

WEATHERING OF PYRITIC TAILINGS IN UNSATURATED COLUMNS: EXPERIMENTAL AND REACTIVE TRANSPORT MODELING

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Abstract

Several columns filled up with pyritic tailings were forced to desiccate by heating, and were dismantled at four successive stages of dryness. Porewaters and solid phases collected at different depths were characterized, and the results were interpreted by thermo-hydro-geochemical reactive transport modeling. Oxygen diffusion in the unsaturated zone leads to pyrite weathering and subsequent silicate dissolution. Evaporation at the top of the columns drove capillary upflow and mass transport to the surface, producing a crust of sulfates. This crust, which has also been identified in the field, caused a decrease in the evaporation rate of the columns, and promoted downwards water vapor flux, which condensed at depth and diluted porewater solutes.

Introduction

To prevent weathering and Acid Mine Drainage, sulphide tailings are usually kept under a layer of water during mining operations. However, once the exploitations are abandoned, this layer may disappear due to evaporation, which enhances the access of oxygen to sulfide minerals. This is especially relevant in the case of abandoned mines placed in sub-arid areas, where scarce rainfall favors evaporation and allows the access of oxygen to greater depths into the tailings.

Earlier works focused on the geochemistry of porewaters and mineral phases in the water-saturated and vadose zones of tailings (Blowes et al., 1990; Gussinger et al., 2006, among many others). Also, an increasing number of works include reactive transport modeling (for revision, refer to Mayer et al., 2002). These studies provide snapshots of the spatial variability of the mine tailings geochemistry at different depths or areas, but no data on the evolution of porewaters and solid phases. On the other hand, column experiments have focused on the evolution of effluent waters and mineral association once the experiment has been dismantled (Malmström et al., 2006 and references therein).

The present study is an attempt to study unsaturated pyrite-bearing wastes during weathering taking into account not only vertical variations of porewaters and mineral phases in the tailings profile, but also their time evolution. This is expected to unravel coupled heat, water and gas flow processes and mineral reactions which have not been described to now.

Methods

Ten columns with inner diameter of 14.2 cm, and length of 30 cm were filled with fresh and water-saturated mine tailings from a tailings impoundment. Each column was placed with the top surface at 60 cm below an infrared bulb, used as a heat source. Bulbs were kept switched on throughout the whole experiment, which lasted for 125 days. Water loss by evaporation was controlled by measuring the weight variations of the columns with time.

Variations in the moisture content, mineralogy and porewater chemical composition with depth were investigated at four dryness stages. Each dismantling column was divided in depth into four sub-samples. Solids were separated for SEM and XRD and also for sequential extractions. The extraction of porewater was carried out by squeezing in the three first stages of dryness. Solute concentrations were measured by ICP-AES and ICP-MS, and Fe(II)/(III) by colorimetry. Moreover, the O isotope ratio was determined by equilibrium with CO₂ and subsequent analysis by IRMS.

Reactive transport calculations were performed with CODEBRIGHT-RETRASO (Saaltink et al., 2004). The columns are represented by an initially homogeneous 1D porous medium. The main thermohydraulic processes controlling the evolution of our system are represented in Figure 1. The evolution of water contents was calculated from the calculated liquid and gas pressures through a Van Genuchten retention curve. Vapor pressure is calculated in equilibrium with the liquid taking into account the temperature and solute concentrations. Gas dissolution was always considered in equilibrium. Hydraulic conductivity, diffusivity and the thermal conductivity are considered to change with porosity and water saturation.

From the geochemical point of view, a homogeneous mixture of minerals has been assumed as initial condition. The reactive area of each mineral phase has been obtained by distributing the measured BET specific surface between the different phases according to their volumetric fraction. The initial composition of the column porewaters has been assumed to correspond to one of the squeezing samples from the first dismantled column.

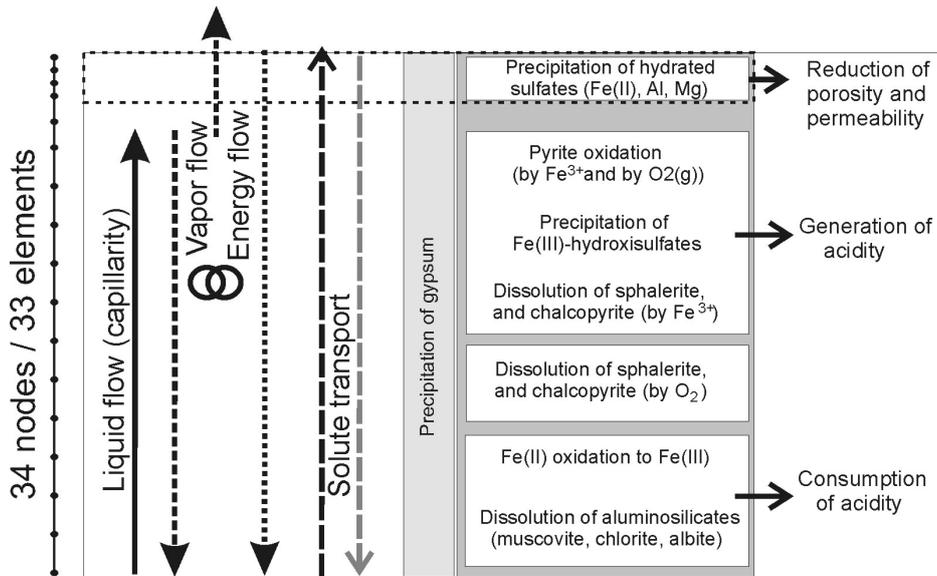


Figure 1. Main thermohydraulic and geochemical processes included in the model.

All porewaters analyzed were very concentrated and the Pitzer ion-interaction approach was used to simulate solute behavior. Mineral dissolution of sulfides and aluminosilicates, precipitation of sulfates, and Fe(II) oxidation by $O_2(aq)$ to Fe(III), however, were considered slow in comparison with processes involved in the water movement, and were simulated using kinetic laws.

Results and Discussion

Heating caused evaporation, which induced upwards liquid phase flux due to capillary forces. Solute concentrations increased progressively in the columns top and caused precipitation of whitish efflorescent salts as early as the second day was on their top surface. Salts continued growing and created a continuous crust which kept increasing its thickness throughout the experiment (up to 20 mm at the end of the experiment). According to XRD results, the main phases identified in the crust were Fe(II)-Mg-Al-sulfates. The same mineral paragenesis has been identified on the surface of several pyrite tailings of the Iberian Pyrite Belt (Buckby et al., 2003).

With the aim of assessing the role of the precipitates crust in the evaporation rates, the crusts in one column were removed mechanically every 3 to 10 days throughout the experiment. In this column, the average evaporation rate was more than double of the evaporation rate in the rest of the columns (Fig. 2). It is clear that the presence of the continuous crust caused a decrease in the evaporation rate in the columns.

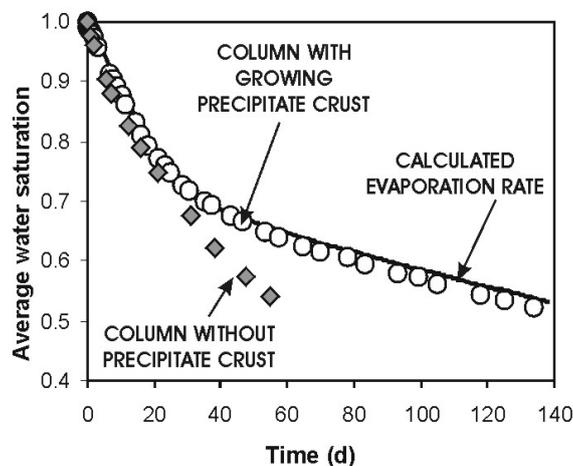


Figure 2. Evolution of the evaporation rate of two representative columns. Comparison with calculations.

All columns with growing precipitate crust displayed very similar desiccation trends throughout the 125 days of experiment (Fig. 2). There were no important vertical variations in water saturation for each dryness stage. The model matches the water content evolution (Fig. 2).

The main geochemical processes controlling column evolution are detailed in Figure 1. Sulfide oxidation generated acidity, SO_4 and metals (especially Fe, Cu, Zn). Fe(II) was subsequently oxidized to Fe(III), which precipitated partially into the pore spaces, releasing more acidity. Acidity promoted the dissolution of aluminosilicates, which buffered porewater pH. As explained above, solute concentrated at the column top and precipitated massively therein.

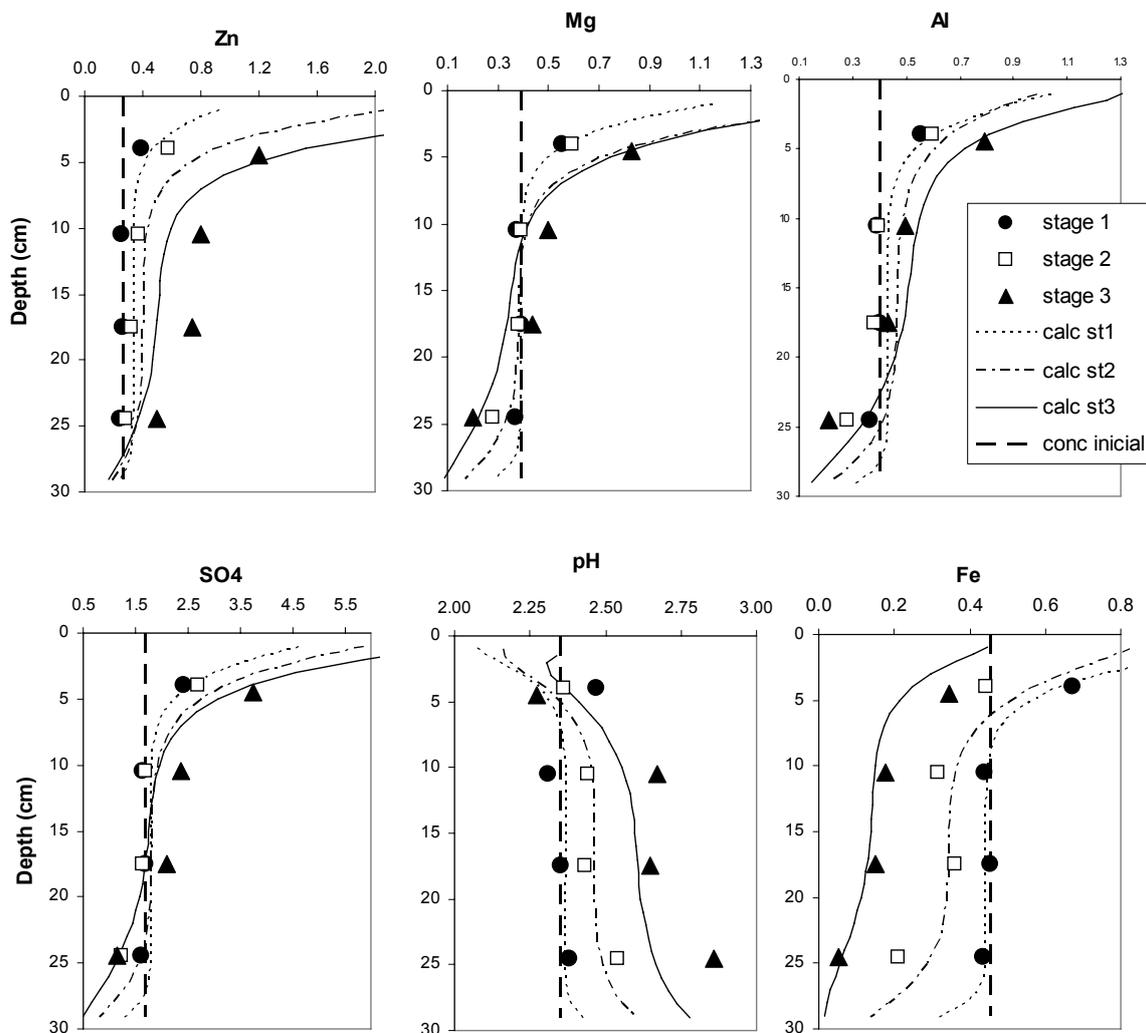


Figure 3. Evolution of concentration ($\text{mol}\cdot\text{kg}^{-1}$) and pH of porewater from the columns. Comparison with calculated values.

The observed behavior of major elements can be divided into three different trends. First, the Zn porewater concentrations increased at all depths with time due to sphalerite dissolution. This increase was more evident in the shallower part of the column, where the evaporation was taking place (Fig. 3). Second, Al, Mg and S increased mainly in the third stage and in the upper part of the column (Fig. 3) due to mineral dissolution (sulfides and aluminosilicates) and water loss by evaporation. However, the most interesting trend is the progressive dilution observed for Al, Mg and S concentrations in the lower part of the columns. Dilution can be explained by the thermally-driven vapour flux from the top to the bottom of the columns, and its subsequent condensation therein. This is consistent with the decrease in the $\text{O}^{18}/\text{O}^{16}$ ratio (not shown) observed for the same samples.

Finally, Fe porewater concentrations decreased with time at all depths. In the light of the sequential extraction results, this decrease is attributed to the precipitation of secondary phases (possibly jarosite, goethite and

schwertmannite). The precipitation of Fe(III)-bearing phases explains also the low proportion of Fe(III) measured (always less than 20% of total iron.).

All these geochemical and thermohydraulic processes were included in the model. Porosity variations with mineral dissolution/precipitation were considered to change hydraulic conductivity and diffusivity. Dissolution rates for sulfides and aluminosilicates phases were calibrated to match the observed porewater evolution. Fe(II)-oxidation rates were increased to take into account the catalytic role of microorganisms. As displayed in Figure 3, the model results matched reasonably the observed porewater evolution. Both the increase in solute concentrations at the column top and the progressive dilution at the column bottom are adequately reproduced by the model. The evolution and composition of the precipitates crust at the column top (not shown) is also reproduced by the model.

Conclusions

A simple methodology based on the successive dismantling of replicated column experiments has been successfully applied to characterizing the evolution of porewaters and solid phases in unsaturated pyritic tailings. This methodology allows detecting processes controlling the temporal evolution of the vadose zone which can not be unravelled in the field or with single-column experiments. It has also been demonstrated that the geochemical evolution of undersaturated pyritic soils is controlled not only by geochemical processes but also by thermohydraulic processes and that coupled thermohydraulic and reactive transport model is imperative to understand and quantify the complex interactions between them.

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