

Red Mud as Sorbent for SO₂ Gas Cleaning

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Abstract— The main purpose of this study was to investigate for SO₂ removal using red mud as sorbent in laboratory for the sake of gas cleaning. The study was carried out by using a laboratory-scale reactor to examine the batch absorption study of SO₂ gas with slurry and liquor of red mud samples from Worsley Alumina Pty. Ltd., Western Australia. The intention of the batch absorption study is not only constrain for gas cleaning of SO₂ using red mud, but this study also revealed how effective the sulfur dioxide in neutralizing the red mud which are verified as hazardous and caustic due to the high pH of 10-13. Prior to the absorption study, the red mud needs to undergo for alkalinity test to determine the intensity of carbonate and hydroxide ions presence in the red mud. From the experiment, the hydroxide and carbonate ions are assumed to be consumed at specific pH of the sample's alkalinity, taking into consideration the fact that hydroxide is commonly present at pH levels greater than 8.3, while carbonate is present at pH between 4.5 and 8.3. In other hand, analysis from the batch absorption studies exhibited good performance of red mud as sorbent with respect to sulfur capacity.

Keywords-Red Mud; Gas Cleaning; SO₂

I. INTRODUCTION

Flue gas generally consists of H₂O, O₂, CO₂, CO, NO_x, SO_x and a variety of particulates [1]. However, regulation requires that industries comply with the imposed emission limits of SO₂ as this is the major problematic constituent in the flue gas due to the detrimental impact on both the environment and health [2]. Sulphur dioxide (SO₂) is a toxic and hazardous gas that is generated by industrial activities such as coal-burning and electric power generation [3]. The development of technology for the removal of SO₂ from flue gas has progressed through several distinct stages [4]. These includes the replacement of fuels with high sulphur content with those containing a much smaller amount [2], conducting a specific combustion processes which result in the generation of SO₂ such as fluidized bed combustion (FBC) and sorbent injection, and finally the advent of flue gas desulphurization (FGD) technology [5]. In other efforts, a variety of sorbents were modified and applied to the present technology for a higher

efficiency of SO₂ removal. Examples of such modified-sorbent processes include the magnesia spray absorption process [6], and those which make use of aluminum organometallic [7], CuO/ γ -Al₂O₃ [8] and Bayer red mud [1,9].

However, not much research has been conducted in waste gas cleaning using red mud. This is because the application of red mud is focusing more on the water treatment such as coagulant production and adsorption of anion, heavy metals, dye, organics and bacteria/virus removal [10].

In 1977, a desulphurisation plant was built by a Japanese company, Sumitomo Chemical Co. Ltd, which discovered the chemical properties of red mud and its use as an agent to remove SO₂ from flue gas [1]. The process, referred to as the Sumitomo Bauxite Residue Desulphurisation System (BRDS), has the capacity to effectively remove up to 96% of the SO₂ in flue gas [1]. However, a detailed description of the BRDS process from authentic sources is still unfounded; hence most information about the plant is uncertain.

On the other hand, red mud is alkaline bauxite residue that has a high pH value, in the range of 10-13, as a result of the presence of hydroxide [11]. The alkaline characteristics of red mud are the main cause of numerous environmental problems such as groundwater contamination, damage to dykes and corrode the pipelines for pumping [12, 13, 14]. As a result, red mud is categorized as hazardous, corrosive and toxic substance due to the presence of high levels of calcium, oxalate and sodium hydroxide [11, 15, 16]. In addition, the capability of sodalite to exchange Na⁺ ions may result in a serious impact to the environment [13]. Therefore, the project will focus on waste remediation technologies whereby red mud is used as economical adsorbent for the removal of SO₂ emission. These studies will not only solve the problems to comply with the stringent environmental regulation of SO₂ emissions limits and gas cleaning, but also neutralize the caustic and hazardous red mud in economical ways.

II. MATERIAL AND METHOD

A. Sample description

Red mud samples supplied from Worsley Alumina Pty Ltd (WAPL), Western Australia, were used in this study. The red mud sample was brown in colour and the pH was 13.16. The properties of the WAPL red mud are listed in Table 1.

TABLE I. PROPERTIES OF WAPL RED MUD

Parameters	WAPL Red Mud
pH	13.16
Moisture Content (%)	60
Particle Size Distribution (µm)	
D ₁₀	1.981
D ₅₀	6.490
D ₉₀	30.667
Chemical phases (wt.%)	
Na ₂ O	25
Fe ₂ O ₃	60
Al ₂ O ₃	15
SiO ₂	5
TiO ₂	5

The characteristics of red mud for pH and moisture content were determined base on the American Public Health Association (APHA) standard method [17]. The particle size distribution analysis was carried out with a Malvern size analyzer (Mastersizer 2000 version 5.40). Distilled water was used as the red mud dispersant for the measurements and the instrument was operated at 2000rpm.

B. Experiment Apparatus

The experimental apparatus in this study consisted of two gas cylinders – (SO₂ and N₂) which function by supplying a gas stream to a reactor containing red mud. The gas stream for each cylinder was controlled by different valves, each of which is connected to a separate gas-mass flow meter. To ensure a good mixture of the gases, both valves are connected to another main valve before the gas stream enters the reactor. The gas flow rates for an experiment in such a set-up can reach a maximum of 850ml/min. The absorption reactor used in this study was a stainless steel cylinder vessel with both a diameter and height of 0.15m. Other apparatus include a pH probe which was specifically designed for the reactor and was placed at the conveyor which is connected to the hood. A rotor was used to attain uniform agitation and to avoid sedimentation of red mud at the bottom of the reactor. For all experiments, the rotor was set fixed at speed of 360rpm. A schematic diagram of the experimental apparatus is included in Fig. 1.

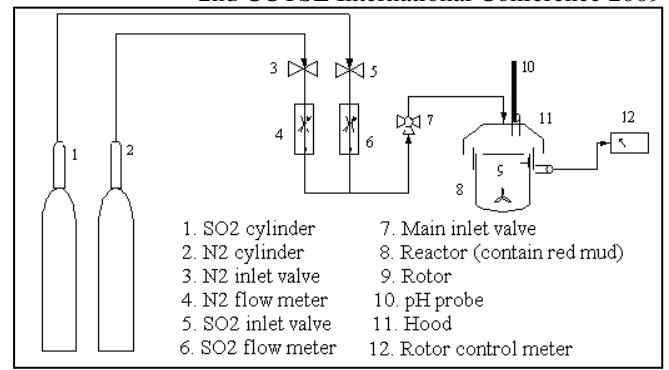


Figure 1. Experimental apparatus

1) Alkalinity

The determination of alkalinity in this study involved the titration neutralization of alkaline red mud (≈ 1M NaOH) with 1M H₂SO₄. The experiments were conducted separately with two different forms of red mud, one consisting of slurry and one of liquor. Their compositions were as follows:

- 10g of red mud slurry were mixed in 500ml of distilled water
- 10ml of red mud liquor were mixed in 500ml of distilled water

Red mud was filled into the reactor (as depict in Fig. 1) and then agitated by a rotor operating at 360rpm. These samples were then titrated with H₂SO₄ which was supplied via a tube to the reactor. Before running the experiment, a pH probe was placed in the hood through a conveyor and was directly connected to a computer running the Tiamo™ program. This software automatically gives the titration curve and the reaction will be stopped at set pH points for sample removal and analysis.

2) Batch Absorption Studies

Absorption of SO₂ with red mud took place in a cylinder vessel covered by a hood, the contents of which were agitated at 360rpm with a gas flow rate of 750ml/min. The process of this experiment is illustrated in Figure 1. The gas streams involved in this reaction were SO₂ and N₂. An analysis of pure SO₂ gas is too dangerous to be conducted in high concentrations. Thus, N₂ was added for the purpose of diluting the concentration of SO₂ gas to 0.1% of the total concentration. The samples of red mud taking part in the absorption with SO₂ were:

- 2 ml of red mud liquor were mixed in 250ml of distilled water
- 2.5g of red mud slurry were mixed in 250ml of distilled water

The samples for both cases were analysed using XRD, XRF and ICP. The mineralogy of red mud in the solid phase was determined using X-ray diffraction (XRD). The analysis requires that the red mud slurry be dried in an oven for 24 hours at 100°C. Then, the solid samples are spread uniformly

on a sample holder before this is placed at the slit of the instrument. The specimens are scanned with the Rigaku Miniflex diffractometer at 2°/min with the range from 5° to 80° 2θ using Co Kα radiation. The standard measurement outputs were analysed using the Traces program.

For ICP analysis, the samples need to be filtered through a 0.22 μm membrane. Then the samples were diluted 20 times with 1M of acid hydrochloric (HCl) and analyzed using ICP-OES to determine the concentration of selected elements. To identify the total elemental composition of red mud, the samples were dried in an oven at 100°C for 24 hours. Then 0.6g of red mud were prepared and analysed using Philip XRF. The machine is directly connected to the Super Q program for X-ray fluorescence (XRF) analysis.

III. RESULT AND DISCUSSION

A. Alkalinity of WAPL Red Mud

Fig. 2 and 3 show the titration curves for the red mud slurry and liquor, respectively. The graphs represent the sample's alkalinity, which is equal to the amount of acid used to neutralize the sample. As depicted in Fig. 2, the alkalinity slowly decrease until a state of equilibrium is reached at around pH 4.5. Once equilibrium has been reached, all of the hydroxide and carbonate ions are assumed to be consumed, taking into consideration the fact that hydroxide is commonly present at pH levels greater than 8.3, while carbonate is present at pH between 4.5 and 8.3 [17]. In Fig. 3, the alkalinity also shows a slow decrease with increasing dose, but drops rapidly at pH 8.3. This may be caused by the carbonate content in the red mud liquor.

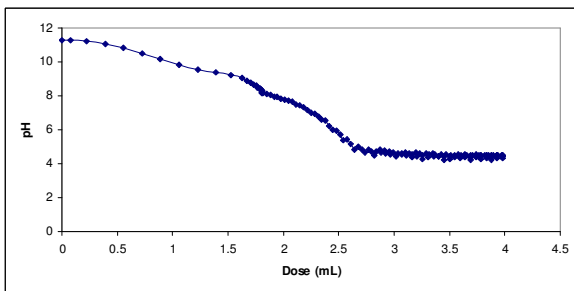


Figure 2. Titration curve for red mud slurry

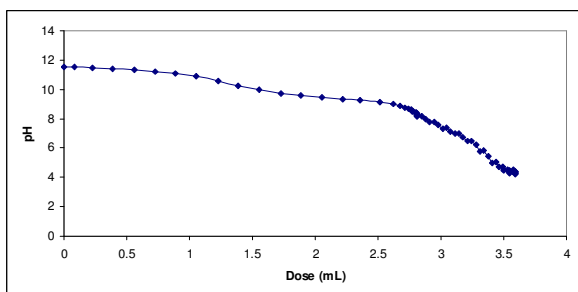


Figure 3. Titration curve for red mud liquor

B. Absorption of SO₂ with red mud

The absorption of SO₂ into the red mud slurry and liquor, were illustrate in Fig. 4 and 5 respectively. Studies on the absorption of SO₂ were only conducted using 2.5 g of red mud slurry and 2.0 ml of red mud liquor. In Fig. 4, the absorption results show a slow decrease in pH during the first 4500 seconds of contact time. This is continued until a state of equilibrium is reached at pH 4.5, implying that equilibrium absorption levels were reached within 4500 to 6000 seconds of contact time. The graph also indicates the existence of two abnormal increases in pH, occurring at pH values of 8.3 and 4.5. These may be due to the changes in hydroxide and carbonate uptake at that specific pH.

Fig. 5 also shows a slow decrease in pH during the first 3000 seconds, as well as depicting clear humps at pH 8.3 and 4.5. The equilibrium absorption of SO₂, at pH 4.5, was reached within 3000 to 4500 seconds of contact time.

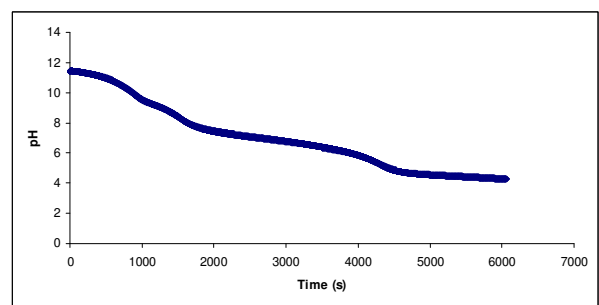


Figure 4. Absorption of SO₂ with 2.5 g red mud slurry

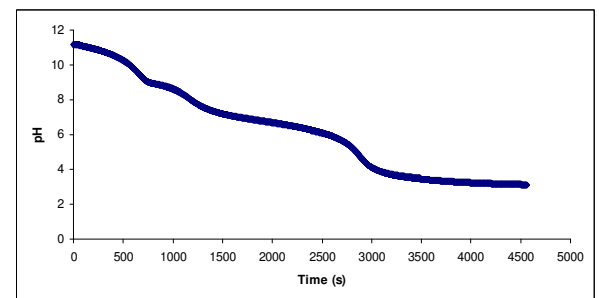


Figure 5. Absorption of SO₂ with 2.0 ml red mud liquor

C. XRD Analysis

Fig. 6 shows the XRD patterns of a number of solids formed as a result of the reaction of 2.5 g red mud slurry with SO₂. The lines represent the solids produced after contact time of (a) 0 s (red mud samples prior to reaction with SO₂) and (b) 6000 s. Upon preliminary analysis, for a contact time of 0 seconds, the stack appears to have low intensity of five main mineral components: goethite, hematite, aluminium silicate, potassium magnesium hydrogen aluminium silicate hydrate, and sodium titanium silicate. However, only minor amounts of aluminium silicate are identified (point 8) with low intensity while the rest of minerals have not yet begun to form. All of

the five main minerals began to form with higher intensity after the reaction with SO₂ for 6000 s. It is observed that goethite is the dominant mineral after the red mud has reacted with SO₂ with sharp peaks at points 1,6,7, and 10.

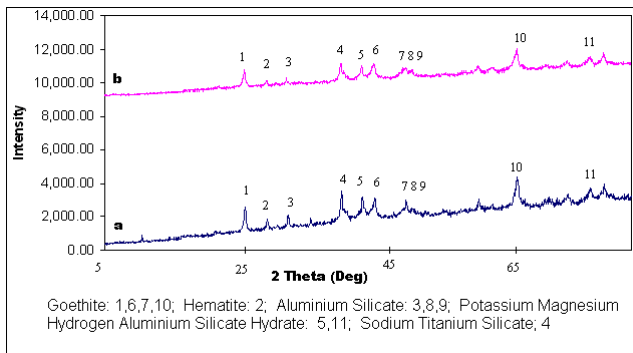


Figure 6. XRD patterns of red mud when react with SO₂ at: a) 0 s b) 6000 s

D. ICP Analysis

It is observed that the concentration of elements such as Co, Cu, Fe, Mn, S, Ti, and Zn was increased after the reaction. However, elements such as Na and Ca were removed tremendously, with 99.14% and 95.07% removal respectively. For elements such as Al and Mg, the percentages of removal are 83.3% and 70.02%, respectively, while other elements (P, K, Ga) have a percentage removal of 35% to 60%. While several of the elements in the treated liquor were outside the limits specified by the ANZECC guidelines [18], all concentrations of elements with no set limit such as Ca, Co, Ga, K, Mg, Mn, Na, P, S, and Ti, are acceptable.

E. XRF Analysis

The XRF results for the red mud prior to reaction with SO₂ indicate that the main element present is iron, which makes up 60.19% of the total element composition. This is followed by aluminium with contribution of 17.65%. Silicon (6.93%), titanium, (4.08%), and sodium, (1.23%) are the next most considerable components.

After the reaction between red mud and SO₂ at 6000 seconds, element such as titanium, phosphorus, sulphur and potassium show that the elements increases with time. However for elements such as calcium, sodium, and magnesium decrease after the reaction with SO₂ at contact time of 6000 seconds. For strontium and zirconium, the results are constant whereby showing the composition of elements are not affected by time. This is in contrast to chromium, vanadium, gallium, silicon, aluminium and iron that show fluctuating results with a slightly dissimilar composition of elements at both contact time of 0 and 6000 seconds.

IV. CONCLUSION

In this research, the efficiency of red mud as an adsorbent

for the absorption of SO₂ and ability of these gases to neutralize the red mud were studied. The alkalinity of the red mud slurry and liquor show a slow decrease with the increase of acid dosage while the results for absorption study show that it takes longer time for SO₂ gas to neutralize the red mud slurry compare to the red mud liquor.

XRD analysis of the red mud shows the five main minerals components; goethite, hematite, aluminium silicate, potassium magnesium hydrogen aluminium silicate hydrate, and sodium titanium silicate were increased in intensity after the reaction with SO₂.

As in the XRF results, elements such as Ti, P, S, and K show that the elements increase with time. This trend is similar with Ca, Na, and Mg during the first 600 s, but then followed by a slow decrease towards the end of contact time of 6000s. These imply that the fluctuations of elements may be due to the changes of elements between the solid and the liquid phase of the red mud when the experiments were carried out. These were proven when the ICP results also fluctuate over time.

Several areas within the experiment should be expanded and considered in further studies. Some of the recommendations are such as determination of the saturation point and the kinetics of the system in batch absorption studies and also determination of the crystal morphology of red mud after being reacted with SO₂ by using Scan Electron Microscopic (SEM).

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