



Experiment title: Geochemistry of oxyanions in Alkaline Matrices: An XAS Study of Binding Mechanisms of Antimony in Alkaline Solid Wastes

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Report:

Introduction: This project aims to identify the mechanisms that control leaching of Sb in alkaline matrices. Industrial residues from high temperature processes contain amongst the highest concentrations Sb found anywhere. All these wastes develop an alkaline porewater pH and the behaviour of Sb is unknown and complex in such matrices. Moreover, the most common procedure to solidify hazardous waste is the inclusion of these wastes in a cementitious matrix. Such an environment is highly alkaline (up to pH 13). Much research has focussed on the behaviour of heavy metals of high concentration and known toxicity in a variety of waste such as Zn, Pb, Cd,... Sb, however, is less studied. It forms oxyanions in solution, the most important one being antimonate: $\text{Sb}(\text{OH})_6^-$. In a recent literature review (Cornelis et al., 2008), we demonstrated that leaching of oxyanions in alkaline wastes are controlled by either precipitation of the calcium metalate, in this case calcium antimonate, or adsorption or solid solution to abundant minerals. To improve understanding of the geochemical mechanisms that govern the Sb-leaching behaviour in alkaline wastes, calcium antimonate precipitation was studied as well as fundamental interactions of Sb with 4 selected minerals: portlandite ($\text{Ca}(\text{OH})_2$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), Calcium silicate hydrates (CSH), and monosulphate ($\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 32\text{H}_2\text{O}$). This knowledge was then applied to MSWI bottom ash and a cement paste spiked with Sb(V). This knowledge could assist in the long-term leaching prediction of these wastes and possibly lead to treatment methodologies.

Experiments: The research was supported by Sb-K edge EXAFS analysis ($E_0=30.491$ keV) of amorphous and crystalline calcium antimonate, sorption complexes of Sb(V) on the aforementioned minerals, and Sb in MSWI bottom ash and a spiked ordinary Portland cement (OPC) paste. For analysis of data we kindly received support of Dr. Grandjean, DUBBLE beamline. The high energy adopted was at the top range possible to attain by the Si(111) monochromator. As a result it was not possible to achieve a very high resolution required for XANES analysis. EXAFS data quality, on the other hand, was very high. Thermal contributions to the Debye-Waller factors were reduced significantly by adopting a cryostat at 12K. In this way, long range information up to 8\AA became available. In total 14 samples were analysed, using 52 successful runs of 1 hour.

Brief summary of results: Figure 1 shows the Fourier Transform (FT) modulus (k^3 weighted) of amorphous (24h aged) and crystalline (60 days aged) calcium antimonate. Dr. Grandjean (DUBBLE) initiated also Rietveld analysis of the crystalline form and it appeared that the formula was not $\text{Ca}[\text{Sb}(\text{OH})_6]_2$, as generally thought in literature, but a more complex structure called *pyrochlore* structure. Fig 1 shows the typical first peak at 1.97\AA corresponds to a hexagonal coordination of pentavalent Sb with 6 oxygens, found through FEFF fitting. The second peak is probably an overlap of Sb and Ca peaks that is much more ordered in the crystalline analogue. Sb-Sb and Sb-Ca bonds found through FEFF fitting roughly corresponded to bond distances found through Rietveld analysis, although FEFF-fitting indicated a small but significant difference between Ca-Sb and Sb-Sb bonds, which is not expected in a cubic pyrochlore structure. Similar Sb-Sb and Ca-Sb distances were found in the amorphous analogue. Not only does this suggest that the amorphous analogue is a true precursor of crystalline calcium antimonate and no real conformation change occurs during aging, but also that FEFF fitting of the 60 days aged product is complicated by the presence of some amorphous material and that aging was therefore not yet complete after 60 days.

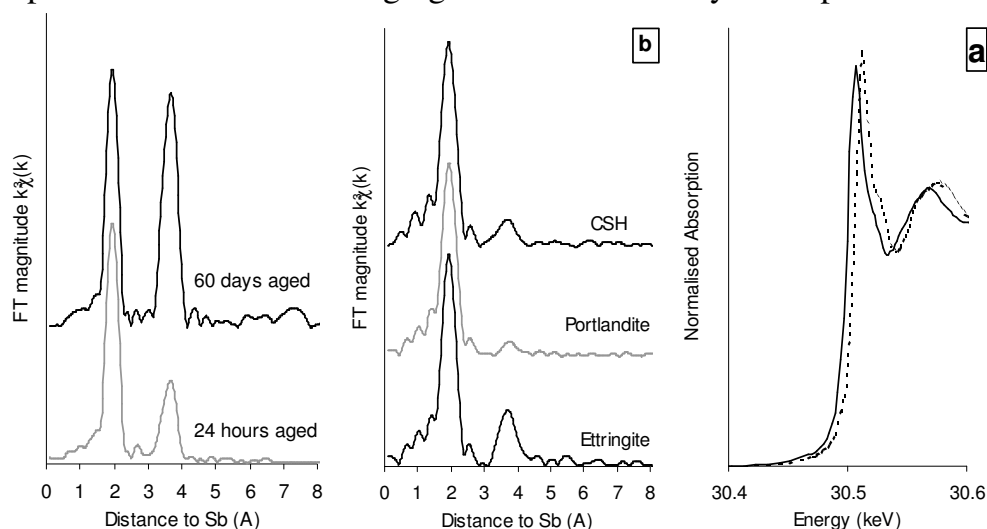


Fig. 1

Fig. 2

Fig. 3

Fig. 2 shows FT moduli of sorption complexes. The second peak again is an overlap of Ca and Sb shells but other evidence indicated that these could not belong to calcium antimonate that could possibly have precipitated on the surfaces of these minerals. The Ca-shells of portlandite and ettringite FT moduli therefore correspond to a binding to the minerals themselves. Moreover, the FEFF fitted distance was calculated using bond-valence theory not to correspond with a bond inside the structure of ettringite or portlandite, but to the surface of

these minerals. The Ca-shell therefore corresponded to surface adsorption, which is relevant for leaching prediction because it is described with totally different thermodynamics than a bond inside the structure.

In case of CSH there was a slight shift in the E_0 to lower values, also seen in fig 3 which shows the EXAFS pattern of Sb in a Sb(V) spiked OPC paste compared to that of calcium antimonate (dotted lines). OPC pastes are known to contain high CSH amounts. This suggests Sb(V) is partly reduced in the presence of CSH to Sb(III) which is much less mobile than Sb(V). This could explain the high affinity of Sb for CSH found in adsorption experiments. This reduction mechanism, however, requires more research because reduction reactions catalysed by CSH are unprecedented in literature.

Other spectra have only underwent minor analysis. The E_0 value of most readings in most Sb(V) spiked cements confirmed a partial reduction of Sb(V). Moreover, this reduction was confirmed using extraction tests and speciation analysis by HPLC-ICP-MS. Sb(III) was also detected in the same way in MSWI bottom ash, accompanied by a decrease in E_0 .

Future works: These will include a more thorough analysis of measured spectra. The sorption complex on monosulphate will be discussed as well as the chemical environment of Sb in differently carbonated OPC paste fractions. Carbonation, the reaction with atmospheric CO_2 , is known to alter leaching characteristics of cement pastes profoundly and therefore deserves attention. The binding mechanism in these pastes is believed to be calcium antimonate precipitation accompanied by adsorption to CSH. For both measurements, standard spectra are now available and semi-quantitative analysis to determine the dominating mechanism controlling Sb is in principle possible. This can be performed by making linear combinations of standard spectra fitted to the spectra of Sb in OPC paste. The reduction of Sb(V) was, however, not expected and this complicated such analyses. Assistance of experts will therefore be sought to determine future research strategies.

Publications: The results summarized above will be published in a Ph.D. thesis entitled: *Cornelis, G., 2008. Leaching mechanisms of oxyanionic metal and metalloid species in alkaline solid wastes. KULeuven.*

In addition the results on calcium antimonate will be part of a presentation: *2nd international workshop on Mechanisms and modelling of waste/cement interactions, October 12-16, 2008, Le Croisic France.*

the proceedings of which will be published in an international journal (It is not yet known which one).

Future publications are in preparation but require more analysis of the data at hand.

Of course, full proper will be given to ESRF and DUBBLE staff. In fact, due to his help with analysis of EXAFS spectra, Dr. Grandjean will be co-author of several publications.