

# Mechanisms of Neutralization of Bauxite Residue by Carbon Dioxide

Sameer Khaitan, A.M.ASCE<sup>1</sup>; David A. Dzombak, F.ASCE<sup>2</sup>; and Gregory V. Lowry, M.ASCE<sup>3</sup>

**Abstract:** Bauxite residue (red mud), an alkaline slurry from alumina refining, is produced in large volumes and disposed of in large surface impoundments. The objectives of this study were to measure the extent of neutralization of bauxite residue by carbon dioxide as a function of CO<sub>2</sub> partial pressure and to determine the geochemical reactions responsible for carbon sequestration. Bauxite residue was exposed to carbon dioxide (CO<sub>2</sub>) at partial pressures ranging from 10<sup>-3.5</sup> to 1 atm and the residue pore-water pH was measured until a steady state pH was achieved. Using pure CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub>=1 atm), a steady state pH of 7.7 was established in 1 day while it took 9 days to reach a pH of 9.8 at P<sub>CO<sub>2</sub></sub>=10<sup>-3.5</sup> atm. The pH rebounded to 9.9 after 1 day when bauxite residue first neutralized at P<sub>CO<sub>2</sub></sub> of 1, 0.1, or 0.01 atm for 10 days was subsequently exposed to P<sub>CO<sub>2</sub></sub>=10<sup>-3.5</sup> atm, indicating that the pH change during short-term carbonation (t ≤ 10 days) was due to reactions of carbonic acid and OH<sup>-</sup> in the pore water. A longer reaction time (30 days) at P<sub>CO<sub>2</sub></sub>=1 atm indicated carbonation of tricalcium aluminate (C3A solid) and conversion to calcite. This was confirmed in aged field samples that had been carbonated in air (P<sub>CO<sub>2</sub></sub>=10<sup>-3.5</sup> atm) for 30 years. The maximum solid-phase CO<sub>2</sub> sequestration (as calcite) potential of red mud can be realized at P<sub>CO<sub>2</sub></sub>=10<sup>-3.5</sup> atm; however, the sequestration rate is limited by slow dissolution of C3A. The CO<sub>2</sub> sequestration potential is small (0.029–0.057 MMT CO<sub>2</sub>/year) compared to annual CO<sub>2</sub> emissions (110 MMT/year) for bauxite refining and red mud production of 30 MMT/year.

**DOI:** 10.1061/(ASCE)EE.1943-7870.0000010

**CE Database subject headings:** Industrial plants; Solid wastes; Waste management; Simulation; Groundwater; Surface water.

## Introduction

The production of alumina by the Bayer process results in the creation of a slurry residue (red mud) containing Ca<sup>2+</sup> and Mg<sup>2+</sup> and having a pH in excess of 12.5. Approximately 3 million tons of red mud are produced in the United States each year and 30 million metric tons/yr globally (on a dry weight basis), with disposal in land-based impoundment reservoirs (Ayres et al. 2001). Problems associated with the disposal of red mud include its high pH (12–13), alkaline seepage into groundwater, and alkaline air borne dust.

Efforts to stabilize red mud typically incorporate a pH-reduction processing step by addition of amendments, followed by vegetation of the storage impoundment surface to control dust release (Wong and Ho 1994; Vachon et al. 1994; Koumanova et al. 1997; Wehr et al. 2006). The large volume of highly alkaline red mud produced annually requires an equally large source of acid to neutralize it. Neutralization of red mud by acidic water

from mine tailings has been demonstrated (Paradis et al. 2006; Duchesne and Doye 2005; Doye and Duchesne 2005). Additionally, neutralization of red mud by acidic fly ash has also been demonstrated (Khaitan et al. 2009b). The use of carbon dioxide from the atmosphere or from industrial emissions is another potentially significant source of acid for neutralizing red mud (Enick et al. 2001). Direct atmospheric emissions of greenhouse gases such as CO<sub>2</sub> from bauxite refining and aluminum smelting have been estimated worldwide at 110 million metric tons of carbon dioxide equivalent per year (IAI 2002; Martchek 2003). The ability to use red mud to sequester CO<sub>2</sub> emitted during the production of aluminium can help to offset these emissions.

The use of carbonic acid to neutralize red mud has been investigated previously. Typically, gas phase CO<sub>2</sub> or flue gas containing CO<sub>2</sub> has been bubbled through aqueous red mud slurries to form carbonic acid in the aqueous phase [Szimai et al., "Method for the multistage, waste-free processing of red mud to recover basic materials of chemical industry," U.S. Patent No. 5,053,144 (1991)]. Enick et al. (2001) contacted liquid carbon dioxide at 295 K and 6.7 MPa with red mud slurry for 10–15 min, resulting in an equilibrium pH of 9.5–10 after several weeks equilibration with the atmosphere. Cardile et al. (1994) bubbled gaseous CO<sub>2</sub> through red mud in a reaction vessel for 14 h yielding an equilibrium pH of about 8. Thus, it has been demonstrated that carbonic acid in liquid form or carbon dioxide in gaseous form can neutralize red mud, with the extent of neutralization dependent on the pressure of CO<sub>2</sub> and time of exposure. A study by Smith et al. (2003) observed pH rebound after treatment. It was hypothesized that dissolution of tricalcium aluminate (C3A) in the neutralized slurries caused this pH reversion.

The objectives of this investigation were to elucidate the pH neutralization processes occurring during red mud neutralization

<sup>1</sup>Hydraulic Design, Caltrans, 1976 E. Charter Way, Stockton, CA 95219. E-mail: sameer\_khaitan@dot.ca.gov

<sup>2</sup>Dept. of Civil and Environmental Engineering, Carnegie Mellon Univ., 5000 Forbes Ave., Pittsburgh, PA 15213. E-mail: dzombak@cmu.edu

<sup>3</sup>Dept. of Civil and Environmental Engineering, Carnegie Mellon Univ., 5000 Forbes Ave., Pittsburgh, PA 15213 (corresponding author). E-mail: glowry@cmu.edu

Note. This manuscript was submitted on August 12, 2008; approved on November 10, 2008; published online on April 3, 2009. Discussion period open until November 1, 2009; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Environmental Engineering*, Vol. 135, No. 6, June 1, 2009. ©ASCE, ISSN 0733-9372/2009/6-433-438/\$25.00.

**Table 1.** Composition of Jamaican Bauxite Residue and Pore Water [from Khaitan et al. (2009a)]; Pore Water Concentrations Measured by Alcoa (Elbicki et al. 2004) Using ICP-OES after Centrifugation Followed by Filtration of the Separated Water through a 0.45  $\mu\text{m}$  Filter to Remove Solids

Component	Dried solids concentration (mg/kg solid)	Pore water (M)
Chloride	470	0.012
Sulfate	430	0.004
Carbonate	4,000	0.12
Al	113,000	0.098
Na	54,000	0.93
Si	26,000	$1.4 \times 10^{-3}$
Fe	237,000	$<1.8 \times 10^{-6}$
Ca	48,000	$7 \times 10^{-4}$
Mg	1,200	$<4.2 \times 10^{-6}$
Cu	200	$<1.7 \times 10^{-6}$
Mn	5,800	$<1.8 \times 10^{-6}$
Ni	600	$<1.7 \times 10^{-6}$

by gaseous carbon dioxide, to identify the equilibrium pH reached for different  $\text{CO}_2$  exposure pressures, and to estimate the capacity for permanent carbon dioxide sequestration by bauxite residue. Red mud pore-water pH was determined as a function of  $\text{CO}_2$  pressure and time of exposure. The chemical stability of the neutralized residue and the phenomenon of pH rebound were also studied. Solution and solid phase reactions controlling the neutralization of the red mud slurry by carbonation were studied with the assistance of chemical equilibrium modeling. A red mud slurry geochemical model developed by Khaitan et al. (2009a) was used to simulate the effect of different  $\text{CO}_2$  pressure values on slurry pH. The experimental values were compared to the simulated values, and differences were used to identify the primary geochemical processes occurring in red mud upon exposure to  $\text{CO}_2$ . Finally, the carbon sequestration potential of red mud was estimated based on the irreversible uptake of  $\text{CO}_2$  to form calcite and on the annual production of red mud.

## Materials and Methods

**Bauxite Residue and Chemicals.** Bauxite residue was procured from an Alcoa storage impoundment in Sherwin, Tex. This residue was primarily from the refining of Jamaican bauxite and is referred to as Jamaican red mud. The residue was  $\sim 40$  wt% solids and the pH as received was 12.5. The elemental compositions of both solids and pore water in the Jamaican red mud are given in Table 1. A complete characterization of the Jamaican residue is available in Khaitan et al. (2009a). Industrial grade carbon dioxide,  $\text{N}_2$  gas, and  $\text{CO}_2$ -free air were obtained from Butler Gas, McKees Rocks, Pa. Each gas was used as received without further purification.

**Neutralization of Bauxite Residue.** To monitor the rate and extent of neutralization of red mud, 5 g of red mud slurry (initial pH=12.5) were placed in a 50 mL plastic beaker and exposed to  $10^{-3.5}$ , 0.01, 0.1, and 1 atm partial pressure of gaseous carbon dioxide in a 50 L glove bag (SS20-20H-3, Glascol, Ind.). The total pressure in all cases was 1 atm. To achieve the desired  $\text{CO}_2$  partial pressures, carbon dioxide was mixed with  $\text{CO}_2$ -free air in

**Table 2.** Experimental Design and Results for Neutralization of Red Mud by  $\text{CO}_2$

Treatment number	$\text{CO}_2$ volume added (mL) to 50 L glovebag	$P_{\text{CO}_2}$ (atm)	Experimental equilibrium pH
1	16	$10^{-3.5}$	9.8
2	500	0.01	9.3
3	5,000	0.1	8.6
4	50,000	1	7.7
Control	$\text{N}_2$ purged	0	12.5

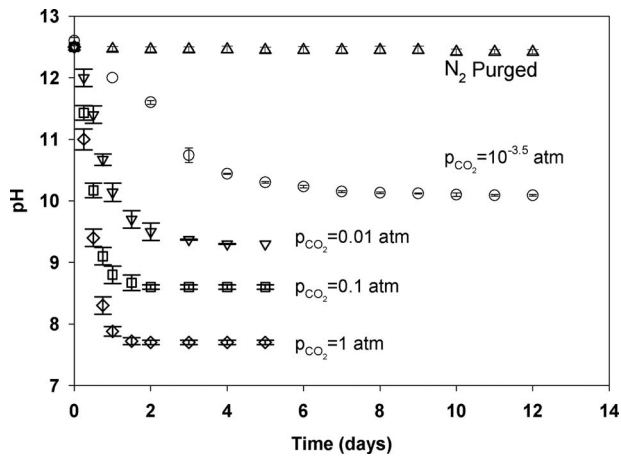
different volume proportions. The volume of  $\text{CO}_2$  added to the 50 L glove bag, the resulting  $\text{CO}_2$  partial pressure, and corresponding equilibrium pH are given in Table 2. In all exposures, gas added to the glove bag ( $\text{CO}_2$ -free air or pure  $\text{CO}_2$ ) was first bubbled through deionized water to saturate the gas with water (RH=100%) to prevent drying of the red mud during the exposure.

The general procedure was as follows. For  $P_{\text{CO}_2} < 1$  atm, the water saturated  $\text{CO}_2$ -free air was flowed into a glove bag containing the red mud samples. Containers filled with pure  $\text{CO}_2$  gas were then placed in the bag and opened to provide  $\text{CO}_2$  at the desired concentration. For  $P_{\text{CO}_2} = 1$  atm, pure water-saturated  $\text{CO}_2$  gas was directly flowed into the glove bag until it was fully inflated. A control experiment without  $\text{CO}_2$  was conducted by filling the bag with water-saturated,  $\text{CO}_2$ -free nitrogen gas. Periodically, the red mud slurry was removed from the bag and the pH was measured according to ASTM method D4972-95a for soils using an Accumet 13-620-07 pH electrode and Orion model 701A meter.

**pH Rebound of the Carbonated Red Mud.** The rate and extent of pH rebound were assessed for red mud carbonated at 0.01, 0.1, and 1 atm pressure of carbon dioxide, followed by exposure to water-saturated air at atmospheric  $\text{CO}_2$  partial pressure. The pH was measured at time intervals of 6 h for 2 days.

**Long-Term Carbonation.** One experiment was conducted to investigate the mineralogical changes due to long-term carbonation of the red mud slurry. Five grams of red mud slurry were placed in a 50 mL plastic beaker and exposed to 1 atm carbon dioxide for 30 days in the glove bag. The carbonated red mud slurry pH was measured at the end of 30 days. Next, the red mud was dried in the oven at  $105^\circ\text{C}$ , ground to a powder, and analyzed by x-ray diffraction (XRD) using a Rigaku instrument (Geigerflex Theta-Theta, Tex., US). The scan ranged from 10 to  $60^\circ$   $2\theta$  with a step size of  $0.05^\circ$  and a dwell time of 2 sec. Peak identification was done using X'pert graphics and identifier software (Ver. 1.2b, Philips, The Netherlands).

**Carbon Dioxide Effect on Bauxite Residue Field Samples.** To assess the effect of long-term exposure to atmospheric carbon dioxide on the geochemistry of bauxite residue in the field, surface core samples were obtained from red mud storage impoundments at Sherwin, Tex. Samples from the edge to the center of several impoundment cells were acquired from a depth of 1.0 to 1.2 m. Detailed information on the pH profiles and carbonate content for the samples is provided in Khaitan (2007). Selected red mud core sample sections were dried in the oven at



**Fig. 1.** Neutralization of Jamaican red mud by carbon dioxide. All treatments used 5 g of red mud slurry.

105 °C, ground to a powder, and analyzed by the x-ray diffraction method as described above for the long-term carbonation experiments.

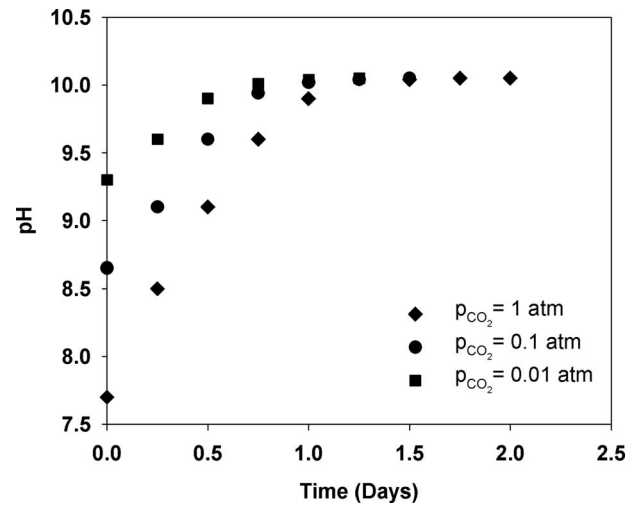
## Results and Discussion

### Carbonation of Bauxite Residue

The stable pH (Table 2) and the time required to achieve the stable pH (Fig. 1) of red mud slurry depended on the CO<sub>2</sub> partial pressure during treatment. The equilibrium pH of the carbonated red mud after 10 days of exposure decreased with increasing partial pressure of carbon dioxide. The steady-state pH ranged from 9.9 to 7.7 for  $P_{CO_2}$  ranging from  $10^{-3.5}$  to 1 atm. The rate of bauxite residue neutralization also increased with increasing CO<sub>2</sub> partial pressure. A stable pH was achieved at  $P_{CO_2} = 10^{-3.5}$  atm after 10 days while at  $P_{CO_2} = 1$  atm a stable pH was achieved after 2 days (Fig. 1).

**pH Rebound of Neutralized Bauxite Residue.** The carbonation data (Fig. 1) indicated that the stable pH established by contact of red mud and carbon dioxide depends on the carbon dioxide pressure and occurs on relatively short time scales. The short times needed for neutralization suggests that the neutralization process is a gas-liquid equilibrium process rather than due to mineral dissolution, which typically occurs on longer time scales and involves precipitation of carbonate minerals.

Proposed red mud neutralization processes with CO<sub>2</sub> typically involve short-term contact of CO<sub>2</sub> with freshly generated red mud, followed by storage in impoundments open to the atmosphere. Thus, we investigated the potential for pH rebound of red mud neutralized at high CO<sub>2</sub> partial pressures and then exposed to atmospheric CO<sub>2</sub> partial pressure. When bauxite residue that was previously carbonated at  $P_{CO_2} > 10^{-3.5}$  atm was contacted with air ( $P_{CO_2} = 10^{-3.5}$  atm), for all treatments the pH rebounded in only 1 day to that observed for neutralization by atmospheric CO<sub>2</sub> (Fig. 2). This further suggests that the experimental carbonation process was indeed limited to acid-base reactions with pore water dissolved species and that the solids did not contribute significantly to the observed neutralization in the time frame of the experiments. The pH rebound occurs because carbonate dissolved through equilibrium with the gas phase buffers the pore water in



**Fig. 2.** pH rebound of carbonated red mud when exposed to a  $P_{CO_2}$  of  $10^{-3.5}$  atm. Initial pH values correspond to final pH values in Fig. 1. Final pH corresponds to residue carbonated at atmospheric  $P_{CO_2}$  in Fig. 1.

the pH range of atmospheric CO<sub>2</sub>-neutralized red mud (pH = 7–10). Thus, higher  $P_{CO_2}$  conditions are largely affecting only the chemistry of the pore water.

**Long-Term Carbonation of Bauxite Residue.** Short-term exposure of red mud to CO<sub>2</sub> decreased the pH due to absorption of CO<sub>2</sub> into the pore water, which is readily reversible with changes in  $P_{CO_2}$ . Bauxite residue was carbonated at  $P_{CO_2} = 1$  atm for 30 days to investigate the potential for mineral dissolution (especially tricalcium aluminate, C3A) to affect the equilibrium pH of the residue during long-term carbonation. The resulting pH was 7.55, which was 0.15 pH units lower than carbonation at 1 atm  $P_{CO_2}$  after 1 day, suggesting that mineral dissolution may be occurring during longer exposure to CO<sub>2</sub>. XRD analysis of the resulting residue indicated the formation of calcite (CaCO<sub>3(s)</sub>) and the disappearance (dissolution) of C3A. In the evaluation of XRD data by Khaitan et al. (2009a), C3A was identified by the peaks at 33.5, 41, and 47.5° (Cu-K $\alpha$ ,  $\lambda = 1.54178 \text{ \AA}$ ), for which the peak at 47.5° was solely attributed to C3A. XRD peaks at 33.5, 41, and 47.5° were observed for the carbonated residue, but all decreased in intensity upon carbonation, implying that C3A dissolved during the 30 days of carbonation at  $P_{CO_2} = 1$  atm. In addition, the XRD peak for calcite at 29.4° 2 $\theta$  increased upon carbonation. The apparent slow dissolution of C3A and formation of calcite may be responsible for the lower pH measured after 30 days carbonation compared to 1 day, and likely explains the difference in the experimental and simulated pH values discussed subsequently. This also implies that atmospheric carbonation of the residue will be a long-term process that causes the slow dissolution of C3A and formation of calcite, which sequesters CO<sub>2</sub>.

**Carbonation of Stored Bauxite Residue in the Field.** Results for the 30-day carbonation in the laboratory at 1 atm partial pressure of CO<sub>2</sub> were similar to those observed for red mud stored for extended periods in confined disposal ponds exposed to atmospheric CO<sub>2</sub> in that the red mud was neutralized and C3A decreased while calcite increased. The magnitude of the pH lowering and the C3A depletion depended on the age of the stored red

**Table 3.** Solid Precipitation/Dissolution Reactions in Bauxite Residue Model (Khaitan et al. 2009a)

Solid formation	Solid phase reactions	log K
Boehmite	$\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{AlOOH}_{(s)} + 3\text{H}^+$	-8.9
Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_{3(s)}$	8.48
Sodium-aluminum-silicate	$\text{Na}^+ + \text{Al}^{3+} + \text{Si}(\text{OH})_4 = \text{NaAlSiO}_{4(s)} + 4\text{H}^+$	-15
Tricalcium aluminate	$3\text{Ca}^{2+} + 2\text{Al}^{3+} + 6\text{H}_2\text{O} = \text{Ca}_3\text{Al}_2\text{O}_6_{(s)} + 12\text{H}^+$	-74
	Liquid phase reactions	
	$\text{Al}(\text{OH})_4^- + \text{H}^+ = \text{Al}(\text{OH})_3^0 + \text{H}_2\text{O}$	22.688
	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^0$	-3.5
	$\text{H}_2\text{CO}_3^0 = \text{HCO}_3^- + \text{H}^+$	-6.3
	$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-10.3

mud. A field study (Khaitan 2007) compared the characteristics of stored red mud from Sherwin, Tex. (located between Ingleside, Tex. and Gregory, Tex.) and Copano, Tex. The red mud at Sherwin was 30–35 years old while the red mud at Copano was only 5 years old. The older cell at Sherwin was neutralized to pH = 9.5 up to a depth of at least 36 in., while the relatively younger cell at Copano had a pH of 10.4 at the surface and a pH of 12.1 at a depth of 36 in.. The depth of neutralization for the younger (Copano) cell was less than that at the older (Sherwin) cell, suggesting that carbonation at atmospheric carbon dioxide partial pressure ( $P_{\text{CO}_2} = 10^{-3.5}$  atm) is indeed a slow process, on the time scale of decades. XRD analyses of surface red mud from Copano (the younger pond) and red mud at a depth of 48 in. (Khaitan 2007) indicated the disappearance of C3A and boehmite (AlOOH) and the formation of calcite and gibbsite [Al(OH)<sub>3</sub>]. This is consistent with the laboratory carbonation results obtained here. The difference in surface pH values of Sherwin and Copano cells can be attributed to kinetic limitations of mineral dissolution (C3A) as demonstrated by Khaitan et al. (2009a).

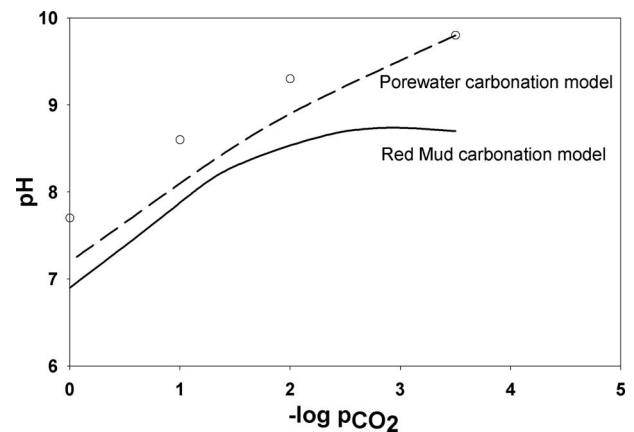
**Simulation of the Carbonation of Bauxite Residue.** Khaitan et al. (2009a) used long-term (55 days) acid-neutralizing capacity (ANC) measurements and equilibrium modeling to demonstrate that the major portion of the ANC (to pH 4.6) of red mud is derived from dissolution of solids in red mud and only a small portion by liquid phase buffering due primarily to OH<sup>-</sup> and Al(OH)<sub>4</sub><sup>-</sup>. A list of solid and liquid phase reactions that were identified as significant contributors to the ANC of bauxite residue is given in Table 3.

To understand better the mechanisms for neutralization of red mud by CO<sub>2</sub>, the equilibrium model for red mud chemistry (Khaitan et al. 2009a) was modified to simulate the stable pore-water pH measured for carbonated red mud exposed to different  $P_{\text{CO}_2}$  values (Fig. 3). Two cases were considered. The first case assumed that both pore-water and solid-phase reactions occur (red mud carbonation), while the second case assumed that only pore-water reactions occur (pore-water carbonation). For these simulations,  $P_{\text{CO}_2}$  was fixed instead of total carbonate (TOTCO<sub>3</sub>) as in the original model of the bauxite residue ANC (Khaitan et al. 2009a). Sensitivity analysis revealed that the predicted pH was highly sensitive to the relative amounts of Ca present as C3A and calcite, and the amount of carbonate in the bauxite residue before carbonation. For the Jamaican red mud (pH=12.5) used here, 40% of the Ca was initially present as calcite and 60% initially present as tricalcium aluminate (C3A). This was determined based on the peak count ratio of C3A/calcite in the initial red mud pattern. An XRD pattern generated by Khaitan et al. (2009a) using C3A/calcite wt% ratios of 90/10, 70/30, and 50/50 was

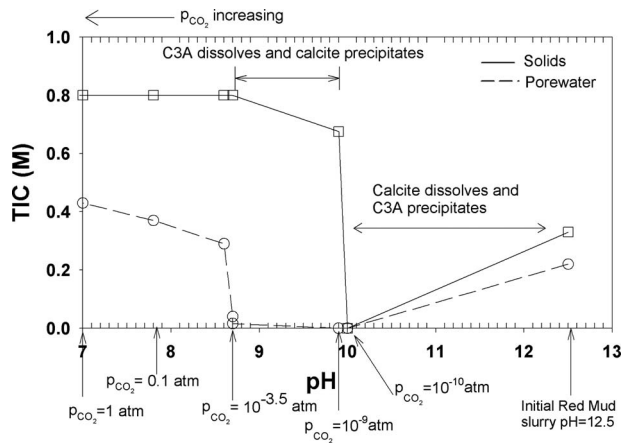
used for calibration. Based on the pore-water carbonate concentration and the total carbonate concentration in red mud (Table 1), it was found that 23% of the carbonate was dissolved while 77% was present as calcite (Khaitan et al. 2009a).

The simulated pore-water pH for red mud carbonation was lower than the measured pH of carbonated red mud for all  $P_{\text{CO}_2}$  values (Fig. 3 solid line), particularly at the lower  $P_{\text{CO}_2}$  values. The difference between experimental and simulated red mud carbonation can be explained by the incomplete dissolution of C3A. At the pH values observed, the equilibrium model predicts complete dissolution of C3A; however, the 30-day carbonation experimental results indicated incomplete dissolution of C3A at  $P_{\text{CO}_2} = 1$  atm. Further, C3A was present in field samples exposed for more than 30 years to atmospheric CO<sub>2</sub> (Khaitan 2007). It was previously shown that C3A dissolution in red mud produces a buffer region at pH 9.9, which drops to pH 8.7 once the C3A dissolves completely (Khaitan et al. 2009a). A buffer region at pH 9.8 was observed experimentally in red mud carbonation at atmospheric  $P_{\text{CO}_2}$  (Fig. 1), which further suggests incomplete dissolution of C3A.

The equilibrium model that included the contribution of solids to the ANC of bauxite residue (red mud carbonation) predicted a greater reduction in pH by CO<sub>2</sub> than was observed, whereas an equilibrium model for pore-water carbonation (ignoring any contribution of solids) agreed more with the experimental carbon-



**Fig. 3.** Comparison of simulated and experimental equilibrium pH for red mud neutralized by CO<sub>2</sub>. The difference between the red mud carbonation model (solid line) and the experimental data (open circles) is due to incomplete dissolution of C3A and calcite precipitation.



**Fig. 4.** Simulated inorganic carbon in the dissolved and precipitated (solid) phases of red mud as a function of pH. Sequestered TIC is fixed at  $P_{\text{CO}_2} \geq 10^{-3.5}$  atm due to a limited amount of  $\text{Ca}^{2+}$  in the system to form  $\text{CaCO}_3$ . The initial slurry pH = 12.5 in a closed system with an initial total  $\text{CO}_3$  concentration of 0.55 M. Symbols are simulated points. The lines are not model fits; they are added to distinguish between the solid phase and dissolved phase TIC.

ation results (Fig. 3), particularly at the lower  $P_{\text{CO}_2}$  values. This again suggests that carbonation carried out in the laboratory was primarily limited to the pore-water ANC phase and that the solids did not contribute significantly towards the neutralization process over the reaction times studied here. This hypothesis was evaluated using equilibrium modeling as described next.

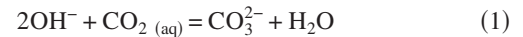
#### Simulation of Change of TIC with pH of Bauxite Residue at Different $P_{\text{CO}_2}$ Values

The sequestration potential of red mud can be determined from its total inorganic carbon (TIC) content before and after carbonation. Inorganic carbon in the red mud slurry exists in the aqueous phase primarily as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , or as  $\text{H}_2\text{CO}_3$ , and as a solid in the form of calcite or C3A. The simulated TIC content (in carbonate solids or in dissolved species) of a red mud slurry equilibrated with different  $P_{\text{CO}_2}$  values versus pH is shown in Fig. 4.

These simulations indicate that atmospheric carbon is sequestered by the red mud slurry primarily due to precipitation of calcite at  $\text{pH} \leq 9.9$ . Starting from the original slurry at  $\text{pH} = 12$  and a total carbonate concentration of 0.55 M, opening the system and equilibrating at  $P_{\text{CO}_2} = 10^{-10}$  atm resulted in calcite dissolution, formation of C3A, and a net decrease in TIC (Fig. 4). Increasing  $P_{\text{CO}_2}$  over the pH range observed for neutralization by gas phase  $\text{CO}_2$  ( $\text{pH} = 7$  to  $\text{pH} = 9.89$ ) increased the  $\text{CO}_2$  uptake. The  $\text{CO}_2$  uptake predominantly yields as precipitated calcite, but the amount formed does not increase significantly as  $P_{\text{CO}_2}$  increases above  $10^{-3.5}$  atm because  $\text{Ca}^{2+}$  is limiting. Conversely, the TIC present as dissolved phase carbonate species increases with increasing  $P_{\text{CO}_2}$ , indicating that most additional  $\text{CO}_2$  uptake at  $P_{\text{CO}_2} > 10^{-3.5}$  atm is as dissolved carbonate species and that fairly rapid pH rebound may be expected if red mud carbonated at  $P_{\text{CO}_2}$  of 1 atm is subsequently exposed to lower levels of  $P_{\text{CO}_2}$ . The  $\text{CO}_2$  sequestered in the solid phase at  $P_{\text{CO}_2}$  of  $10^{-3.5}$  atm is essentially the maximum possible for the red mud system.

**Mechanism for  $\text{CO}_2$  Sequestration by Reaction with Bauxite Residue.** The pore-water pH of red mud slurry is reduced when exposed to gaseous carbon dioxide. The red mud slurry

carbonation involves both pore-water carbonation and solid phase reactions of tricalcium aluminate dissolution and calcite precipitation. The pore-water carbonation occurs by the rapid absorption of carbon dioxide that forms carbonic acid and neutralizes the excess base in the form of  $\text{NaOH}$ ,  $\text{NaCO}_3^-$ , and  $\text{Al}(\text{OH})_4^-$  in the pore water. The rate and extent of pore-water neutralization is directly proportional to the partial pressure of carbon dioxide (Fig. 1). Initial  $\text{CO}_2$  additions to red mud convert pore-water hydroxide [ $\text{Al}(\text{OH})_4^-$  and  $\text{NaOH}$ ] alkalinity to carbonate ( $\text{CO}_3^{2-}$ ) alkalinity, which dominates at pH values greater than 10.3

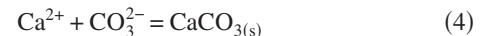
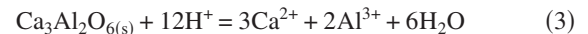


With further  $\text{CO}_2$  addition, pore-water carbonate alkalinity is converted to bicarbonate ( $\text{HCO}_3^-$ ) alkalinity, which dominates at pH values less than 10.3



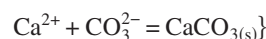
A summary of the dominant aqueous phase reactions (Cardile et al. 1994) is given in Table 3.

The long-term carbonation process involves dissolution of C3A and precipitation of calcite, which initiate at  $\text{pH} \approx 9.9$  and result in lowering of the pH of the slurry. The relative amounts of C3A and calcite present in the fresh bauxite residue control the pH values achieved upon neutralization with  $\text{CO}_2$ , as these solids determine the amount of calcium present and available to react with added  $\text{CO}_2$ . The key solid phase reactions in long-term carbonation are given by Eqs. (3) and (4)

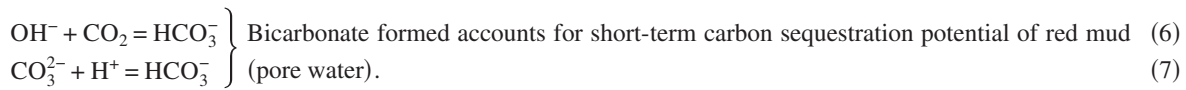


Further, over the long term, boehmite ( $\text{AlOOH}(\text{s})$ ) initially present in the bauxite residue is converted to the more stable phase gibbsite [ $\text{Al}(\text{OH})_3(\text{s})$ ]. The dissolution of tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6(\text{s})$ ) occurs slowly as the residue is carbonated, and the dissolved Ca precipitates as calcite, lowering the equilibrium pH of carbonated residue. Based on the experimental and field data presented earlier and in Khaitan (2007), it appears that the dissolution of C3A is kinetically limited, but may be accelerated by increasing the pressure of the carbon dioxide.

**Carbon Sequestration Potential.** The amount of carbon dioxide potentially sequestered by red mud slurry can be estimated as the sum of bicarbonate ( $\text{HCO}_3^-$ ) ion formed in the pore water and the calcite precipitated in the solid phase for exposure of red mud to a particular  $P_{\text{CO}_2}$ . The total carbon dioxide sequestered by red mud is the change in concentration of calcite in the precipitated phase and change in the bicarbonate ion in the pore-water phase



Calcite formed in solid phase accounts for the long term carbon sequestration potential of red mud (5)



The theoretical carbon dioxide sequestration potential (pore water and solids) was determined from the change in TIC assuming that all of the C3A dissolves to form  $\text{CaCO}_3(s)$  at a residue  $\text{pH} < 9.8$ . Assuming a final equilibrium  $\text{pH}$  of 8.7, the carbon dioxide sequestration potential for pore water is estimated to be 0.132 M (moles C/L PW) or 5.8 mg  $\text{CO}_2/\text{g PW}$  while the corresponding long-term estimate for whole bauxite residue was found to be 0.27 M (moles C/L RM) or 8.5 mg  $\text{CO}_2/\text{g RM}$  (21 mg/g RM solids). These estimates agree with those reported by Enick et al. (2001) who calculated 23 mg  $\text{CO}_2/\text{g RM}$  solids under high pressure (6.9 MPa). Based on an annual production of 30 MMT for red mud (Ayres et al. 2001) and the corresponding 18 MMT of pore water, long- and short-term estimates of carbon sequestration potential are 0.057 and 0.029 MMT C/year, respectively. The long-term, solids-related carbon sequestration estimate is larger than the corresponding short-term value, as red mud slurry carbonation is a slow process requiring the dissolution/precipitation of solids. Even though liquid phase pore-water carbonation occurs relatively quickly, it contributes less to carbon sequestration than the Ca present in C3A.

The estimated long-term sequestration potential will be realized only if C3A dissolves completely, which was not observed in the field results discussed before. In addition, the sequestration potential is only realized within the surface material in the storage impoundment exposed to atmospheric carbon dioxide. Thus, only a fraction of the total annual production of red mud will be available for atmospheric  $\text{CO}_2$  sequestration unless the red mud is neutralized to a  $\text{pH} < 9.9$  prior to storage and enough time elapses to ensure complete dissolution of C3A.

Considering the limitations noted, the above estimates represent theoretical upper limits of the  $\text{CO}_2$  that can be sequestered in solid and water. Even assuming that the total annual RM production is available for sequestration, the total  $\text{CO}_2$  that could be sequestered in this manner is much smaller than the total annual  $\text{CO}_2$  production of 110 MMT/year associated with the alumina industry (IAI 2002; Martchek 2003), which implies residue is not a large potential sink of carbon dioxide.  $\text{CO}_2$  neutralization of surface residue is, however, a "green" process that does not require additional chemical additives for neutralization and allows for vegetation of the residue impoundment surface (Khaitan 2007).

## Acknowledgments

This project was supported by the National Science Foundation (BES-0329424) and by Alcoa, Inc., Pittsburgh, Pa. The writers thank Jaw Fu, John Smith, Dennis Fulmer, and Keith Schmidt of Alcoa for providing samples, data, and information about bauxite residue.

## References

- Ayres, R. U., Holmberg, J., and Anderson, B. (2001). "Materials and the global environment: Waste mining in the 21st century." *MRS Bull.*, 26, 477–480.
- Cardile, C. M., Hughes, C. A., and Summers, K. J. (1994). "Evaluation of carbon dioxide treatment of red mud." *Proc., 6th AusIMM Extractive Metallurgy Conf.*, 317–320.
- Doye, I., and Duchesne, J. (2005). "Column leaching test to evaluate the use of alkaline industrial wastes to neutralize acid mine tailings." *J. Environ. Eng.*, 131(8), 1221–1229.
- Duchesne, J., and Doye, I. (2005). "Effectiveness of covers and liners made of red mud bauxite and/or cement kiln dust for limiting acid mine drainage." *J. Environ. Eng.*, 131(8), 1230–1235.
- Elbicki, J. M., Fu, J. K., Adamek, G., and Weightman, R. L. (2004). "Jamaica residue evaluation." *Alcoa RD&E Report No. 04-029*, Alcoa Technical Center, Alcoa Center, Pa.
- Enick, R. M., Beckman, E. J., Shi, C. M., Xu, J. H., and Chordia, L. (2001). "Remediation of metal-bearing aqueous waste streams via direct carbonation." *Energy Fuels*, 15(2), 256–262.
- Int. Aluminium Institute (IAI). (2002). *Aluminium Industry's Sustainable Development Rep.*, Int. Aluminium Institute, London.
- Khaitan, S. (2007). "Field evaluation of the effects of carbon dioxide, vegetation, and organic amendments on neutralization of bauxite residue." Ph.D. thesis, Carnegie Mellon Univ., Pittsburgh, Pa.
- Khaitan, S., Dzombak, D., and Lowry, G. (2009a). "Chemistry of the acid neutralization capacity of bauxite residue." *Environ. Eng. Sci.*, in press.
- Khaitan S., Dzombak, D. A., and Lowry, G. V. (2009b). "Neutralization of bauxite residue with acidic fly ash." *Environ. Eng. Sci.*, 26(2), 431–440.
- Koumanova, B., Drame, M., and Popangelova, M. (1997). "Phosphate removal from aqueous solutions using red mud wasted in bauxite Bayer's process." *Resour. Conserv. Recycl.*, 19, 11–20.
- Martchek, K. J. (2003). "Measuring, reporting and verifying greenhouse gas emissions from aluminum reduction operations." *Proc., Light Metals Conf.*, 227–231.
- Paradis, M., Duchesne, J., Lamontagne, A., and Isabel, D. (2006). "Using red mud bauxite for the neutralization of acid mine tailings: A column leaching test." *Can. Geotech. J.*, 43(11), 1167–1179.
- Smith, P. G., Penniford, R. M., Davies, M. G., and Jamieson, E. J. (2003). "Reactions of carbon dioxide with tri-calcium aluminate." *Proc., 5th Int. Symp. Honouring Professor Ian M. Ritchie*, C. Young, A. Alfanzazi, C. Anderson, A. James, D. Dreisinger, B. Harris, eds., The Minerals, Metals, and Materials Society, Warrendale, Pa., 1705–1716.
- Vachon, P., Rajeshwar, D. T., Auclair, J. C., and Wilkinson, K. J. (1994). "Chemical and biological leaching of aluminum from red mud." *Environ. Sci. Technol.*, 28, 26–30.
- Wehr, J. B., Fulton, I., and Menzies, N. W. (2006). "Revegetation strategies for bauxite refinery residue: A case study of Alcan Gove in Northern Territory, Australia." *Environ. Manage. (N.Y.)*, 37(3), 297–306.
- Wong, J. W. C., and Ho, G. E. (1994). "Effectiveness of acidic industrial wastes for reclaiming fine bauxite refining residue (red mud)." *Soil Sci.*, 158, 115–123.