



Título: MOBILIZATION AND NATURAL ATTENUATION OF ARSENIC IN ACID MINE DRAINAGE (AMD)

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Resumen: Acid mine drainage (AMD) generated by sulfide oxidative dissolution is a major cause of water

contamination world-wide. Arsenic is one of the main AMD pollutants whose concentration can reach up to hundreds of mg L⁻¹

, i.e. 5-6 orders of magnitude higher than the limit of 10 µg L⁻¹

for potable water

established by the European Union in 1998. This thesis is concerned with the impact of arsenic mobilization along AMD discharges.

Oxidation of As-bearing sulfides such as arsenopyrite (AsFeS), As-rich pyrite (FeS₂) or marcasite (FeS₂) is one of the main sources of arsenic release. The first part of this thesis is focused on the



dissolution kinetics of arsenopyrite and marcasite at acidic to neutral pH using long term flow-through experiments. The effects of pH, dissolved oxygen and temperature on their dissolution were assessed. The respective dissolution rate laws were proposed on the basis of the steady-state rates, taking into consideration the slight pH effect and the strong dissolved oxygen effect on dissolution. The incorporation of these rate laws into the kinetic databases of geochemical and reactive transport codes allows us to obtain better realistic simulations.

The environmental impact of released arsenic into waters depends on its natural attenuation. The arsenic oxidation state is considered given that the main process that controls the fate and mobility of aqueous arsenic is arsenate sorption onto precipitated Fe-phases. The second part of the thesis discusses arsenic oxidation and arsenic sorption. Oxidation was studied by means of batch experiments under abiotic and biotic conditions at typical AMD water pH and water composition. Simultaneous oxidation of Fe(II) to Fe(III) and arsenite to arsenate occurs under biotic conditions, the former mediated by bacteria, and the latter by the presence of Fe(III). Under abiotic conditions, oxidation of arsenite to arsenate in the presence of Fe(III) is slow, but is enhanced by increasing dissolved Fe(III) and chloride concentrations in the presence of light. Arsenic sorption at AMD sites, and hence arsenic attenuation, occurs via arsenate sorption on new iron-oxyhydroxide and iron-oxyhydroxide-sulphate precipitates (mainly, schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{5.5}(\text{SO}_4)_{1.25}$), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and goethite (FeOOH)). The

sorption capacity of goethite and jarosite was studied and compared with the one reported for schwertmannite. To this end, batch experiments were conducted using synthetic powders of K-jarosite and goethite at highly acidic pH. In the absence of competitive effects of other anions, K-jarosite presented better removal efficiency for arsenate, and ionic strength and pH had little effect on the sorption capacity of the two minerals. In contrast, these sorption capacities diminished considerably in the presence of sulfate, which is the main anion in AMD waters.

A deeper understanding of the dominant mechanisms controlling arsenic content in waters demands the study of the processes not only under laboratory but also under natural conditions. Accordingly, the third part of this thesis deals with the arsenic attenuation processes in a natural system. To this end, the acidic water and sediments of the abandoned Tinto Santa Rosa mine discharge, located in the Iberian Pyritic Belt, were studied. The most striking feature of the water was a pH decrease accompanied by a systematic decrease in ferrous iron, total iron, arsenite, arsenate and total arsenic concentration.

Additionally, bed-stream sediments showed high arsenic contents. The main processes that control the fate and mobility of arsenic in waters in the field were iron and arsenic oxidation, precipitation of Fe(III)-minerals and sorption of As(V) onto them. A 1-D reactive transport model using the PHREEQC code was used to explain and quantify the aforementioned processes that had been studied previously under laboratory conditions.