Geology, Geophysics & Environment • 2012 • Vol. 38 • No. 4 • 545–546

DISSOLUTION OF MIMETITE $Pb_5(AsO_4)_3Cl$ IN MALIC ACID SOLUTIONS

Piotr TUREK, Tomasz BAJDA & Maciej MANECKI

AGH University of Science and Technology, Faculty of Geology,
Geophysics and Environmental Protection, Department of Mineralogy,
Petrography and Geochemistry; al. Mickiewicza 30, 30-059 Krakow, Poland

Pentavalent arsenic and lead are presently considered to be one of the major soil pollutants. Theseand widespread elements t occur in very low concentrations. Their natural concentrations in soils and waters are the results of leaching from rocks containing Pb and As(V) minerals. However, concentration of these elements in environment can be drastically raised by anthropogenic processes, such as coal combustion, mining, metallurgy, pesticides application or glass manufacturing. Leaching of Pb and As(V) from soils and residues containing lead arsenates may cause contamination of the pedosphere.

Arsenic and lead minerals are relatively numerous but in nature occur occasionally. The most common secondary As(V) and Pb minerals are schultenite ($PbHAsO_4$), mimetite ($Pb_5(AsO_4)_3Cl$), hydroxymimetite ($Pb_5(AsO_4)_3OH$) and sahlinite ($Pb_{14}(AsO_4)_2O_9Cl_4$), though mimetite is considered to be prevalent (Bajda 2011). Mimetite, as a slightly soluble and thermodynamically stable mineral, especially at pH above 5 characteristic to natural waters and soil solutions, is considered to have great possibilities to be applied in remediation procedures (Bajda 2010). Mobility and bioavailability of lead and arsenic can be controlled by mimetite crystallization at mentioned pH range, then important aim arises, to determine stability of $Pb_5(AsO_4)_3Cl$ at pH below 5. Solubilization of extremely insoluble apatite through efficient ligand-promoted organic complexation of metals has been observed before, which suggests that mimetite dissolution may be similarly enhanced by low-molecular-weight organic acids (LMWOAs) (Bajda 2011). The influence of LMWOAs on mimetite stability was investigated, but malic acid was not included in these experiments, which is a purpose of this research.

Batch dissolution experiments were carried out with use of mimetite synthetized of $Na_2HAsO_4 \cdot 7H_2O$, KCl and $Pb(NO_3)_2$. Malic acid concentrations selected to these experiments were 0.1 mM; 0.5 mM; 1 mM; 5 mM; 10 mM. As a control there were used three non-organic solutions with pH set using HNO_3 to be similar to the primary pH measured in certain organic acid solutions. The purpose of performing non-organic samples was to compare effect of pH on mimetite dissolution at parallel pH value in organic and inorganic acid solutions. Duration of the experiment was 120 hours and samples were taken after 24, 48, and 120 hours. The total Pb concentration was determined by atomic absorption spectroscopy (AAS) and pentavalent As concentration were determined colorimetrically by the molybdene blue method (UV-Vis).

Data obtained for the experiment allowed to notice that the state of equilibrium was reached before 24 hours regardless of pH and organics concentration. It was found that lower values of pH enhance mimetite dissolution, which is confirmation of previously run studies (Bajda 2011, Magalhales & Silva 2003). Solubility of mimetite expressed by the amount of As(V) and Pb released to the solution was significantly higher at low pH. Similar correlation was observed investigating solubility and acid concentration: the higher the acid concentration is, the more elements were released to the solution. The total concentration of As(V) in 10 mM acid solution was about 20 times greater than in 0.1 mM. For lead this ratio was lower and equaled 11.4.

This mechanism mainly depends on free protons concentration and the process of protonation, which is proved by released curves for controls where samples containing inorganic nitric acid instead of malic also exhibit higher solubility of mimetite at low pH. However, because of Pb-malate complexes formation, presence of organic anions can noticeably increase the scale of mimetite decomposition. Complexation and protonation of mimetite surface are complementary and additive processes, which speeds up and intensifies mimetite dissolution. The difference between total As(V) in samples and controls was 12.5% for 5 mM and 26.5% for 1 mM while for Pb it was respectively 5.6% and 8.6%. This suggests that soil organic acids can potentially liberate Pb and As(V) from mimetite and thereby comprise a probable risk to the groundwater quality.

The research was financed by the AGH University of Science and Technology statutory grant.

REFERENCES

Bajda T., 2010. Solubility of mimetite $Pb_5(AsO_4)_3Cl$ at 5–55^{o}C. *Environmental Chemistry*, 7, 268–278.

Bajda T., 2011. Dissolution of mimetite in low-molecular-weight organic acids and EDTA. *Chemosphere*, 83, 1493–1501.

Magalhaes M.C.F. & Silva M.C.M., 2003. Stability of lead arsenates. *Monatshefte für Chemie*, 134, 735–743.