Oxidative Dissolution Rate of Aznalcóllar Sulphide Sludge (SW Spain)

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On April 25th 1998, the wall of the tailing dam of Aznalcóllar pyrite mine (SW Spain) failed. As a consequence, 4×10^6 m^3 of sludge covered a farmland and river flat extension of nearly 4×10^7 m^2 in a layer of 5cm to 1m thick.

Although the largest part of the sludge has been removed mechanically, a small percentage remains within the soil and so forms a hazard for ground- and surface water contamination. This abstract focuses on laboratory flow-through experiments done with the objective of defining an oxidative dissolution rate equation of the sludge to perform realistic predictions.

The sludge used in the experiments is rich in Fe (36.44%) and S (39.75%) with significant amounts of Zn (9448μg/g), Pb (7141μg/g), As (5223μg/g), Cu (1968μg/g), Sb (474μg/g), Cd (31μg/g), As (29μg/g) and Bi (47μg/g). It is mainly composed of pyrite (76%) and contains lesser amounts of quartz (8%), gypsum (6%) and clays (10%). A few grains of sphalerite, galena and chalcopyrite were detected by SEM-EDS (Alastuey et al., 1999).

The sludge was not pre-treated before the experiments. However, BET measures were also done to a sample of sludge cleaned with acetone and to another cleaned with acetone and hydrochloric acid in order to see any differences due to the possible formation of sulphates on the pyrite surface. BET measures were also done with two types of gases, a mixture of N2 and He (30% N$_2$) and a mixture of Kr and He (0.1% Kr). No significant differences were observed between the measures and a BET area of 1.4 ±0.2m^2 g^{-1} of sludge has been chosen. The size of particles is quite heterogeneous having an average of (3.9 ±0.2)μm. This size gives a theoretical area of 0.30 ±0.23 m^2 g^{-1} of sludge following Nicholson (1994).

The flow-through experiments have been done at different pH (3, 4 and 5 fixed with 10^{-3}, 10^{-4} and 10^{-5} M HCl solutions) and at different partial pressures of O$_2$(g) (0±0.000007, 0.045±0.009, 4.5±0.045 and 21±1%). Experiments at 0% and 0.045% PO$_2$ have been done in a closed box with and atmosphere equal to the gas used in the experiment.

Different rate values (at different pH and PO$_2$ experimental conditions) have been obtained from iron concentrations at the steady state. Considering the theoretical area corresponding to the amount of pyrite in the sludge an equation rate has been fitted as:

$$R = 10^{-(8.3 \pm 0.3)} [O_2(aq)]^{(0.14 \pm 0.03)} a_{H^+}^{(0.22 \pm 0.07)} \text{ (mol m}^{-2}\text{ s}^{-1})$$

This equation agrees with Nicholson et al (1988) and shows good correlation with their values at higher pH. However, the equation reported here shows a dependence on pH that contradicts the dependence proposed by Williamson and Rimstidt (1994).

From this results it can be deduced that the sludge dissolution rate decreases when oxygen is not easily available. Thus, in less permeable areas where the oxygen diffusion is slow, the sludge oxidation will be slow and will become controlled by the oxygen transport rate.

Although the experiments have been carried out at a very slow flow rate, some elements (Cd, Na, Ba and V) have not been properly measured because they were below the detection limit. The elements Mg, Tl, Pb, Mn, Cr and Al increase their concentration in solution at low oxygen concentration and acidic pH, while Ni increase at high pH. As, Co and Sb have higher concentrations at oxidant and acidic conditions. Finally, Zn and Cu increase their concentrations in oxidant conditions and they have not dependence on pH. The behaviour of Ca is quite random.

There are several reasons that could explain these different behaviours. The determination of the element concentrations is quite difficult because they are close to the detection limits. Moreover, adsorption processes on silicate surfaces could modify the final concentration. Finally, there are other sulphides that are being dissolved. If the oxidation of those metals does not depend on the same way on pH and [O$_2$(aq)] than pyrite, an evolution of Zn, Cu and Pb similar to the Fe evolution cannot be expected. As they are trace minerals, their dissolution does not appear as a simultaneous chemical process, but a process that modifies the main dissolution.

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