Red Mud Minimisation and Management for the Alumina Industry by the Carbonation Method

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ABSTRACT

Bauxite residue (red mud), a waste from the Bayer process for refining bauxite to alumina, is highly alkaline (pH~13) and its treatment and management have posed environmental challenges to the alumina industry. Carbonation of red mud using carbon dioxide (CO_2) has previously been demonstrated to be feasible in both permanently capturing the CO_2 and neutralising this solid waste. A systematic study of the neutralisation of red mud by CO_2 over a range of different operating conditions is essential in order to optimise the carbonation process and maximise the volume of CO_2 captured by red mud.

The objectives of this study were to determine the acid neutralisation capacity of red mud and its solid and aqueous phase contribution to the acid neutralisation capacity via the analyses of red mud compositions. A red mud sample, provided by Rio Tinto Alcan, was carbonated in a range of different operating conditions with the intent of establishing the optimal condition for the carbonation process. The carbonation was carried out at room temperature and atmospheric pressure using a stirred tank reactor operating at different conditions such as total gas flow rate, CO_2 concentrations, stirring speeds, and solids concentrations in red mud. A range of analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray (EDX), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Carbon-Hydrogen-Nitrogen Elemental Analyser (CHN) were used to ascertain the different mineral phases, change of chemical composition before and after carbonation, and carbonation capacity of the mud. Finally, based on the information of red mud composition, an equilibrium chemical model using MINEQL+ version 5.0 was developed for the carbonation process.

The acid neutralisation capacity of red mud was measured by both rapid and long-term titration of red mud slurries to pH endpoint of 4.5, 6, 8, and 10. At the endpoint of pH 4.5 corresponding to the bicarbonate endpoint, the acid neutralisation capacity of the red mud was found to be 0.79 and 1.91meq/g red mud for rapid and long-term titration, respectively. Furthermore, it is estimated that the solid phase contributed approximately 81% to the acid neutralisation capacity, while contribution from the liquid phase was only 19% in the final long-term acid neutralisation capacity determination.

The carbonation process was observed to be significantly dependent on concentration of CO_2, total gas flow rate and stirring speeds, whereas the concentration of solids in red mud seemed to have a little effect based on only three concentrations studied. For the carbonation of red mud slurry, it took from 30-75 minutes to establish the equilibrium pH of 7.5-6.6 in the range of CO_2 concentrations of 10%-100%. In contrast, when the carbonation of red mud liquor only was performed at the same range of CO_2 values, the stable pH of 7.0-6.3 (0.3-0.5 pH unit lower) was reached within 15-30 minutes. After carbonation, the pH from carbonated red mud slurries, exposed to atmosphere CO_2, rebound quickly and took about 20-25 days to reach pH of 9.7. The carbonated liquor, however, showed a lower rate of pH recovery, and took a month to equilibrate to pH of 9.7.

The XRD patterns of carbonated red mud revealed the appearance of calcite and the increase of gibbsite due to the dissolution of sodalite and the breakdown of cancrinite minerals in the carbonation of red mud. The quantifications confirmed the precipitation of calcite from 0% to 1.51%, and the increase of gibbsite from 1.04% to 5.15% in raw red mud and carbonated red mud, respectively. XRD patterns and the quantifications associated with other results such as EDX and CHN analyses

indicated that the most optimal conditions for carbonation process were 30% CO_2 concentration and total gas flow rate of 200mL/min. At this condition, the amount of CO_2 captured for the whole red mud (both solid and liquid phases) was highest at 65g CO_2/kg of red mud, and the alkalinity decreased from 11,610mg/L to 2,104mg/L as $CaCO_3$. Stirring speeds were found to be effective in boosting the extent of red mud carbonation and the amount of CO_2 sequestration. The results showed that when stirring speeds rose from 250rpm to 700rpm, the amount of CO_2 sequestration increased by 3.4g/kg of red mud, from 65 to 68.4g CO_2/kg of red mud.

The simulation for heavy metals dissolved in long-term titration of red mud at different pH levels of 4.5, 6, 8, 10, and 12.5 was performed using chemical equilibrium modelling system MINEQL+ 5.0. The modelling suggested that four key dominant metals Al, Na, Ca, and Fe were found to govern the aqueous chemistry of the red mud carbonation process due to their presence in both soluble and solid forms in red mud. Measured metal concentrations from long-term titration at various pH values indicated that boehmite (AlO(OH)) and hematite (Fe_2O_3) did not dissolve in the system, therefore, both Al and Fe were not responsible for the control of carbonation process as their concentrations remained unchanged. However, Na and Ca were considered the major solids controlling the process. The dissolution of sodalite ($Na_8(AlSiO_4)_6(OH)_2.4H_2O$) and cancrinite ($Na_6(AlSiO_4)_6(CaCO_3)(H_2O)_2$) were attributable to Na and Ca concentrations in the system. The key reactions are as below:

$$Na_8(AlSiO_4)_6(OH)_2.4H_2O + 18H^+ = 8Na^+ + 6Al^{3+} + 6Si(OH)_4 + 2H_2O$$

$$Na_6(Al_6Si_6O_{24})(CaCO_3)(H_2O)_2+24H+ = 6Na^+ + 6Al^{3+} + 6Si(OH)_4 + Ca^{2+} + CO_3^{2-} + 2H_2O$$

For carbonation process, a chemical model was formulated in MINEQL+ 5.0 to calculate the final equilibrium pH values for both carbonation of RM slurry and RM liquor at different concentration of CO_2. The results revealed that the simulated pH values for the carbonation process at different P_{CO_2} were 0.3-0.45 pH units higher than the experimental pH values. In other words, the difference in final pH equilibrium values between experimental and simulated carbonation of red mud varies from 4.0-6.0%. This difference is about 2 times lower than that of previous work done by Khaitan (2009b). The key reactions of carbonation of red mud are as follows:

Liquid phase reactions:

$$2OH^-_{(aq)} + CO_{2(aq)} \leftrightarrow CO_3^{2-} + H_2O$$

$$H_2O + CO_3^{2-} + CO_{2(aq)} \leftrightarrow HCO_3^-{}_{(aq)} + H^+_{(aq)}$$

$$[Al(OH_4)^-]_{(aq)} + CO_{2(aq)} + Na^+_{(aq)} \leftrightarrow Al(OH)_{3(s)} + Na^+_{(aq)} + HCO_3^-{}_{(aq)}$$

Solid phase reactions:

$$Na_8(AlSiO_4)_6(OH)_2.4H_2O + 18H^+ \leftrightarrow 8Na^+ + 6Al^{3+} + 6Si(OH)_4 + 2H_2O$$

$$Na_6(AlSiO_4)_6CaCO_3(H_2O)_2 \leftrightarrow 6NaAlSiO_4 + CaCO_{3(s)} + H_2O$$

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