PASSIVE TREATMENT OF AMD WITH A FILTER OF CEMENTED POROUS PELLETS OF TRANSFORMED RED MUD

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Abstract

The successful passive treatment of Acid Mine Drainage (AMD) by means of a Permeable Reactive Barrier (PRB) is a function of (i) the composition and volumetric flow rate of the AMD, (ii) the hydraulics and architecture of the filter, and (iii) the reactants used. Cemented porous pellets of transformed Red Mud are an innovative mineral reactant that can be tailor made to suit the specific properties of the AMD and PRB. It is shown how, in a bench-scale column test, the cemented porous pellets of transformed Red Mud efficiently remove aluminium and other metals from SE Sardinian AMD, whereas more classical reactants like crushed marble failed due to premature clogging of pore space and sealing of reactants by $Al(OH)_3$ precipitates.

Introduction

The long-term active treatment of acid and metal-contaminated ground water flowing from (abandoned) mines (Acid Mine Drainage) is perceived as costly. Consequently, the last decades showed development of passive AMD treatment by means of more cost-effective filters (Permeable Reactive Barriers), not requiring continuous presence of operating personnel or the use of powered equipment. The appropriate type of PRB appears to be a function of (i) the composition and volumetric flow rate of the AMD, (ii) the hydraulics and architecture of the filter, and (iii) the reactants that are used to neutralize acid and/or immobilize metals (Younger, 2000).

A regularly encountered problem during the operation of a PRB is premature exhaustion of its capacity due to clogging of pore space and sealing of reactants by metal precipitates. For instance, treatment of AMD from an abandoned mine gallery in SE Sardinia by means of a conventional filter of crushed limestone, appeared hardly feasible due to massive aluminium hydroxide precipitation in the first centimeters of the column. The same AMD can be effectively treated with a filter column of cemented porous pellets of transformed Red Mud, which can be designed to suit the properties of the AMD and the architecture of the filter. It is expected that this innovative reactant finds application in the remediation of the widespread environmental pollution caused by the abandoned mines of Sardinia and, at the same time, contributes to the sustainable management of Sardinian Red Mud waste, of which about 1 million m^3 is generated each year during bauxite refining and deposited in several tens of million m^3 large tailings dams, occupying valuable land in the SW of Sardinia (European Commission, 2004; Teodosi, 2004).

The idea to use caustic (pH > 13) Red Mud in environmental remediation is not new. During the second half of the last century, studies showed that Red Mud, mainly composed of micron-sized particles of hematite, gibbsite and sodalite, mixed with caustic liquor of sodium carbonate and hydroxide (McConchie et al., 1999, 2000; Hanaban et al., 2004), could be effectively used to bind phosphate (Shannon and Verghese, 1976; Vlahos et al., 1989), neutralize and decontaminate heavy metal-rich acid to slightly alkaline (mine) waters (Glenister and Thornber, 1985; Apak et al., 1998; López et al., 1998), and neutralize acid-sulfate soils (McConchie and Clark, 2000). However, systematic re-use of Red Mud in environmental remediation was not regularly practiced, until recently, when an industrial method was developed (BASECON^{TM} process) in order to transform the caustic Red Mud, by means of reaction with Mg and Ca salt, into a more benign environmental remediation product of pH ~ 8.5 (BAUXSOL^{TM}, McConchie et al., 1996; Brunori et al., 2005a, b; Zijlstra et al., 2005). The fine-grained transformed Red Mud mixed with a supportive matrix of quartz sand was first used in a PRB to successfully treat low volumetric flow AMD (Munro et al., 2004; Lapointe et al., 2006). Subsequently, the transformed Red Mud was cemented into sub-angular porous pellets of mm-cm-dm size (Fig. 1), also allowing the use in PRB for treatment of AMD flowing at relatively high volumetric rate.

This paper describes the results of the use of cemented porous pellets of transformed Sardinian Red Mud on bench scale, demonstrating the effective neutralization of the before mentioned SE-Sardinian AMD and the removal of metals by means of adsorption and/or precipitation, even in case of massive precipitation of aluminium hydroxide gel.

Methods

SE Sardinian mine gallery water with a few ppm of ferric hydroxide in suspension was collected during spring time at the end of the rainy season (AMD0) and during autumn, after onset of the rainy season (AMD1 and AMD2, kindly provided by IGAG – CNR). Spring and autumn mine waters were titrated with 0.02 M NaOH

solution up to pH 9.5, over a period of 24 hours, in order to define the acidity. Sub-samples of 100 ml of AMD0, AMD1 and AMD2 were first acidified with 1 ml 65% nitric acid to dissolve suspended iron (and any adsorbed arsenic) and then filtered through 0.45 μm membrane before analysis of Al, As, Cd, Cu, Fe, Mn, Pb and Zn by means of ICP-MS.
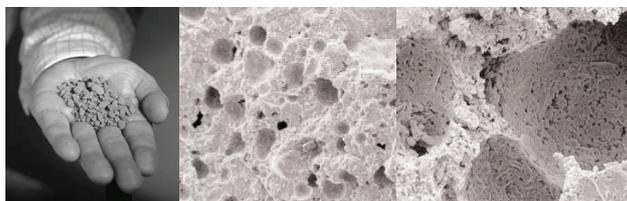
Figure 1. Porous transformed Red Mud pellets of cm-size (left-hand picture), with macro-pores of ~ 100 micron (middle SEM picture), occurring in a matrix with interconnecting micro-pores of ~ 1 micron (right-hand SEM picture).

A porous pellet was prepared with a relatively low Acid Neutralizing Capacity (ANC) of 4 mol/kg at end-pH 5.5, a specific density of 1.15 kg/dm^3, an internal porosity of 50%, and an average size between 1 and 4 mm. The pellet was finely crushed and 500 milligram quantities were stepwise added to 1 L of continuously mixed AMD0, until a pH of 9.2 was reached after 120 minutes, in order to define the approximate amount of pellet reactant required for neutralization and metal removal from AMD in batch and column test.

An about 12 cm high bed of 89 g of pellets, with 145 ml bed volume and 46% inter-pellet porosity, was added to a plexi-glass column with an inner diameter of 3.9 cm, and with a plastic sieve at the bottom. After saturation of intra- and inter pellet pore space with tab water, AMD1 was pumped from a 5 L HDPE container, through a silicon rubber tube, by means of a Watson Marlow 101F peristaltic pump, into a funnel filled with mm-sized glass beads, connected to the bottom of the column. Effluent was collected in another 5 L HDPE container, via a silicon rubber tube, connected to a plexi-glass tube, opening into the top side of the column.

First 5 L of AMD1 and then 20 L of slightly less concentrated AMD2 were pumped through the column in upward saturated, interrupted, flow mode, and at a volumetric rate between 2.5 and 3.0 ml/min. At regular time intervals, 100 ml sub-samples of clear effluent were collected. After measurement of pH and EC (Electrical Conductivity), sub-samples were first acidified with 1 ml 65% nitric acid to dissolve eventual (re-)suspended metal precipitates (e.g. particulate aluminium hydroxide), and then filtered through 0.45 μm membrane before analysis of Al, As, Cd, Cu, Fe, Mn, Pb and Zn by means of ICP-MS.

Results and Discussion

Analysis of AMD, collected at the end (AMD0) and at the beginning (AMD1 and AMD2) of the rainy period of SE Sardinia, clearly shows a seasonal variation of pH, EC and metal concentrations (Table 1). Metal concentrations almost double and acidity, as defined by OH$^-$ consumed during titration with NaOH, increases from 2.2 for AMD0 to 3.3 mmole/L for AMD1. The reason for this seasonal variation might be sought in the relatively low volumetric flow rate of 0.3 – 0.5 L/sec of the AMD, in combination with summer evaporation, concentration of acid and metals in the groundwater, production of new acid and dissolved metals during ongoing (microbially catalyzed) oxidation, finally followed by flushing out of relatively concentrated groundwater during the first rain fall.

Table 1. Analysis of AMD collected at the end (AMD0) and at the beginning (AMD1 and AMD2) of the rainy season of SE Sardinia. EC expressed in μS/cm, and metal concentrations in mg/L.

	pH	EC	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
AMD0	4.4	1192	8.5	0.09	0.06	0.22	1.9	1.9	0.20	7.9
AMD1	3.6	1223	14.6	0.19	0.10	0.96	4.0	3.4	0.77	13.8
AMD2	3.8	1252	11.6	0.32	0.07	0.45	5.1	2.7	0.55	9.3

The results of the column test (Fig. 2) show that, during treatment of 25 L and passing of about 176 bed volumes, pH effectively raises from around 3.8 for influent to on average 7.6 for effluent, while effluent EC is slightly higher than influent EC. Only at the very beginning of the column test, EC of the effluent is about 3 times the EC of the influent; this can be attributed to calcium and magnesium salts initially washed from the cemented porous pellets of transformed Red Mud.

As far as concerns the removal efficiency for metals, one might distinguish very good overall removal efficiency for As, Pb and Fe; good for Al and Cu; fair for Cd and Zn; and very poor overall removal efficiency for Mn. The

concentration profile of Al and, to a lesser extent, the profiles of Cu, Fe and As show an initial removal efficiency that is lower than successively. Such an effect might be contributed to an initially still relatively strong pH gradient between AMD flowing in pores and alkaline fluid in and around pellets, causing metal precipitation in solution, rather than on and in pellets, so that an appreciable amount of suspended metal precipitate is transported out of the column. Concerning the improving removal efficiency for As after some bed volumes have passed, it is assumed that the adsorption capacity of, in particular, the hematite in the pellets improves significantly (> 1 mg/g BAUXSOL[TM], Genc-Fuhrmann et al., 2004) when the pH inside, and around the pellets starts to drops below 6.5. This occurs after sufficient acid mine water has flowed in order to consume at least a substantial part of the pellet ANC at the entrance or up-current part of the column.
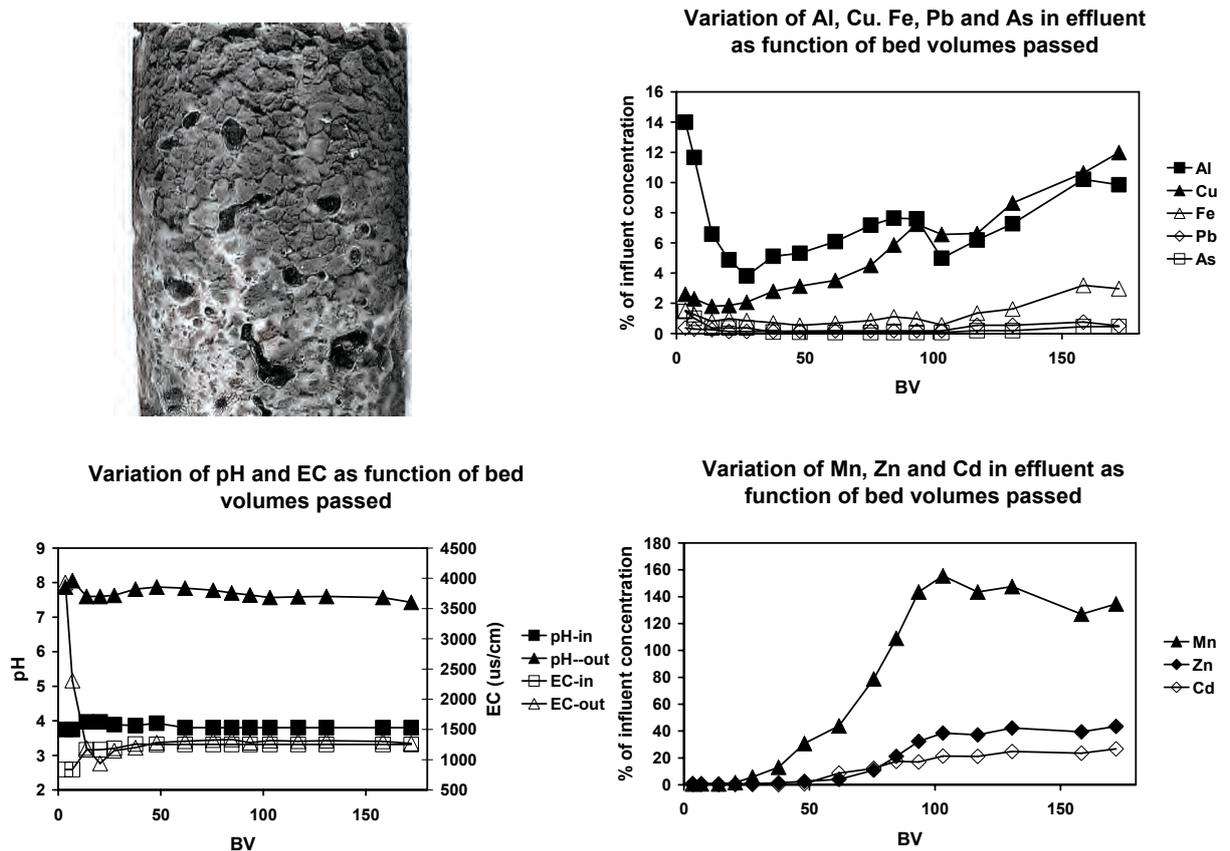

Figure 2. Upper left: Detail of the 12 cm high and 3.9 cm wide pellet bed as it appears at the end of the test (width of view ~ 4.5 cm, flow from bottom to top); the transition from a lower zone, where the inter pellet pore-space is filled with light-grey colored Al(OH)$_3$ precipitate and dark colored preferential flow paths are visible, to an upper zone, where pellets and initial packing seem relatively un-affected by precipitation and 'dissolution', can be seen. Lower left: Variation of pH and EC of influent and effluent as function of 25 L or 176 bed volumes passed. Upper right: Variation of Al, Cu, Fe, Pb and As concentrations in effluent as function of bed volumes passed, and expressed as percentage of metal concentration in influent. Lower right: Variation of Mn, Zn and Cd concentrations in effluent as function of bed volumes passed, and expressed as percentage of metal concentration in influent.

The gradual decrease of the metal removal efficiencies for Al, Cu, Fe, Pb and As might not be as much a consequence of exhaustion of the column by reactant consumption or pellet sealing, in particular because the effluent pH remains well above the pH at which these metals precipitate. It is likely that the massive Al(OH)$_3$ precipitation and progressive decrease of pore space causes a substantial increase of flow velocity and consequently a decrease of the already limited residence and reaction time (22 minutes) in this rather short column. The concentration profiles of Mn, Zn and Cd show a very high initial removal efficiency, in line with the relatively high pH at which they precipitate. The gradual decrease of removal efficiency for Zn and Cd, with increasing bed volumes passed, may again be explained by an increase of flow velocity and decrease of reaction

time. However, for these metals, also the decrease of pH in the initial part of the column may reduce the immobilization efficiency considerably, and as demonstrated by the Mn profile in particular, it is evident that a substantial part of the initially immobilized metal goes into solution again and is then transported out of the column.

When comparing the batch and column average metal removal efficiencies (Table 2), it appears that for Al, As, Cu, Fe and Pb, the pellet column performs better than the crushed pellet in batch. This most likely reflects the substantially larger volume of the solid-fluid boundary layer of the column, as compared to that of the batch test, notwithstanding the slightly lower pellet reactant concentration of 3.5 g/L and contact time of <22 minutes for the column, as compared to the respective values of 3.7 g/L and 120 minutes for the batch test. For the metals Cd, Mn and Zn, the reversed is observed, reflecting the lower overall pH of the column as compared to the end-pH of the batch test, and additionally, the effect of the dissolution/desorption in the up-current part of the column, as reaction fronts move further down-current.

Table 2. Reactant use (g/L), pH, EC (µS/cm) (time averaged for column) and metal removal efficiencies (%) for AMD0 mixed 2 hours with crushed pellet material in beaker, and AMD1 and AMD2, pumped during 9 days through the column.

	g/L	pH	EC	Al	As	Cd	Cu	Fe	Mn	Pb	Zn
Batch	3.7	8.9	1219	90.4	91.9	95.8	81.0	87.5	66.1	94.0	98.1
Column	3.5	7.6	1345	92.8	99.8	86.0	94.4	98.6	13.4	99.7	78.7

The current column test is performed in order to demonstrate that cemented porous pellets of transformed Red Mud, combining a relatively high specific reaction surface with a relatively low ANC and reaction rate, can be used to decrease $Al(OH)_3$ precipitation rate, stretch the $Al(OH)_3$ precipitation zone along the length-axis of the column, and prevent the clogging and premature exhaustion of filter capacity. The simultaneous efficient removal of metals like Mn, Zn and Cd is not attempted and requires a longer column or the use of a higher ANC type of cemented porous pellet of transformed Red Mud at the down-current end of the column.

Conclusions

The use of cemented porous pellets of transformed Red Mud for treatment of Acid Mine Drainage is an example of Geochemical Engineering and the application of minerals to manage adverse anthropogenic influences on the natural geochemical cycle (Vriend and Zijlstra, 1999). The pellet filter effectively treats AMD whereas other types of natural mineral filters may fail due to clogging of pore space and sealing of reactants by massive metal salt precipitation. The artificially produced mineral pellets are an innovative instrument for combating environmental pollution by AMD, as they can be specifically designed and adapted to its composition, volumetric flow rate, and the architecture of the Permeable Reactive Barrier. Pilot tests of substantially larger dimension are planned in order to demonstrate that the cemented porous pellets of transformed Red Mud can effectively treat AMD at volumetric flow rates that are 10^5 times larger than those of the above described bench-scale column test, while filter bed life time is in the order of years, instead of days.

Acknowledgements

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