing 10 wt% As^{III} (from NaAsO₂) in various binders cured for various times

Binder	Leachate Concentration (mg l ⁻¹)		
	28 Days	1 Year	3 Years
OPC	2.1	1.7	2.3
OPC, no gypsum	2.7	3.1	2.2
4:1 OPC: Class F fly ash	3.1	36	
1:1 OPC: Class F fly ash	540	430	560
1:4 OPC: Class F fly ash	1300	1400	
20:1 OPC:silica fume	2.4	2.3	3.2
20:1 OPC:Na ₂ SiO ₃	3.5	2.0	1.4
10:1 OPC:bentonite	30	2.4	
10:1 OPC:organoclay	3.0	1.1	1.8
20:1 Type 1A:silica fume	3.1	2.5	2.8
20:1 Type 1A:Na ₂ SiO ₃	1.2	1.6	2.6
White cement	1.7	0.9	0.4
20:1 White:Na ₂ SiO ₃	2.5	1.0	1.1
Lumnite	140	240	230
Refcon	150	190	160

OPC: Type I portland cement.

Na₂SiO₃: Type N soluble silicate.

Type 1A is a Type I portland with air entraining agent added.

White cement is low-iron-content portland.

Lumnite and Refcon are high alumina refractory cements.

vials were capped and sealed with parafilm and maintained at room temperature during the cure time. Each measurement made at a different cure time used a different sample vial.

2.2. TCLP leachability

Each sample was prepared in duplicate and the toxicity characteristic leaching procedure (TCLP) was run according to specifications in SW-846 [12], with the following exceptions. In order to run large numbers of samples, we routinely use small samples, as described above, and carry out the TCLP on 10 g of sample rather than 100 g. A correspondingly smaller amount of leachant is used. Otherwise, the procedure was that described in USEPA documents. Arsenic concentration in the aqueous leachate was determined on a Jarrell–Ash AtomComp direct-reading inductively coupled argon plasma spectrometer, with the lower limit of detection for arsenic being 35 µg l⁻¹. The data reported in the Tables 1 and 2 is the average of at least two duplicate runs with samples prepared in separate vials. Under these conditions, reproducibility is rarely worse than ± 5%.

2.3. MAS–NMR

Specimens were characterized using ²⁷Al and ²⁹Si high resolution solid-state magic angle spinning NMR at various cure times. The vial containing the sample was broken

Table 2

Arsenic concentrations in TCLP leachates from samples containing 10 wt% As^V (from Na₂HAsO₄) in various binders cured for various times

Binder	Leachate concentration (mg l ⁻¹)		
	28 Days	1 Year	3 Years
OPC	1.7	1.4	0.7
4:1 OPC: Class F fly ash	2.5	2.4	
1:1 OPC: Class F fly ash	7.9	94	130
1:4 OPC: Class F fly ash	530	1400	
20:1 OPC:Na ₂ SiO ₃	0.1	0.4	0.7
20:1 Type 1A:silica fume	0.1	0.4	0.5
White cement	3.6	10	
20:1 White:Na ₂ SiO ₃	8.0	15	34

and the solidified sample crushed using a mortar and pestle and then sieved through a 100 mesh sieve. ²⁹Si solid-state NMR studies were performed on a 200 MHz (4.7 Tesla) Bruker MSL-200 wide bore NMR spectrometer. A 5 μ s 90° pulse with a relaxation delay of 5 s was used to acquire the spectra at a resonance frequency of 39.7 MHz. The spectra were obtained using ca. 300 mg of sample in a zirconia rotor spinning at 5 KHz, and are reported relative to external tetramethylsilane. Enough scans were acquired to obtain a signal-to-noise ratio of 40. Al spectra were obtained on the same spectrometer using ca. 150 mg of sample in Torlon rotors spinning at 7 KHz and are reported relative to external aqueous AlCl₃. A 3 μ s 30° pulse with a relaxation delay of 0.02 s was used to acquire the spectra at a resonance frequency of 52.1 MHz. In both cases the peaks were integrated using the window integration method and Bruker software. From many determinations using duplicate and triplicate samples prepared in separate vials, integrations were reproducible to $\pm 4\%$.

2.4. XRD

X-ray diffraction analyses were performed with a Scintag PADV automated X-ray diffractometer. The samples were crushed to a fine powder with porcelain and agate mortars and sieved through a 200 mesh sieve. The XRD scan was made with copper K α radiation from 3° to 70° two-theta with 0.02° step-width and 1 to 3 s counting time.

2.5. DTG

The derivative thermogravimetric runs were made from 25 to 1000°C with the following steps: 25 to 40°C at 5°C min⁻¹; held for 10 min at 40°C; 40 to 200°C at 5°C min⁻¹; and 200 to 1000°C at 10°C min⁻¹ using a Seiko TA 220 Thermal Analyzer. The samples were ground with an agate mortar and a pestle and passed through a 200 mesh sieve. The samples were not oven-dried or otherwise treated because trial runs suggested that Aft will decompose by 105°C. The samples were analyzed immediately after grinding. The amount of sample ranged from 15 to 25 mg.

3. Results

3.1. As leaching from various binders

TCLP leaching results for samples containing As^{III} (from NaAsO₂) and As^V (from Na₂HAsO₄) are summarized in Tables 1 and 2, respectively. The results are quite variable, with leachabilities ranging from < 1 to > 1000 mg l⁻¹. Portland cement without additives shows considerable promise for treatment of both oxidation states of As. Furthermore, in cases where reasonable results are obtained, such as with portland cement alone, there is no indication of degraded performance after very long cure times. Thermodynamics predicts conversion of calcium arsenate to calcium carbonate on exposure to CO₂, with resultant release of soluble arsenate. Nevertheless, concretes exposed to air undergo only extremely slow carbonation, with CaCO₃ appearing first at the surface, then becoming visible below the surface at an average rate of about 0.1 mm year⁻¹. We cannot eliminate the possibility that our OPC-stabilized samples will show greater As leachability due to CO₂ penetration after very long times, but it is not evident after 3 years of cure.

A variety of additives that are commonly used in S/S practice, like Type N soluble sodium silicate or clays of various types, may even marginally improve performance of portland cement as binder. It does not seem necessary to use such additives to control As leachability, but they may be desirable additives because a waste contains other hazardous species in addition to As. In those circumstances, As leachability would not be expected to be compromised.

A very striking result in the Tables 1 and 2, however, is the poor performance of mixtures containing fly ash. In most cases, leachability of As is much greater from OPC-fly ash mixtures than from OPC alone, and the data overall clearly indicate that leachability increases with increasing cure time. Since fly ash is a common component of S/S binders, it is important to be aware of its potentially detrimental interactions with As wastes.

Several specialty cement materials have been included in this study. White cement is a low-iron-content cement, produced mainly for decorative purposes. We have often included it in our studies, because we commonly characterize the matrices using nuclear magnetic resonance spectroscopy, and the low concentration of ferromagnetic species is a major advantage. In addition to low iron content, the white cement used had elevated CaO content. It showed reasonable performance with As^{III}, but somewhat poorer performance with As^V. The high alumina, low silica cements have not shown significant promise (in this study or others) for metal or metalloid containment. Another common component of the binders for S/S is ground granulated blastfurnace slag. We have not included slag in this study, but previous work from this laboratory on As-contaminated soils showed considerably increased leachability for a 1:1 OPC:slag binder compared to OPC alone [13]. The reducing environment in the slag matrix may be responsible for reduction of As^V to As^{III}, but we have no direct evidence for that.

3.2. Spectroscopic and thermal analysis

We have periodically monitored our samples by powder X-ray diffraction in order to attempt to identify crystalline phases that are forming as a result of waste addition. In

most cases of S/S products, any new crystalline salts, if formed, are present in such low concentration that they are not evident in the already complex diffraction pattern of the cement. This is not true with arsenates when the arsenic is added as sodium arsenate. A crystalline material is formed in major amounts, $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$, and this species is present in both cement and cement–fly ash binders. Fig. 1 and Fig. 2 show the diffraction patterns of binder alone, then binder with As^{III} and binder with As^{V} , all cured for one year. In Fig. 1, the binder is portland cement alone, while in Fig. 2 it is 1:1 cement–fly ash. Diffraction measurements were made at other time intervals as well. Even when As^{III} is solidified with cement–fly ash (but not cement alone), minor amounts of the As^{V} product, $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$, are formed. The formation of this salt depends, of course, upon the availability of significant amounts of Na as well as Ca, a condition which may not be met in all cases of arsenate treatment. The XRD patterns show other notable differences. Calcium hydroxide (CH) peaks are very prominent in cement alone, but much less so in cement–fly ash mixtures. The presence of either arsenic species in the cement greatly reduces the CH. Monosulfate (AFm) is also prominent in the 1 year old cement, but not in the cements containing arsenic. Thus, despite the substantial degree of hydration of the binder materials when arsenic is present (see below), the matrix components other than calcium silicate hydrate gel (C–S–H) are significantly altered by the presence of the arsenic salts.

Because of the observation that leachability increased over time with some of the cement–fly ash samples, these were examined in more detail by both XRD and thermal analysis. XRD showed that all samples contained phases which could be divided into two components: those present in the Class F fly ash and those due to the hydration–pozzolanic reactions in cement–fly ash. Mullite and quartz were the two principal phases from the fly ash. XRD of the samples with As^{III} indicated the As salt $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$ was absent in the 14 day old sample but present in the 1 year old sample. Calcium hydroxide was not detected. Strätlingite was tentatively identified, but only one peak at 1.260 nm could be associated with it. XRD of the samples containing As^{V} showed that calcium hydroxide was present in samples up to 14 days of age but absent later. Ettringite was present in a 14 day sample but was absent in a 1 year old sample. The As salt, $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$, was observed as early as 7 days. Numerous peaks of $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$ were detected in the XRD patterns of As^{V} -containing samples; fewer were observed in the As^{III} -containing samples. The reaction product is presumably more crystalline in the former group of samples.

The residue was analyzed by XRD after TCLP tests of these samples. Mullite and quartz were the residual crystalline phases, which is not surprising considering their inert nature. Calcium carbonate was also common. Carbonation from atmospheric carbon dioxide must have resulted in this calcium carbonate.

Derivative thermogravimetric (DTG) analysis was carried out on hydrated 1:1 OPC–Class F fly ash (Fig. 3), cement–fly ash containing As^{III} (Fig. 4), and OPC–fly ash containing As^{V} (Fig. 5). DTG measurements were made after 7 days, 1 year and 3 years of cure. The DTG curve of Class F fly ash alone was featureless, indicating the absence of any hydrated or carbonated phases. The 7 and 14 day samples of hydrated cement–fly ash (Fig. 3) were practically identical. The principal hydration products of the mixture are calcium hydroxide and ettringite (Aft); a broad hump is also present

Binder - OPC

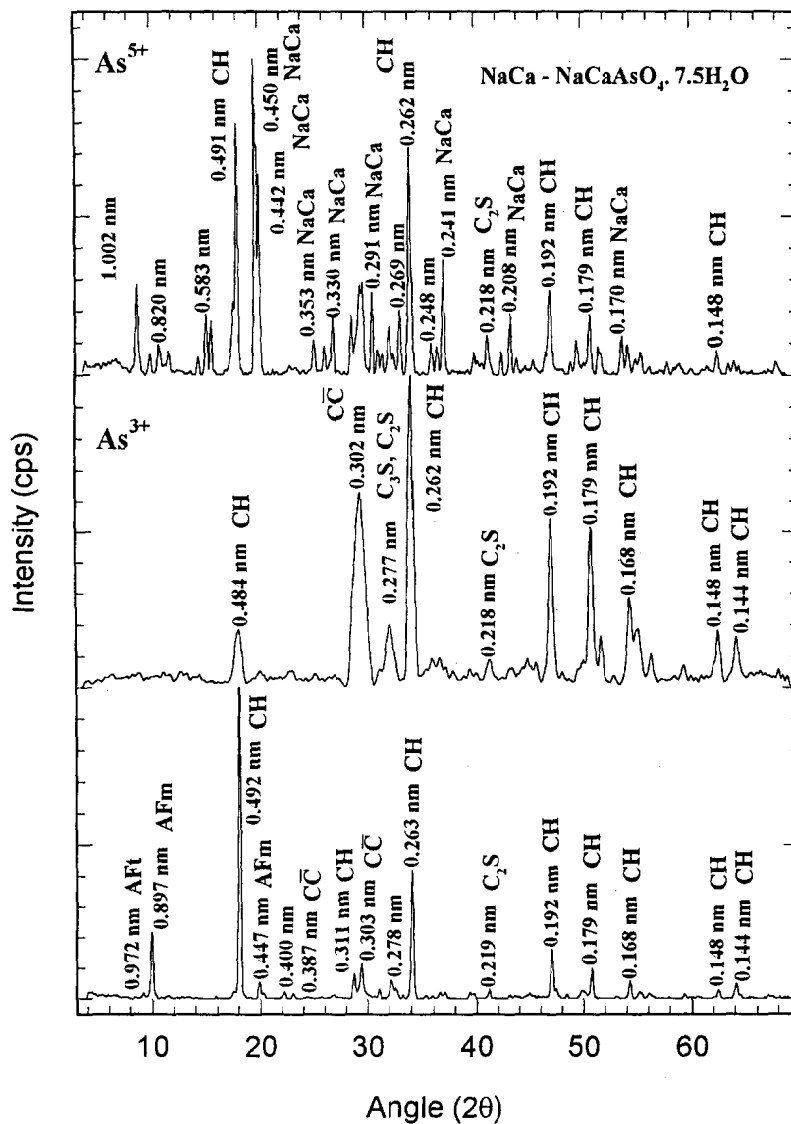


Fig. 1. X-ray diffraction of OPC, OPC + As^{III} and OPC + As^V. Peak identifications are: CH: calcium hydroxide, C₂S: dicalcium silicate, C₃S: tricalcium silicate, NaCa: NaCaAs₄·7.5H₂O, CC: calcium carbonate, AFt: ettringite, AFm: monosulfate.

over the range 200 to 400°C. The hump is due to the solid solution between C₄AH₁₃ and AFm [14]. With time, the amount of calcium hydroxide decreases and completely disappears in the three-year old sample, presumably being consumed in the pozzolanic

Binder - CFA

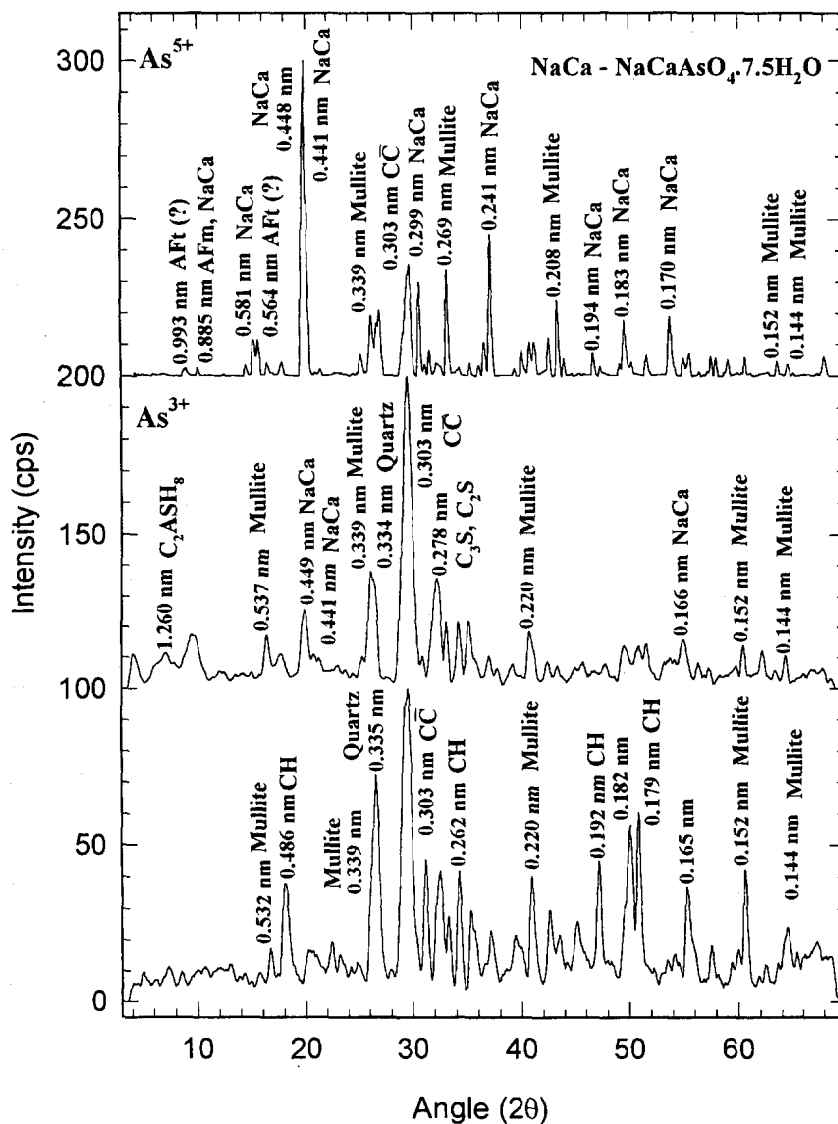


Fig. 2. X-ray diffraction of OPC-FA, OPC-FA + As^{III} and OPC-FA + As^V. Peak identifications are: CH: calcium hydroxide, C₂S: dicalcium silicate, C₃S: tricalcium silicate, NaCa: NaCaAsO₄·7.5H₂O, CC: calcium carbonate, AFt: ettringite, AFm: monosulfate, C₂ASH₈: strätlingite.

reactions of the glassy phase in the fly ash (which can be seen in the NMR, as discussed below). The broad hump over the range 200 to 400°C grows stronger and sharper with time, and the peak also moves towards lower temperature. The move towards lower

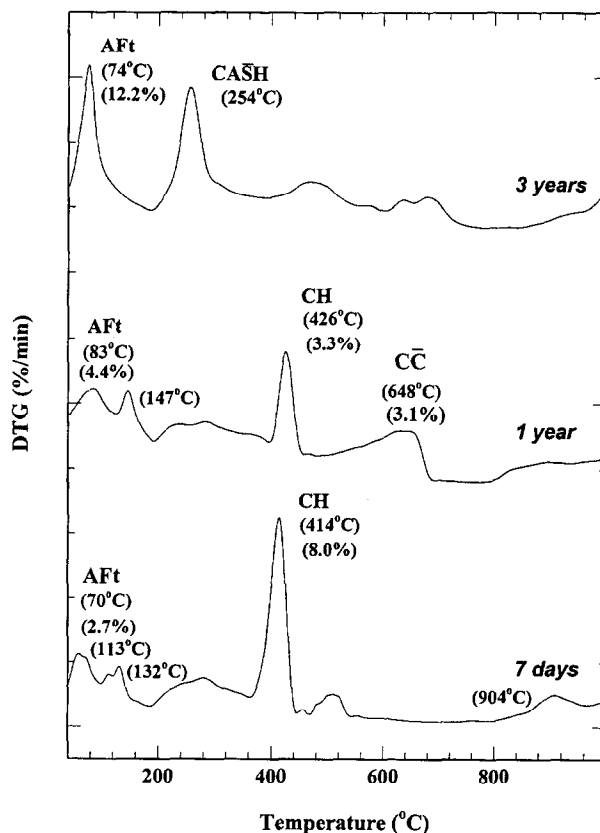


Fig. 3. Derivative thermal gravimetry of OPC-FA after cure times of 7 days, 1 year and 3 years. Peak identifications are: CH: calcium hydroxide, CC: calcium carbonate, AFt: ettringite, CASH: solid solution of calcium aluminate hydrate with monosulfate.

temperature may indicate the growth of more SO_3 -rich end members of the solid solution series. The ettringite peak also increases in intensity with time. A moderate peak is present around 900°C in samples of intermediate age. Some workers have correlated this high temperature peak with calcium silicate hydrate [13]; on the other hand, Berry, et al., associate this peak with breakdown products of complex sulfates [15]. Whatever the origin, It appears reasonable that the extent of the pozzolanic reaction of fly ash can be estimated from the $900\text{--}930^\circ\text{C}$ peak. In OPC-fly ash mixtures, this peak is prominent in the 7 day old sample, less so in the 1 year old sample, and completely vanished in the 3 year old sample. At the same time, all the CH has been consumed, and the AFt peak has become prominent.

In the DTG curves of As^{III} -containing samples (Fig. 4) calcium hydroxide and ettringite are absent at an early age but appear in 3 year old samples. The 3 year old sample is similar to the 1 year old cement-fly ash sample without any added arsenic. As^{III} certainly affects hydration of cement-fly ash. The limited data set, however, does

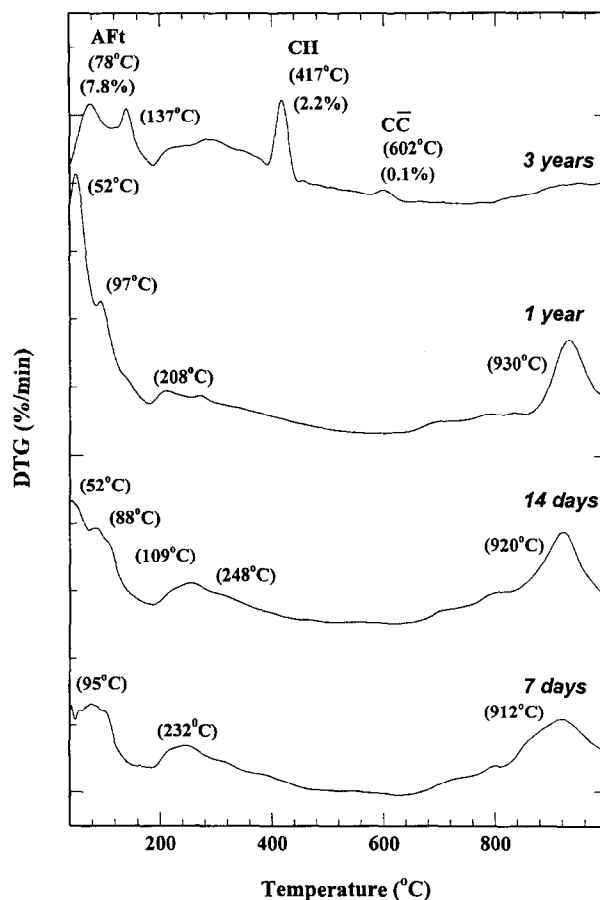


Fig. 4. Derivative thermal gravimetry of OPC-FA + As^{III} after cure times of 7 days, 14 days, 1 year and 3 years. Peak identifications are: CH: calcium hydroxide, CC: calcium carbonate, AFt: ettringite.

not indicate whether the amount of calcium hydroxide is increasing or decreasing with time. Compared to the As^V samples, a strong peak at 54°C is absent in these samples but could be hidden below the peaks in the 50 to 150°C range. The peak at 924°C is stronger at an early age but decreases in intensity later. Some calcium carbonate is observed in the 1 year old sample. NMR does show decreasing amounts of the glassy silicate from fly ash up to one year of cure, but little change thereafter.

The samples containing As^V (Fig. 5) have some calcium hydroxide at an early age, similar to the cement-fly ash samples without arsenic, but it is absent later. The amount of calcium hydroxide present in the young samples is very low compared to the samples without As^V. The peak at 54°C becomes sharper with time. A comparison of these samples with the As^V with lime sample (see below) suggests that the 54°C peak is due to the As-salt; with lesser amounts of this salt or finer grain size a shift towards lower temperature is possible [16]. Some contribution to this peak from ettringite is also

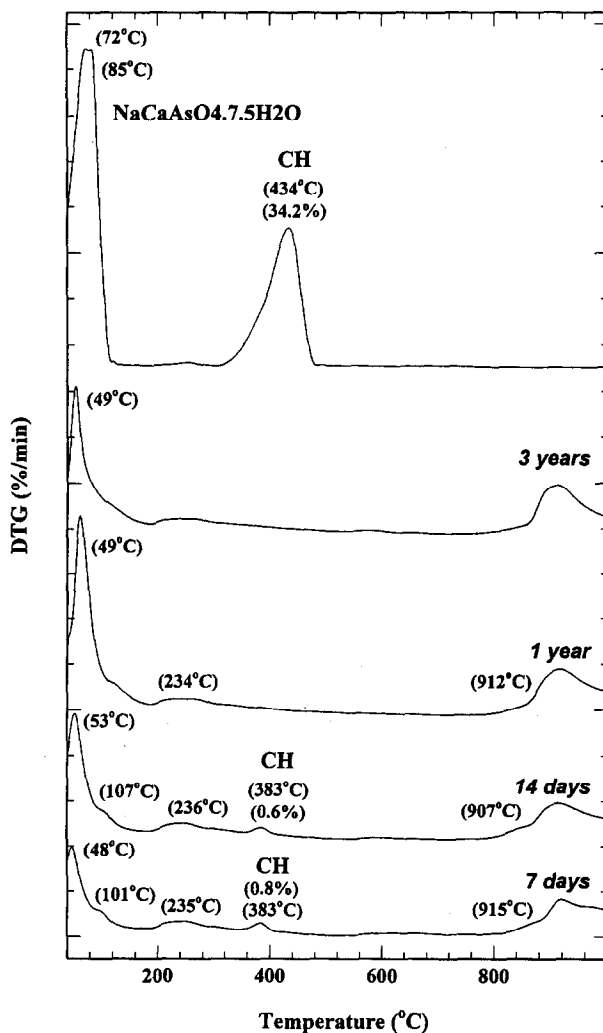


Fig. 5. Derivative thermal gravimetry of OPC-FA + As^V after cure times of 7 days, 14 days, 1 year and 3 years; (top) DTG of NaCaAsO₄. CH: calcium hydroxide.

possible. All samples with As^V have a peak in the range 910–925°C, similar to the As^{III} samples of up to one-year age and cement-fly ash mixtures of early age, but the peak is stronger in the presence of As^V. For all these samples, there is broad agreement between the results obtained by XRD and DTG, although the two techniques provide some complementary information.

A sample of NaCaAsO₄·7.5H₂O was prepared by mixing NaH₂AsO₄ with Ca(OH)₂ and water. The formation of NaCaAsO₄·7.5H₂O in this mixture was confirmed by XRD. The DTG curve of the sample is shown in Fig. 5 (top). There are two peaks: one with an overlapping doublet in the range 70–84°C and another at 433°C (Ca(OH)₂). The

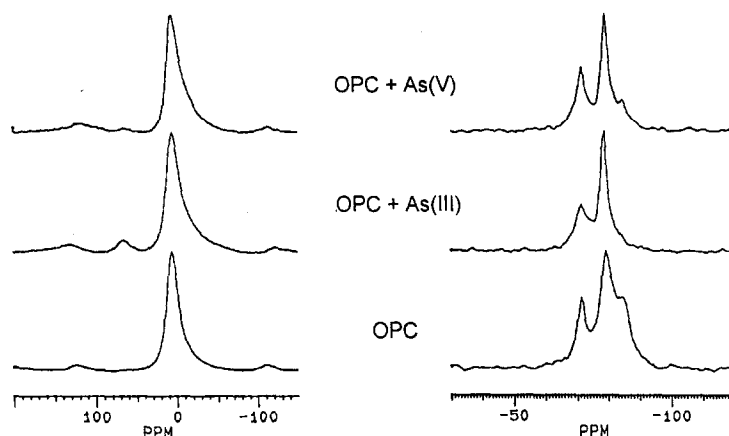


Fig. 6. Al (left) and Si (right) NMR of OPC, OPC + As^{III} and OPC + As^V cured for 28 days.

doublet presumably represents a multi-step dissociation process of the arsenic salt $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$ [16]. The doublet is probably completely overlapping at low concentrations of the salt.

The progress of hydration for these samples has also been followed by ^{27}Al and ^{29}Si solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR). Fig. 6 shows spectra for cement alone and cement containing the two arsenic salts after 28 days of cure. Although in the early hours of cement hydration, arsenic salts may act as set retarders [17], after 28 days hydration has proceeded to a significant extent. NMR spectra of hydrating portland cement are interpreted in terms of percent hydration by taking the proportion of the Q^0 peak to represent unhydrated cement. As seen in Fig. 6, the Q^0 peak is diminishing normally during hydration of cement with arsenite and arsenate present. The notable difference in the spectra is the contribution from Q^2 , which is much diminished in the case of both of the arsenic salts. Thus, the salts are retarding the polymerization of the silicate species in the matrix. Hydration of the aluminate phase can be followed by NMR as conversion of tetrahedrally coordinated Al in the clinker to octahedrally coordinated Al minerals in the mature cement paste. Arsenic salts retard the aluminate conversion in portland cement, but after 28 days, most of the tetrahedral Al has been converted into octahedral Al. There is almost no change in the Al spectra comparing 28 days and one year of cure. The effects of arsenic on the cement–fly ash mixtures are much more dramatic, as described in the next section.

3.3. Long-term changes in leachability and structure

There is increasing interest in the S/S literature in long-term effects. Using ‘dynamic’ leaching procedures, like ANS 16.1, it is possible to determine effective diffusion coefficients for waste constituents in cementitious matrices, and to use that information, along with particle size information, to predict leaching potential of the solidified wastes far into the future. Of course, the projections do not have validity if the

matrix is changing over time in ways that alter leachability. Most of the currently available data on long-term effects in S/S (usually in the form of TCLP leaching results) indicate reduced leachability with increasing cure times.

Considering only the progress of matrix development, it is reasonable that leachability should decrease with time, at least up to a year or so, since cement hydration reactions are very slow ones. Pore waters are continuing to be used up in hydration processes up to that time, and the matrix is continuing to become less porous and permeable. Indeed, the data for portland cement alone in Tables 1 and 2 show either unchanged or modestly decreasing leachability over a 3 year period. However, there are a few reports of significantly increased leachability over time, and the present data for As in OPC–fly ash mixtures is perhaps the most dramatic yet published. For As^{III} in Table 1, the result for 4:1 OPC–fly ash obtained after 28 days is a very reasonable one, but after a year of cure, the TCLP leachability is unacceptably high. The 1:1 OPC–fly ash results in Table 2 for As^V also show very large changes between 28 days and 1 year of cure.

Our structural studies provide a rationale for those observations. In contrast to

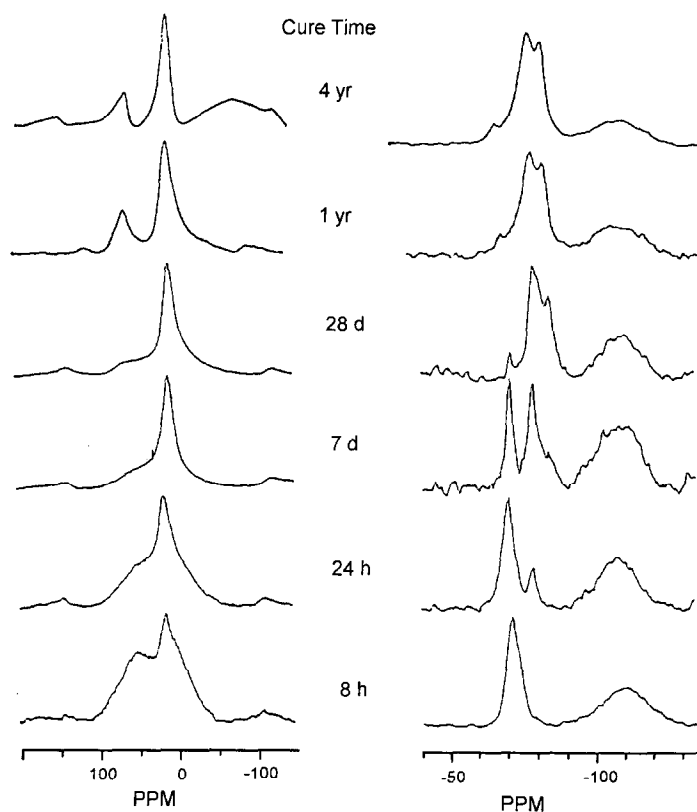


Fig. 7. Al (left) and Si (right) NMR of OPC–FA at various times of cure.

hydrating OPC alone, mixtures of OPC and fly ash show a much wider range of transformations occurring after long cure times. An aluminum-containing mineral phase that is commonly associated with cement–fly ash mixtures is strätlingite. For instance, Tenoutasse and Marion [18] investigated cement–fly ash samples of various compositions by XRD and SEM–EDAX after two and three years of hydration and reported the presence of crystalline C_2ASH_8 . Strätlingite is a complex calcium aluminosilicate hydrate that contains Al in both tetrahedral and octahedral coordination, and ^{29}Si - and ^{27}Al -NMR studies of synthesized strätlingite have recently been published [19] and indicate a variable Al(4)/Al(6) ratio depending upon method of synthesis. Fig. 7 shows NMR spectra as a function of cure time for the 1:1 OPC–FA matrices prepared in the present study. The Si spectra (on the righthand side of this and the other NMR figures) show distinct differences from those of OPC alone. There is a broad hump around -110 PPM coming from the silica fraction of the fly ash. Up through 7 days of cure, this silica does not appear to become involved in the hydration reactions, but is slowly consumed thereafter. The progress of formation of Q^1 and Q^2 peaks from the initial Q^0 is quite

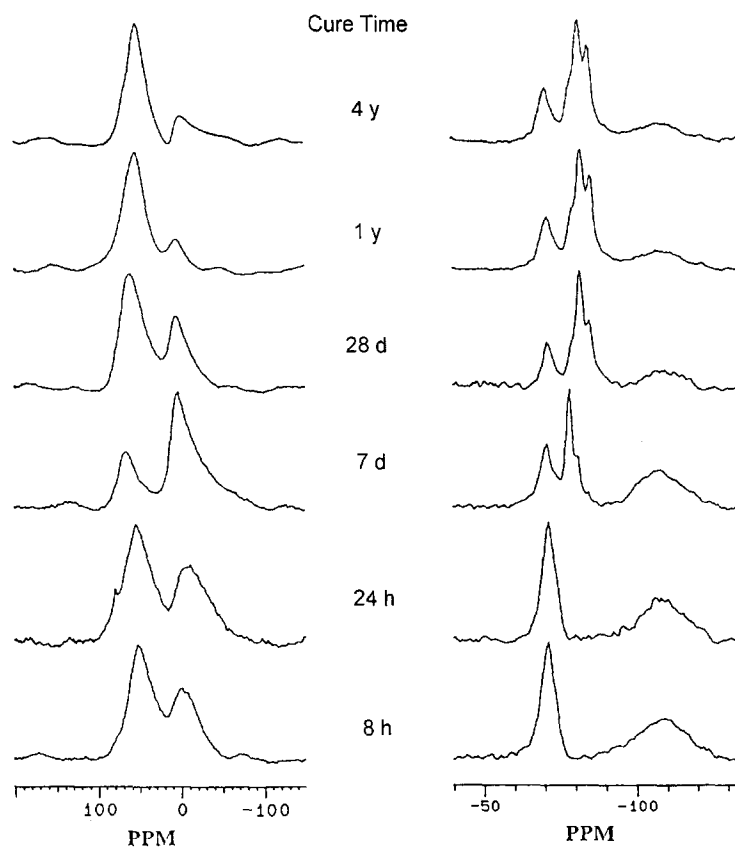


Fig. 8. Al (left) and Si (right) NMR of OPC–FA + As^{III} at various times of cure.

comparable to that observed with OPC. Some Q^0 still remains even after 4 years of cure, but the bulk of the silicate units appear as Q^1 and Q^2 . The progress of conversion of Al(4) to Al(6) is slower than in OPC alone, but nevertheless appears to be essentially complete after 28 days. At much later times, however, Al(4) reappears and is still a prominent peak after 4 years of cure. Integration under the peaks shows the Al(4):Al(6) ratio to be approximately 25:75. We presume that the 4-coordinate Al that appears at later cure times is associated with strätlingite formation.

Fig. 8 and Fig. 9 show Al- and Si-NMR spectra of the 1:1 OPC:FA matrices in the presence of 10% by weight As^{III} and As^V , respectively. The rate of conversion of orthosilicate to more complex silicate oligomers is slower to start in the presence of arsenic salts, but then accelerates to get ahead of the OPC-FA at 7 days of cure (reduced Q^0 peak). From that point on, however, the presence of As appears to almost freeze the silicate hydration, more dramatically so in the presence of As^{III} than As^V . Even bigger differences are apparent in the aluminate phases. The arsenic salts have a major effect in slowing the aluminate transformations, but they appear to be going in the normal direction of conversion of tetrahedral Al to octahedral Al. In OPC alone, conversion of Al(4) to Al(6) is essentially complete within 24 h. That transformation takes 7 days in OPC-FA, but never reaches completion in the presence of As. The most notable effects in the OPC-FA-As samples occur later, however. After 28 days of cure the conversion of Al(4) to Al(6) has begun to reverse itself, and after a year almost all the Al(6) has reverted to Al(4). The OPC-FA control samples containing no waste show similar effects in the aluminum spectra, as noted above, but the extent of reversion to Al(4) is much lower at 1 year in the absence of As. The NMR spectra show that while both As^{III} and As^V appear to have little effect on OPC matrices in the long term, both

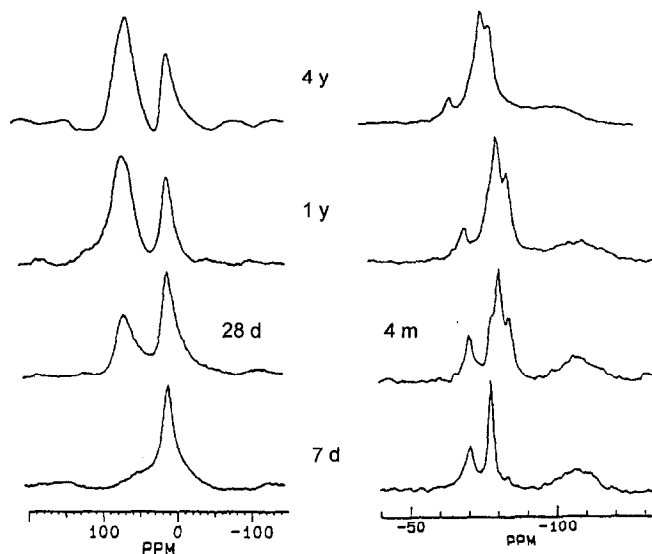


Fig. 9. Al (left) and Si (right) NMR of OPC-FA + As^V at various times of cure.

accelerate the aluminate phase changes that are characteristic of OPC–FA and induce them to proceed further to completion at long cure times, with As^{III} having a greater effect than As^V.

4. Conclusions

We have observed what we believe is the first example of a waste catalyzing a long-term matrix change in a common binder used for solidification–stabilization. Arsenic appears to catalyze the formation of the aluminate mineral, strätlingite, during hydration of portland cement–fly ash mixtures, and that mineral respeciation is associated with (if not responsible for) increased arsenic leachability. It is not common practice to perform physical or chemical testing of S/S products at long times after the matrix has been prepared. Testing even after 28 days is uncommon, but even such ‘long-term’ testing would not have detected the changes observed in the present study. Long-term effects that alter the matrix, such as those described here, have serious consequences for the application of leach modeling to long-term predictions of release rates for contaminants. The OPC–FA matrix containing As is quite different in mineral composition at 7 or 28 days from that at a year or later. Obviously, effective diffusion coefficients and TCLP measurements of leachability will have little meaning when the matrix is changing over time.

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