

Interaction of gypsum with Pb-bearing aqueous solutions

J.M. ASTILLEROS¹, J.D. RODRIGUEZ-BLANCO²,
A. GODELITSAS³, L. FERNÁNDEZ-DÍAZ¹ AND M. PRIETO²

¹Dpto. Cristalografía y Mineralogía. Universidad Complutense de Madrid. E-28040 Madrid, Spain [jmastill@geo.ucm.es, lfdiaz@geo.ucm.es]

²Dpto. de Geología. Universidad de Oviedo, E-30005 Oviedo, Spain [juandiegorodriguez@gmail.com, mprieto@geol.uniovi.es]

³University of Athens, Faculty of Geology and Geoenvironment, Athens, Greece [agodel@geol.uoa.gr]

Sorption of heavy metals on mineral surfaces plays an important role in controlling both the dispersion and accumulation of these pollutants as well their geoavailability and bioavailability in near-surface environments. Among sedimentary rocks-forming minerals, gypsum arises as potentially useful to uptake a broad spectrum of dissolved metals because of the high reactivity of its surfaces and its abundance in nature.

With the aim of investigating the effectiveness of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as a Pb-sequester, we have carried out macroscopic experiments in which 2 g of pure gypsum fragments (selenite variety) millimetre-sized (1.00-1.40 mm) were put in contact with 100 cm³ of Pb-bearing aqueous solutions. The initial concentrations of Pb in the solution were in the range between 10 and 1000 mg/l). Experiments were conducted at room temperature under atmospheric CO₂ pressure in a closed batch type experimental set-up. Independent experimental runs were carried out for each Pb(NO₃)₂ aqueous solution concentration. After specific reaction periods (ranging from 1 minute to a week), crystals were separated from the solution. The evolution of the aqueous solution composition was monitored using AAS, Ion Chromatography, and occasionally ICP-OES. Our experimental results show that the concentration of Pb²⁺ in the solution rapidly decreases during the first minutes of the interaction. The uptaking process takes place by the rapid dissolution of gypsum ($\text{pK}_{\text{sp}} = 4.58$) and the simultaneous formation of an anglesite (PbSO₄, $\text{pK}_{\text{sp}} = 7.79$) precipitate (identified by XRD and SEM-EDX) on the gypsum surface. Speciation calculations using PHREEQC (Parkhurst and Appelo, 2000) demonstrate that solutions tend to reach equilibrium with respect to both gypsum and anglesite phases after long interaction periods. The behaviour observed can be interpreted as a result of the coupling between gypsum dissolution and anglesite precipitation. The kinetics and effectiveness of this process is discussed. The macroscopic study is completed with some AFM observations.

References

Parkhurst D.L., and Appelo C.A.J., (2000) User's guide to PHREEQC (version 2). *US Geological Survey Water-Resources Investigations Report 99-4259*, 2000, p. 312.

Toxic metals in runoff from acid sulphate soils

MATS E. ÅSTRÖM

Kalmar University, School of Pure and Applied Natural Sciences, 39182 Kalmar, Sweden (mats.astrom@hik.se)

A massive supplier of toxic metals

A largely unrecognised geogenic source delivering massive amounts of toxic metals to the aquatic environment is presented. The source is a soil type – acid sulphate (a.s.) soil – that cover more than 17 million ha worldwide. This soil is located mainly on coastal plains and is developed when sulphide-rich sediments once formed under anoxic conditions in lakes or oceans are exposed to atmospheric oxygen. The pH of this soil is between 2 and 4.

The awareness of the problem

It is well known that from a.s. soils large amounts of acidity is leached, in particular during heavy rains or snow melting, causing severe acidification of downstream waters and inner estuaries. Associated fish kills have been reported from a variety of regions, including northern Europe, eastern Australia and south-east Asia. The metal problem associated with these soils is, however, largely unrecognised and unknown.

The mechanisms and extent of metal release

The behaviour of chemical elements, including potentially toxic trace metals, in a.s. soil landscapes has been sparsely studied. One exception is the largest a.s. soil occurrences in Europe, found on the coastal plains of western Finland, where a number of hydrogeochemical studies have been carried out. These have shown that the Finnish a.s. soils deliver to the aquatic environment large amounts of highly toxic metals such as Be, Tl and Cd, produces in low order streams concentrations of Al up to 300 mg/L and Mn 20 mg/L, and supplies much larger amounts of metals to the aquatic environment than the entire Finnish industry. Preliminary studies in Asia and others in Australia have indicated similar patterns in tropical and subtropical areas. The mechanisms and extent of the metal release from these nasty but also socioeconomically valuable soils are presented.