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Weathering of the Pyritic Sludge Remaining in the Soil after the Aznalcóllar Accident (SW Spain)

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Introduction

On April 25th 1998, the tailing dam of Aznalcóllar pyrite mine (70km north of Doñana National Park) collapsed and the valleys of the Agrio and Guadiamar rivers were flooded with nearly $4x10^6$ m^3 of sulphide sludge. As a consequence, 4 $x10^7$ m^2 of river flats and farmlands were covered with a blanket of sulphide sludge ranging from 5cm to 1m thick.

The bulk of the sulphide was removed during the months following the failure. However, a percentage of this sludge (0.1 to 10%wt) remains in some areas that are difficult to clean (e.g. gravel soils). These areas are placed in the subsaturated zone, very near to the phreatic level, and they represent a potential source for future pollution.

The rate of dissolution-oxidation of sludge (mol m^{-2} s^{-1}) has been determined as a function of pH and aqueous concentration of oxygen ($[O_{2(aq)}]$, (mol l^{-1})) by means of flow-through experiments and its equation is:

$$r=10^{-(8.3\pm0.3)}\,[O_{2(aq)}]^{(0.14\pm0.03)}\,{}^{a}H_{+}$$

In order to determine the influence of others factors not studied in the flow-through experiments (such as the saturation degree of soils) in the rate of oxidation, as well as the existence of additional metal retention processes, two column experiments have been carried out. The columns have been filled with a mixture of a sandy soil and sludge and a clayey soil and sludge (10% wt of sludge in each column), being the soils the most representative soils of the area affected by the Aznalcóllar accident. Quartz, k-feldspar, hornblende, albite and minor amounts of clay mainly compose the sandy soil, while the clayey soil is basically composed by quartz, calcite and illite, chlorite and kaolinite. At the bottom of the columns a quartzitic sand layer is placed to facilitate the drainage. At different time intervals, a known volume of Millipore MQ water has been added and the lixiviate obtained has been chemically analysed and the pH measured.

Results and Discussion

The pH of sand column drops to values around 2 after 260 days. The experimental values have been compared to the values that would have been obtained if the sludge would have dissolved at the maximum rate regarding aqueous oxygen concentration ($[O_{2(aq)}]$ in equilibrium with atmosphere). The experimental values for Zn, Cd and Co follow the same trend than the expected values. From those results it can be concluded that the oxidation rate in the sand column is maximum and that there are not effective retention processes for Zn, Cd and Co. Those elements are directly released to the media.

At the beginning of the experiment, when pH is higher than 4-4.5, the concentrations of Fe and Al are very low. The saturation indexes shows that the solution is in equilibrium with $Fe(OH)_{3(a)}$ and $Al(OH)_{3(a)}$. The evolution of copper with time suggests the co-precipitation of Cu with $Fe(OH)_{3(a)}$. When pH decreases, these minerals dissolve and the concentrations of Al and Cu increase in solution up to the expected values and in the case of Fe, they not reach the predicted values suggesting the existence of another retention process. Although jurbanite ($AlOHSO_4$) is in equilibrium with solution at pH lower than 4-4.5, it does not control Al concentration in solution.

Na and K concentrations are around the expected values at the beginning of the experiment, but when pH decreases, their concentrations also suffer a significant decrease. The saturation indexes of iron minerals suggest that the mineral in equilibrium with solution at low pH is natrojarosite $(Na, K)Fe_3(SO_4)_2(OH)_6)$. The precipitation of this mineral agrees with the observed decrease of Na and K in solution and with the observed concentrations of Fe and SO_4 always lower than the expected values. This mineral allows the introduction of trace elements in their structure (Scott, 1987) and from values obtained, it is clear that Pb and As precipitates within the structure of jarosite.

The pH of the clay column has a constant value around 7.5 due to the dissolution of calcite and to a bad O_2 diffusion across the column lessening the sludge oxidation-dissolution rate and enhancing metal retention in the soil. The solution is saturated in $Fe(OH)_3$ and in equilibrium with gypsum.

Scott, KM, *American Mineralogist*, **72**, 178-187, (1987).