

# CARBON DIOXIDE SEQUESTRATION VIA pH REDUCTION OF RED MUD USING LIQUID CO<sub>2</sub>

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## ABSTRACT

The pH of red mud, waste from the Bayer process for alumina manufacture, can be lowered by contacting the aqueous red mud slurry with liquid carbon dioxide. The carbonic acid that forms in the water in the presence of liquid CO<sub>2</sub> (pH of 2.8 - 2.9) neutralizes the basic compounds of the red mud via the formation of metal carbonates. The pH of a 45% red mud slurry can be reduced from 12.5 to a stable value of 9.0-9.5 via the contact of liquid CO<sub>2</sub> at 298 K and 6.7-10 MPa. The required reaction time is 5-15 minutes if the slurry is well mixed with the liquid CO<sub>2</sub>. The carbonates were not removed from the red mud because pH reduction was the only process requirement. The approximate amount of sequestration is about 2.3 gr CO<sub>2</sub> per 100 gr dewatered red mud.

## INTRODUCTION

The Bayer process, developed by Karl Josef Bayer 110 years ago, remains the most widely used means of manufacturing calcined commercial alumina from bauxite (40-60% Al<sub>2</sub>O<sub>3</sub>). Typically, the alumina in the crushed bauxite feed is dissolved aqueous caustic soda at high temperature. Red mud, the insoluble impurities of bauxite, is then separated from the soluble alumina and caustic soda and washed. The soluble sodium aluminate is then partially hydrolyzed, yielding an aluminum trihydroxide precipitate. Calcination of the aluminum trihydroxide yields the anhydrous alumina product (Anderson and Haupin 1985). Aluminum is subsequently produced by the electrolysis of alumina.

The major by-product from the Bayer process is red mud, the insoluble residue of the alumina extraction from the bauxite (Hind et al.1999, Prasad et al.1996). Approximately 70 million tons of red mud is generated annually throughout the world. Red mud disposal methods include traditional closed cycle disposal (CCD) methods and modified closed cycle disposal (MCCD). A new class of dry stacking (DS) technology has also emerged which requires much less land. Problems associated with the disposal of red mud waste include its high pH (12-13), alkali seepage into underground water, safety in storage, and alkaline air borne dust impact on plant life. Efforts to ameliorate red mud typically and possibly, use it as a raw material usually incorporate a pH-reduction processing step (Wong and Ho 1994, Vachon et al. 1994, Koumanova, et al. 1997, Rodriguez et al.1999). Various aqueous acidic solutions have been considered for this application, including acidic industrial wastewater (Wong and Ho 1994). The use of carbonic acid has also been considered. Gas phase CO<sub>2</sub> or CO<sub>2</sub>-containing flue gas has been bubbled through aqueous slurries to form carbonic acid in the aqueous phase (Sziirmai, et al. 1991). The carbonic acid results with basic components of the red mud, lowering its pH. However, the pH of water exposed to gaseous CO<sub>2</sub> is not likely to drop below 5.5 (approximately), and hence the rate of reaction/neutralization of the solids in the aqueous slurry is typically not fast enough to satisfy industrial needs. At the short contact times which industrial process rates demand, only a fraction of the alkaline material in red mud is neutralized using gaseous CO<sub>2</sub>. Hence although the pH of the aqueous phase drops rapidly upon exposure to CO<sub>2</sub> gas, it soon rises again to unacceptable levels as additional alkaline material leaches from the mud.

The focus of this investigation was the use of high-pressure *liquid* carbon dioxide, rather than *vapor phase* carbon dioxide, for the pH reduction of red mud. The pH of water in contact with liquid CO<sub>2</sub> is 2.80-2.95 over the 298-343 K temperature range and 70-200 atm pressure range (Toews, et al. 1995). This is significantly lower than the pH of 5.0-5.6 that can be attained with gas-phase carbon dioxide. Therefore, we expected that a more rapid and effective neutralization of the red mud would be achieved using liquid carbon dioxide. The apparatus used for this remediation would need to operate at elevated pressures, however.

## MATERIAL AND METHODS

Dewatered red mud was provided by Alcoa. Its approximate composition is provided in Table 1.

Table 1. The Composition of the Red Mud Sample

Compound	Formula	Content	
		In Red Mud	MW
Hematite	$\text{Fe}_2\text{O}_3$	10-30wt%	160
Alumino-geothite	$(\text{Fe,Al})\text{OOH}$	10-30	75
Sodalite	$3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{SO}_4$	4-40	994
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	2-20	378
Anatase/Rutile	$\text{TiO}_2$	2-15	80
Calcite	$\text{CaCO}_3$	2-10	100
Quartz	$\text{SiO}_2$	0-30	60
Boehmite	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	0-20	120
Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	0- 5	156
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	0- 5	258
Muscovite	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	0-15	796

Two slurries were prepared from this sample by mixing it with distilled water. The 45wt% red mud and 10% red mud slurries had pH values of 12.5 and 11.8, respectively. The slurry was contacted with liquid carbon dioxide at 297 K and 10 MPa in an attempt to neutralize both the free soda and bound soda in the red mud. In a typical experiment, 40 gr of the slurry and 40 ml of liquid carbon dioxide at 297 K at 10 MPa psia were introduced to a variable volume, windowed cell. This amount of carbon dioxide used was sufficient to keep the aqueous phase saturated with  $\text{CO}_2$ , and a clear liquid carbon dioxide phase resided above the slurry in each experiment. The system was then gently mixed via rocking throughout the duration of the treatment, which ranged from 1 minute to 4 hours, at 297 K and 10 MPa. After specified reaction time had elapsed, the mixing was stopped and the liquid  $\text{CO}_2$  was slowly vented from the top of the vessel.

In order to estimate the amount of liquid  $\text{CO}_2$  that was sequestered during this experiment, a non-sampling,  $\text{CO}_2$  material balance experiment was conducted. The initial pressure of this experiment was set at 5000 psia. In the control experiment, only water and  $\text{CO}_2$  were introduced to the cell. The pressure in the cell dropped due to cooling of the vessel (which was heated as the  $\text{CO}_2$  was compressed into the sample volume) and dissolution of the  $\text{CO}_2$  into the aqueous phase. The experiment was then repeated with the same amount of water and carbon dioxide, but with a specified amount of dewatered red mud. The pressure in the vessel dropped more rapidly and reached a lower limiting value due to the neutralization reaction that removed  $\text{CO}_2$  from the liquid phase and transformed it into a carbonate via the formation of carbonic acid and reaction in the aqueous phase. The additional pressure drop, temperature, initial pressure, knowledge of  $\text{CO}_2$  density as a function of temperature and pressure and volume of liquid  $\text{CO}_2$ , were then used to perform a material balance that indicated the amount of  $\text{CO}_2$  that formed carbonates.

A one-liter fixed volume cell with turbine impeller mixing was employed for the neutralization experiments because of the poor mixing observed during the rocking of the smaller, variable volume view cell. Approximately 900 gr of the 45% red mud slurry was introduced to this vessel, which was then blanketed with liquid carbon dioxide. The aqueous slurry and the liquid carbon dioxide were mixed at 297 K and 6.7 MPa using several axial flow impellers spinning at 300 rpm.

## RESULTS

The pH reduction results for the smaller vessel with mixing by rocking are illustrated in Figures 1 and 2. The results, shown on the following figures, indicate that

- (1) there is a reduction in pH immediately following the exposure to liquid  $\text{CO}_2$ ,
- (2) the pH slowly rises and then levels off following the treatment due to the release of bound soda via desilication,
- (3) the 10% red mud slurries approached an equilibrium pH of approximately 9, regardless of the duration of the mixing
- (4) the efficiency of the treatment was comparable for all of the 10wt% red mud slurries
- (5) the 45% red mud slurries approached an equilibrium value, with lower pH values attained for solutions that were mixed for longer times during treatment (e.g. 4 hr. of mixing was required to attain an equilibrium pH of 9

The material balance experimental results are shown in Figure 3. The difference between the curves represents a "sequestration" of carbon dioxide. Using the data at 5000 minutes, approximately 2.3 grams of CO<sub>2</sub> can be sequestered for each 100 grams of dewatered red mud.

The effect of neutralizing the red mud with more vigorous mixing is shown in Figure 4. Reaction times of 5-15 minutes were capable of lowering the ultimate pH value to approximately 9.5, as opposed to the 4 hours required to lower the pH to 9 with poor mixing (Figure 2). The pH of the treated mud reached its equilibrium value within two weeks of treatment as shown in Figure 4, while several months were required for equilibration of the sample that was poorly mixed (Figure 2).

## DISCUSSION

The neutralization of red mud can be achieved with liquid carbon dioxide at ambient temperature due to the pH value of carbonic acid at high pressure being in the 2.8 - 2.9. As expected and previously reported for red mud treated with gaseous CO<sub>2</sub>, the pH of the red mud was close to 7 immediately after the treatment, it soon rose again as additional alkaline material leached from the mud. Effective treatment was obtained within minutes by reducing mass transfer limitations with vigorous mixing with impellers, rather than rocking the contents of the vessel. The process simultaneously remediated the red mud while sequestering about 2% (based on dewatered red mud mass) CO<sub>2</sub>. The process requires the use of high pressure, corrosion resistant equipment, however, and power for the operation of the high-pressure pumps.

## CONCLUSIONS

Liquid carbon dioxide was more effective for pH reduction of red mud than vapor phase CO<sub>2</sub> because carbonic acid pH values less than 3 can be realized with high-pressure carbon dioxide (6.7 - 10 MPa in this study). The initial red mud pH of 12-13 was lowered to 7-8 immediately after treatment, then slowly rose to values of 9.0-9.5 due to desilication reactions of the treated red mud. The processing time was reduced to 5-15 minutes using vigorous mixing of the liquid carbon dioxide and aqueous red mud slurry. Approximately 2 gr of carbon dioxide per 100 gr of red mud were bound in carbonate products when the process was conducted at 297 K.

## ACKNOWLEDGMENTS

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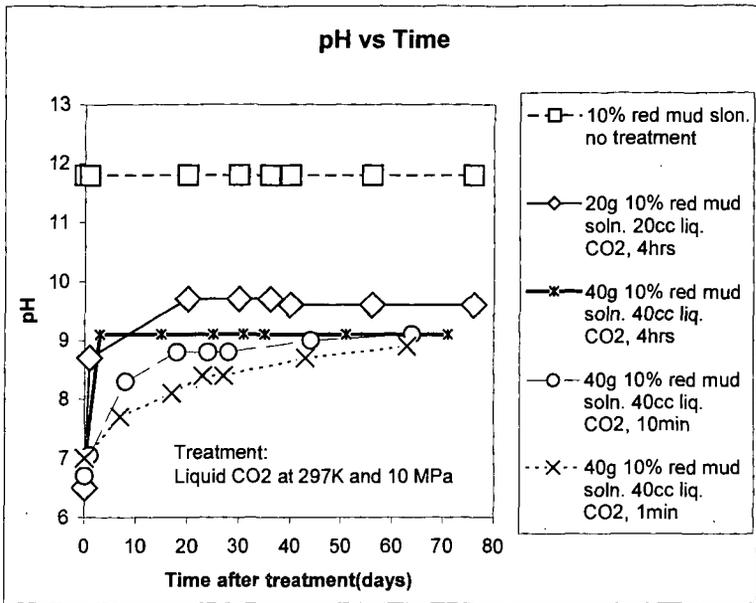


Figure 1. pH reduction of 10% Red Mud Slurries, Small Vessel, Poor Mixing via Rocking

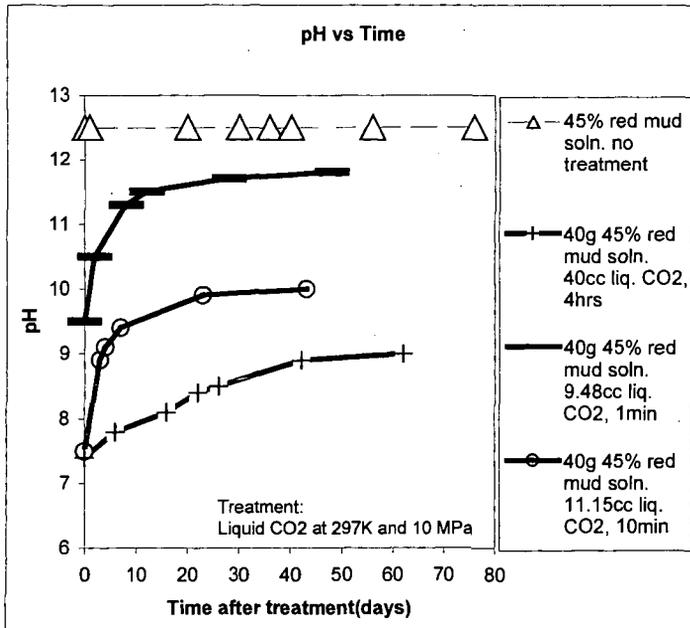


Figure 2. pH Reduction of 45% Red Mud Slurries, Small Vessel, Poor Mixing via Rocking

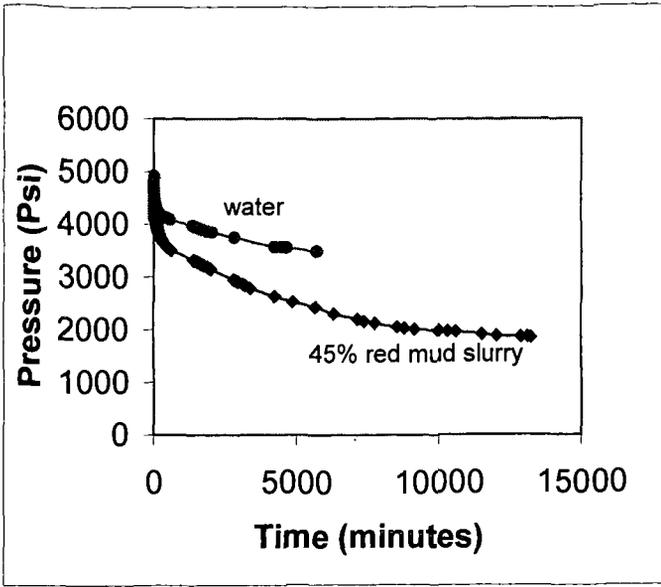


Figure 3. Pressure Decline Measurements at 298 K, 10 ml CO<sub>2</sub>, 43 gr Water, Difference Between the Curves Corresponds to the CO<sub>2</sub> in Liquid CO<sub>2</sub> that Formed Carbonates

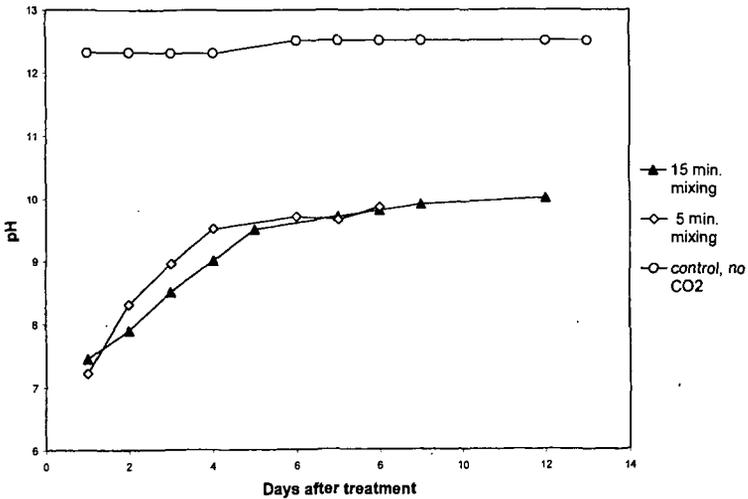


Figure 4. pH Reduction of 45% Red Mud Slurries, Large Vessel, Vigorous Mixing with Impellers, 900g slurry, 130g CO<sub>2</sub>, 6.7 MPa