Hydraulic performance of laboratory PRBs for the decontamination of acidic mine waters

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ABSTRACT

In this paper the hydraulic performance of laboratory-scale PRB treatment systems, using red mud and fly ash is studied. Factors such as the hydraulic conductivity of each reactive medium and the residence time required for efficient operation over a long period of time, the quality of the leachates, the loss of reactivity and porosity over time and the main removal mechanisms are taken into account and discussed. Geochemical modelling of the process and interpretation of the results is attempted by using the speciation/mass transfer computer code PHREEQC and the MINTEQ database. Experimental results provide useful information regarding the long-term efficiency of PRBs, constructed by low cost materials, when used for the clean up of acidic mine waters and the prevention of groundwater contamination.

INTRODUCTION

Acid mine drainage generated from mining activities is a well-recognized source of environmental contamination. Oxidation of metal sulfides in mines, mine dumps and tailings impoundments generates waters characterized by low pH, elevated concentrations of dissolved SO_4^{2-}, Fe^{2+}, and low to moderate concentrations of metals, that have a significant impact to soils, surface- and groundwater (Kontopoulos et al., 1999).

In the last years, the use of permeable reactive barriers for the decontamination of waters impacted by AMD has been well documented (Benner et al., 1997; Waybrant et al., 1998; Blowes et al., 2000; Amos & Younger, 2003) Permeable reactive barriers are placed in the path of a migrating contaminated plume. Reactive materials within the barrier are selected to promote geochemical reactions that result in the removal or stabilization of the contaminants. As migrating plumes flow through a PRB, several reactions within the reactive media cause mineral precipitation and therefore the effective porosity of the reactive medium is reduced due to clogging. Another potential problem, the preferential flow through the reactive barrier has received so far less attention. Preferential flow through high conductivity zones usually reduces the contact time between contaminated plume and reactive media, so that treatment effectiveness is impaired. In addition, dissolution of reactive media enhances porosity and permeability at pore scale structure, leading to focusing of flow and fingering of the reaction front (Ortoleva et al., 1987).

Several materials have been investigated as reactive media for treating acid mine water such as leaf mulch, sawdust, sewage sludge, wood chips (Waybrant et al., 2002; Gilbert et al., 2003), limestone (Komnitsas et al., 2004b,c) and apatite (Chen et al., 1997). By far, the most successful PRB medium for heavy metals removal to date is zero-valent iron (Cantrell et al., 1995; Shokes & Möller, 1999; Wilkin et al., 2003). Nevertheless, there is a considerable effort for the use of low-cost industrial by-products as reactive media (Bailey et al., 1999, Lee et al., 2004).

Fly ash and red mud are industrial by-products that can be obtained for little or no cost. Previous studies have demonstrated the potential of fly ash and red mud as low-cost reactive barrier materials for treating acid mine waters (Komnitsas et al., 2004a,b,c; Zoumis et al., 2000). However, issues related to the long-term performance of these reactive media have received so far little attention. From a critical design standpoint, the long-term efficiency of red mud and fly ash barriers is mainly dependent upon their ability to maintain a reactive surface and on hydraulic parameters (porosity and hydraulic conductivity). Currently, there is still much uncertainty and limited information in predicting the long term effectiveness and the hydraulic performance of these reactive media over long periods of time along with the need to predict the type of precipitates formed under given conditions.

In the present study, column experiments using low-cost reactive media (red mud and fly ash) were carried out and the changes in solution chemistry and hydraulic performance were observed. More specifically, (1) preliminary hydraulic conductivity tests were carried out to determine the optimal reactive mixture ratio for each media (2) tracer tests for each column configuration using non-reactive tracer were carried out; (3) moment analysis of the results was used to evaluate temporal changes in the mean residence time (Young & Ball, 1995); (4) tracer test derived estimates of water-filled porosity were compared with gravimetric measurements within the column to determine mineral precipitates; (5) results were interpreted using the equilibrium computer code PHREEQC (version 2.0) (Parkhurst & Appelo, 1999).

MATERIALS AND METHODS

Column tests

Red mud was obtained from former Aluminium de Gréce S.A. Class C fly ash was obtained from a Northern Greece thermal power station. The composition of both reactive media is seen in Table 1. The fly ash used has cementitious and pozzolanic properties due to its increased CaO content.

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	TiO_2	Na_2O	SO_3	LoI*
Red mud	6.96	14.84	15.65	45.58	0.19	0.07	7.07	3.26	-	6.42
Fly ash	31.85	33.89	13.04	5.56	4.48	0.76	0.71	0.29	6.83	2.67

Table 1: Red mud and fly ash composition (wt %)

*Loss of ignition

Continuous column experiments, using two 5 cm internal diameter and 45 cm long columns placed in a series were carried out in duplicate at room temperature. Each reactive medium was initially mixed with 0.84-0.60 mm silica sand, at a specific volume ratio (see heading 3.1), so that the mixture obtained appropriate permeability and therefore changes in hydraulic residence time resulting from heterogeneity, preferential flow path development and clogging due to precipitation that affected the long term PRB performance were minimized (Kamolpornwijit et al., 2003).

The reactive mixture was homogeneously packed in the mid-section of each column between two 3 cm of silica sand layers placed at both ends. The packed bed was supported by 2.0 cm thick glass wool. A 5 cm long tapered conic supporter was used to hold each column, distribute the incoming flow and prevent transfer and loss of fine particles. Prior to testing, nitrogen was introduced in each column for 5 min to remove air from the bed pores.

A synthetic solution simulating AMD was prepared in HCl-cleaned glassware from concentrated stock analytical grade sulfate solutions. Its initial concentration was 1500 mg/L for Fe, 500 mg/L for Al, 200 mg/L for Zn, 25 mg/L for Cd and 50 mg/L for Cu, Mn, Ni and Co. Sulfate concentration was 8400 mg/L. No further pH adjustment of the incoming feed was required as its natural acidity (pH=1.8) prevented precipitation of metal phases. The solution was pumped upwards using a variable-speed peristaltic pump (Gala/4W) at a Darcy velocity of 152 ± 0.5 cm per day (~5ft/day) corresponding to average flow rate of 987 mL/day for fly ash and 897.3 mL/day for red mud columns respectively. These values represent the mean of pore-water velocities reported so far for PRBs installed in the field (McMahon et al., 1999; Phillips et al., 2000). The use of fast-flow (typical groundwater velocity ~1ft/day) was selected in order to accelerate exhaustion of the reactive media and thus to simulate long-term operation of the barriers within a shorter actual time frame. Average total porosities of 0.33 (total pore volume 569 ml) and 0.30 (total pore volume 518 ml) were measured in each system respectively. Hence the total residence time, defined as the ratio total column length: average pore-water velocity was 850 min.

Chloride pulse tracer tests were periodically conducted to assess the hydraulic performance and estimate the mean residence time of the column systems during operation. Approximately 1 L of a NaCl solution (500 mg/L Cl^-) was pumped through the columns at ~5ft/day. The chloride ion concentration at the column outflow was frequently determined by titrating 10 mL of aliquot against standard $AgNO_3$ using 5% K_2CrO_4 as an indicator (Richards, 1968). The concentration-versus-time plots, or breakthrough curves (BTC), provide information about residence times and heterogeneities that are seen due to continuous application of simulated AMD.

Sampling ports installed along the column walls at a distance of 20 cm (sampling port A) and 60 cm (sampling port B) from the inlet allowed solution sampling at frequent intervals. Sampling port C was installed at the exit of the second column.

All liquid samples were measured by an atomic absorption spectrometer (Perkin Elmer 2100) for total Fe, Zn, Mn, Al, Cd, Cu, Co and Ni. Sulfate concentration was determined gravimetrically by addition of saturated $BaCl_2$ solution to form a $BaSO_4$ precipitate. Solution pH and redox potential (Eh) were measured with a pH/Conductivity meter (Metrohm 691 pH meter). All samples were filtered using sterile acrodisc filters (Gelman Science, 25 mm diameter, 0.45 μm pore size).

Prior to solution recirculation, preliminary hydraulic conductivity tests for each reactive mixture were performed using the constant and falling head methods (ASTM D5084, D5856) in order to define the optimum volume sand:PRB media ratio.

Geochemical modeling

The main reactions and processes taking place within the PRB systems were simulated using the PHREEQC (Version 2) computer program for speciation and one-dimensional transport. The PHREEQC code enabled calculation of mineral saturation indices for predicting mineral precipitation. Thermodynamic constants were retrieved from the MINTEQA database (Allison et al., 1991).

Data analysis

Concentration–time histories (breakthrough curves) for the tracer were evaluated through moment analysis. Column tests using fly ash and red mud as reactive medium were run for 85 and 109 pore volumes respectively until each medium showed clear signs of exhaustion. Although the concentration of a number chemical species was periodically measured in the columns, only pH, redox, major cations and sulfate are seen in this paper.

RESULTS AND DISCUSSION

Column hydraulics

Preliminary hydraulic conductivity tests. The results of the preliminary hydraulic conductivity tests for the different ratios of ‘‘fresh’’ Sand/Fly ash and Sand/Red mud mixtures by using distilled water and simulated AMD are presented in Figures 1a and 1b, respectively.

The use of an AMD solution as permeant for the hydraulic conductivity tests, was selected in order to closely approximate conditions anticipated in the field. Results showed that permeation of the sand/red mud mixtures with AMD increased slightly the hydraulic conductivity, by almost one order of magnitude, as a result of the contraction of electrical double layers surrounding oxide particles and dissolution of red mud.

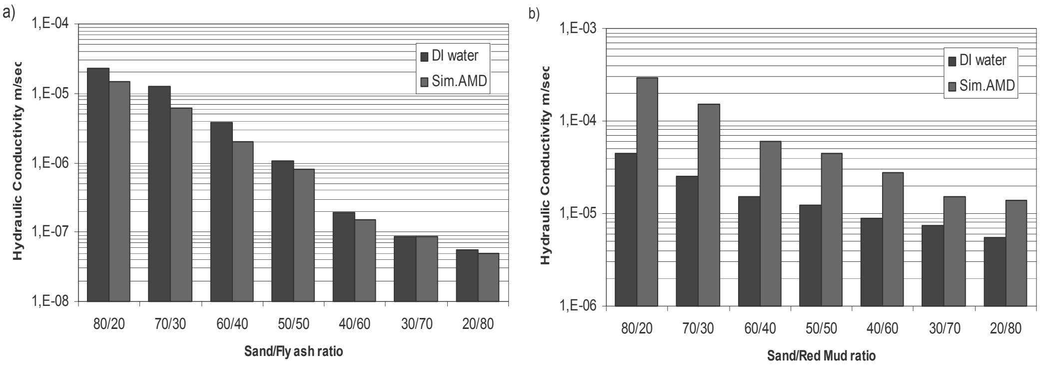

Figure 1a,b. Results of hydraulic conductivity for different sand/fly ash and sand/red mud volume ratios

On the other hand, the hydraulic conductivity of the sand/fly ash mixtures (20–80% w/w) was significant lower than that of sand/red mud mixtures due to the lower grain size of fly ash (Figure 1a). The permeation of the sand/fly ash mixtures with AMD decreased hydraulic conductivity due to chemical reactions between AMD and fly ash particles.

The 50:50 red mud/sand and 30:70 fly ash/sand mixtures were chosen as optimum reactive media for the column tests. Previous studies (Benner et al., 1997) have suggested that the optimum permeability for a reactive barrier is one order of magnitude greater than that of the aquifer in which it is placed.

Fly ash column tests

Tracer tests. Effluent Cl^- breakthrough curves of the fly ash column are presented in Figure 2 for three tracer tests conducted on day 11, 25, and 39. On day 11 (after 18 pore volumes), column fly ash barrier exhibited a clear-sighted plug flow pattern with a mean residence time of ~825 min, thus the porosity can be calculated as 32%. This porosity is in excellent agreement with the value (~33%) obtained from the direct gravimetric measurement of the packed column.

Chloride breakthrough occurred much faster on day 25 (after 42 pore volumes) with 780 min residence time and the significant tailing of the tracer suggesting preferential flow development (porosity ~29%). These changes became more evident on day 39 (after 67 pore volumes) with 600 min residence time (porosity ~23%). The latter is the result of the formation of mineral precipitates and temporal clogging due to pozzolanic reactions (Komnitsas et al. 2004, Xenidis et al. 2002). Moment analysis of the tracer breakthrough curves indicates that pore water velocity within the column displays a modest increase over time for day 11 and 25 (157.09 and 170.53 cm/day, respectively). Initially the pore water velocity was 152.4 cm/day; on day 39 it increased by 27%. Conclusively, Figure 2 shows that mean tracer residence time varied considerably and that tracer spreading tended to increase over the period of operation. In general, not only does the residence time increase over time, but the breakthrough curves become also increasingly asymmetric by exhibiting enhanced tailing. Previous works have also suggested that these changes indicate the development of preferential flow due to the formation of mineral precipitates (Kamolpornwijit et al., 2003). Furthermore, as discussed in other studies conducted with several reactive mixtures (Vikesland et al., 2003, Lee et al., 2004) changes in residence time are believed to alter the pore-scale chemical reactivity of the surface.

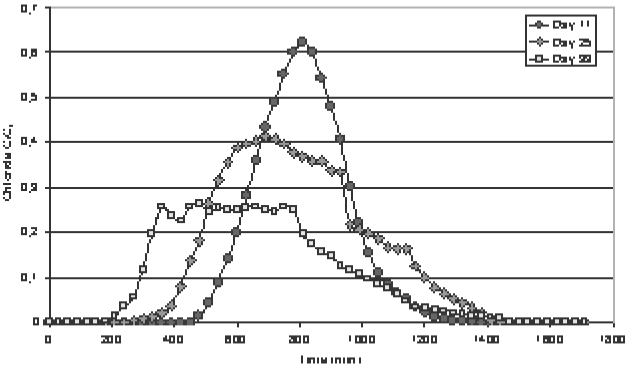

Figure 2. Chloride breakthrough curves obtained at three different times after the start of the fly ash column operation

Variabily of aqueous solution chemistry. During the early stages of treatment (until day 11), pH at sampling ports B and C remained constant (~12). However, the pH at sampling port A decreased rapidly on day 11 and after 42 pore volumes (day 25) reached 2.15 while the drop of pH at sampling port B was actually initiated after 56 pore volumes (Figure 3a).

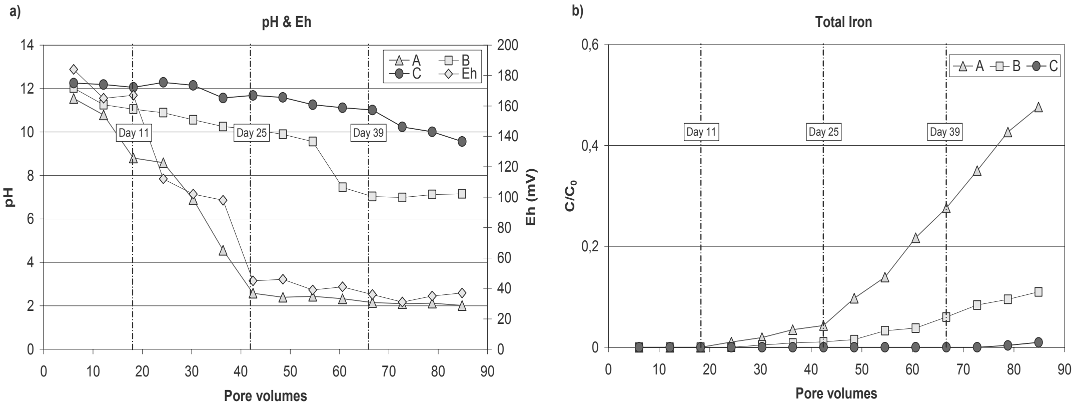

Figure 3. Experimental breakthrough curves at sampling ports A, B and C as a function of pore volumes a) pH & effluent Eh b) total dissolved iron

The effluent pH remained high for the entire period of operation indicating that although the lower parts of the PRB, coated with precipitates (25% loss of porosity was determined by tracer tests), lose part of their efficiency to buffer pH, the upper parts retain their reactivity over a long period. Over the same period redox potential was maintained at low values and varied between 30 and 190 mV, indicating that poor oxidation conditions prevail within the entire reactive mass.

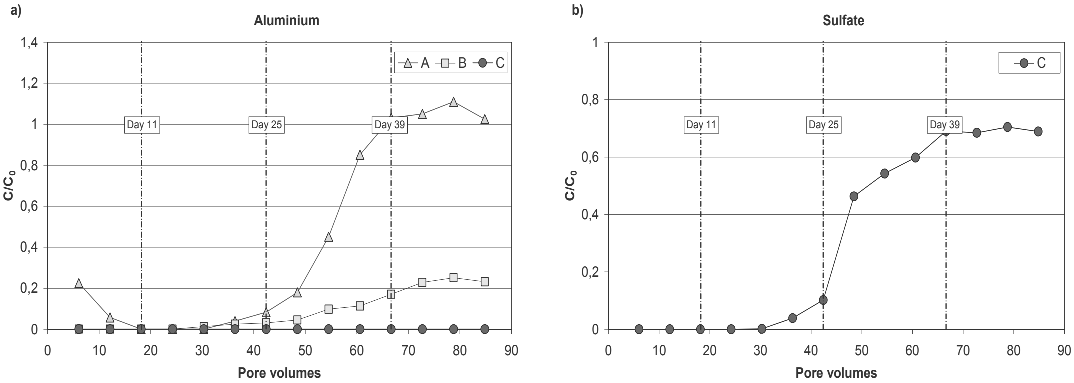

Figure 4. Experimental breakthrough curves at sampling ports A, B and C as a function of pore volumes a) Aluminium b) Effluent Sulfate

The early concentration profiles (<11 days) indicated that most of the contaminants (data not shown) were almost immediately removed and could not to be detected even at sampling port A. On day 11, tracer tests also confirmed plug flow pattern (constant reactivity) suggesting that no preferential flow has developed. On day 25, column reactivity regarding Al (Figure 4a), Cu, Cd, Mn, Zn, Co and Ni (data not shown) has started to decrease such that most of those metals were detected later at sampling port B (day 39). As seen in Figures 3b and 4b the concentrations of total dissolved iron and sulfate after day 25 indicates clear signs of reactive media exhaustion.

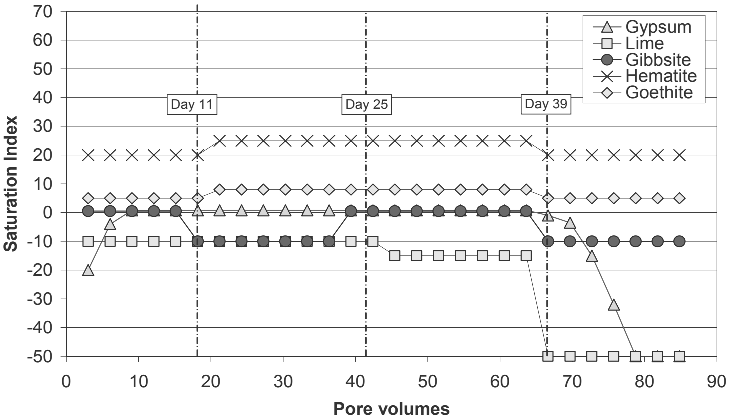

Figure 5. Saturation indices of gypsum, lime, gibbsite, hematite and goethite vs. pore volumes for fly ash column configuration

Geochemical modelling with PHREEQC also confirmed loss of column porosity due to the formation of mineral precipitates. Calculated saturation indices (Figure 5) indicate that the high load feed remains for about 42 pore volumes (day 25) saturated with respect to gypsum, goethite and hematite and simultaneously undersaturated with respect to gibbsite and lime, suggesting thus gradual depletion of lime and simultaneous precipitation of gypsum. On day 25, the incoming feed becomes also saturated with respect to gibbsite but after 67 pore volumes (day 39) total depletion of lime is seen.

Red mud column tests

Tracer tests. Effluent Cl^- breakthrough curves are presented in Figure 6 for four tracer tests conducted on day 11, 25, 39 and 52. On day 11 and 25 (after 18 and 42 pore volumes, respectively), the system exhibited clear plug flow patterns with a mean residence time of ~840 min and ~825 min. From these values the porosity can be calculated as 29.6% and 29.1%. These values are in very good agreement with the value (~30%) obtained from direct gravimetrically measurement of the packed column suggesting no significant loss of porosity for the first 42 pore volumes.

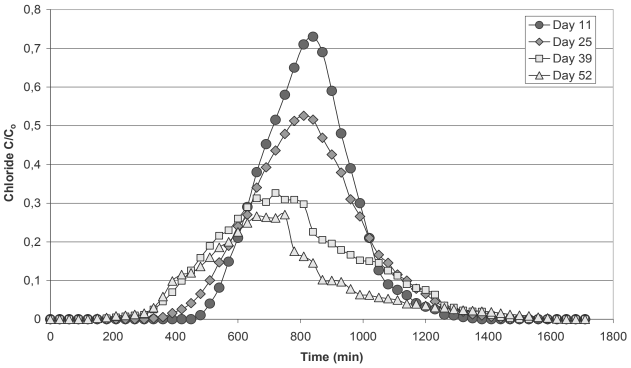

Figure 6. Chloride breakthrough curves obtained at four different times after the start of the red mud column operation.

Chloride breakthrough occurred much faster on day 39 (after 67 pore volumes) with 780 min residence time and significant tailing of the tracer (Figure 6); this suggests development of preferential flow (porosity ~27%). These changes became more evident on day 52 (after 91 pore volumes) with 600 min residence time (porosity ~25.4%) suggesting mineral precipitation. Moment analysis of the tracer breakthrough curves indicates that pore water velocity (initially 152.4 cm/day) displays trivial increase over time for day 11 and 25 (154.28 and 157.09 cm/day, respectively). Even on day 39 it slightly increased by 8% reaching the final value of 180 cm/day on day 52 (18%). Conclusively, Figure 6 shows that the red mud column differs significantly from the fly ash column by exhibiting constant reactivity and maintaining its porosity over a long period.

Variability of aqueous solution chemistry. Effluent pH values at sampling port C remained slightly constant (8~10). However, the pH at sampling port A decreased rapidly on day 11 and after 67 pore volumes (day 39) reached 2.89 while the decrease of pH at sampling port B was actually initiated after 42 pore volumes (Figure 7a).

The buffering capacity of red mud decreased gradually over time but maintained its reactivity near the exit of the system (tracer tests, pH profile). pH and redox exhibited similar trends to those seen in fly ash columns.

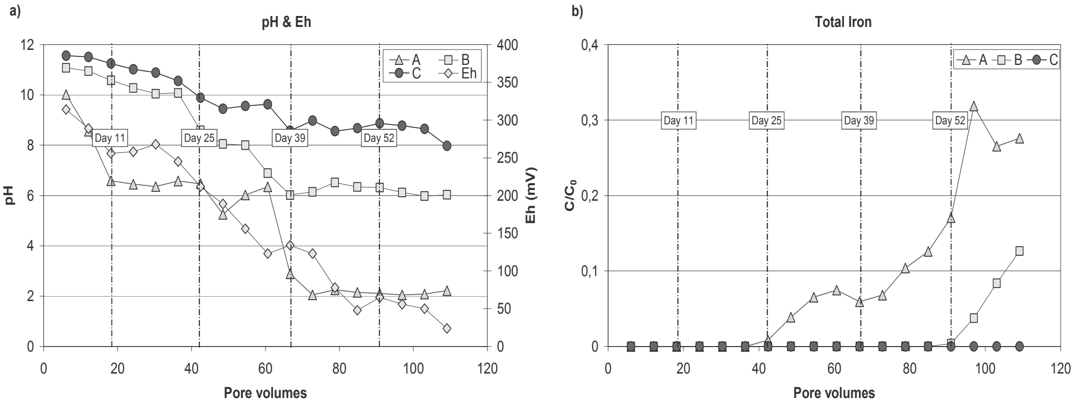

Figure 7. Experimental breakthrough curves at sampling ports A, B and C as a function of pore volumes a) pH & effluent Eh b) total dissolved iron

The ion profiles obtained indicate that most of the contaminants (data not shown) removed over the entire operation period (63 days). On day 11 and 25, their concentration (data not shown) remained below detection limits. For this period, tracer tests showed plug flow operation suggesting that no preferential flow was developed. On day 39, dissolved Al (Figure 8a), Cu, Cd, Mn, Zn, Co and Ni (data not shown) appears at sampling port A. Total dissolved iron concentration exhibited a constant increase after day 39 (Figure 7b). Throughout column operation, sulfate concentrations compared with those recorded in fly ash columns remained low. This is due to gypsum precipitation and suggests long-term reactivity (Figure 8b).

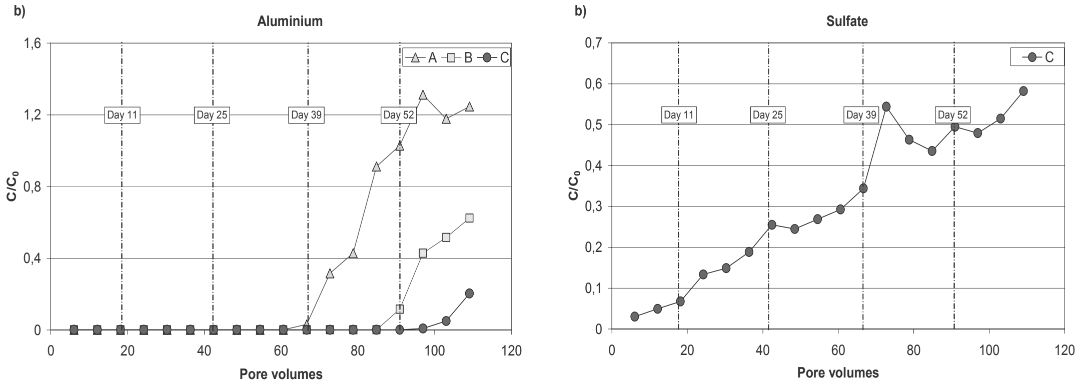

Figure 8. Experimental breakthrough curves at sampling ports A, B and C as a function of pore volumes a) Aluminium b) Effluent sulfate

PHREEQC also verified loss of column porosity as a result of the formation of certain mineral precipitates. Calculated saturation indices (Figure 9) indicate that the simulated AMD solution remains for almost 42 pore volumes (day 25) supersaturated with respect to gypsum, goethite, saturated with respect to ferrihydrite and slightly saturated with respect to gibbsite and lime. On day 39, the high load feed shows undersaturation with respect to lime suggesting strong evidence of its depletion.

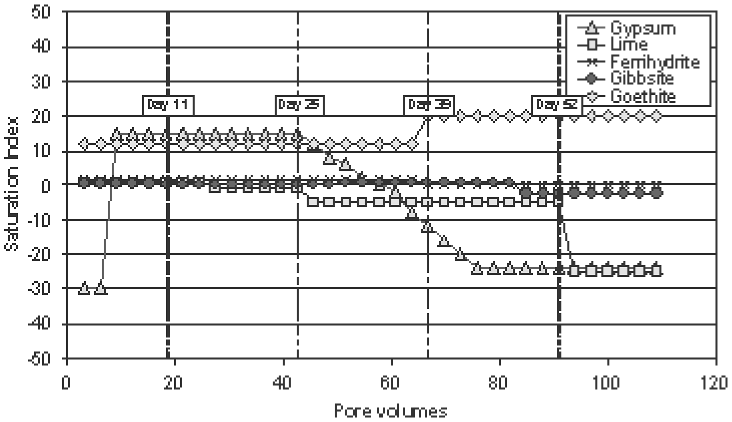

Figure 9. Saturation indices of gypsum, lime, ferrihydrite, gibbsite and goethite vs. pore volumes for red mud column configuration

CONCLUSION

The three most important factors to assess the suitability of fly ash and red mud as permeable reactive barrier media are pore water chemistry, hydraulic conductivity and loss of porosity. Laboratory tests (hydraulic conductivity tests, tracer tests, analysis of ion profiles) and geochemical modeling provide indications as to where precipitation occurs and how heterogeneous flow develops. The longer-term declines in reactivity observed for fly ash systems, is due to the formation of mineral precipitates and temporal clogging as pozzolanic reactions take place. On the contrary, red mud columns maintain their reactivity and porosity over long periods.

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