Semi-Empirical Modelling for Dissolution of Calcium from Ironmaking Slag in Ammonium Acetate for CO₂ Utilisation

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Abstract: It is a great technique to use iron and steel slags as feedstock for a mineral carbonation reaction to use carbon dioxide gas because they are easily accessible, contribute to land pollution, and have a reasonable quantity of lime and magnesia. The rate at which ironmaking blast furnace ironmaking slag dissolves in an aqueous solution of ammonium acetate was investigated in relation to pH, stirring speed, solvent concentration, and temperature. A one-factor-at-a-time experiment was conducted pH was monitored to the maximum value of 11, stirring speed ranged from 100 to 200 rpm, solvent concentration was adjusted from 0.01 to 1 M, whereas the reaction temperature was maintained between 25 and 80 °C. The dissolution kinetics of ironmaking slag was calculated by fitting experimental data to a model of a diminishing core. Using AAS, the leach liquor was characterized under various experimental conditions. The results of the trial revealed that this reaction is driven by chemical reaction model equation. A semi-empirical model was also developed from the experimental data to better describe the dissolution kinetics.

Keywords: Dissolution Reaction; CO₂ utilisation; Ironmaking Slag; Shrinking Core Models; Semi-Empirical Modelling

1. Introduction

Ironmaking slag is a waste product of the iron and steel industry that has been generated in large quantities globally. The disposal of ironmaking slag poses a significant environmental problem due to its potential impact on land pollution and water quality. Therefore, finding sustainable ways to reuse this waste material is an important goal. One potential application is to use ironmaking slag as a feedstock for mineral carbonation, a process that converts CO₂ into stable carbonates through a chemical reaction with the alkaline components in the slag. This process has the potential to store large amounts of CO₂ over geological timescales, thus mitigating the impact of anthropogenic emissions on the climate.

The dissolution of ironmaking slag in aqueous solutions is a crucial step in the mineral carbonation process. In addition, the dissolution of calcium from the slag is important since it provides the alkalinity necessary for the CO₂ sequestration reaction. Previous studies have investigated the dissolution kinetics of ironmaking slag in various solvents, including water, acetic acid, and ammonium acetate. However, the dissolution behaviour of ironmaking slag is complex and depends on various factors such as pH, temperature, particle size, and solvent concentration. Therefore, further research is needed to develop a comprehensive understanding of the dissolution process [1, 2].

Additionally, the development of a semi-empirical model for the dissolution process can aid in the design and optimisation of mineral carbonation reactors. Overall, this study contributes to the development of a circular economy for ironmaking slag, which can reduce the environmental impact of the iron and steel industry while providing a valuable

resource for CO_2 sequestration [3]. The Shrinking Core Models (SCMs) denotes that the reaction first occurs at the surface of the particle then moves to the centre. As the reaction continues, the unreacted core of the particle is reduced in size while more solid and aqueous layers are created. Therefore, chemical reaction rate and the fluid film diffusion expressions are denoted as equation 1 and 2 respectively [4]:

$$X = \frac{3bk_i C_A}{\rho_B R_0} t = k_r t$$

(1)

$$1 - (1 - X)^{\frac{1}{3}} = \frac{bk_s C_A}{\rho_B R_0} t = k_r t$$

(2)

The temperature dependence on the reaction rate constant is denoted by Arrhenius equation:

$$K_r = K_0 e^{(-E_a/_{RT})}$$

(3)

Where K_0 is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the temperature. Moreover, the values of the activation energy E_a and K_0 are obtained from a linear relationship between $-\ln K_r$ and $1/T$. The activation energy for a product layer diffusion-controlled reaction mechanism is normally below 20 kJ/mol while for the chemically-controlled reaction mechanism the energy is from $40 - 80$ kJ/mol [5, 6].

A semi-empirical model including all process variables can be depicted as follows:

$$K_r = K_0 C^a N^b (\tfrac{S}{L})^c P^d e^{(-E_a/_{RT})}$$

(4)

By substituting Equation (2) into (4), the following expression is obtained:

$$1 - (1 - X)^{\frac{1}{3}} = K_0 C^a N^b (\tfrac{S}{L})^c P^d e^{(-E_a/_{RT})} t$$

(5)

Where a,b,c and d are the reaction orders evaluated from the rate constants. C is the concentration, N is the stirring speed, (S/L) is the solid-to-liquid ratio, and P is the pH.

1. Materials and Methods

1.1. Materials

Blast furnace ironmaking slag was obtained from a local steel mill in Vanderbijlpark, South Africa. High purity ammonium acetate salt and calcium standards for Atomic Adsorption Spectrometry (AAS) analysis was supplied by United Scientific PTY LTD. A laboratory scale jaw crusher and a rod mill were used to reduce the slag particles from 10 cm down to 75 μm. In addition, a portable orbital shaker was used for leaching process of a solution in 500 ml Erlenmeyer flasks.

1.1. Methods

A finely milled blast furnace slag was added to the 500 ml Erlenmeyer flask with distilled water placed in a portable orbital shaking vessel. The reaction temperature, solid-to-liquid, solvent concentration, stirring speed, as well as pH were varied according to the experimental design. This was done by setting up the required temperature and stirring speed on the orbital shaker. The pH of the solution was monitored by Thermo Scientific Alpha pH 2000P Panel Mount pH/ORP Controller. Samples were then removed, filtered and analysed for calcium concentration (in ppm) by Varian AAS (AA140) instrument with a hollow cathode lamp for calcium element analysis.
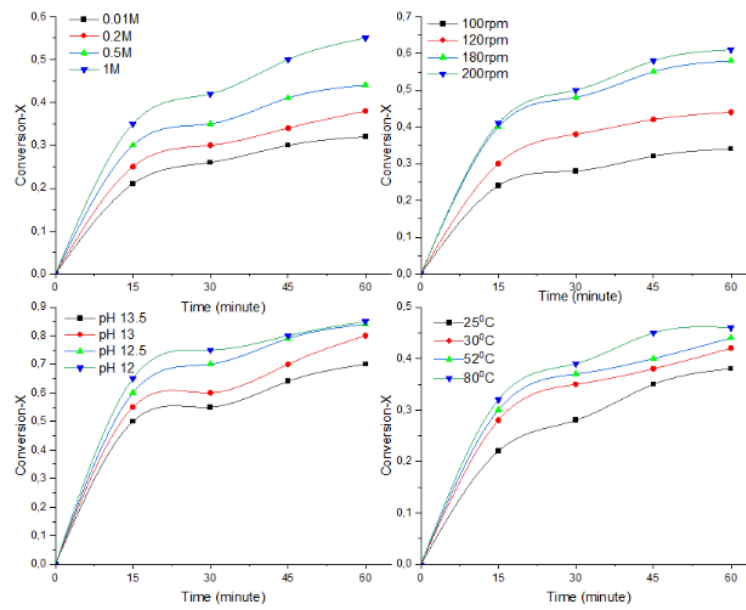
1. Results and Discussion

Figure 1. Effect of different (a) solvent concentration, (b) stirring speed, (c) pH values, and (d) temperature on dissolution of calcium from ironmaking slag in ammonium acetate solution.
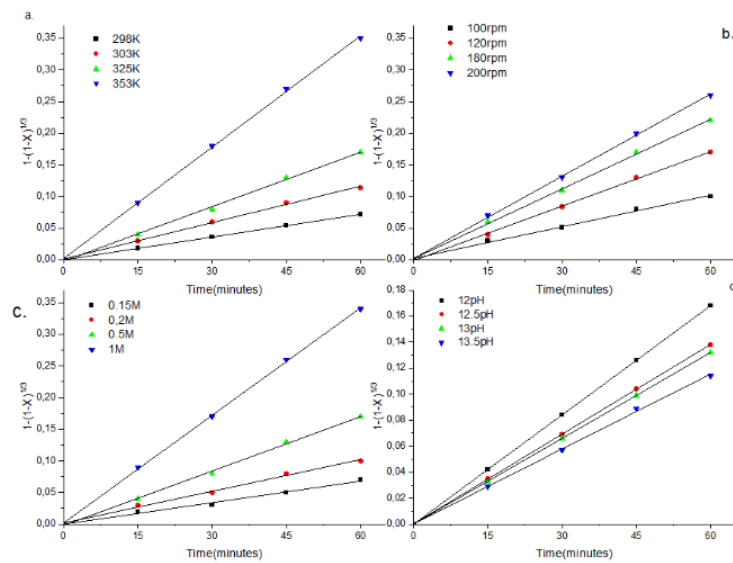

Figure 2. Variation of $1-(1-X)^{1/3}$ different with times for various (a) temperature, (b) stirring speed, (c) concentration, and (d) pH values.
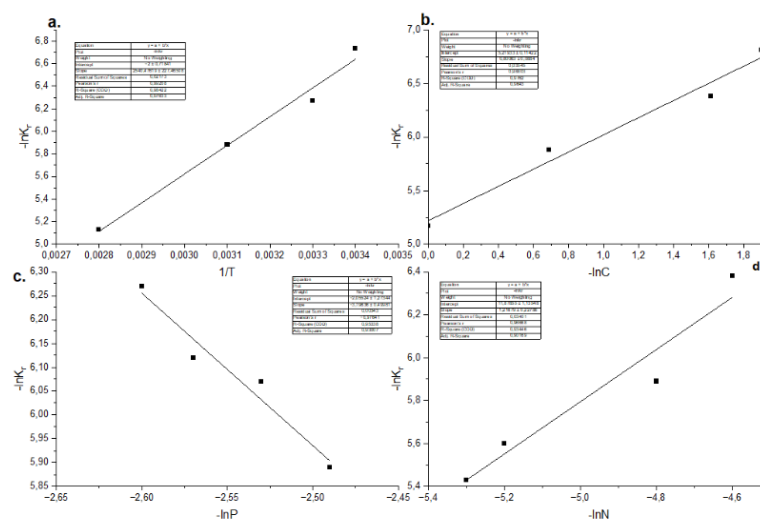
Figure 3. Arrhenius plot for dissolution of calcium from ironmaking slag.

3.1. The effect of solvent concentration on the dissolution of calcium

Experiments by using 0.15, 0.2, 0.5, and 0.1 M ammonium acetate were carried out to examine the impact of concentration on the dissolution of calcium from blast furnace ironmaking slag. The pH, stirring speed, and temperature were all held constant at 12.5 pH, 303 K, and 120 rpm, respectively. As shown in Figure 1, as the concentration increases, more calcium ions are converted, which improves the flow of fluid reactant from the liquid bulk to the surface of the solid particle. As a result, the leaching rate increases with high amenability of calcium dissolution in ammonium acetate aqueous phase.

3.2 The effect of stirring speed on the dissolution of calcium

A concentration of 0.01 to 1 M ammonium acetate was used to analyse the impact of stirring speed on the dissolving of used beverage cans at 303 K and pH 12.5. There were four different stirring speeds: 100, 120, 180, and 200 rpm. According to the experimental findings in Fig. 1b, the dissolution of calcium from ironmaking slag rises with increased stirring speed. A higher stirring speed results in a reduction in the resistance of the film layer, which in turn increases the rate of dissolution.

3.3. The effect of solution pH on the dissolution of calcium

Four experiments were conducted at a constant temperature of 303 K, 0.2 M concentration, and 120 rpm stirring speed to examine the impact of pH on alkaline leaching of calcium from blast furnace ironmaking slag. After filtering, the pH of the solution was monitored, and the results were 12, 12.5, 13, and 13.5. The findings in Fig. 1c show that lower pH resulted in a higher conversion of iron steel particularly calcium ions. Reduced dissolution results from a larger apparent mass transfer coefficient, which is induced by a higher pH. Because there is a large concentration of H^+, which speeds up the dissolving interaction between the fluid reactant and the solid particles, high values of the rate constant were achieved at low pH [7].

3.4. The effect of reaction temperature on the dissolution of calcium

Under constant conditions of 0.2 M concentration, 120 rpm stirring speed, and pH 12.5, the temperature was changed between 298 K, 303 K, 325 K, and 353 K. The experimental results shown in Fig. 1d allow the conclusion that greater temperatures result in a faster rate of dissolution. As a result of an effective power collision between molecules brought on by high temperatures, many types of reactions between the solid reactant and the fluid reactant occur.

The rate constant was 0.0012 min^{-1} at temperature 298 K, and it further increased to 0.0059 min^{-1} at temperature 353 K. The values obtained at 298 K and 353 K had a significant large difference. This is due to the fact that high temperatures change the kinetics of the leaching process, which causes increased reactivity [8].

3.5 Kinetic analysis for the dissolution of calcium from ironmaking slag

Figs. 2 a–d show the linear relationship between $1-(1-X)^{1/3}$ and the reaction time for different (a) temperature, (b) stirring speed, (c) concentration and (d) pH values respectively. The slope of a plot of $\ln K_r$ vs $\ln C$ in Fig. 3b was used to determine the reaction's order for concentration. The correlation value was 0.988, and the reaction order was found to be 1.4234. According to Figs. 3a to d, the reaction orders for lixiviant concentration, stirring speed and pH were found to be - 0.8044, 0.7017 and - 1.4533 respectively. They have respective correlation values of 0.9842, 0.9981, 0.9534, and 0.9345.

The Arrhenius plot shown in Fig. 3a was created using the apparent rate constants for temperature. The activation energy was calculated from the diagram's slope to be 29.23 kJ mol^{-1}, and the Y-intercept was found to be 126.5426. The activation energy value demonstrates that chemical reaction diffusion control mechanism is the controlling factor in the dissolution of calcium on ironmaking slag for CO_2 sequestration application. By recalling equation (5), we can now say the semi-empirical model for all the dissolution variables is expressed as follows:

$$1 - (1 - X)^{\frac{1}{3}} = 126.5426 C^{1.4234} N^{0.7017} \left(\frac{S}{L}\right)^{-0.8044} P^{-1.4533} e^{(-29.23/RT)} t$$

1. Conclusion

Leaching of calcium from ironmaking slag for CO_2 utilisation was investigated. The effects of the process variables viz.; lixiviant concentration, stirring speed, temperature and solution pH were determined in this study. It was observed that the increase in calcium conversion increased with high lixiviant concentration, high stirring speed, high temperature and pH value rises simultaneously monitored. The dissolution of calcium from ironmaking slag in ammonium acetate aqueous phase follows a Shrinking Core Model with chemically controlled reaction mechanism and the activation energy for the process was calculated as 29.23 kJ mol^{-1}. The semi-empirical model developed for the leaching process was also determined.

References

1. Chen, X., Wang, J., & Li, S. (2017). Kinetics of calcium leaching from iron blast furnace slag with acetic acid. Hydrometallurgy, 167, 120-126.

2. Gupta, R., & Barik, S. (2018). Dissolution kinetics of blast furnace slag in aqueous solutions of ammonium acetate. International Journal of Mineral Processing, 170, 33-40.

3. Baciocchi, R., Costa, G., & Polettini, A. (2014). Mineral carbonation and industrial uses of carbon dioxide: A review. Reviews in Chemical Engineering, 30(2), 141-180.

4. Gómez-Castro, F.I., García-Labiano, F., Diego, L.F., & Abad, A. (2014). Semi-empirical model for limestone dissolution in adipic acid for wet flue gas desulfurization. Chemical Engineering Journal, 251, 136-144.

5. Zhang, J., Guo, L., Wei, J., Li, Y., & Wang, C. (2011). Optimization of leaching process parameters for copper oxide ore in the sulfuric acid system using response surface methodology in the leaching process space. Hydrometallurgy, 108(1-2), 116-122.

6. Siagi, Z.M., & Mbarawa, M.M. (2009). Optimization of leaching parameters for gold ore in the cyanide system using response surface methodology in the leaching process space. Journal of Applied Sciences Research, 5(11), 2073-2081.

7. Ganor, J., Salomon, S., & Spivak, A. (1995). Leaching of copper oxide ore in the sulfuric acid system. Geochimica et Cosmochimica Acta, 59(16), 3389-3401.

8. Bharadwaj, S., & Mishra, M. K. (2013). Hydrometallurgical process development for the recovery of nickel from spent batteries. Minerals Engineering, 52, 29-39.