Neutralization and Decontamination of Acid Leachates using Bauxite Red Mud

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Abstract The feasibility of red mud, a bauxite refining residue, for the treatment of acid leachates was studied. Acid neutralization capacities (ANC) at pH 4 and at pH 2 of red mud were calculated as ≈2.0 and 4.8 mmol H^+ kg^{-1} RM, and they were dependent on the time of reaction. Permeation of red mud with acidic solutions (pH 2) showed that the effluent pH was maintained ≥8 after the percolation of ≈8 pore volumes of acidic solutions. Neutralization was accompanied by the dissolution of mainly Na, Ca, Si and Al. Red mud has noteworthy potential applications for the neutralization and depuration of acidic mine waters.

Key Words red mud, acidic mine waters, neutralization capacity, reutilization

Introduction

Besides the important and strategic contribution of mining industry to the European economy, mining activities also cause environmental problems, especially in the case of closed mines abandoned without proper safety and restoration. Acid mine drainage (AMD) is one of the most critical environmental problems resulting from mining activities, and it is a major cause of ground and surface water pollution in the EU. Estimation suggests that as much as 4500 km of European watercourses are currently polluted by contaminated drainage from abandoned mines (Younger 2002). AMD polluted waters are generated by the biologically enhanced oxidation of metal sulphides, which results in ore dissolution and the release of sulphates, protons and heavy metals in soil solution. The negative effects of AMD are often diminished by neutralization, since heavy metals precipitate at high pH. The usual techniques for this process can be classified according to different approaches, but a distinction is usually made between both chemical and biological, and passive or active treatments.

As the costs associated to the remediation of contaminated sites can be extremely high, it is interesting to develop low–cost methods to prevent and/or to treat AMD. One well known technique to mitigate AMD is the addition of alkaline materials to reactive tailings to increase the pH, reduce the proliferation of bacteria, fix metals and reduce the activity of Fe (III) via the precipitation of Fe oxyhydroxide. Neutralization of AMD with various liming agents such as lime, sodium hydroxide and limestone has been widely used. Also, some industrial wastes produced in large volumes (e.g. rotary kiln fines, lime kiln dusts, cement kiln dust and fly ashes, among others) present very interesting alkaline properties that make them susceptible of being used as additives to avoid the generation of AMD and the release of toxic metals from acid mine tailings. Towards this direction, some research groups have tested successfully red mud (RM) for limiting AMD generation and/or to treat it (Doye and Duchesne 2003). Red mud is the fine residue of bauxite refining using the Bayer process to obtain alumina. RM is generated in enormous quantities worldwide (≈90 million tonnes per year) (Kumar *et al.* 2006), so the search of alternative uses of this material is a priority for the society in general and for the aluminium industry in particular. Chemically, RM is a strongly alkaline and oxide–rich (mainly Fe, Al and Ti oxides) material and therefore it has a high capacity to neutralize acid solutions and to retain metals and metalloids by sorption/precipitation processes (Altundoğan *et al.* 2000; López *et al.* 1998). RM is also the basis of Bauxsol™ technology (sea water–neutralized RM, Virotec International Ltd), which has been used to treat contaminated wastewater with arsenic (Genç *et al.* 2003), AMD (Davies-McConchie *et al.* 2002), and to immobilize metals in polluted mine soils (Brunori *et al.* 2005).

Therefore, all these neutralizing and adsorbent properties of red mud acting combined suggest that RM may be used to prevent/control/treat acidic leachates and to avoid leachability and movement of toxic metals, therefore protecting soil and water from contamination. However, considering the high variability in the RM chemical and mineralogical composition, a detailed study of RM from different factories is needed in order to definitely evaluate the potential reuse of this residue to treat acidic waters. Moreover, the mechanisms and components of RM responsible of these neutralization properties in the different pH ranges and types of acids remain still unclear.

In this work, the interaction of RM and acidic solutions was studied. Acid neutralization curves, dissolution tests in function of pH, and continuous flow percolation test of RM with acidic solutions were carried out to evaluate the feasibility of RM to neutralize/treat acid leachates and to elucidate the mechanisms and the components of RM controlling the process at different pH conditions and reaction times.

Methods

Red Mud Pre-treatment and Characterisation

The RM studied was obtained as fresh alkaline suspension (≈50% water content) from the ALCOA-San Cibrao alumina factory (Lugo, NW Spain). RM was air-dried (≈20°C) during three weeks, then crushed and sieved (<0.250 mm). The main chemical constituents of the RM used were (%w/w): 37.22±0.33% Fe_2O_3, 20.10±0.59% TiO_2, 12.40±1.07% Al_2O_3, 6.30±0.20% CaO, 4.64±0.41% Na_2O, 3.81±0.16% SiO_2, 0.51±0.02% P_2O_5, 0.36±0.02% ZrO_2 and 0.14±0.00% MgO, loss on ignition 11.34±0.02%. The main mineral phases (X-Ray diffraction) were hematite, rutile, magnetite, boehmite, ilmenite and zeolite-type minerals (≈9%). The BET-surface area of the red mud was 23.7 m^2g^{-1}. The RM studied had a pH (as a 1:5 mixture in water) of 9.7±0.1 and a pH_{pzc} of 8.29 in 0.01M NaCl. Cation exchange capacity (ammonium acetate pH 7) of RM was 10.83±0.02 $cmol_c\ kg^{-1}$.

Acid Neutralization Curves for Red Mud

Acid neutralization properties of RM were studied by developing rapid and pseudo–equilibrium acid neutralization curves by additions of HCl from an initial pH of ≈9.3 to final pH ≈2. Rapid neutralization curve of RM was made using a rapid titration procedure of a suspension of RM (100 mg) in CO_2 – free deionized water (25 mL) by adding small aliquots (100 µL) of 0.1M HCl under N_2 continuous flow, using a Metrohm 702SM Titrino automatic titrator. Reaction time between each addition of acid was 5 min and the final pH of the titration was set at pH = 2. Neutralization curve for RM was constructed representing the recorded pH values against the corresponding concentration of added H^+. Once the final pH was reached, the suspension was centrifuged (14400 g), filtered (0.45 µm) and analysed for Fe, Al, Si, Ti, Ca, Mg and Na by atomic absorption spectrophotometry (AAS). Titrations were repeated, and solutions were analysed, following an identical procedure, but setting the final pH at pH 6 and pH 4.

Equilibrium acid neutralization curve for RM was developed by shaking (t = 24 h, rotary shaker) a series of N_2–purged PP centrifuge tubes containing a fixed amount of RM (5 g) with HCl aqueous solutions (50 mL) of increasing concentration, resulting in acid additions between 0 and 7.18 mol $H^+\ kg^{-1}$. After the reaction period, pH values of the suspensions were measured using a combined glass electrode, then centrifuged, filtered and analysed as described above.

RM dose versus pH curve was developed to estimate the amount of RM required to raise the pH of an acid solution to a desired final pH value, by reaction of increasing amounts of RM (ranged between 1 and 5000 mg) with 100 mL of an CO_2 – free 0.01M HCl solution (pH ≈2). The suspensions were shaken during 72 h in a rotary shaker and then their final respective pH values were measured.

Acid Dissolution Tests

Two types of experiments were carried out to study the dissolution of the main components of RM when exposed to acid conditions: (i) pH_{stat} leachability tests, where a suspension of RM in DI water (solid:solution ratio 1:100) was leached at constant pH_{stat} = 3 during a period of 24 h. pH was adjusted and controlled during all the leaching period by small additions of 1M HCl using a Metrohm 702SM automatic titrator working in pH_{stat} mode. After the leaching period, the suspension was centrifuged and filtered (0.45 µm), and the concentrations of dissolved Fe, Al, Ti and Si in the extracts were measured by AAS, and (ii) Batch dissolution tests in strongly acidic solutions, where RM was leached (solid:solution ratio 1:20, t = 24 h) with 0.1, 0.25, 0.5, 1, 3 and 6 M HCl solutions, respectively. After the extraction period, the suspensions were centrifuged, filtered and analysed as described above.

Percolation Experiment

In this experiment a probe of compacted (Proctor standard test) RM (40 mm height × 56 mm diameter, dry density = 1.60 Mg m^{-3}, water content = 30%, porosity e = 1.2) was sequentially percolated initially with DI water, then with acetic acid solutions of pH 4 and pH 2, and finally again with water. A total of ≈10 pore volumes of influent were passed through the red mud probe. The effluents were periodically sampled and analysed for pH, EC, suspension solids, turbidity and main constituents of red mud (Fe, Al, Si).

Results and discussion

Acid Neutralization Curves for Red Mud

The rapid acid neutralization curve obtained for RM (Figure 1a) presented the typical shape of RM curves with different origin and composition (Snars *et al.* 2004). It was characterized by a sudden drop of pH from its initial pH = 9.3 to pH ≈5 after addition of 0.44 mol $H^+\ kg^{-1}$. However, addition of acid beyond this pH value only caused a slight decrease of pH, which was reflected in the levelled shape of the curve in the pH range 5–4, corresponding to an acid addition of 2 mol $H^+\ kg^{-1}$. Addition of acid beyond this value caused a slow and progressive decrease of pH until the final pH was reached (≈5.5 mol $H^+\ kg^{-1}$ added to the suspension). From this curve, immediate ANC of RM at pH 6.5, 4.3 and 2.3 were calculated as 0.1, 1.7 and 4.8 mol H^+kg^{-1}. The initial pH of the neutralisation curve represents the free alkali in solution, which corresponds with the residual alkali in RM from the bauxite digestion step. This free alkali reacts first and it is quickly consumed above pH 7, causing an abrupt drop of pH. The buffered region observed between pH ≈5 and 4 is consequence of the interaction of H^+ with the solid components of RM. Neutralization of added H^+ may occur by adsorption of H^+ onto the negative charged sites of RM surface or may be due to the consumption of H^+ by dissolution of some components of RM. Since RM is a heterogeneous material, it is plausible that the dissolution of the different RM components –and the corresponding neutralization of H^+– are different in each pH interval. To clarify this question, dissolution of main components of RM at final pH 6, 4 and 2 was measured (Table 1).

The addition of acid to pH 6 caused mainly the dissolution of Ca and Na of RM, although the low percentages of total Na and Ca dissolved at this pH are indicative of the slow release of both elements from RM. A decrease in pH to pH 4 caused an increase in the dissolved Na and Ca concentration, although their rates of dissolution within this pH range were lower than within the first region of the neutralisation curve. Significant amounts of Al and Si were dissolved at pH 4, which suggests that the dissolution of the zeolitic aluminosilicates of RM at pH ≤5 is responsible of the buffering region observed in the neutralization curve. Dissolution of Fe at pH 4 was negligible (Table 1). When the pH was lowered to pH 2, the concentrations of Na, and especially of Ca (which was almost twice the concentration dissolved at pH 4), still continued to increase. This additional Ca may proceed from the previously undissolved calcite and other alkaline components of RM, and from the zeolite-type minerals containing Ca. Al and Si dissolution increased markedly at this pH, and the dissolved amounts of both elements were almost equivalent, which agrees with the stoichiometry of the main zeolitic minerals identified in the RM: sodalite, nosean and cancrinite. The dissolved percentages of Al and Si represented the 33 and 100% of total contents in RM, respectively, which suggests the complete dissolution of desilication product (DSP) of RM at pH 2. Acidification at pH 2 increased the dissolved Fe concentration, although the total dissolved Fe was very low, reflecting the high crystallinity and chemical stability of Fe oxides of RM. Ti was not detected in none of the extracts analyzed.

The acid neutralization curve obtained for a 24 h period (Figure 1a) showed that acid neutralization properties of RM are dependent on the time of reaction, visualized in a displacement of the neutralization curve to higher pH values as the reaction time increased, due to the slow dissolution kinetics of some components of the RM. The 24 h neutralization curve was also different in shape, exhibiting buffered regions not visualized in the instantaneous neutralization curve, which suggests that also different mechanisms act at different reaction times. Three main buffered regions were observed in the neutralization curve: (i) pH ≈7 – 6, (ii) pH ≈4 – 3, and (iii) pH ≈0.8 – 0.5, and a less evident region between pH ≈9.3 – 8. In general, the ANC of RM increased with the reaction time, and the differences between both curves were evident especially at low acid addition rates. However, for very high acid addition rates (pH ≤2.5), the RM equilibrated during 24 h experimented a higher decrease in pH than the RM equilibrated during 5 min. This may be attributed to the alkalinity remaining unreacted in RM at short-times, which was however released for a 24 h period as it is evidenced in the displacement of the curve observed at acid addition rates below 2 mol H^+ kg^{-1}.

Figure 1b shows the amounts of cations dissolved from RM after 24 h as a function of added acid concentration and equilibrium pH. In the first part of the curve (pH 9.3 – 8) the main dissolved cation was Na (≈10% of total Na). At pH 8 – 7 the dissolved Ca concentration increased significantly (≈13 times) to 1.65 g kg^{-1} (≈4% of total Ca). The concentration of Si also increased progressively as a consequence of the partial dissolution of DSP, which started at pH 8.3. The addition of acid up to pH 6 (1.4 mol H^+ kg^{-1}) caused the dissolution of Na (22.5 g kg^{-1}, ≈65% of total Na) and Ca (9.3 g kg^{-1}, ≈21% of total Ca) of the RM solids. Most of the released Ca at this pH proceeds from the dissolution of calcite. The dissolved Si at pH 6 represented only ≈2% of total Si, whereas Al, Fe and Ti

Table 1 *Elements (mg kg^{-1}, % of total content in parenthesis) dissolved by acidification (rapid neutralization procedure) of RM suspensions to final pH 6, 4 and 2.*

pH	Na	Ca	Mg	Fe	Al	Si
6	4003 (11.6)	4220 (9.4)	23 (2.7)	71 (0.03)	101 (0.2)	680 (3.8)
4	15500 (45.1)	8910 (19.9)	19 (2.2)	223 (0.08)	9792 (15.5)	13840 (77.8)
2	18540 (59.9)	17250 (38.5)	94 (10.8)	623 (0.23)	20980 (33.3)	20970 (100)

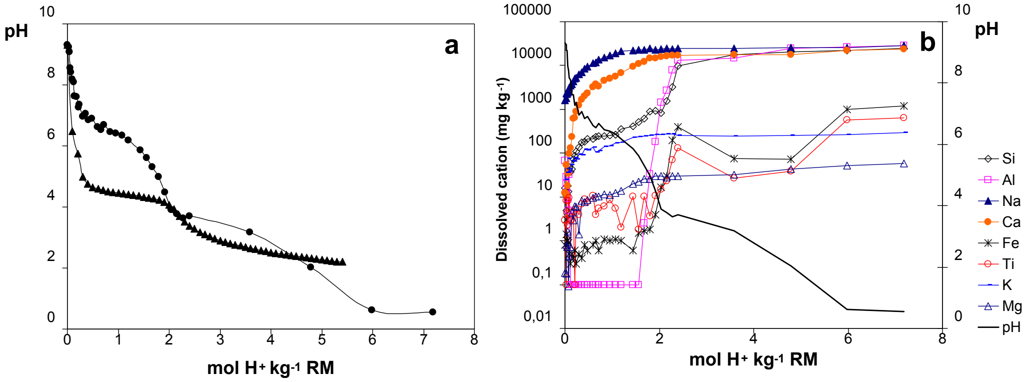

Figure 1 (a) Rapid (▲) and equilibrium (●) acid neutralization curves of RM, (b) Dissolution of cations (Y-axis) from red mud as a function of H^+ *addition rate and pH (reaction time = 24 h). pH values are showed in the secondary Y-axis. Corresponding pH values to each added acid concentration are obtained by crossing the acid concentration with the acid neutralization curve in Fig. 2b and extrapolation to the secondary Y-axis.*

dissolution was negligible in this region of the curve. The concentration of dissolved Al increased suddenly (≈14000 times) between pH 6 and 4 up to 1.43 mg kg^{-1} (≈2.3% of total Al), which corresponds with the increase in Al solubility from its minimum value of $10^{-6.5}$ to 10^{-1} mol L^{-1} at pH<5.4. Al dissolution was accompanied by the concomitant dissolution of Si, which suggests the dissolution of zeolitic Al– Si phases of RM. Fe and Ti dissolution was also promoted at pH<5 (≈1.80 mol H^+kg^{-1}), although the dissolved amounts at pH 4 represented only the 0.006 and 0.013% of total Fe and Ti in RM. Thus, the contribution of these both elements to the buffering capacity of RM in this pH region was less important. Therefore, it may be concluded that Al and Si dissolution is mainly responsible of acid buffering capacity of RM between pH 6 and 4.

A buffered region in the neutralization curve was observed between pH 4 and 2 (acid addition rates between 2 and 4.8 mol H^+ kg^{-1}). Within this pH range the dissolved Al concentration increased quickly from 1.43 to 24.58 g kg^{-1}, which represented ≈39% of total Al content. This is in accordance with the amount of amorphous Al oxides in RM (≈37%) extracted by oxalic/oxalate at pH 3. Similarly, dissolved Si concentration increased up to 20.30 g kg^{-1} at pH 2, which represented almost total dissolution of Si of RM, suggesting the complete dissolution of DSP at pH 2. These results indicate that the acid buffering capacity of RM between pH 4 and 2 is due to the dissolution of DSP and re–dissolution of previously precipitated Al at near neutral pH. Once the pH was decreased below 2, Fe dissolution started and the concentration of dissolved Fe increased from 73 mg kg^{-1} at pH 2 to 1187 mg kg^{-1} at pH 0.6. The dissolved Ti concentrations also increased within the same pH range up to 651 mg kg^{-1}. Anyway, these amounts represented as much as the 0.4 and 0.6% of total Fe and Ti, respectively, reflecting the very high stability of these both components of RM even under strong acidic conditions. The dissolved Al concentration also increased in this pH range, although at a lower dissolution rate. Therefore, Fe and Al dissolution is the mechanism responsible for the buffering capacity of RM in the lower part of the curve.

RM dose versus pH curve (not shown) showed that the pH of the suspension increased abruptly as the RM concentration increased from 0.01 to 10 g L^{-1}, but increased slightly for higher RM concentrations. The capacity of RM to neutralize H^+ increases as pH decreases, as the active components of RM are progressively dissolved and the variable charge surface sites of RM are progressively protonated. From the obtained curve, it was calculated that a dose of 7 g RM/l raises the pH of a solution from 2 to ≈ 6.5.

Acid Dissolution Tests

pH_{stat} leaching test showed that Fe dissolution at pH_{stat} 3 was very low, accounting for 0.01% of total Fe. The dissolved Ti was negligible. However, higher amounts of Al (21.4% of total) and Si (56.8% of total) were dissolved after 24 h of leaching at pH_{stat} 3, which is in accordance with the results of acid neutralization experiments. Altogether, the RM dissolution at pH_{stat} 3 accounted for ≈3% (w/w) of RM components. Extractions of RM with acidic solutions with concentrations ranged between 0.1 and 6M HCl showed that dissolution of RM components increased as the acid concentration increased. Main dissolved components were Al and Si oxides (maximum dissolution of 41 and 100% of total amount, respectively). For both elements, the dissolved amount only increased slightly at HCl concentrations >0.1M (RM suspension pH = 2). Maximum dissolution of Fe and Ti was 2.9 and 15.4% of total content, respectively, extracted by 6M HCl.

Percolation Experiments

The results obtained for the permeation of RM with acidic solutions are shown in Figure 2. Effluent pH did not decrease when 3 pore volumes of solution at pH 4 were percolated through RM. A progressive decrease in pH was observed as a pH 2 solution passed through the RM layer, although the effluent pH was always ≥8, even after the percolation of ≈ 5 pore volumes of pH 2 solution. The concentration of solids in the effluent increased initially, but it decreased progressively and it did not increase again when water was reintroduced as influent after percolation of acidic solutions. A progressive increment of effluent dissolved concentrations of Al, Si, and lower amounts of Fe, were observed as acid solutions passed through RM. This suggests that, in addition to the neutralization of H^+ by residual alkali, dissolution processes of the more soluble fractions of RM occurred when reacted with the pH 2 solution, concretely aluminosilicates integrating the DSP and amorphous oxyhydroxides. It was estimated that a volume of ≈ 116 PV of solution at pH 2 would be required to pass through the RM probe so that the effluent pH would be equal to the influent pH. It means that a period of ≈ 300 years of continuous percolation of acidic solution (pH 2) through a ≈10 cm thick layer of RM with a permeability of 1×10^{-7} cm s^{-1}, is needed so that the effluent pH would decrease to pH ≈2.

Conclusions

Red mud exhibited a high ANC as a consequence of the interaction of H^+ with the different components of RM, causing the dissolution mainly of Na, Ca, Si and Al. This suggests that the residual alkali, carbonates and amorphous aluminosilicates are the main components of RM involved in the neutralization of H^+. ANC strongly depended on the reaction time between the RM and the acid, resulting in neutralization curves with different shape at shorter and longer reaction times, respectively. This time dependence was evidenced by the displacement of the neutralization curve towards higher pH values and the visualization of new buffered regions as reaction time increased from 5 min to 24 h. The sequential permeation of RM with acidic solutions showed that RM was able to maintain the effluent pH above 8 after the percolation of ≈10 PV of acidic solutions. RM has potential utility for the neutralization and depuration of acid mine waters.

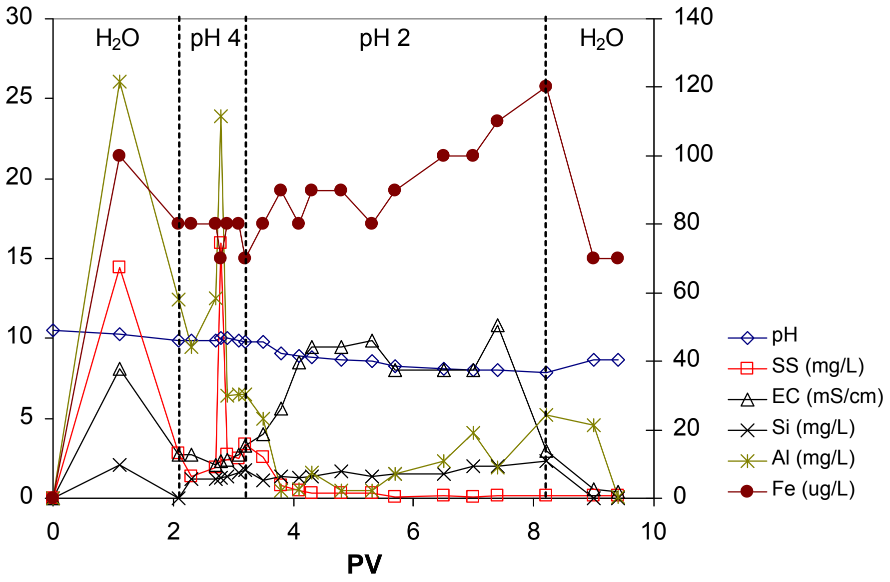

Figure 2 Chemical parameters of the effluent from sequential percolation of water and acidic solutions with pH 4 and 2 through a compacted layer of red mud as a function of pore volumes (PV). pH, suspended solids (SS), electrical conductivity at 25 ºC (EC), Si and Al dissolved concentrations (mg L^{-1}) are showed in the main Y-axis. Dissolved Fe concentrations (µg L^{-1}) are showed in the secondary Y-axis.

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