

Dissolution of Zeolite as a Sorbent in Flue Gas Desulphurization Process Using a pH Stat Apparatus

Hilary Rutto, John Kabuba

Abstract—Sulphur dioxide is a harmful gaseous product that needs to be minimized in the atmosphere. This research work investigates the use of zeolite as a possible additive that can improve the sulphur dioxide capture in wet flue gas desulphurisation dissolution process. This work determines the effect of temperature, solid to liquid ratio, acid concentration and stirring speed on the leaching of zeolite using a pH stat apparatus. The atomic absorption spectrometer was used to measure the calcium ions from the solution. It was found that the dissolution rate of zeolite decreased with increase in solid to liquid ratio and increases with increase in temperature, stirring speed and acid concentration. The activation energy for the dissolution rate of zeolite in hydrochloric acid was found to be 9.29kJ/mol. and therefore the product layer diffusion was the rate limiting step.

Keywords—Calcium ion, pH stat apparatus, wet flue gas desulphurization, zeolite.

I. INTRODUCTION

SULPHUR dioxide is highly detrimental to human health since it causes respiratory problems and irritation of the nostrils, pulmonary system, throat and it has also been linked to cases of visual impairment [1]. Sulphur dioxide dissolves in water and from acid rain which poses adverse effects on the ecosystems and infrastructure [2], [3]. There are technologies that have been designed to remove sulphur dioxide from flue gas, flue gas desulphurization (FGD) is largely used to curb sulphur dioxide emission from large electric utilities such as boilers in coal combustion. FGD systems are mostly used because of high sulphur dioxide removal efficiency. FGD systems are categorized as wet, dry and semi dry FGD. In wet FGD systems high degree of SO₂ removal is usually achieved with high level of sorbent utilization. SO₂ in flue gas is removed by contacting it with CaO in aqueous phase in which it reacts with sulphur dioxide to form calcium sulphate. The main sorbents used in flue gas desulphurization are limestone, magnesite and dolomite, other sorbent used as sorbent in wet flue gas desulphurization used include fly ash, coal fly ash which are added in small quantities to improve flue gas desulphurization process [4]-[7]. The dissolution of sorbent in both wet and flue gas desulphurization form a critical step to determine the percentage of sulphur dioxide capture. Siagi et al. [8] studied the dissolution of South African calcium based

material; he found out that the dissolution of limestone is largely dependent on its sources and its process variables. Rutto et al. [9] studied dissolution magnesite and developed a semi-empirical model which predicts dissolution using a pH stat apparatus, from the study he found out that the dissolution of magnesite as sorbent for wet flue gas desulphurization depend on the process conditions. Fly ash is a siliceous material that contains calcium and aluminum compounds, studies have shown that the SO₂ removal efficiency improves when fly ash is mixed with limestone [10]-[12]. Studies show that silica undergoes a hydration and a pozzolonic reaction with CaO to form calcium silicate hydrate sorbent with high specific surface area. Zeolite is a silicious material that contains largely silica both in amorphous and crystalline form, aluminum oxide and calcium oxide which can improve the total SO₂ removal efficiency in both wet and dry flue gas desulphurization systems [13]. The main objective study is to determine the feasibility of using zeolite as a source of calcium ions in flue gas desulphurisation using hydrochloric acid as a leaching agent. The effect of the process variables namely: temperature, concentration of acid, solid to liquid ratio and pH are investigated using a pH stat apparatus.

II. MATERIALS AND METHODS

Zeolite sample was obtained from partly mining industry, washed and dried on an oven with 100°C temperature for 24 hours. The XRF (X-ray fluorescence), Phillips Magix Pro, chemical composition of zeolite was as follows: SiO₂ 51.81%, Al₂O₃, 30.49%, Fe₂O₃ 4.67%, CaO 6.82%, MgO 0.26%, K₂O 0.97%, P₂O₅ 0.37%, and SO₃ 0.61%. The chemical used were hydrochloric acid, distilled water and calcium standard which were obtained from a local chemical supplier. The physical properties of the zeolite are [14]: Main phase: 80-85% Clinoptilolite (XRD, BET & analysis); main impurities: Paline Cristobalite, K-Feldspar & trace of Sanidine; refractive index: 1.484; density or specific gravity: 2.2 g/cm³; bulk density of the ore: 1.92g/cm³, packing density: 0.99kg/m³, thermal stability: it can be heated to over 700°C before the aluminosilicate framework collapses; acid and alkaline stability: stable from pH3 to 12; color: reflection white: 80% [Mg = 85%]; Hardness is 3.5-4.0 MOH; pore size: 3.5-6 Angstroms; pore volume: approximately 5-10%, the bulk density of the rock as determined by immersion in mercury is 1.92g/ml³. The XRD (X-ray power diffractometer) Phillips X'pert Model 0.993 gives the following results: 70% SiO₂, 12% Al₂O₃, 2% Na₂O, 5% K₂O, 2%CaO, 2.5%Fe₂O₃ with traces of other elements was observed and their BET surface area analysed. The measured BET surface areas and pore sizes

H.L. Rutto is with the Department of Chemical Engineering, Vaal University of Technology, South Africa (phone: +27 16 -950-9243; fax: +27 16-950-9796; e-mail: hilaryr@vut.ac.za).

J. Kabuba is with the Department of Chemical Engineering, Vaal University of Technology, South Africa (phone: +27 16 -950-9887; fax: +27 16-950-9796; e-mail: johnka@vut.ac.za).

for the air and oven dried natural clinoptilolite were (26.03 m²/g, 0.081 cm³/g) and (20.88 m²/g, 0.068 cm³/g) respectively. This showed that oven drying started already to close up the zeolite structure, Fig. 1[15].

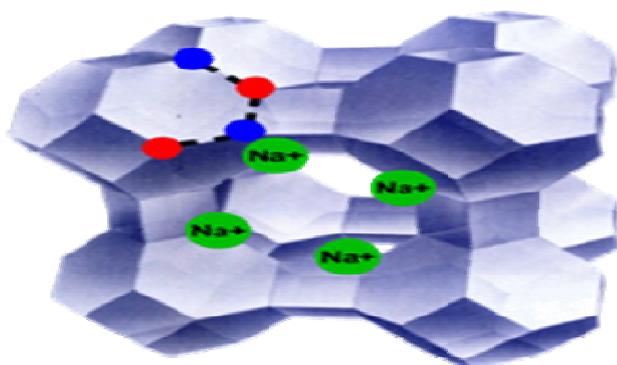


Fig. 1 A representative structure of clinoptilolite [15]

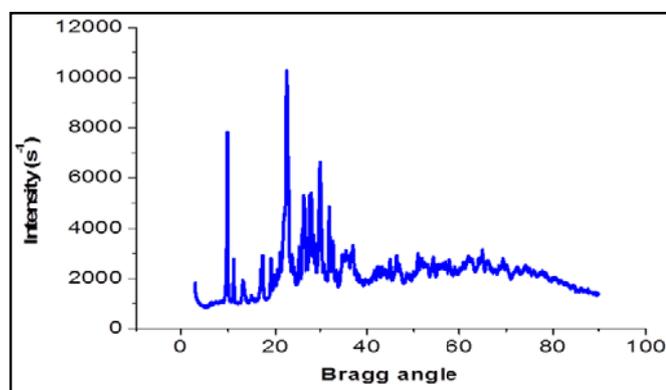


Fig. 2 Diffraction pattern of the natural clinoptilolite

The X-Ray Fluorescence (XRF) and X-Ray Diffractometry (XRD) characterization done by Reference [15] showed that clinoptilolite contained exchangeable ions of sodium, potassium, calcium and magnesium. This zeolite (clinoptilolite) has a Si/Al ratio of 5.96 (mol/mol) and the corresponding ratio of (Na⁺ + K⁺/Ca²⁺) was 3.4. XRF also confirmed that the zeolite was a high silica clinoptilolite enriched with Mg²⁺, K⁺ and Na⁺. Fig. 2 shows a typical mineralogical diffraction pattern of a crystallite with a composition of 70% SiO₂, 12% Al₂O₃, 5% K₂O, 2.5% Fe₂O₃, 2% Na₂O, 2% CaO and traces 0.2% of TiO₂. The XRF composition suggested that the clinoptilolite was a silicon based zeolite when taking into account that its major component was silicon dioxide [15]. The XRF and XRD determinations to a very large extent were thus in agreement particularly with the dominance of the silicon species followed by aluminum. Traces of other elements not accounted for in the XRD determinations were probably the titanium and magnesium moieties, which XRF analysis could not detect and thus the percentage composition detected by XRF did not add up to 100% [15].

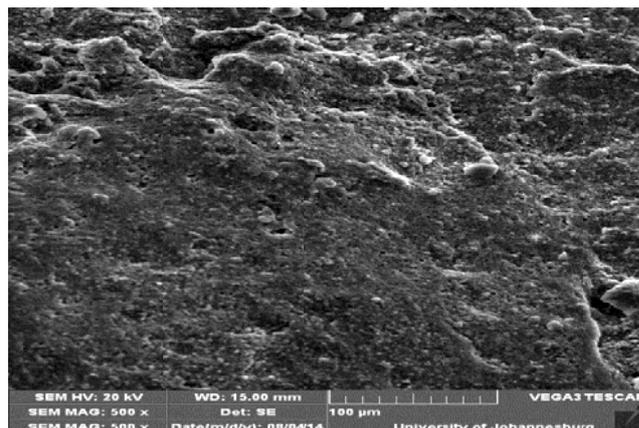


Fig. 3 SEM image of original clinoptilolite

Fig. 3 illustrates the surface texture and porosity of clinoptilolite with holes and small opening on the surface which will increase the contact area of the adsorbent and consequently lead to the pores diffusion during adsorption

A. Method

The ground sample was sieved into different particle sizes ranging from an average of 63-150 μm. A predetermined amount of zeolite was added to the reactor vessel and the temperature, acid concentration, solid to liquid weight ratio, stirring speed, and pH were varied. The pH was controlled using a pH electrode with an accuracy of 0.01 if the pH surpasses a given set value the pump is automatically activated to dose hydrochloric up to the set point. The experimental set up is shown in Fig. 4. The samples were filtered and the filtrate was analyzed for calcium ion content using the Atomic Absorption Spectrophotometer (AAS). The dissolution fraction was calculated using the following formula below:

$$x = \frac{\text{Calcium in filtrate}}{\text{Total amount calcium in original simple}} \quad (1)$$

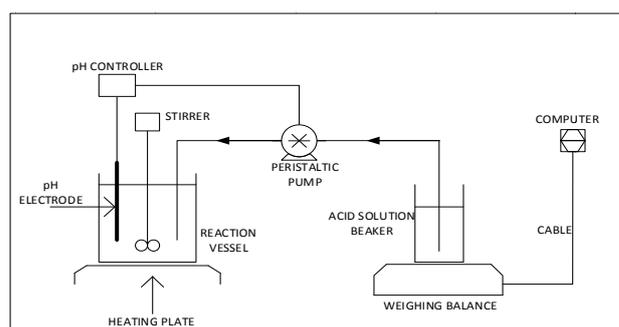


Fig. 4 Schematic pH stat experimental set up for zeolite dissolution

III. RESULTS AND DISCUSSION

A. Mechanism for the Dissolution of Zeolite

From XRF analysis shows that zeolite consists of CaO, Al₂O₃ and SiO₂ which affect dissolution process Hydrochloric acid dissociates into solution to form chloride and hydronium ions:



CaO dissolution by hydrogen complexation



Calcium ions from supersaturation (3) can be utilised more in pozzolanic reaction to form aluminosilicate complex compounds as shown in (4) [16]. Pozzolanic reaction:



The product formed (calcium aluminosilicate hydrate) from the pozzolanic reaction leads to an increase in the surface area of the sorbent which thus improves its SO₂ absorption capacity during flue gas desulphurization.

B. Effects of Reaction Variables

1. Effect of Stirring Speed on the Dissolution Rate of Zeolite

The dissolution rate of zeolite was investigated by varying stirring speed from 150-400 rpm. The temperature, pH, concentration of HCl and solid to liquid ratio were kept constant at 55°C, 0.5M and 1.5g/100ml respectively. As shown in Fig. 5(a), it was observed that the dissolution rate increased as the stirring speed increased. The increase in stirring speed causes a decrease in film layer, therefore causing an increase in dissolution rate.

2. Effect of Acid Concentration on the Dissolution Rate of Zeolite

Effect of HCl acid concentration on the dissolution rate of zeolite was examined by varying the acid concentration from 0.1-1M. The temperature, pH, stirring speed and solid to liquid ratio were kept constant at 55°C, 5.5, 0.5M, 200 rpm and 1.5g/100ml respectively. Result depicted in Fig. 5(b) shows that as the concentration of the acid is increased, the dissolution rate increases and vice versa. The increase in dissolution at high acid concentration is attributed to presence of more H⁺ which reacts with the calcite as shown in (3).

3. Effects of Solid-Liquid Ratio on the Dissolution Rate of Zeolite

The effect solid-to-liquid ratio on the dissolution rate of the zeolite was investigated by varying the solid-to-liquid ratio from 1 to 2.5g/100 ml. The temperature, pH, concentration of HCl and stirring speed were kept constant at 55°C, 5.5, 0.5M and 200 rpm respectively. The result in Fig. 5(c) shows that the dissolution rate decreased as the solid to liquid ratio increases. This is attributed to the decrease in the fluid reactant per unit weight of the solid as solid to liquid ratio increases.

4. Effects of Temperature on the Dissolution Rate of Zeolite

The effect of temperature on the dissolution rate of zeolite was examined by varying the temperature from a range of 25-55°C. The stirring speed, pH, concentration of HCl and solid to liquid ratio were kept constant at 200 rpm, 5.5, 0.5M and 1.5g/100ml respectively. As shown in Fig. 5(d) dissolution

rate increases with increase in temperature. Increase in temperatures increases the molecular collision which increases the dissolution rate.

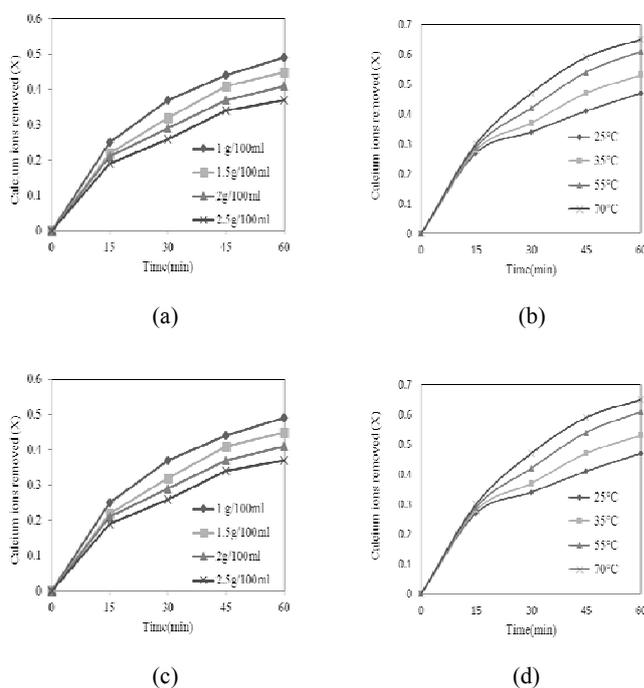


Fig. 5 Effect of stirring speed (a), HCl acid concentration (b), solid to liquid ratio (c) and temperature (d) on the dissolution rate of zeolite

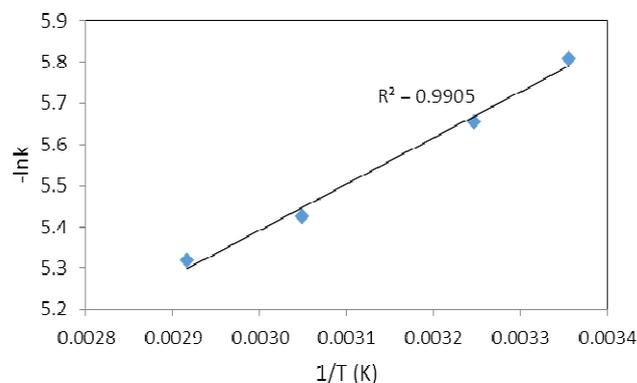


Fig. 6 Arrhenius plot for the dissolution rate

The activation energy was determined to be 9.29 kJ/mol by plotting lnk versus T. As shown in Fig. 6 it was found out that when the activation is 9.29 kJ/mol, the product layer is the rate limiting step [17] this could be because a pozzolonic reaction occurs which forms product layer of calcium hydrated silicate which limits the reaction [18],[19].

IV. CONCLUSION

The work showed that it possible to leach out calcium ions out of zeolite using a pH stat apparatus with hydrochloric solution. Results showed that the dissolution rate increased as temperature, concentration, and stirring speed were increased

and decreased as solid-to-liquid ratio and particle size was increased dissolution rate of zeolite in hydrochloric acid was controlled by the product later diffusion control step with activation energy of 9.29kJ/mol.

[19] Z. I. Zafar. "Determination of semi empirical kinetic model for dissolution of bauxite ore with sulfuric acid: Parametric cumulative effect on the Arrhenius parameters", Chem. Eng. J., 2008, vol.141, pp.233-241.

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REFERENCES

- [1] Z. Klimont, S. J. Smith and J. Cofala, "The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions", Environmental Research Letters, 2013, vol. 14, pp. 1-3.
- [2] D. Kunkel, H. Tost and M. Lawrence, "Impact of anthropogenic emissions from major population centers on global and regional aerosol budgets", EGU General Assembly Conference Abstracts, 2013, vol. 7083.
- [3] National Environmental Management, South Africa, Air and Quality Act, Act No. 30 of 2004, 2005.
- [4] C. You and Y. Li, "Desulfurization Characteristics of Rapidly Hydrated Sorbents with Various Adhesive Carrier Particles for a Semidry CFB-FGD System", Environ. Sci. Technol., 2013, vol. 47, pp. 2754-2759.
- [5] H. Song and J. Park, "Improvement of SO₂ removal by the solubility change of Ca (OH)₂ in the spray dryer system", Environ. Technol., 2001, vol. 22, pp. 1001-1006.
- [6] H. Rutto and C. Enweremadu, "A study on dissolution of a South African calcium based material in acetic acid solution for flue gas desulphurization", Electrical and Control Engineering (ICECE) International Conference. 2011, pp. 5701-5705.
- [7] S. Shih, J. Lin and G. Shiau, "Dissolution rates of limestones of different sources", J. Hazard. Mater., 2000, vol.79, pp.159-171.
- [8] Z. Siagi and M. Mbarawa, "Dissolution rate of South African calcium-based materials at constant pH", J. Hazard. Mater., 2009, vol.163, pp.678-682.
- [9] H. Rutto and C. Enweremadu, "The dissolution study of a South African magnesium-based material from different sources using a pH-stat", Chemical Industry and Chemical Engineering Quarterly, 2011, vol. 17, pp.459-468.
- [10] N. Karatepe, A. Mericboyu and S. Küçükbayrak, "Effect of Hydration Conditions on the Physical Properties of Fly Ash-Ca (OH)₂ Sorbents", Energy Source. 1998, vol.20, pp. 505-511.
- [11] A. Garea, I. Fernandez, J. Viguri, M. Ortiz, J. Fernandez, M. Renedo and J. Irabien, "Fly-ash/calcium hydroxide mixtures for SO₂ removal: structural properties and maximum yield", Chem. Eng. J., 1997, vol.66, pp. 171-179.
- [12] C. Jorgensen, J.C.S. Chang and T.G. Brna, "Evaluation of sorbents and additives for dry SO₂ removal", Environmental Progress. 198, vol.6, pp. 26-32.
- [13] N. Karatepe, N. Erdog˘an, A.E. Meriçboyu, S. Küçükbayrak, "Preparation of diatomite/Ca(OH)₂ sorbents and modelling their sulphation reaction", Chemical Engineering Science. 2004, vol. 59, pp. 3883-3889.
- [14] S.A. Abdulkareem, E. Muzenda, A.S. Afolabi, J. Kabuba, "Treatment of clinoptilolite as an Adsorbent for the Removal of copper Ion from Synthetic Wastewater solution", Arab. J. Sci. Eng., 2013, vol. 38, pp. 2263-2272.
- [15] J.D. Gilchrist, Extraction Metallurgy, Pergamon Press.1989
- [16] B.B. Mamba, D.W. Nyembe and A.F. Mulaba-Bafubiandi, "The effect of conditioning with NaCl, KCl and HCl on the performance of natural clinoptilolite's removal efficiency of Cu²⁺ and Co²⁺ Synthetic solution", Water SA., 2009, vol. 36, pp. 437-444.
- [17] K.T. Lee, M.A. Mothar, N.F. Zainudin, S. Bhatia and A.R. Mohamed, "Optimum conditions for the preparation of flue gas desulphurization sorbent from rice husk ash", 2004, vol.84, pp. 143-151.
- [18] E.M. Van der Merwe and C. Strydom, "Hydration of medium reactive magnesium oxide using hydration agents", Journal of Thermal Analysis and Calorimetry. 2006, vol. 84, pp. 467-471.