Synthesis and thermodynamic properties of arsenate and sulfate-arsenate ettringite structure phases

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Abstract

Arsenic is a toxic and carcinogenic contaminant of potential concern. Ettringite [Ca₆Al₂(−SO₄)₃(OH)₁₂·26H₂O] has the ability to incorporate oxyanions as a solid solution with SO₄²⁻, which could lower the soluble oxyanion concentrations. Therefore, ettringite containing SO₄²⁻ and AsO₄³⁻ has been synthesized. Results indicated that AsO₄³⁻ could substitute for SO₄²⁻ inside the channels of ettringite in the form of HAsO₄²⁻, and a linear correlation existed between X_{initial} solution and X_{solid}. The thermodynamic characterization of the solid samples was investigated by means of Visual MINTEQ, a freeware chemical equilibrium model, and the solubility product logK of -48.4 ± 0.4 was calculated for HAsO₄−-ettringite at 25°C. The Lippmann phase diagram and X_{HasO₄−}−X_{HasO₄,aq} plot showed that the solid solution series containing arsenate has HASO₄-poor aqueous solutions in equilibrium. These findings can be helpful to arsenate solidification and arsenate leaching modeling projects.

Introduction

Arsenic (As) is known to be toxic, carcinogenic, and possibly teratogenic to humans [1–3]. In nature, As is released to the environment through volcanism and weathering. As is also produced by anthropogenic activities, such as mineral processing and melting, coal combustion, and extensive use of As-containing compounds, such as wood preservatives, desiccants, and herbicides, resulting in high concentrations of As in water and soil [4].

Ettringite, a hydrous calcium aluminum sulfate mineral with the formula Ca₆(Al(OH))₂(SO₄)₃·26H₂O, is an important hydration product of cement and alkaline wastes [5, 6]. Ettringite forms a hexagonal prismatic crystal, which is constructed of the columns of composition [Ca₆(Al(OH))₂·24H₂O]⁶⁺ through electrostatic interactions with [(SO₄)₃·2H₂O]⁶⁻ in the channels between the columns [7]. The full or partial SO₄²⁻ ions in the channels can be replaced by some oxyanions (i.e., CrO₄²⁻, SeO₄³⁻, SeO₃²⁻, MoO₄²⁻, and VO₄³⁻) to form a solid solution [8–13]. Ettringite and its solid solution have low solubility. Robert reported on SO₄−-ettringite and CrO₄−-ettringite with the pK_{sp} of -44.8 [14] and -41.4 [5], respectively. Therefore, ettringite and...
ettringite analogs are important potential candidates for the immobilization of contaminant ions.

Indeed, AsO$_4^{3-}$ substitution for SO$_4^{2-}$ in ettringite has been previously observed [15, 16]. However, to date there are no investigations focusing on the solid composition analysis and thermodynamic data of AsO$_4$/SO$_4$-ettringite solid solutions. The purpose of the present study is to investigate the changes in solid-phase characteristics, solid composition, and solubility resulting from AsO$_4^{3-}$ substitutions in the ettringite structure. The results of this investigation will be helpful in modeling the potential for ettringite to control AsO$_4^{2-}$ concentrations.

**Experimental materials and methods**

**Materials**

All chemicals used in this study were at least of pro-analytical grade. The following substances were used: CaCO$_3$ powder, NaAlO$_2$ powder, Na$_2$SO$_4$, Na$_3$AsO$_4$·12H$_2$O, sucrose, and HNO$_3$. Deionized water used in this study was boiled, followed by cooling under soda lime in a N$_2$ (g)-filled glove box to eliminate CO$_2$(aq).

All polyethylene bottles, tubes, and glassware were soaked in acid solution (5% HNO$_3$) for at least 24 h and rinsed using ultrapure water three times prior to each experiment. All handling of materials, the solid solution synthesis, the sample filtration, the sample drying, and the pH measurements were conducted in a glovebox filled with N$_2$ to prevent possible CO$_2$ contamination.

**Solid solution synthesis and experiments**

The solid solution was synthetized on the basis of Hassett and McCarthy’s "modified saccharate method" [17]. Initially, a solution containing a mixture of NaAlO$_2$, Na$_2$SO$_4$, and Na$_3$AsO$_4$·12H$_2$O was prepared with a range of arsenate/sulfate ratios (the total number of moles of SO$_4$ and AsO$_4$ was constant). A soluble calcium complex prepared by dissolving CaO in a 10% sucrose solution was added slowly (4 mL/min to 7 mL/min) to the mixed solution while stirring. A twofold excess of NaAlO$_2$ was used to prevent the precipitation of calcium arsenate or sulfate, which would be difficult to separate from the ettringite solid solution. The liquid-to-solid ratio was 20 mL/g. The sample was stirred for 12 h and equilibrated in a thermostatic oscillator for 48 h at a constant temperature of 25˚C. Afterward, the sample was centrifuged for 15 min at 4,500 rpm. The supernatant was filtered using 0.45 μm nylon membrane filters following pH measurement. The solution was stored at 4˚C for analyzing for elemental composition after being acidified with concentrated HNO$_3$. The solid phase was washed with acetone after being filtered, and was dried in a desiccator.

**Characterization of the solid phase**

After drying, part of the solid phase was ground with an agate mortar to <60 μm for analysis by X-ray diffraction (XRD), infrared (IR) analysis, and chemical analysis. XRD analysis was used to determine the purity and crystallinity of the phases, and data were collected on an X’Pert PRO Polycrystalline X-ray Diffractometer from PANalytical Company using Cu Ka radiation. The diffraction scans ranged from 5˚ to 60˚ 2θ with a step interval of 0.0263˚ 2θ and a counting time of 4 s/step. The IR spectra were recorded on a Thermo Nicolet Nexus Series using potassium bromide pellets in the range of 4,000 cm$^{-1}$ to 400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ to confirm arsenate in the samples. The morphology of the samples was determined by scanning electron microscopy (SEM) using a ZEISS SIGMA 500 equipped with a Bruker Quantax EDS detector, which can also provide the information on the surface composition.
Chemical analysis

Part of powder sample was dissolved in a 1% solution of HNO$_3$. Then, solid stoichiometry was determined using ICP-OES for calcium, sodium, aluminum, and arsenic and using ion chromatography for sulfur.

Solubility study and geochemical model

Finely ground synthetic solid samples were mixed with distilled deionized water (1:10 (w/v)) and equilibrated in a shaker bath for 100 days at 25 ± 1°C. The supernatant was isolated by centrifugation and passage through a 0.45 μm nylon membrane filter, and the concentrations of calcium, sodium, aluminum, arsenic, and sulfur in the filtrate were determined. Ionic species and their activities were calculated from the experimental values of ionic concentrations and pH values using Visual MINTEQ (Version 3.1).

Visual MINTEQ is a freeware chemical equilibrium model, which was developed from the DOS program MINTEQA2 and originally coded by the US EPA. Visual MINTEQ can calculate the speciation of inorganic ions and complexes in water [18]. And the databases used by Visual MINTEQ (Version 3.1) included pertinent and updated thermodynamic data from available literature (Table 1).

Results and discussion

Solid phases of the solid solution series

Table 2 lists the chemical composition of the solid solution series, which shows that the solids had relatively constant Ca and Al ratios at variable SO$_4$:AsO$_4$ ratios in the initial solution. The ideal stoichiometry of ettringite is 6Ca:2Al:3SO$_4$. However, small deviations from the ideal stoichiometry were observed, which might have resulted from the synthesis method and the amount of water present [25]. Nevertheless, the Ca/Al ratio in the solid with no sulfur was 4.7, and far greater than the ideal value 3, which occurred in despite of the two-fold excess of soluble Al in the synthesis solution. This could be the result of the production of Ca phases (such as portlandite, calcite or calcium-arsenic compound). Furthermore, the molar ratio of AsO$_4$ to (AsO$_4$ + SO$_4$) in the initial solution (which is represented by $X_{\text{initial solution}}$) was not obtained in the solid. At low molar ratio ($X_{\text{initial solution}} < 0.3$), the solids were more enriched in AsO$_4$ than the original solution, whereas the solids had more SO$_4$ at high molar ratio ($X_{\text{initial solution}} > 0.3$). Linear regression analysis of the data of the molar ratio of AsO$_4$ to (AsO$_4$ + SO$_4$) in solids (which is represented by $X_{\text{solid}}$) and the initial solution led to the following equation: $X_{\text{solid}} = 0.7858X_{\text{initial solution}} + 0.0409$ with a coefficient of correlation of 0.994. This equation can be used to approximately estimate the solution mix ratio of SO$_4$ to AsO$_4$ required to prepare a particular solid solution composition.

Sharp peaks in the X-ray diffractograms (Fig 1) of the synthesis products indicated good crystallinity, and ettringite was the only stable crystalline phase except the sample h. Although the low intensities of the diffraction peaks are obtained in the pure As-sample (Fig 1h), the ettringite phase clearly can be recognized. The peaks showed slight shifts to higher angles (smaller $d$-spacing) with substitution of AsO$_4$ for SO$_4$ (including the sample h). This decrease in basal spacing implied that the interchannel for sulfate and water molecules was compressed after AsO$_4$ uptake, which can be attributed to the intercalation of an arsenate anion in exchange for sulfate and the displacement of the ordered water molecules [26, 27]. The solids with high arsenic content ($X_{\text{solid}} > 0.5$) evidently had lower intensities of the diffraction peaks, which indicated lower crystallinity of samples. The peak intensity (around 9.9°) decreased with increasing As content in the solid solution series, and disappear when there was no sulfur.
Table 1. Thermodynamic data supplemented to the Visual MINTEQ (Version 3.1) database.

| Reaction | logKsp | Source |
|----------|--------|--------|
| H₂O-H⁺ = OH⁻ | -13.99 | [19] |

**Aqueous species**

| Reaction | logKsp | Source |
|----------|--------|--------|
| Ca²⁺ + AsO₄³⁻ = CaAsO₄⁻ | 4.36 | [20] |
| Ca²⁺ + H⁺ + AsO₄³⁻ = CaHAsO₄⁰ | 14.31 | [20] |
| Ca²⁺ + 2H⁺ + AsO₄³⁻ = Ca₂H₂AsO₄⁺ | 19.66 | [20] |
| Ca²⁺ + H₂O-H⁺ = CaOH⁺ | -12.83 | [19] |
| Al³⁺ + H₂O = AlOH²⁺ + H⁺ | -4.97 | [21] |
| Al³⁺ + 2H₂O = Al(OH)³⁺ + 2H⁺ | -10.11 | [21] |
| Al³⁺ + 3H₂O = Al(OH)₃ + 3H⁺ | -16.67 | [21] |
| Al³⁺ + 4H₂O = Al(OH)₄ + 4H⁺ | -23 | [21] |
| AsO₄³⁻ + H⁺ = HAsO₄²⁻ | 11.8 | [22] |
| AsO₄³⁻ + 2H⁺ = H₂AsO₄²⁻ | 18.79 | [22] |
| AsO₄³⁻ + 3H⁺ = H₃AsO₄³⁻ | 21.09 | [22] |
| Al³⁺ + 2SO₄²⁻ = Al(SO₄)₂ | 5.58 | [23] |
| Al³⁺ + SO₄²⁻ = Al₂(SO₄)³⁻ | 3.84 | [23] |
| SO₄²⁻ + H⁺ = HSO₄⁻ | 1.99 | [23] |
| Ca²⁺ + SO₄²⁻ = CaSO₄⁰ | 2.36 | [23] |

**Solid phases**

| Reaction | logKsp | Source |
|----------|--------|--------|
| Ca₅(AsO₄)₂.9OH = 5Ca²⁺ + 3AsO₄³⁻ + H₂O - H⁺ | -26.12 | [20] |
| Ca₃(AsO₄)₂-xH₂O = 3Ca²⁺ + 2AsO₄³⁻ + xH₂O | -21.25 | [20] |
| Ca₄(AsO₄)₂.4H₂O = 4Ca²⁺ + 2AsO₄³⁻ + 6H₂O - 2H⁺ | -1.20 | [20] |
| Ca(H₂AsO₄)₂ = Ca₂⁺ + 2H⁺ + 2AsO₄³⁻ | -35.62 | [20] |
| CaHAsO₄ = Ca²⁺ + H⁺ + AsO₄³⁻ | -10.55 | [20] |
| Ca(OH)₂ = Ca²⁺ + 2H₂O - 2H⁺ | 22.7 | [19] |
| Al₂O₃.corundum = 2Al²⁺ + 3H₂O - 6H⁺ | 16.93 | [21] |
| Al₂O₃.9.γ-alumina = 2Al²⁺ + 3H₂O - 6H⁺ | -18.33 | [21] |
| Al(OH)₃.3.δ-alumina = Al³⁺ + 3H₂O - 3H⁺ | 10.8 | [24] |
| AlOOH.gunnite = Al²⁺ + 2H₂O - 3H⁺ | 7.64 | [19] |
| AlOOH.kasapite = Al²⁺ + 2H₂O - 3H⁺ | 7.01 | [19] |
| Al(OH)₃.3.γ-alumina = Al³⁺ + 3H₂O - 3H⁺ | 7.75 | [19] |
| CaSO₄.2H₂O = Ca²⁺ + SO₄²⁻ + 2H₂O | -4.61 | [23] |
| CaSO₄.2H₂O = Ca²⁺ + SO₄²⁻ | -4.36 | [23] |
| Al₂(SO₄)₃ = Al²⁺ + SO₄²⁻ + 3H₂O | -3.23 | [23] |
| Al(OH)₃SO₄ = 4Al⁺ + SO₄²⁻ + 10H₂O - 10H⁺ | 22.7 | [23] |

Ca₄[Al(OH)₃]₂(SO₄)₃.26H₂O = 6Ca²⁺ + 2Al(OH)₄⁺ + SO₄²⁻ + 4OH⁻ + 26H₂O | 44.8 | [14] |

That was due to the elevated electron density in the structure, which resulted from the substitution of SO₄ by AsO₄. A new peak (around 12.6°) appeared when As contents in the samples were higher than 0.65. This could be attributed to CaAl₂O₄·10H₂O. And there was another new peak at 30.4° in sample h, which was due to Ca₅(AsO₄)₂·10H₂O. The peak intensity around 37.3° rapidly decreased with As increasing in solid samples, which may be attributed to As substitution for partial H₂O in the channel of ettringite. And the rapid decrease of the peak (37.3°) caused a false appearance of peak split in f, g and h.

The poorer crystalline solid with increasing As content in the samples could also be observed through the SEM micrographs of the samples (Fig 2). The club-shaped ettringite particles were approximately 5 μm to 12 μm in length when arsenic was absent. However, the grain length of ettringite decreased to <1 μm with increases in solid-phase arsenic concentration, and the
Table 2. Chemical composition of solid digest analyses of synthesized solid solution series.

| Initial solution (AsO$_4$) / (SO$_4$+AsO$_4$) | Measured solid digest concentrations in mol/L | Molar ratios Ca:Al:(SO$_4$+AsO$_4$) normalized to 6Ca | Solid product (AsO$_4$) / (SO$_4$+AsO$_4$) | Final solutions in precipitation experiments |
|---------------------------------------------|-----------------------------------------------|---------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| X$_{\text{initial solution}}$ | Ca | Al | SO$_4$ | AsO$_4$ | Ca | Al | SO$_4$ | AsO$_4$ | SO$_4$+AsO$_4$ | X$_{\text{solid}}$ | pH | log (HAsO$_4$) | X$_{\text{HAsO}_4, \text{aq}}$ |
| 0.00 | 2.35 | 0.75 | 1.14 | 0.00 | 6.0 | 1.9 | 2.9 | 0.0 | 2.9 | 0 | 11.53 | 0 | 0 |
| 0.03 | 2.35 | 0.74 | 1.09 | 0.05 | 6.0 | 1.9 | 2.8 | 0.1 | 2.9 | 0.04 | 11.53 | -5.17 | 0.0018 |
| 0.07 | 2.31 | 0.71 | 1.03 | 0.11 | 6.0 | 1.8 | 2.7 | 0.3 | 2.9 | 0.09 | 11.52 | -5.12 | 0.0051 |
| 0.10 | 2.31 | 0.71 | 0.99 | 0.14 | 6.0 | 1.8 | 2.6 | 0.4 | 2.9 | 0.12 | 11.51 | -4.76 | 0.0053 |
| 0.30 | 2.33 | 0.65 | 0.79 | 0.34 | 6.0 | 1.7 | 2.0 | 0.9 | 2.9 | 0.3 | 11.43 | -4.82 | 0.0051 |
| 0.60 | 2.08 | 0.63 | 0.49 | 0.55 | 6.0 | 1.8 | 1.4 | 1.6 | 3.0 | 0.53 | 11.48 | -4.76 | 0.0078 |
| 0.80 | 2.30 | 0.66 | 0.43 | 0.80 | 6.0 | 1.7 | 1.1 | 2.1 | 3.2 | 0.65 | 11.52 | 5.2 | 0.0203 |
| 1.00 | 2.11 | 0.45 | 0.00 | 1.12 | 6.0 | 1.3 | 0.0 | 3.2 | 3.2 | 1 | 11.54 | -4.85 | 1 |

Fig 1. X-ray diffractograms of the solid solution series of AsO$_4$-ettringite and SO$_4$-ettringite. a, b, c, d, e, f, g, and h correspond to the samples with X$_{\text{solid}}$ of 0, 0.04, 0.09, 0.12, 0.30, 0.53, 0.65, and 1.00, respectively.

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length-to-diameter ratio was lower. Typical ettringite rods dominated when As contents in samples were low (<0.3), while some irregular particles attached to the rods with short length at higher As content. The irregular particles also contained the same elements with the prisms, which were showed from EDS mapping (Fig 3).

Oxyanion speciation could be confirmed by Fourier transform infrared (FTIR) spectroscopy. Fig 4 shows the spectra of the solid solution series of AsO$_4$–SO$_4$–ettringite. The assignments of vibration are shown in Table 3. As indicated by the peak intensities, the SO$_4$
concentration in the solid solutions decreased with the increase in the solid phase AsO$_4$ concentration. The FTIR spectra of solid solutions exhibited an As–O stretching peak at 855 cm$^{-1}$, which was higher than 810 cm$^{-1}$ reported by Siebert H. [28]. AsO$_4$$^{3-}$ was protonated to form HAsO$_4$$^{2-}$, which caused the As–OH symmetric stretch to shift to higher wavenumbers [29]. Thus, AsO$_4$$^{3-}$ substituted SO$_4$$^{2-}$ inside the channels in the form of HAsO$_4$$^{2-}$, which was also

Fig 4. FTIR spectra of the solid solution series of AsO$_4$–ettringite and SO$_4$–ettringite. a, b, c, d, e, f, g, and h correspond to the samples with $X_{\text{solid}}$ of 0, 0.04, 0.09, 0.12, 0.30, 0.53, 0.65, and 1.00, respectively.

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Table 3. IR spectra of the solid solution series of AsO$_4$–ettringite and SO$_4$–ettringite and band assignments.

| Frequency (cm$^{-1}$) | Vibrations          |
|----------------------|---------------------|
| 553                  | Al(OH)$_6$          |
| 619                  | SO$_4$              |
| 855                  | HAsO$_4$            |
| 1112                 | SO$_3$              |
| 1421                 | Possible CO$_3$     |
| 1668                 | H$_2$O              |
| 3432                 | H-bonded OH         |
| 3635                 | Non-H-bonded OH     |

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demonstrated in dissolution experiments because HAsO$_4^{2-}$ was the dominant form of arsenic in the equilibrated solutions. Strong and broad OH bands around 3432 cm$^{-1}$ and 2950 cm$^{-1}$ developed with increases in solid phase AsO$_4^{3-}$ concentration, and the new band (around 2950 cm$^{-1}$) may have been due to the formation of H-bonds between AsO$_4^{3-}$ and structural OH or H$_2$O. Possible weak carbonate bands at 1421 cm$^{-1}$ existed in the spectra [30, 31], which could indicate carbonate contamination, but in less than 5%, because no compound containing carbonate was observed from the X-ray diffractograms.

**Solid solution solubility products**

The ion concentrations in solution of the dissolution experiments were shown in Table 4. And the Ca:Al:SO$_4$3:AsO$_4$ ratios in solution were different from those of the solid, suggesting non-stoichiometric dissolution. This was expected, since the presence of secondary phases (Ca-As compound, gypsum and Al-hydroxide) leaded to reduction of dissolved Ca, Al, SO$_4$ and AsO$_4$ concentrations in solution.

The chemical speciation of the ions and saturation index (SI) calculations were performed using the geochemical speciation model Visual MINTEQ 3.1. Activity coefficients of aqueous species were calculated with the geochemical speciation model Visual MINTEQ 3.1 using the Davies equation:

$$\log g_i = -AZ_i \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.24I \right)$$ (1)

In the precipitation experiments, the results showed the saturation index (SI) of ettringite, Ca$_4$(OH)$_2$(AsO$_4$)$_3$·4H$_2$O, Ca$_3$(AsO$_4$)$_2$·xH$_2$O at low molar ratio ($X_{initial}$ solution, <0.3), and ettringite, Al(OH)$_3$, boehmite, Ca$_5$(AsO$_4$)$_2$OH, Ca$_3$(AsO$_4$)$_2$·xH$_2$O, diaspor, gibsite, boehmite at higher molar ratio, and Al(OH)$_3$, boehmite, Ca$_5$(AsO$_4$)$_2$OH, Ca$_3$(AsO$_4$)$_2$·xH$_2$O, diaspor, gibsite, without sulfate were above 0. However, ettringite was the only the stable phase except the sample without sulfate. This indicated the content of the other phases was below XRD detection limit even though these phases were present. However, both the XRD result of the sample without sulfate and the saturation index (SI) indicated Ca$_5$(AsO$_4$)$_2$·10H$_2$O was present. In the dissolution experiments, the saturation index (SI) of Al(OH)$_3$, boehmite, Ca$_3$(AsO$_4$)$_2$OH, diaspor, ettringite, gibsite at $X_{solid}$ <0.3, and Al(OH)$_3$, boehmite, Ca$_5$(AsO$_4$)$_2$OH, diaspor, ettringite, gibsite, Ca$_4$(OH)$_2$(AsO$_4$)$_3$·4H$_2$O at higher $X_{solid}$ were above 0.

FTIR spectroscopy analysis of the solid samples and chemical analysis of the liquid phase revealed that AsO$_4^{3-}$ substituted for SO$_4^{2-}$ inside the channels in the form of HAsO$_4^{2-}$. Thus, HAsO$_4^{2-}$ will be used for the thermodynamic study of the solid solution series.

**Table 4. Ion concentrations in solution in the dissolution experiments (mmol/L).**

| Sample($X_{solid}$) | Ca  | Al  | SO$_4$ | AsO$_4$ | pH  | log(HAsO$_4$) | $X_{HAsO_4,aq}$ |
|----------------------|-----|-----|--------|---------|-----|---------------|-----------------|
| 0.00                 | 2.984 | 1.032 | 5.261  | 0.000   | 10.85 | 0             | 0               |
| 0.04                 | 3.004 | 1.010 | 5.105  | 0.020   | 10.80 | -5.3          | 0.0019          |
| 0.09                 | 2.692 | 0.857 | 4.452  | 0.081   | 10.90 | -4.89         | 0.0053          |
| 0.12                 | 2.677 | 0.811 | 4.067  | 0.088   | 10.97 | -4.91         | 0.0056          |
| 0.30                 | 2.530 | 0.842 | 4.315  | 0.094   | 11.09 | -4.94         | 0.0049          |
| 0.53                 | 1.745 | 1.912 | 2.902  | 0.131   | 11.32 | -4.87         | 0.0082          |
| 0.65                 | 1.836 | 2.206 | 1.268  | 0.160   | 11.34 | -4.86         | 0.0186          |
| 1.00                 | 1.751 | 1.579 | 0.000  | 0.174   | 11.41 | -5.06         | 1               |

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The solubility products of the solid solution series was calculated according to the following reaction:

$$\log K_{sp} = 6 \log \{Ca^{2+}\} + 2 \log \{Al(OH)_4^{-}\} + 3\{x \log \{HAsO_4^{2-}\} + (1-x)\log \{SO_4^{2-}\}\}$$
$$+ 4 \log \{OH^-\} + 26 \log \{H_2O\}$$

The curly brackets {} denote aqueous activities. The $K_{sp}$ calculated are shown in Fig 5. The calculated AsO$_4^{2-}$-ettringite and SO$_4^{2-}$-ettringite solubility products change as a function of $X_{HAsO_4}$ for mixed phases, with a linear correlation between $\log K_{sp}$ and $X_{HAsO_4}$. This finding indicates that solid solutions exist. Solubility calculations of all precipitation and dissolution experiments resulted in a mean $\log K_{As\text{-ettringite}} = -48.4 \pm 0.4$ and $K_{SO_4\text{-ettringite}} = -43.9 \pm 0.6$. The solubility of SO$_4^{2-}$-ettringite in the current study was higher than that determined by Barbara and Thomas (-44.9) [14, 32], which could be due to a small CO$_2$ amount in the system that lowers the pH. Certainly other factors, such as the choice of the activity coefficient model, analytical errors, and the presence of other complexes not included in the activity calculations, may affect estimates based on minimizing the variance in $K_{sp}$.

Fig 5. Solid mole fraction/solubility products plot for the system HAsO$_4^{2-}$-ettringite and SO$_4^{2-}$-ettringite solid solution at 25°C. The calculated $K_{sp}$ of the solid solutions fits best to the nonideal model.

[Link](https://doi.org/10.1371/journal.pone.0182160.g005)
The aqueous solubility of the binary solid solution system HAsO$_4$$^-$-ettringite and SO$_4$$^-$-ettringite could be predicted by plotting the Lippmann’s solidus and solutus relationships on the ordinate against two superimposed scales, i.e., $X_{\text{HAsO}4}$ and $X_{\text{HAsO}4,aq}$, on the abscissa, which could provide the solid-phase and aqueous-phase compositions for a series of possible thermodynamic equilibrium states [33–35]. In this case, the solidus and solutus equations can be expressed as follows:

$$
\Sigma \Pi_{eq} = \{\text{Ca}^{2+}\}^6\{\text{Al(OH)}_4^{-}\}^2\{\text{SO}_4^{2-}\} + \{\text{HAsO}_4^{2-}\}^3\{\text{OH}^-\}^4\{\text{H}_2\text{O}\}^{26}
$$

and

$$
\Sigma \Pi_{eq} = \frac{1}{K_{\text{HAsO}4}\gamma_{\text{HAsO}4} + K_{\text{SO}_4}\gamma_{\text{SO}_4}}
$$

where the curly brackets {} denote aqueous activities; $X_{\text{HAsO}4}$ and $X_{\text{SO}_4}$ are the mole fractions of HAsO$_4$ and SO$_4$ ($X_{\text{SO}_4} + X_{\text{HAsO}4} = 1$) in the solid, respectively; $X_{\text{HAsO}4,aq}$ and $X_{\text{SO}_4,aq}$ are the activity fractions of HAsO$_4$$^-$ and SO$_4$$^-$ ions in the aqueous solution, respectively; $K_{\text{HAsO}4}$ and $K_{\text{SO}_4}$ are...
$K_{SO_4}$ are the solubility products of pure HAsO$_4$–ettringite and SO$_4$–ettringite, respectively; and $\gamma_{HAsO_4}$ and $\gamma_{SO_4}$ are solid activity coefficients.

The solid-phase activity coefficients determined from the modified Guggenheim regular excess free energy model [36] can be expressed as follows:

\[
\ln \gamma_{HAsO_4} = X_{SO_4}^2 [a_0 - a_1 (3X_{HAsO_4} - X_{SO_4}) + a_2 (X_{HAsO_4} - X_{SO_4})(5X_{HAsO_4} - X_{SO_4}) + \ldots] \]  

(5)

\[
\ln \gamma_{SO_4} = X_{HAsO_4}^2 [a_0 - a_1 (3X_{SO_4} - X_{HAsO_4}) + a_2 (X_{SO_4} - X_{HAsO_4})(5X_{SO_4} - X_{HAsO_4}) + \ldots] \]  

(6)

Regular nonideal solid solutions only need one Guggenheim fitting parameter ($a_0$), which was determined by the MBSSAS code [33, 37]. A value of $a_0 = 1.69$ was obtained. Thus, Eqs 5 and 6 can be simplified as follows:

\[
\ln \gamma_{HAsO_4} = X_{SO_4}^2 a_0 \]  

(7)

\[
\ln \gamma_{SO_4} = X_{HAsO_4}^2 a_0 \]  

(8)

The Lippmann diagram for this system at 25˚C is shown in Fig 6. The calculated $\Sigma\Pi$ of the solid solution series fits best to the nonideal model.

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**Fig 7. Solid mole fraction/aqueous activity fraction plot for the system HAsO$_4$/SO$_4$–ettringite solid solutions at 25˚C.**

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The pure HAsO$_4$$^-$-ettringite and SO$_4$$^2-$-ettringite endmember solubility products in this system differ by four orders of magnitude. As a result, a strong preferential distribution of the less soluble endmember toward the solid phase was observed. This expression (Eq 9) can be used to construct a $X_{\text{HAsO}_4}$–$X_{\text{HAsO}_4,\text{aq}}$ plot (Fig 7), which describes the coexisting compositions of solid and aqueous solutions under equilibrium conditions.

$$X_{\text{HAsO}_4} = \frac{K_{\text{SO}_4}\gamma_{\text{HAsO}_4,\text{aq}}}{(K_{\text{SO}_4}\gamma_{\text{SO}_4} - K_{\text{HAsO}_4}\gamma_{\text{HAsO}_4})X_{\text{HAsO}_4,\text{aq}} + K_{\text{SO}_4}\gamma_{\text{SO}_4}}$$ (9)

Fig 7 shows that the $X_{\text{HAsO}_4}$–$X_{\text{HAsO}_4,\text{aq}}$ curve approximates to two straight lines forming a right angle, which implies that HAsO$_4$$^-$-poor aqueous solutions are in equilibrium with HAsO$_4$$^-$-rich solid phases in a wide $X_{\text{HAsO}_4}$ range.

In summary, ettringite containing SO$_4$$^2-$ or HAsO$_4$$^2-$ has been synthesized, and its thermodynamic data were first published. The results revealed that HAsO$_4$$^-$-ettringite and SO$_4$$^2-$-ettringite solid solutions exist and that this solid solution had HAsO$_4$$^-$-poor aqueous solutions in equilibrium. This finding implies that ettringite (AFt-phase) may play an important role in AsO$_4$$^3-$ solidifying mechanisms in the cement matrix and should be considered in AsO$_4$$^3-$ leaching modeling projects.

**Supporting information**

S1 File. X-ray diffraction data of the solid solution series of AsO$_4$$^-$ and SO$_4$$^2$-ettringites. a, b, c, d, e, f, g, and h correspond to the samples with $X_{\text{solid}}$ of 0, 0.04, 0.09, 0.12, 0.30, 0.53, 0.65, and 1.00, respectively. (ZIP)

S2 File. FTIR spectral data of the solid solution series of AsO$_4$$^-$ and SO$_4$$^2$-ettringites. a, b, c, d, e, f, g, and h correspond to the samples with $X_{\text{solid}}$ of 0, 0.04, 0.09, 0.12, 0.30, 0.53, 0.65, and 1.00, respectively. (ZIP)

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