Performance of the Aznalcóllar permeable reactive barrier

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ABSTRACT

An experimental permeable reactive barrier was constructed in September 2000 to remove heavy metals and acidity from the groundwater of the Rio Agrio aquifer in southern Spain contaminated by the 1998 Aznalcollar mine tailings spill. It spans across the width of the alluvial plain (110m) and has three modules containing different proportions of limestone chips, compost, organic sludge and zero-valent iron. During the first three months after barrier construction, the relative metal and acidity removal was very high (almost 100%). In December 2000, exceptionally high rainfalls generated a flood that modified the morphology of the river bed and floodplain. During the following three months, metal concentrations and acidity showed very high values downstream of the barrier, but since April 2001 barrier efficiency has been rising again, attaining removal values of 90% for Al and acidity and 60-90% for Zn and Cu at the end of the two year monitoring period. Barrier hydraulic conductivity varied strongly between the three reactive mixtures: the right margin module had a low hydraulic conductivity and thus did not function, while the centre and left margin module performed better. Bacteriological and mineralogical studies showed that bacterial activity was low and that sulphate reduction processes occurred only sporadically, probably due to the kind of compost used. We conclude that pH increase was caused by calcite dissolution and that metal removal took place by coprecipitation with amorphous Al-S-Fe hydroxides and sorption on organic matter surfaces, still leading to good metal removal values. Extraction of barrier material after two years of operation showed only small consumption of calcite, suggesting that pH will remain high for a long time, stabilising the immobilised metal compounds.

INTRODUCTION

Acid mine drainage (AMD) is one of the most serious environmental threats caused by the mining industry, not only during mine operation but also after mine closure. The generation of AMD can continue throughout decades after mining activity has ceased. Conventional remediation strategies often consist in pump-and-treat technologies with the addition of an alkaline agent or sulphide in order to promote metal precipitation as hydroxides or sulphides. This approach requires a high level of maintenance and a continuous input of energy and reactive agents in order to maintain the treatment process, resulting in high treatment costs. Usually, these active treatment systems are shut down after mine closure, exposing the environment to high levels of contamination.

Passive remediation systems, which after system installation require no input of energy or reactive agents and only infrequent monitoring, may provide a long-lasting solution to AMD. Permeable reactive barriers (PRB) have been used widely throughout the last years for passive remediation of groundwater pollution by chlorinated solvents, but only few PRB for the treatment of AMD exist up to now (Benner et al., 1997; Carrera et al., 2001a+b, Ludwig et al., 2002; Younger, 2002).

The scope of this paper is to present the results from the performance assessment of the Aznalcóllar PRB after two years of operation.

THE AZNALCÓLLAR CASE STUDY

The Aznalcóllar mine tailings dam failure of April 25th, 1998, released about 5 million cubic meters of toxic tailings slurries and acidic water into nearby Agrio river, a tributary to Guadiamar river. The slurry wave covered the floodplain of these rivers up to 40 km downstream of the failure point, and it threatened the Doñana National Park, a UN World Heritage Area. The sludge was retrieved, but the affected floodplains were left bare of vegetation and topsoil. The groundwater near the mine remained contaminated by heavy metals and acid water. As one of the remediation measures, in September 2000 an experimental permeable reactive barrier (PRB) was built across the floodplain of Agrio river in order to remove heavy metals and acidity from the ground water.

SITE, PERMEABLE REACTIVE BARRIER DESIGN AND PERFORMANCE EVALUATION METHODS

SITE AND GEOLOGY

Aznalcóllar is located within the Iberian Pyrite Belt in the province of Seville in south-western Spain (fig. 1). In this region, mining activities have been carried out for thousands of years. From 1975 until its closure in 2002, the Aznalcóllar Mine was operated as an open pit mine. The ore was extracted from the Paleozoic formations north of the mine compound, while the settling pond for mine tailings was built south of the mine compound on the quaternary alluvial terraces of Agrio river. The impermeable base of the alluvial aquifer and of the tailings pond is formed by the Miocene “Blue Marls” formation. The groundwater to be treated by the PRB had a pH of 4 and contained Al (10 mg/L), Zn (10 mg/L) and Cu (1 mg/L). Remarkably, the water in the alluvial aquifer and in the Agrio river has high concentrations of sulphate (around 1000 mg/l), but only a very low iron content (<0.1 mg/l).

The alluvial aquifer drains the adjacent formations, and is itself drained by the river. A very good hydraulic connection between the river and aquifer is believed to occur throughout the valley axis. A drinking water dam is present in the Agrio river 2 Km upstream of Aznalcóllar supplying water to the village and formerly to the mine. The water level of the Agrio river depends mainly on the operation of this dam, and piezometric heads in the alluvial aquifer equilibrate with river stage very rapidly (minutes to hours).

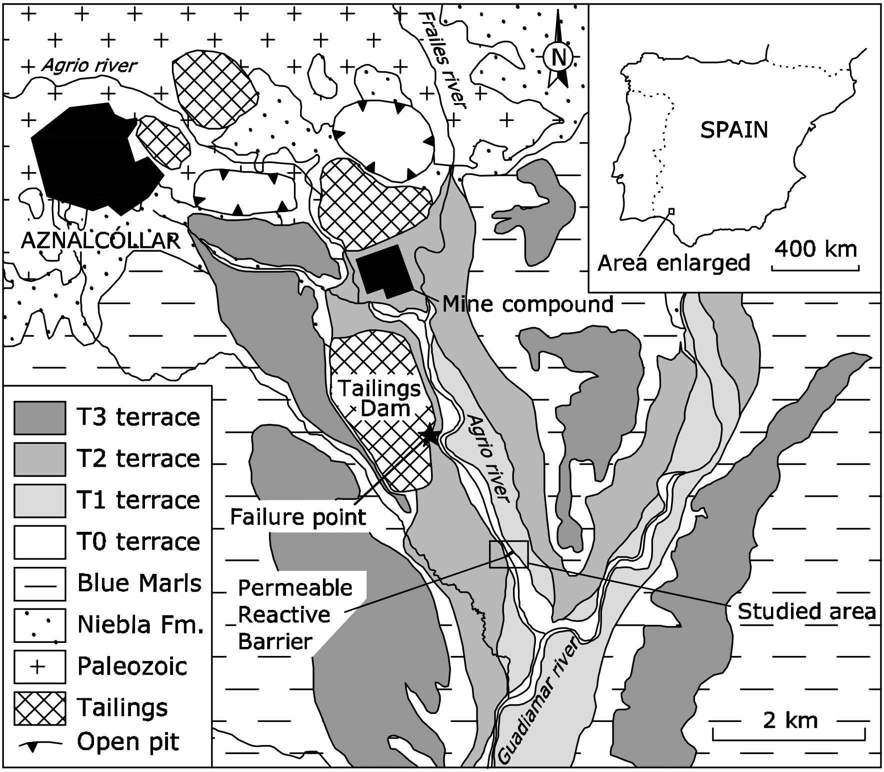

Figure 1: Studied site with geologic and geomorphologic formations

PRB DESIGN

The Aznalcóllar experimental PRB was designed to remove heavy metals and acidity by bacterial sulphate reduction (ALCOLEA ET AL., 2001). It consists of three reactive modules containing different mixtures of limestone chips, organic material (gardening compost and sewage sludge) and iron cuttings (table 1). The limestone adds alkalinity to the water, raises pH and creates suitable conditions for the sulphate reducing bacteria (SRB). The organic material provides electron donors for the SRB. The sulphide produced by SRB activity precipitates with heavy metals, removing them from the ground water. The central module additionally contains zero-valent iron in order to increase anoxic conditions within the barrier. Each module is 30 m wide, 1.4 m thick and on average 6 m deep, penetrating the underlying marls by about 0.5 m (figs. 2+3). The three modules are separated by two 10 m wide non-reactive sections of low hydraulic conductivity, and the whole barrier is covered with the same low-permeability material. The PRB was constructed in September 2000 two kilometres downstream of the tailings dam failure point and one kilometre upstream of the confluence with Guadiamar river. It spans the full width of the actual floodplain (terrace T0) of the Agrio river.

Table 1: Volumetric composition of reactive mixtures used in the three modules of the PRB

Module	Right margin barrier (RMB)		Central barrier (CB)		Left margin barrier (LMB)	
Composition	60%	Limestone chips	60%	limestone chips	60%	Limestone chips
	40%	Gardening compost and sewage sludge	35%	gardening compost	40%	Gardening compost
			5%	iron cuttings		

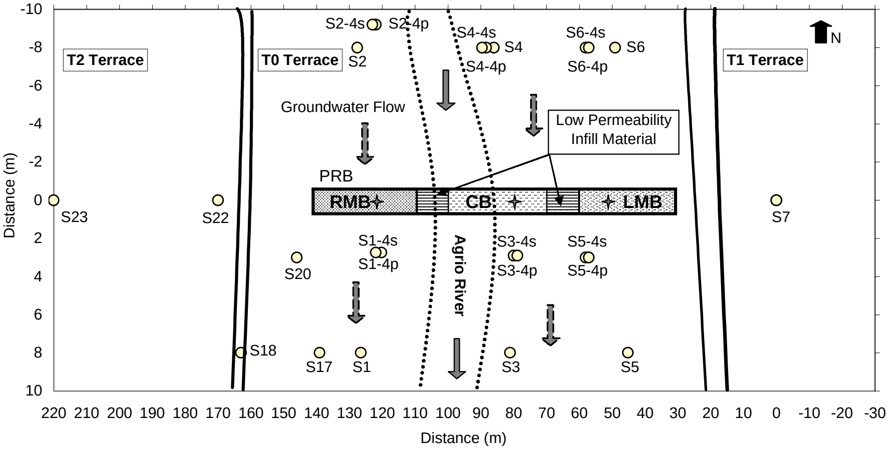

Figure 2: Plan view of permeable reactive barrier (PRB) emplacement and monitoring well network. Circles represent monitoring wells, the stars inside the three PRB modules represent piezometer nests sampling water from inside the barrier near the inflow and outflow at three different depths.

Each PRB module contains two piezometer nests which allow sampling of water and reactive material at three depths inside the barrier, one nest near the inflow and one near the outflow. The monitoring wells upstream and downstream of the PRB are used to measure the hydraulical and geochemical performance of the barrier.

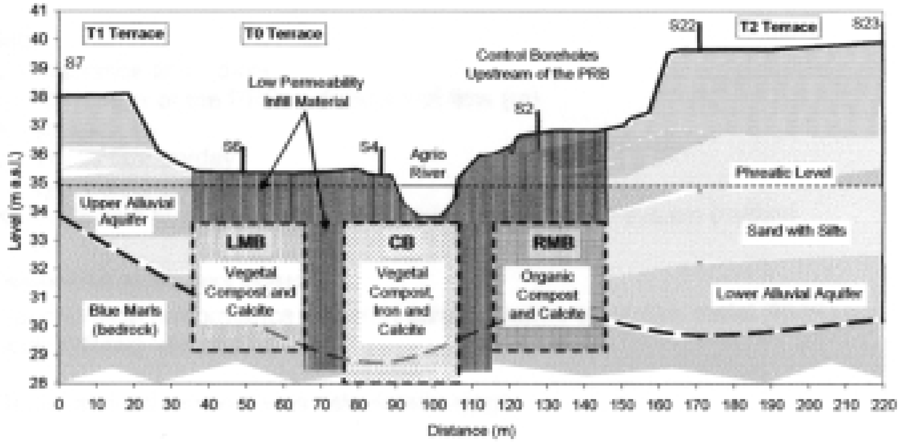

Figure 3: Cross section of the PRB and the alluvial aquifer seen from upstream.

HYDRAULIC PERFORMANCE ASSESSMENT

Hydraulic performance was evaluated in terms of flow rates and residence time of water flowing through the PRB. Flow rate was determined applying Darcy's Law using measured effective hydraulic conductivity and hydraulic gradients. Hydraulic gradient was measured between the monitoring wells situated 8 m up- and downstream of the PRB (wells S1-S6, fig. 2). Hydraulic conductivity of the aquifer was measured by cross-hole pumping tests (Alcolea et al., 2001), hydraulic conductivity of the reactive modules of the PRB by slug tests. Effective hydraulic conductivity of the aquifer-PRB-system was calculated according to:

$$K_T = \frac{x_T}{\frac{x_1}{K_1} + \frac{x_b}{K_b} + \frac{x_2}{K_2}}$$

with:
KT – effective hydraulic conductivity of the aquifer-PRB-system (m/day)
K_1, K_2 – hydraulic conductivity of the aquifer up- and downstream of the PRB (m/day)
K_b – hydraulic conductivity of the PRB (m/day)
x_T – total distance between monitoring wells (m),
x_1, x_2 – distance between up- or downstream monitoring well and PRB (m),
x_b – thickness of the PRB in direction of flow (m)

Residence time was calculated according to:

$$t_r = \frac{x_b * n}{q} = \frac{x_b * n}{i * K_T}$$

with:
t_r – residence time (days)
x_b – thickness of the PRB in direction of flow (m)
n – porosity (-)
q – Darcy flux (m/day)
i – hydraulic gradient (m/m)
K_T – effective hydraulic conductivity of the aquifer-PRB-system (m/day)

GEOCHEMICAL PERFORMANCE ASSESSMENT

Geochemical performance was measured in terms of relative metal (RMR) and acidity (RAR) removal.

Relative metal removal was calculated using:

$$RMR\ (\%) = (M_{up} - M_{down}) * 100 / M_{up}$$

with:
RMR – relative metal removal (%)
M_{up} – metal concentration upstream of PRB (mg/l)
M_{down} – metal concentration downstream of PRB (mg/l)

Relative acidity removal was calculated in a similar way, with metal concentrations being replaced by acidity (A) calculated as:

$$A = 3*Fe + 3*Al + 10^{-pH}$$

$$RAR\ (\%) = (A_{up} - A_{down}) * 100 / A_{up}$$

with:
A – acidity (mol/l)
Fe – molar iron concentration (mol/l)
Al – molar aluminium concentration (mol/l)
RAR – relative acidity removal (%)
A_{up} – acidity upstream of PRB (mol/l)
A_{down} – acidity downstream of PRB (mol/l)

BACTERIOLOGICAL PERFORMANCE ASSESSMENT

Bacterial activity was assessed in terms of total bacteria and sulphate reducing bacteria population in PRB material. Samples of PRB material were obtained from the open bottom of the piezometers installed in the PRB.

CONSUMPTION AND TRANSFORMATION OF PRB MATERIAL

After two years of operation, cores from the entire depths of the PRB modules were obtained using a large diameter (7 cm) penetrometer. Cores were inspected visually for calcite consumption and under an electron microscope for the formation of precipitates.

RESULTS AND DISCUSSION

It is important to point out that the evolution of the barrier was significantly affected by the Agrio river floods. Extraordinarily heavy rains (estimated return period of 50 years) occurred between December 2000 and February 2001, three months after emplacement of the barrier. The Aznalcóllar drinking water dam released very high discharge rates during several weeks, flooding the entire valley of the Agrio river. The valley morphology was reshaped, the river bed was deeply excavated and its relation with the aquifer was modified, probably resulting in an even better hydraulic connection between river and aquifer. This was the first flood after the tailings pond breakdown.

HYDRAULIC PERFORMANCE ASSESSMENT

The right margin barrier module had a very low hydraulic conductivity (table 2), because the sewage sludge used in this mixture contained very fine-grained material that clogged the pores of the reactive material. The central barrier module had the highest hydraulic conductivity of the three modules. The left margin barrier module performed almost as well as the central barrier module. However, permeabilities of these two modules were still lower than that of the aquifer (coarse gravel). The flux took place through the central and left margin barriers and the lower hydraulic conductivity led to a higher gradient inside the two barriers with respect to the aquifer. In the following, only the results from the central barrier module will be presented.

Table 2: Hydraulic conductivity of the three PRB modules as determined by slug tests

	Right Margin Barrier	Central Barrier	Left Margin Barrier
Hydraulic conductivity K (m/day)	<0.1	1.0	0.6

The hydraulic conductivity of the aquifer near the central barrier module was 640 m/day. Consequently, the effective hydraulic conductivity of the aquifer-PRB-system (central module) was 11 m/day. The effective porosity of the aquifer and the barrier as determined by tracer tests was 10%. This leads to an average Darcy flux of 0.05 m/day and an average residence time of 2.7 days during the monitored period (fig. 4). The high water flow rates calculated for the three first months are attributed to the effect of pumping during the construction of the rest of the barrier modules. This may have influenced piezometric heads in the monitoring wells, causing an overestimation of hydraulic gradient and calculated fluxes.

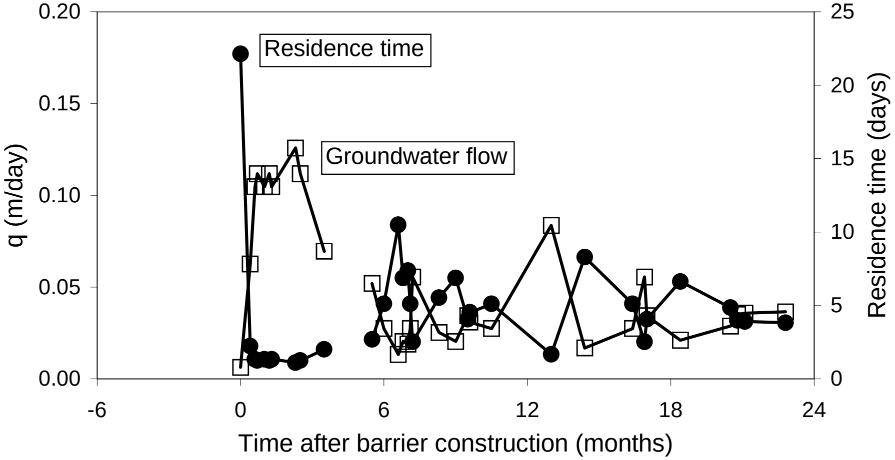

Figure 4: Residence time (filled circles) and Darcy flux (open squares) in the central barrier module.

The aquifer geometry turned out to be more complex than expected. In the pit excavated for barrier emplacement a silty layer was found which had not been described in the borehole profiles executed until that moment (SALVANY ET AL., submitted). The aquifer, which had been expected to be laterally limited to the width of the actual floodplain T0, was found to extend laterally below the higher right margin terrace T2 (fig. 3). Therefore, untreated ground water may flow around the PRB and mix with treated water downstream.

GEOCHEMICAL PERFORMANCE ASSESSMENT

The pH evolution reflects the overall behaviour of the barrier. It had a very efficient performance until January 2001 (fig. 5). The pH downstream of the barrier initially rose to near neutral values, but it dropped to pH 4 after three months, concurrent with the Agrio river flood. The pH increased gradually during the last months of the monitoring period, recovering to near pre-flood values.

The evolution of pH within the barrier was heterogeneous. The bottom and middle piezometers showed higher pH values than the downstream well for the entire monitoring period. However, the top piezometer showed an evolution similar to downstream evolution (S-3). The top piezometer behaviour can be explained by consolidation processes within the reactive material. The top piezometer was initially located within the barrier material, but it may have became surrounded by the clayey barrier cover due to consolidation of the barrier infill, hence sampling a mixture of treated and untreated water.

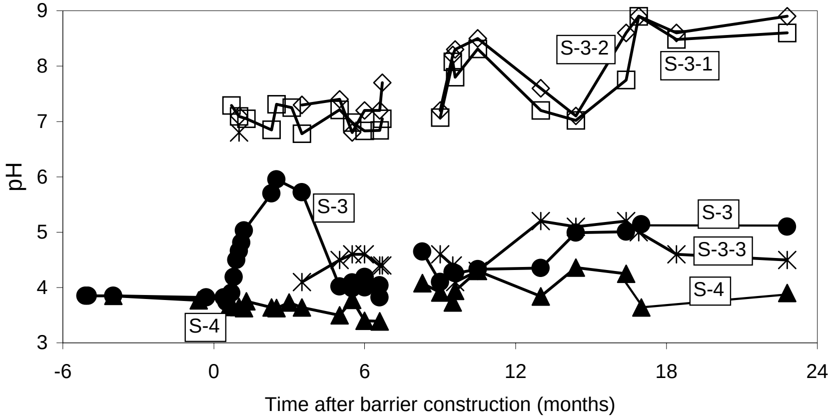

Figure 5: pH evolution upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central barrier (open symbols): top (S-3-3), middle (S-3-2) and bottom (S-3-1).

The evolution of metal concentrations, especially Al, is similar to that of pH. During the first three months, downstream metal concentrations are almost zero (figs. 6+7). After the Agrio river floods, Al downstream concentration rises almost to upstream values (fig. 6), while Zn (fig. 7) and Cu (not shown) rise but do not attain upstream concentrations. All metal concentrations decrease again during the rest of the monitoring period.

The metal concentrations inside the barrier are consistent with pH behaviour. The concentrations are very low throughout the monitored period in the two lower piezometers and higher in the upper piezometer. Note that the upstream concentration (S-4) of all metals decrease over the monitored period.

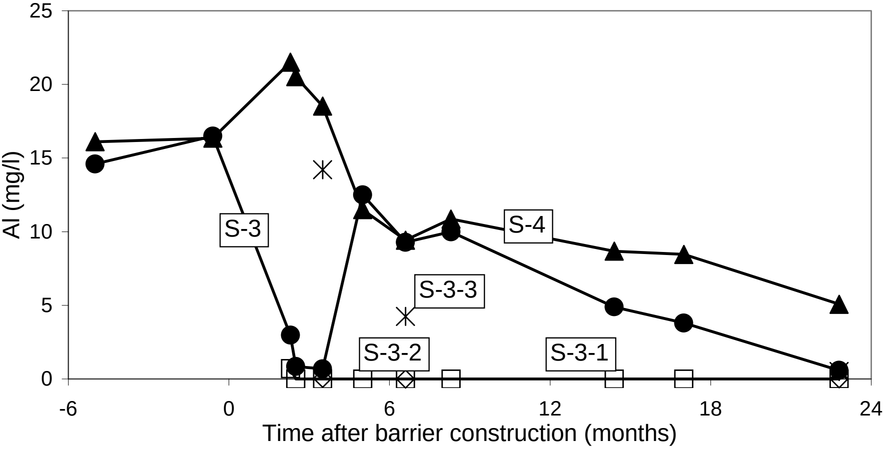

Figure 6: Al evolution upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central Barrier (open symbols): top (S-3-3), middle (S-3-2) and bottom (S-3-1).

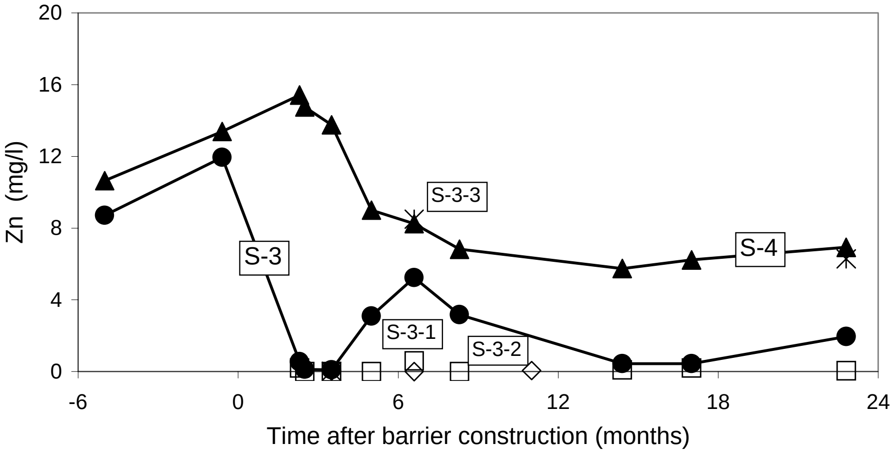

Figure 7: Zn evolution upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central Barrier (open symbols): top (S-3-3), middle (S-3-2) and bottom (S-3-1).

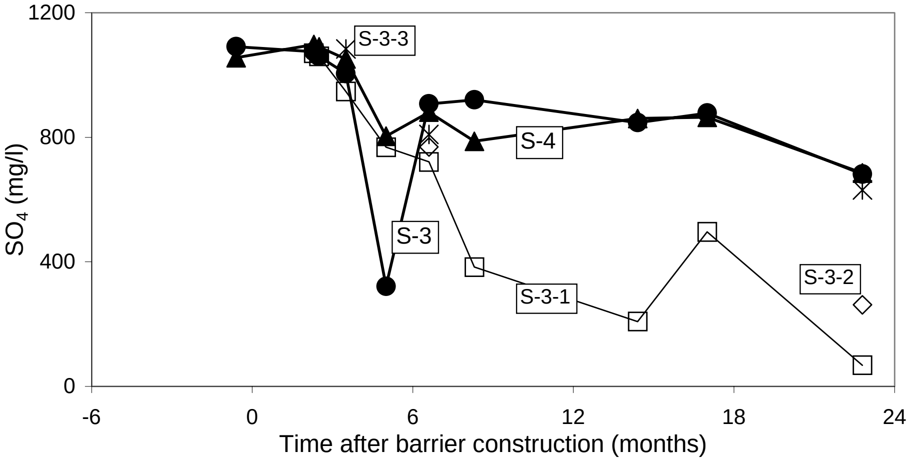

Figure 8: SO_4 evolution upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central Barrier (S-3-1: open squares).

Sulphate concentrations were always very high and almost equal up- and downstream of the PRB (fig. 8). Nevertheless, significantly lower concentrations were measured inside the barrier in the deeper piezometers at the end of the first and during the second year of operation. As described for metal concentrations, a slight decrease of sulphate was observed with time.

The relative metal and acidity removals (fig. 9) were almost 100% until the Agrio river floods, dropped sharply afterwards, but rose again to values of 90% for Al and acidity and 60-90% for Zn and Cu at the end of the two year monitoring period.

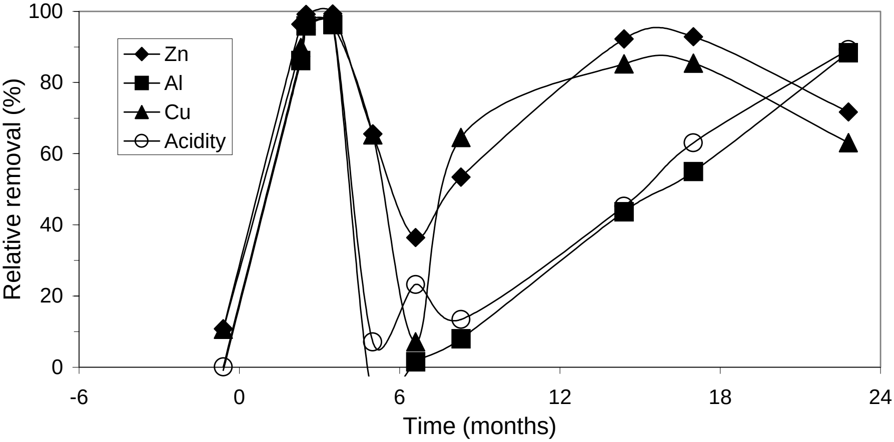

Figure 9: Evolution of relative metal and acidity removal in central barrier.

The Agrio river floods may also have had a geochemical effect on the aquifer system and apparent PRB performance. The heavy rains of December 2000 were the first strong precipitations after a drought period that had begun before the 1998 tailings spill. Therefore, residual salts and sludge not removed by the cleanup process may have been present in the vadose zone. The rain and the floods may have mobilised heavy metals and acidity and washed them down to the saturated zone both up- and downstream of the barrier, leading to a rise of downstream concentrations. Probably, the PRB worked properly throughout the entire monitoring period. This is supported by the geochemical results from the lower piezometers inside the barrier, showing very low metal concentrations and high pH values even during and shortly after the floods. Afterwards, decontaminated water gradually replaced this ephemeral pollution in the downstream aquifer.

BACTERIOLOGICAL PERFORMANCE ASSESSMENT

The microbiological studies show that the population of sulphate-reducing bacteria were too low (<10^{-6} cells/g) for biologically mediated processes to be significant (fig. 10). These data were confirmed by H_2S analyses which were always below detection limit (15 µM), and Eh measurements rarely below -150 mV. The low sulphate concentrations measured inside the barrier (fig. 8) may therefore reflect local spots of sulphate-reduction. They seem to affect only a small part of the volume of the PRB, having no apparent influence on the downstream sulphate concentration.

The lack of sulphate reduction may be due to the kind of compost used in PRB construction which was different from the compost used in previous laboratory column studies. Subsequent laboratory tests showed that the compost used has only a low fraction of biodegradable material (Gibert et al., 2003; Gibert et al., submitted)

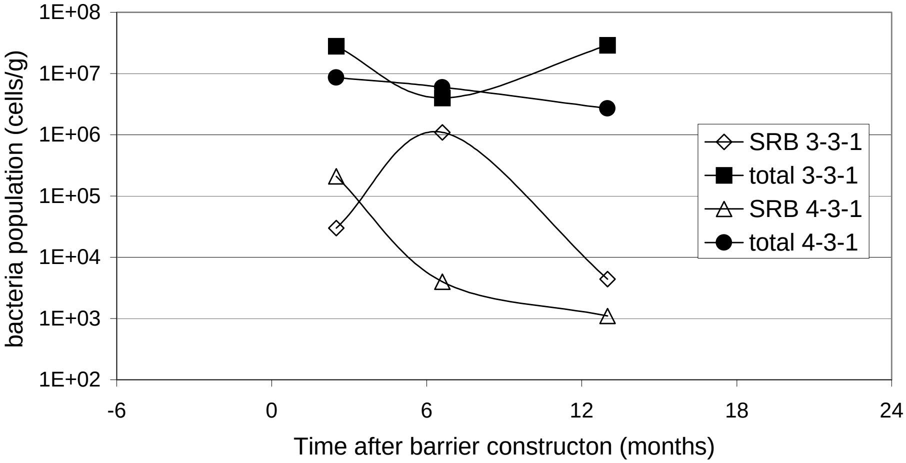

Figure 10: Total bacteria (solid symbols) and sulphate reducing bacteria (SRB: opens symbols) populations in the deepest piezometers inside the central barrier module near the inflow (“4-3-1”) and the outflow (“3-3-1”).

CONSUMPTION AND TRANSFORMATION OF PRB MATERIAL

Visual inspection of extracted PRB material showed only a small consumption of calcite. Electron microscopy showed only few metal precipitates and hardly any sulphides. We found clusters of amorphous Al-S-Fe hydroxides, suggesting that heavy metals may coprecipitate with them. At the elevated pH values measured inside the barrier, metal retention could also take place as sorbed species on the organic matter surface, although no conclusive data on this point are available.

CONCLUSIONS

The central barrier module containing 60% limestone chips, 35% gardening compost and 5% zero-valent iron cuttings performs best both hydrologically and geochemically. The drop in metal and acidity removal was only a temporary effect of the heavy rains and Agrio river floods of December 2000. Relative metal and acidity removals have recovered to values between 60% and 90%.

Metal removal seems to be a consequence of the rise in pH caused by calcite dissolution rather than an effect of SRB activity. Probable reaction mechanisms are coprecipitation of metals with amorphous Al-S-Fe hydroxides and possible sorption on organic matter surfaces. As only a small amount of calcite has been consumed after two years of PRB operation, pH is likely to remain high for a long time, maintaining metal removal reactions and stabilising the immobilised metal compounds.

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