

## Arsenate interactions with CaO: Formation of johnbaumite

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In hyperalkaline environments such as concretes and alkaline wastes, the aqueous geochemistry of arsenate should be controlled by reactions of arsenate ions with alkaline phases such as portlandite, calcite and ettringite. This should result in the formation of surface complexes, and/or solid solutions of metal-arsenate precipitates. At present, insufficient thermodynamic data is available to facilitate prediction of Ca-arsenate precipitates. In addition, little spectroscopic data is available for As(V) interactions with Ca mineral phases or for Ca-arsenate precipitates. The present study examined the sorption of arsenate by CaO. Examination of reaction products with direct physical methods (XRD, SEM, FTIR, Raman and XAS) indicated the formation of johnbaumite ( $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ ).

### Materials and methods

Adsorption experiments were conducted by reacting 0.1 g of reagent grade CaO, with arsenate (AsV) (0–3.6 mM) for 24 h. Chemical analyses of the solutions were made by Inductively Coupled Plasma spectroscopy. The solid reaction products were examined with vibrational spectroscopy (FTIR and Raman), Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques.

In a different sorption experiment, CaO was exposed to  $\text{AsO}_4$  concentrations (71.4 mM) in an attempt to precipitate a calcium arsenate mineral phase. The reacted solids were characterized for their crystal structure (XRD) and arsenate coordination (FTIR and EXAFS).

### Results and discussion

Lime readily formed portlandite, when it was allowed to react with water, which may indicate

that during sorption reactions As(V) actually interacted with portlandite. For the remainder of this abstract, portlandite refers to the CaO phase.

Arsenate reactions with portlandite (As(V) < 3.6 mM) resulted in a decrease in aqueous phase Ca(II) concentrations. In all samples examined, As(V) was below the detection limit (< 1  $\mu\text{M}$ ) and the equilibrium pH remained constant ( $\sim 12.6$ ). XRD patterns of the reacted solids showed that the dominant solid phase in the samples was portlandite followed by traces of calcite. No new minerals were observed in these XRD studies. Interestingly the peak widths corresponding to portlandite increased with increases in the sorbed As(V). However, at very high initial As concentrations (As(V)  $\sim 70$  mM), the XRD patterns of the solid precipitate indicated the presence johnbaumite. SEM studies showed that portlandite was fine grained (< 1  $\mu\text{m}$ ) and upon reaction with  $\text{AsO}_4$  solutions portlandite crystals did not exhibit any recognizable changes in morphology. Saturation index calculations for the solution in equilibrium with these samples were difficult to estimate, since As(V) were below detection.

Raman and IR studies of As(V)-reacted CaO showed distinct splitting in the peaks corresponding to As-O  $\nu_3$  vibrations. Peaks attributed to As-O vibrations were observed at 885, 879, 837, 812 (broad)  $\text{cm}^{-1}$  for samples with low sorbate concentrations. The position of these peaks remained stable with further increases in As(V) concentration; however, new shoulders were developed at 905 ( $\pm 5.0$ )  $\text{cm}^{-1}$  and 795 ( $\pm 10.0$ )  $\text{cm}^{-1}$ . These results indicated that the  $\nu_1$  vibrations were close to 800  $\text{cm}^{-1}$ , suggesting that the As(V) tetrahedron was linked to Ca and remained unprotonated in this sample. Hydroxyl stretching frequencies of Ca-OH (3642  $\text{cm}^{-1}$ ) in the reacted solids decreased with increases in solid phase As(V) concentrations. Other vibrational modes of Ca-O (659, and 527  $\text{cm}^{-1}$ ) however, did not exhibit major changes. These

vibrational spectra, combined with XRD indicate that As(V) formed inner-sphere complexes with Ca by replacing the surface hydroxyls of portlandite.

One of the As(V)-reacted CaO samples was studied using XAS (solid phase As(V) = 0.172 mol kg<sup>-1</sup>). The Fourier transform of this sample had 4 distinct peaks at 1.35, 2.8, 3.2, and 4.5 Å (uncorrected for phase). The fits for the Fourier filtered first peak gave a coordination of 3.73 for first shell O at 1.688 Å. The  $\sigma^2$  values obtained for these As-O fits were close to 0.0005. This low value for Debye-Waller parameter may indicate that all As-O bond lengths were similar. The next major peak at 2.88 Å (not corrected for phase) in Fourier transforms corresponded to the second neighbour Ca (first shell Ca). However, these fits for Ca produced very small  $\sigma^2$  values ( $\sim 0$ ) when coordination number (N) of Ca was floated (N  $\sim 0.35$ ). Since model compounds showed relatively high values for  $\sigma^2$  ( $\sim 0.005$ – $0.01$ ), N is expected to be larger than the obtained value. On the basis of this preliminary data fitting, N for Ca was fixed at 1.0 and 2.0. The final fits were found to be good for both values of N. This leads to an uncertainty in the value of N for Ca atoms at this distance. Calcium atoms were also identified in the second and third shells at 3.55 and 3.70 Å, with a smaller  $\sigma^2$  value ( $\sim 0.004$ ) for the later (corresponding to a peak at 3.2 Å). Arsenic as a backscatterer was also identified at 4.94 Å. These bond distances for different backscatterers indicate that the As(V) tetrahedron formed bidentate mononuclear (Ca at 3.22 Å); and bidentate binuclear and/or monodentate complexes (Ca at 3.55 and 3.70 Å) with Ca polyhedra. However, it was difficult to ascertain, whether johnbaumite actually precipitated at these low solid phase concentrations of As(V).

Lime, when reacted with 71.4 mM of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O for 24 h in deionized water (suspension density: 4 g L<sup>-1</sup>), at ambient temperature, and in the presence of atmospheric CO<sub>2</sub>; precipitated johnbaumite Ca<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>(OH), an arsenate analogue of apatite. These precipitated solids were fine grained < 1 μm (SEM), and their XRD patterns were very similar to johnbaumite. Chemical composition of the solutions in contact with johnbaumite precipitate showed 10.69 mM of As(V) and very small concentrations of Ca (< 0.05 mM).

Vibrational spectroscopic studies of these precipitates produced a sharp OH peak at 3562 cm<sup>-1</sup> corresponding to hydroxyls in the sample. A small and broad band was observed at around 3058 cm<sup>-1</sup> corresponding to crystalline water. Its low intensity indicated a relatively low water content in the precipitated solids. The position of this band indicates that the structural water is coordinating to As(V), since its frequencies are similar to the water around aqueous As(V). The presence of water in these samples (as indicated by OH bending vibrations) may indicate the probable presence of another hydrated calcium arsenate impurity or poorly crystalline johnbaumite. Arsenate ions in this sample exhibited splitting of their ν<sub>3</sub> vibrations producing peaks at 940, 877, 859, 834 and 824 cm<sup>-1</sup>. Symmetric stretching vibrations of As-O-X (X = Ca, H, or water) were observed at 798 and 736 cm<sup>-1</sup>, which may correspond to As(V) polyhedra bonding with a Ca; or relatively large number of Ca atoms/protons respectively. As-O asymmetric bending vibrations are difficult to interpret since they produced a broad band at 470 cm<sup>-1</sup> in IR. Ca-OH librational vibrations at 659 cm<sup>-1</sup> in unreacted portlandite shifted to 630 cm<sup>-1</sup> in johnbaumite, indicating strong interactions between Ca and As(V) polyhedra.

EXAFS analysis of johnbaumite showed 4 distinct peaks in the Fourier transform. The peak at 1.35 Å (uncorrected for phase) corresponds to first shell oxygens, 2.8 to Ca, 3.2 to Ca, and 3.85 to As. The Fourier filtered first peak fits well with four oxygens in the first shell around As at an average distance of 1.688 Å. Data fits for this shell produced a relatively large  $\sigma^2$  value (0.0015). This may indicate non-uniform As-O bond distances in the As(V) tetrahedra. Fourier filtered data for the peaks at 2.8, 3.2, and 3.85 Å were fit well with 1.08 Ca, 1.91 Ca and 1.06 As, and the obtained  $\sigma^2$  values were in the range observed for calcium arsenate model compounds.

In summary, the As(V) tetrahedra participates in extensive bonding and is distorted, as is evidenced by vibrational spectra and  $\sigma^2$  value of As-O shell. In johnbaumite, As(V) forms both bidentate mononuclear, bidentate binuclear and/or mononuclear complexes.