

Arsenate uptake by brucite in the presence of silicate at alkaline pH condition

Eistine Opiso^{1*}, John Charnock², Tsutomu Sato¹, Chiya Numako³, Sohtaro Anraku¹, Yoneda Tetsuro¹

¹Hokkaido University, ²Manchester University, ³Tokushima University

The generation of alkaline pore water during the chemical weathering of slag and coal fly ash recycled as cement aggregates can release toxic anions such as arsenic, fluorine, chromium and boron from these alkaline waste materials. Therefore, the need to address this environmental issue is very important.

This work investigated the effectiveness of brucite as possible sorbent of anionic species in alkaline condition using As(V) as an analog. The sorption experiments were performed during and after mineral formation in batch experiments and conducted in the presence of silicate which is an ubiquitous anion in the natural environment. Solutions containing 0.03 M of Mg(NO₃)₂·6H₂O (90 mL) and 0.03 M of Na₂SiO₃ (10 mL) were mixed and adjusted to pH 11 by adding 5 M NaOH. For coprecipitation experiments, appropriate amounts of Na₂HAsO₄·7H₂O solutions were added instantaneously during the mixing of Mg and Si solutions (with a final As concentration of 10 and 100 ppm, respectively) and were shaken for 7 days. In the case of adsorption experiments, As(V) was added after minerals synthesis (7 days) and the suspension was shaken for additional 7 days prior to collection and analysis. The effect of temperature on the sorption behavior of As(V) by brucite was also carried out at 25, 50 and 75 degrees Celsius. To understand arsenic association with brucite, leaching test using phosphate bearing solution was conducted. The various binding mechanisms of adsorbed and coprecipitated arsenic with brucite was investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy while the speciation of arsenic was determined from the XANES spectra.

The results of sorption experiments after 7 days of reaction time revealed that brucite have very large uptake capacity for As(V) and completely removed arsenic from the solution even in the presence of silicate as competing anion. However, the results of desorption experiments of coprecipitated and adsorbed As(V) by brucite at 25 degrees Celsius indicated that arsenic can easily be released from the brucite surface (more than 80%) by anions with stronger affinity than As(V). The absence of second shell bonding environment for arsenic detected by EXAFS in these samples may prove that As(V) was only adsorbed via outer-sphere complexation in the brucite surface. At higher temperature, the high desorption rate of As(V) was reduced significantly by as much as 40 percent. This strong binding of sorbed arsenic at higher temperature may imply that As(V) could either be imbedded in the brucite surface by displacing the hydroxyl group coordinated to Mg or forming inner-sphere complexes with near surface-exposed Mg. These findings were confirmed by the results of EXAFS analysis which detected arsenic to be 4-fold coordinated to oxygen and surrounded by Mg shells only. However, the presence of amorphous and unknown crystalline phase on these samples which could probably be attributed to Mg-arsenate precipitate may also account for this As-Mg bonding environment.

The results of this experiment highlighted the large uptake capacity of brucite for arsenic and can

limit arsenic mobility at hyperalkaline condition. However, the long-term immobilization of arsenic by brucite cannot be guaranteed since it can only retain arsenic via outer-sphere complexation at temperatures typical of most hydrogeological environments and can easily be released by anions with stronger affinity .

Keywords: Arsenate, Brucite, hyperalkaline, Slag, Coal fly ash