AN EXPERIMENTAL APPROACH TO THE STUDY OF THE PASSIVATION OF PERMEABLE CARBONATE BARRIERS FOR THE REMEDIATION OF ACID MINE SOLUTIONS

Marco Boi[1], José Luis Mogollón[2], Josep M. Soler[1], Carlos Ayora[1] and Jordi Cama[1]
[1]Institut de Ciències de la Terra "Jaume Almera"(CSIC), 08028 Barcelona, Spain
[2]Instituto de Ciencias de la Tierra, Univesidad Central de Venezuela,Caracas, Venezuela

Abstract

The formation of secondary mineral coatings reduces the lifetime of passive barrier systems to treat acid mine water. This process is studied here. Two different types of synthetic solution (Cl^- or SO_4^{2-} as anions) with Fe(III) concentrations ranging between 250 ppm and 1500 ppm and pH 2 have been injected into columns packed with calcite grains. Initially the columns eliminate the acidity and 100% of the input Fe(III), but calcite deactivation causes a drop in removal efficiency from 100% to less than 30%. Mineralogical, chemical and textural changes have been measured by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Tracer tests with Br^-have also been applied to study possible porosity changes. All the experimental results will be used in the formulation of a reactive transport model that takes the effect of mineral coatings into account.

Introduction

In recent years engineering designs have been developed for the in-situ treatment of acidic water resulting from the drainage of sulfide mine tunnels and dumps. Water is circulated through infiltration ponds including a bed of organic matter and calcium carbonate at the bottom (Younger, 2000; Younger et al., 2002). The aims of these RAPS (Reduction and Alkalinity Producing Systems) are to encourage biologically mediated reduction of SO_4^{2-} and precipitation of metal sulfides, to cause a reduction of acidity and to precipitate metal hydroxides. A reduction of the metal content can be often observed, although removal is not complete.

During a previous work, we have evaluated the efficiency of a potential RAPS for the treatment of the Odiel Basin waters (SW Spain). The results are hardly encouraging:

1) Common organic matters (manure, plants) are not very reactive and require water residence times longer than a week, with the consequent demand of space and engineering works (Gibert et al., 2004, 2005). In addition, the high concentrations of Zn in the water seem to inhibit the development of sulfate-reducing bacteria (Gibert et al., 2005).

2) The high Fe and Al concentrations in the water (up to two orders of magnitude higher than that in commonly treated water) cause a large volume of precipitates which a) quickly coat the grains of the reactive agent hindering its dissolution, and b) clog porosity eliminating the system's permeability in a few weeks.

We have started an experimental program to address these issues. To target the issue of loss of reactivity due to coating of the reactive grains by secondary precipitates or clogging of porosity (reduction of permeability), we have designed column experiments using calcite sand and synthetic acidic solutions.

Experiments

In a first set of experiments, input solutions were prepared with Cl^- or SO_4^{2-} as anions, initial concentrations of Fe(III) ranging from 500 to 1500 ppm and pH 2. These solutions were injected into column reactors packed with calcite grains, with grain size between 2 and 5 mm. Flow rate was maintained constant during the experiments. Average flow rate was 0.1 ml/min, with column diameter and length equal to 6.4 cm and 6 cm, respectively.

Seven experiments, with durations ranging from 9 to 48 weeks, were completed successfully, i.e. at least until calcite deactivation caused Fe removal efficiency to drop from 100% to less than 30%.

1. Change in output concentrations with time and distance

In early time stages, as input solution flows through the columns, pH rises from 2 to ~ 6 -7 due to the dissolution of calcite. After a period, in both Cl^- and SO_4^{2-} systems, output pH and Ca concentration drop abruptly. Fe(III) output concentrations remained below detection limits as far as output pH was larger than 5.

pH profiles along the column, measured at intermediate sampling ports, showed variations with time that followed the observed evolution of the coating of the grains with brown-orange precipitates. Output pH showed two typical types of behavior with time. For Cl^- solutions, after the first pH drop occurred, short-lived transitory rises of pH were observed (Fig. 1). These were probably linked to the transport of fines. For SO_4^{2-} solutions, once pH dropped it remained close to input values for weeks.

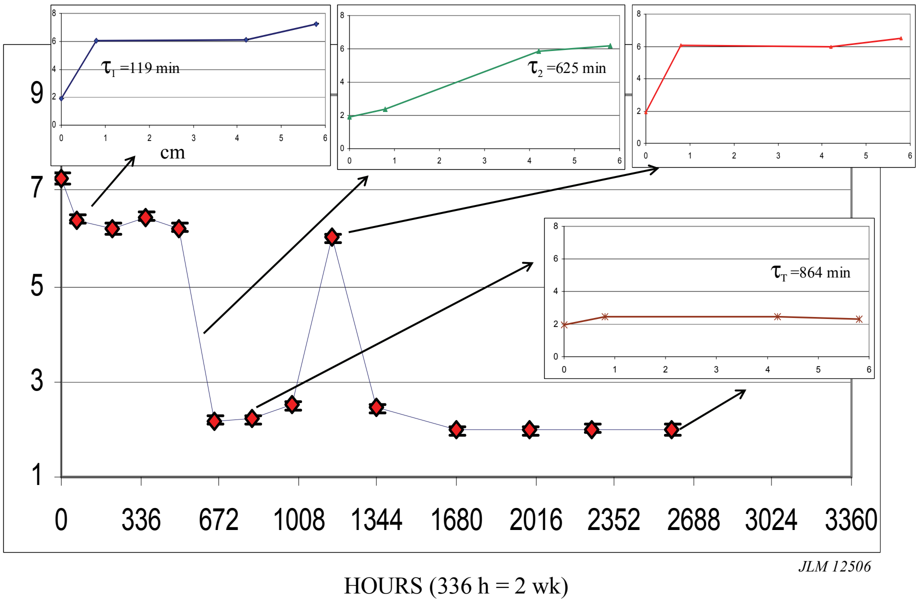

Figure 1. Output pH vs. time (hours). Insets show pH profiles (pH vs. distance in cm) at different times. τ values are residence times at 1, 4 and 6 cm.

2. Porosity and mineralogical variations with time

The initial porosities, determined by means of calcite weight and density, ranged from 43.2 to 48.5% for the different column reactors. In average, the differences between the determinations by calcite and water weight were 1 ± 3%. Porosities determined from the weight of water after the column was saturated ranged from 40.6 to 49.1%.

Porosity (ϕ) determined by Br^- tracer tests showed an average value of 32.6 ± 3 %. The comparison with the above porosity values indicates the presence of non-effective porosity.

According to the accumulated Ca and Mg output, ϕ increase due to calcite dissolution ranged from 1.5 to 11% of the initial porosity. Moreover, the remaining calcite mass was higher than 78% of the initial mass. Clearly, calcite mass was not the limiting factor of the processes.

Considering the possible stoichiometries, molar volumes and densities of the secondary precipitates, it is expected that, per mole of Fe precipitated, schwertmannite should produce the largest pore volume reduction. In fact, the values of precipitate volume per mass of Fe(III) removed from solution (cm^3/g) are 0.95 for schwertmannite, 0.57 for akageneite, 0.37 for goethite and 0.27 for hematite.

As shown by XRD, the dominant secondary minerals were schwertmannite and gypsum in the Fe-SO_4 system and akaganeite in the Fe-Cl system. Mass balance calculations showed that even in the worst scenario, at the time reactors deactivated, the decrease in porosity should be less than 11% of the initial porosity.

Based on these observations, it is to be expected that pore volume increase due to calcite dissolution is counterbalanced by the precipitation of secondary minerals. The magnitudes of both contributions are also rather small.

Examination of reacted samples under the SEM showed no significant modification of porosity compared to an unreacted system. However, the coating of calcite surfaces by secondary precipitates was evident (Fig. 2).

Figure 3 shows a non-linear dependence between the normalized lifetime of the system (passivation time divided by residence time) and input Fe(III) concentration. The strong change in slope between 500 and 1000 ppm Fe(III) suggests that two different mechanisms may be at work.

Our hypothesis is that under larger Fe(III) concentrations (larger supersaturation) nucleation is faster and crystal growth slower than under lower Fe(III) concentrations. Under larger Fe(III) concentrations, coating of the calcite grains is very fast, leading to a quick deactivation of the columns. Under lower supersaturation, crystal growth contributes to the process more significantly. Bigger grains and fewer nuclei form and growth advances more dominantly perpendicular to the calcite surfaces. Therefore, shielding is less effective and more Fe(III) may be removed from solution before surface deactivates. Also, as growth of mineral grains becomes more perpendicular to the calcite substrate, significant pore structure and permeability changes may occur. This concept is summarized in Figure 4.

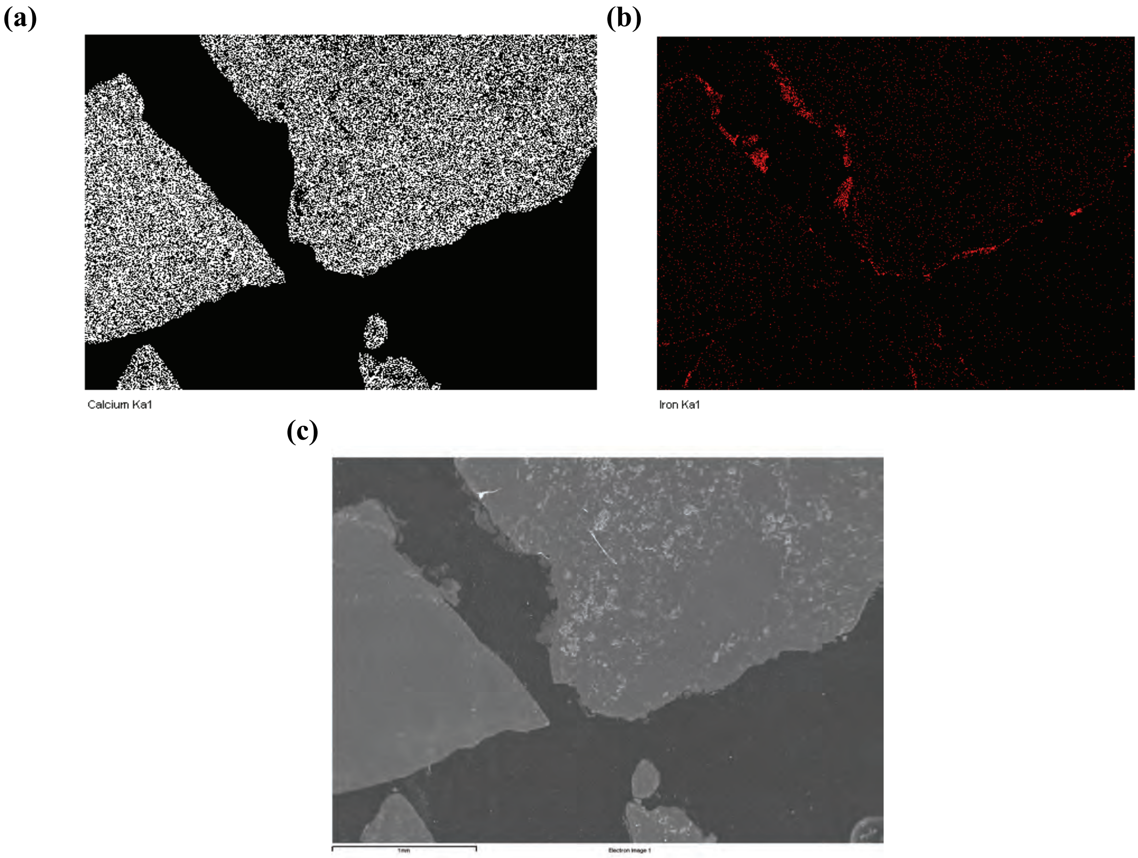

Figure 2. SEM-EDX elemental maps from a section of one of the experiments (input: 1500 ppm Fe, pH 2, Cl^-). Calcite dissolved and akaganeite precipitated during the experiment. (a) Calcium, (b) iron, (c) SEM image. The scale bar is 1 mm in length.

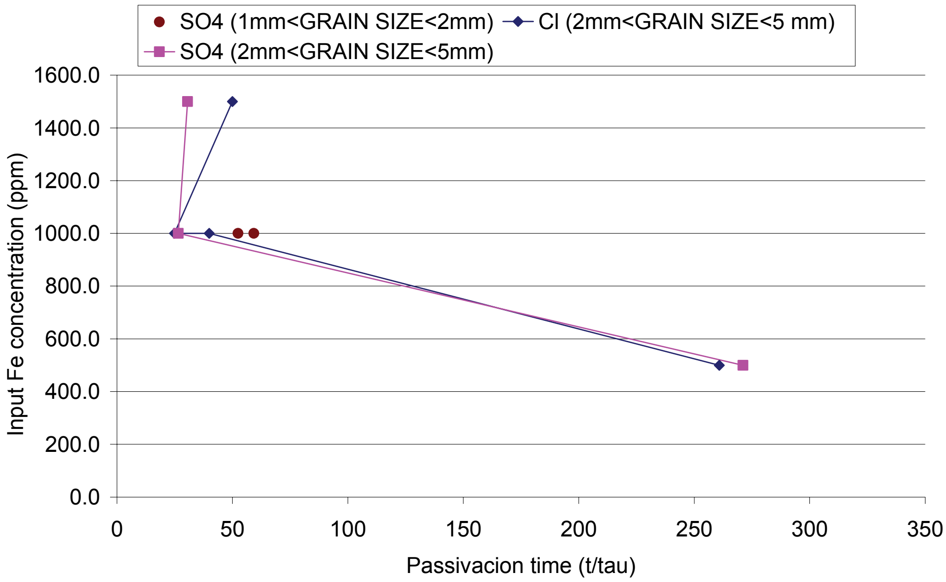

Figure 3. Input Fe concentration (ppm) vs. Passivation time (t/tau). t (t_0-t_{end}) is total time calculated from experiment start time until deactivation time (removal efficiency less than 30%). tau is the residence time (pore volume / flow rate). SO_4 and Cl are the anions utilized for the preparation of iron synthetic solutions.

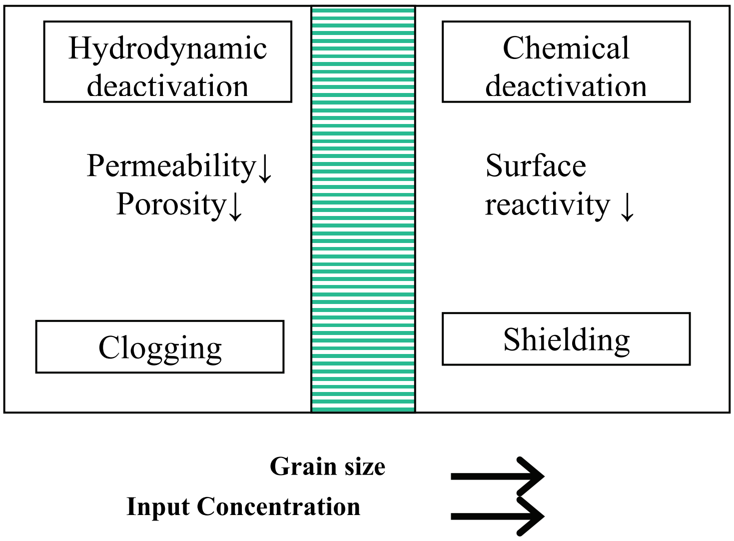

Figure 4. Diagram illustrating the change in the type of deactivation as a function of input metal concentration and available surface area (grain size).

3. A new set of experiments

The aim is to confirm the trends observed in the previous experiments and to perform experiments with a smaller grain size. According to our hypothesis, the amount of available surface is larger using a smaller grain size and the system should be able to retain a larger amount of Fe(III) before deactivation. At some point, significant porosity and permeability changes could also occur.

Currently we have started column experiments using calcite with grain size between 1 and 2 mm. The current design uses small columns (Fig. 5), in order to have a relatively fast deactivation of the systems. Flow is also about a factor of 3 faster than in the first set of experiments. Current columns are 2.5 cm in diameter. Figure 3 shows results for the two sets of experiments. The first results with the second set of experiments seem to confirm an increase in the time necessary for passivation with decreasing grain size. For the new experiments with input Fe(III) equal to 1000 ppm, the normalized lifetime of the system has increased by a factor of about 3.

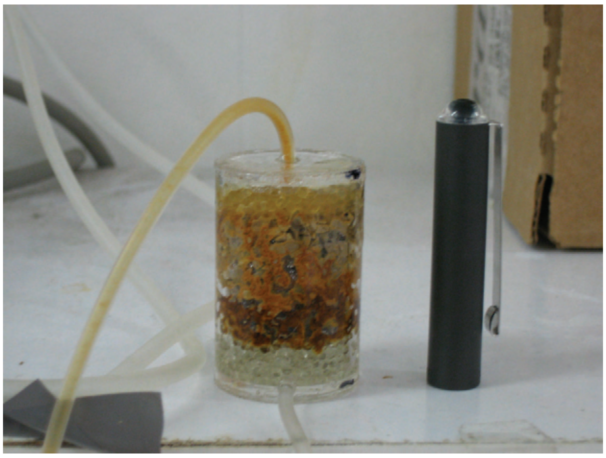

Figure 5. New experimental columns. The reactive part of the column is 2.5 cm in height and 2.6 cm in diameter.

Future plans

The changes in mineralogy, chemical composition and pore structure in the experiments are going to be investigated by X-ray diffraction, Electron Microprobe analyses, Scanning Electron Microscopy and Transmission Electron Microscopy. Plans are also being made to apply the X-ray Microtomography technique to the study of grain and pore structure evolution in this type of systems. The ultimate goal of the investigation will be to formulate a quantitative model of the evolution of the systems using a numerical reactive transport code. An empirical approach to treat the loss of calcite reactivity due to the formation of coatings on the calcite grains is being formulated.

Acknowledgements

This work was supported by the research project 2003-09590-c04 from the Spanish Government.

References

Gibert O., de Pablo J., Cortina J.L., Ayora C. (2004). Chemical characterisation of natural organic substrates for biological mitigation of acid mine drainage. Water Research 38, 4186-4196.

Gibert O., de Pablo J., Cortina J.L., Ayora C. (2005). Municipal compost-based mixture for acid mine drainage bioremediation: metal retention mechanisms for permeable reactive barriers. Applied Geochemistry 20, 1648-1657.

Younger P.L. (2000). The Adoption and Adaptation of Passive Treatment Technologies for Mine Waters in The United Kingdom. Mine Water and the Environment 19, 84-97.

Younger P.L., Banwart S.A., Hedin R.S. (2002). Mine Water: Hydrology, Pollution, Remediation. Kluwer Acad. Press, Dordrecht, 442 pp.