Dissolution Study of a South African Industrial Calcium-based Waste

Nelson Masilela, and Hilary Rutto

Abstract—Wet flue gas desulphurization (FGD) systems are commonly used to remove sulphur dioxide by contacting it with industrial calcium-based waste (limestone) in aqueous phase in which it reacts with industrial calcium-based waste to form either calcium sulfite or calcium sulfate. In this study, the dissolution of industrial calcium-based waste in HCl acid was investigated over a wide range of parameters. The effects of pH, stirring speed; solid to liquid ratio and acid concentration on the dissolution of industrial calcium-based waste was studied. It was found out that the dissolution rate of industrial calcium-based waste increased with increase in acid concentration, temperature, stirring speed and it decreased with an increase in solid to liquid ratio and pH. An activation energy of 20.26 kJ/mol was obtained, this indicate that chemical reaction was the rate limiting step.

Keywords—Activation Energy, Coal Fly Ash, Desulphurization, Dissolution.

I. INTRODUCTION

Emissions of sulphur dioxide into the atmosphere have increased steadily with industrial development, the combustion of coal produces sulphur dioxide. Legislation to curb the emission of sulphur dioxide was introduced in early 1990 in South Africa and there is an urgent need to conduct research in this field [1,2]. Flue gas desulphurization (FGD) system has been identified as a process for better performance and reliability so as to ensure that sulphur dioxide emissions are within the obligatory limits. There are several ways of removing sulphur dioxide from the flue gas. These include dry, semidry and wet flue gas desulphurization (FGD) process methods. Petrochemical industries produce polyvinyl chloride using ethylene and chloride. Chlorine is manufactured from soda ash. The reaction process produces mega tonnes of calcium compound is very important in wet flue gas desulphurization [3,4,5]. The dissolution on calcium and magnesium based waste have been studied [6,7,8,9,10]. Several other studies have focused on dissolution rates have been carried out. Raschman [11] studied the dissolution of calcined magnesite in ammonium chloride solution at constant pH. The effect of acetic acid solution in the dissolution of magnesite in acetic acid solutions has been studied [12], it was established that the dissolution rate was controlled by chemical reaction. Bakan et al., [13] studied the dissolution kinetics of natural magnesite in lactic acid solutions and determined that the dissolution rate is controlled by surface chemical reaction. The main objective is to study the feasibility of using calcium industrial waste as a sorbent in wet flue gas desulphurization to reduce the levels of SO2 in the atmosphere. Moreover with more electricity in demand in South Africa, more coal power station has been built which require desulphurisation to reduce the levels of SO2 in the atmosphere. The use of calcium industrial waste as a sorbent in wet flue gas desulphurization will lead to feasible way to address the issue of landfill and environmental pollution. Calcium sulphate (Gypsum) can be generated in flue gas desulphurisation which is nontoxic and has several application in the building and agriculture sector. Therefore a study on dissolution kinetics of calcium compound is very important in wet flue gas desulphurisation [3,4,5]. The dissolution in this study was controlled by chemical reaction. Experiments were carried out on a predetermined amount of industrial calcium based waste added to the reactor vessel and the temperature, solid to liquid weight ratio, particle size and pH on dissolution rate of calcium industrial waste was investigated using a pH-stat apparatus.

II. MATERIALS AND METHOD

A. Materials

Calcium industrial-based waste was obtained from a petrochemical industry that manufactures polyvinyl chloride. The waste material was crushed using a ball mill and sieved to different particle sizes using shaking screen sieves. The chemicals used were HCl and calcium ions standard and were obtained from local chemical suppliers.

B. Method and experimental design

A predetermined amount of industrial calcium-based waste was added to the reactor vessel and the temperature, solid to liquid weight ratio, particle size, acid concentration, agitation and pH was varied according to the experimental design. The reaction temperature was controlled by a hot plate stirrer. The
pH of the reaction mixture was determined using pH electrode inserted in the solution and connected to a pH 200 1/8DIN pH controller. The controller has specific pH range of pH 0.01. When the pH exceeds the set value, the pump is activated to add acid to the reaction vessel and lower the pH value to the set point. A sample was then be removed, filtered and analyzed for calcium using Atomic Absorption Spectrophotometer (AAS). The dissolution fraction was evaluated as:

\[ X = \frac{[\text{Calcium ions in solution}]}{[\text{Total amount of calcium ions in original sample}]} \]

The experimental setup for the experiment is illustrated in Figure 1.

III. RESULTS AND DISCUSSION

A. Mechanism for dissolution of industrial calcium waste

The mechanism for dissolution of CaCO\(_3\) in industrial calcium based waste in the presence of HCl is as follows:

- **HCl acid dissociation:**
  \[ HCl(aq) \rightarrow Cl^-(aq) + H^+(aq) \]  
  (1)

- **CaCO\(_3\)** dissolution by hydrogen complexation:
  \[ CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+} + CO_2 + H_2O(aq) \]  
  (2)

Fig. 2 The effect of stirring speed on the dissolution rate of calcium based industrial waste

**Fig. 3 The effect of solid to liquid ratio on the dissolution of industrial calcium based waste**
B. The effect stirring speed on the rate of dissolution of the calcium industrial waste.

The experiment was carried out by varying the stirring speed as follows: 100 rpm, 200 rpm, 300 rpm, 400 rpm, to evaluate the effect of agitation on the rate of dissolution. Figure 2 illustrates that the rate of dissolution increases with the increase in stirring speed. Stirring also increases the kinetic energy of the molecules providing more chance of contact with the product layer.

C. The effect solid to liquid on the rate of dissolution of the calcium industrial waste.

The effect of solid to liquid ratio was carried out in the experiment between the ranges of (5% - 20%) to determine the effect of varying the amount of particles. Figure 3 illustrates that the increase in solid to liquid ratio has an inverse effect on the rate of dissolution. This is attributed by the increase in the solid weight per constant amount of product fluid available.

D. The effect acid concentration on the rate of dissolution of the calcium industrial waste.

Acid concentration was varied as follows, 0.05M, 0.075M, 0.1M, 0.15M to determine the effect on the rate of dissolution. As shown in figure 4, an increase in acid concentration increases the rate of dissolution. This is because there is more H+ ions to dissolve the calcium industrial waste.

E. The effect particle size on the rate of dissolution of the calcium industrial waste.

Different size fractions were used in the experiment to determine the effect of particle sizes during dissolution. Particles were varied as follows, <63µm, 63µm - 75µm, 75µm - 150µm, 150µm - 300µm. Figure 5 illustrates that the
dissolution rate of calcium industrial waste, the dissolution rate increases with a decrease in particle size. The finer the particles are, the more surface area increases and that means more particles exposed for leaching.

F. The effect pH on the rate of dissolution of the calcium industrial waste.

Different pH of 5.5, 6, 6.5, and 7 were used in the experiment to analyse the effect of pH on the rate of dissolution. From figure 6, the dissolution rate decreases with an increase in pH. This could be because the no of H+ decreases as the pH increases.

G. The effect of Temperature on the rate of dissolution calcium industrial waste.

The experiment was carried out in the following temperature splits, 30°C, 50°C, 70°C, 90°C to investigate the influence of temperature on the dissolution rate. Figure 7 depicts that an increase in the temperature with time increases the dissolution rate of the calcium industrial waste. This is as a result of high kinetic energy available for the reacting molecules. According to figure 8, the activation energy was determined to be 20.26 kJ/mol this indicates chemical reaction was the rate limiting step [14,15,16].

IV. CONCLUSION

The work demonstrated that it was feasible to use an industrial calcium based waste to produce sorbent that can be used in wet flue gas desulphurization. In this study, The effects of pH, stirring speed, solid to liquid ratio and acid concentration were studied in order to determine the dissolution of industrial calcium based waste. It was found out that the dissolution rate of industrial calcium based waste increased with increase in acid concentration, temperature, stirring speed and it decreased with an increase in solid to liquid ratio and pH. An activation energy of 20.26 kJ/mol was obtained, this indicate that chemical reaction was the rate limiting step.

REFERENCES


