Extraction of calcium from red gypsum for calcium carbonate production

Amin Azdarpour [a,b], Mohammad Asadullah [b,*], Radzuan Junin [a], Erfan Mohammadian [b], Hossein Hamidi [b], Ahmad Rafizan Mohamad Daud [b], Muhammad Manan [a]

[a] *Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 Johor, Malaysia*
[b] *Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*

ABSTRACT

Red gypsum can be considered as a long term storage of carbon dioxide through mineral carbonation. However, for the efficient carbonation, the calcium ions need to be extracted in the solution phase, followed by the carbonation reaction. Therefore, the extraction step is the key of successful mineral carbonation. In this study, solvent extraction of calcium and iron ions has been carried out using different types of acids and bases. In addition, the kinetic study of the extraction has also been performed. The study showed that the base solution was not capable of extracting significant amounts of calcium and iron, while acid solution was very efficient in extracting the ions. However, H_2SO_4 resulted in higher calcium extraction efficiency as compared to HCl and HNO_3. Increasing reaction temperature from 30 to 70 °C and also increasing reaction time from 5 to 120 min were found to be effective in enhancing the degree of extraction for all the three acids used. Kinetic analyses found that the dissolution rate of red gypsum is controlled by the combination of product layer diffusion and chemical reaction control. The calculated activation energy of calcium extraction was 44.02, 37.68, and 42.73 kJ/mol for H_2SO_4, HCl and HNO_3, respectively.

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1. Introduction

Increasing atmospheric carbon dioxide (CO_2) concentration due to excessive fossil fuel consumption has led to various investigations in order to find a suitable way of reducing atmospheric CO_2 concentration. The CO_2 is mostly emitted into the atmosphere from industries such as steel and iron manufacturing industry, cement industry, coal-fired power plants, and oil refineries. Capturing the generated CO_2 followed by long-term storage is called carbon capture and storage (CCS). The basic steps of CCS method consist of CO_2 capture; transportation to the sites; and finally CO_2 storage and sequestration [1–6].

Captured CO_2 from oxy-fuel combustion or from industrial process streams can be stored and sequestered in geological storage, ocean storage, storage below seabed and using mineral sequestration. Geological storage seems to be favorable and feasible for large scale applications and thus it is already practiced due to its minimal operational cost. However, the lack of permanency and continuous site monitoring required are the two major disadvantages of this method. Ocean carbon sequestration has large storage capacity; however, negative impacts on living organisms and CO_2 transport (through pipelines or tankers) to the sites are the major challenges in this method. The CO_2 storage below seabed is still a new idea and requires more study and understanding before implementation on industrial scales. Mineral

carbonation is the only known permanent CO_2 storage and seems to be practically feasible [7–10].

The mineral carbon dioxide sequestration is an exothermic chemical reaction of a metal-bearing oxide (usually calcium, magnesium, or iron) with CO_2 to form stable solid carbonates. Carbonation can take place either in-situ or ex-situ. The in-situ carbonation is the reaction of CO_2 with magnesium and calcium mineral which occurs underground where the CO_2 is being injected while the ex-situ carbonation represents the same reaction above ground in a chemical processing plant. Mineral carbonation involves exothermic reaction of metal oxide with CO_2 to form magnesium and calcium carbonates [10–13].

Natural minerals together with industrial by-products and wastes rich in calcium and magnesium are the two main raw materials suitable for mineral carbonation process. Of all natural minerals, olivine, wollastonite, and serpentine are the most widely used minerals. In addition to natural minerals, some industrial wastes such as asbestos-mining tailings, electric arc furnace (EAF) dust, steel-making slag, cement-kiln dust, waste concrete, coal fly ash, air pollution control (APC) residues, pulverized fuel firing (PF) and circulating fluidized bed combustion (CFBC) ashes as well as ash transportation waters have received lots of attention for CO_2 fixation through mineral carbonation. Utilization of these industrial wastes as calcium and magnesium sources for CO_2 storage through mineral carbonation is also environmentally beneficial considering the hazardous nature of these materials [10,14–18].

Red gypsum ($CaSO_4 \cdot 2H_2O$) is one of the most important industrial wastes produced from titanium dioxide manufacturing industry using

Ilmenite as raw material. Ilmenite which contains approximately 43–65% titanium dioxide (TiO_2) was widely used as raw material. The TiO_2 is extracted through stepwise processes whereby the acidic byproduct usually sulfuric acid is produced at the final step. The neutralization of the spent sulfuric acid during TiO_2 extraction with limestone and lime produces a by-product named red gypsum. The titanium dioxide industry in Malaysia produces about 400,000 tonnes of red gypsum annually that could be utilized for CO_2 sequestration [17,19].

The present study was aimed to find a suitable solvent for efficient extraction of calcium from red gypsum. The potential of calcium and iron extraction (the main constituents of red gypsum) from red gypsum using several acids and bases was investigated. In addition, the dissolution kinetic study was performed using H_2SO_4, HCl, and HNO_3 as solvent.

2. Materials and methods

2.1. Material preparation

In the laboratory, red gypsum samples were oven-dried (45 °C) until complete dryness, ground and homogenized. Subsequently, it was sieved and categorized in terms of average particle size of 100–212 μm. The samples were stored under vacuum condition in a desiccator prior to analysis. In this study, three different acids including H_2SO_4, HCl, and HNO_3 and three bases including NaOH, NH_4OH and KOH were tested for calcium and iron extraction from red gypsum.

2.2. Characterization of red gypsum

The major elements in the red gypsum were quantified using X-ray fluorescence (XRF). Particle size of red gypsum was analyzed using particle analyzer (Malvern MASTERSIZER 2000). Crystalline phases of the samples and mineral composition were determined by X-ray diffraction (XRD) in a diffractometer with Cu Kα radiation source in a 2θ range of 5–70° at a scanning rate of 1°/min.

2.3. Dissolution experiments

In the present study, the dissolution efficiency of calcium and iron in different acidic and basic solutions was determined. Generally, two sets of dissolution experiments were conducted in this study. The first set of experiments involves the dissolution of metal ions in all six solvents (acids and bases). In this experiment, 200 mL solvent of different concentrations ranging from 0.1 M to 4 M was used under constant reaction temperature of 25 °C and time of 60 min. The second set of experiments was conducted with 200 mL of 2 M acid solutions as the selected solvent. In this set, the reaction temperature from 30 °C to
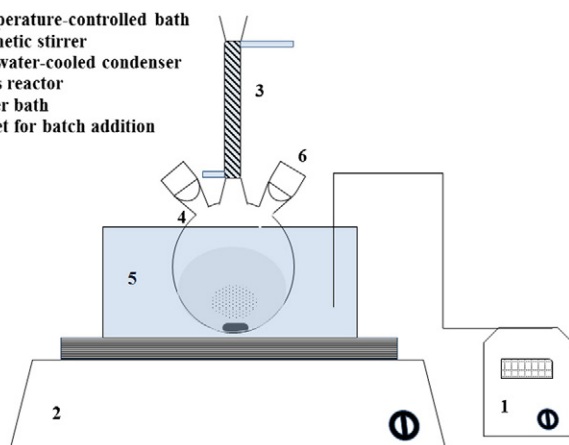
Table 1
Kinetic models used in this study.

Kinetic model	Equation
Product layer diffusion	$kt = 1-3(1-x)^{\frac{2}{3}} + 2(1-x)$
Chemical reaction control	$kt = 1-3(1-x)^{\frac{1}{3}}$
Film diffusion	$kt = x$
Combination of product layer diffusion and chemical reaction control	$kt = \left(1-3(1-x)^{\frac{2}{3}} + 2(1-x)\right) + \left(1-3(1-x)^{\frac{1}{3}}\right)$
First-order pseudo-homogenous	$kt = -\ln(1-x)$
Second-order pseudo-homogenous	$kt = (1-x)^{-1} - 1$
Arrhenius law equation	$k = k_o e^{-E/RT}$

70 °C and the reaction time from 5 min to 120 min were employed. A fixed 10 g of red gypsum with average particle size of 100–212 μm was used constantly in all experiments.

The dissolution studies were conducted in a 500 mL open spherical glass batch reactor using the experimental set up as described by Teir et al. [20] as shown in Fig. 1. A batch of 2 M acid was prepared and poured into the reactor. A temperature controlled water bath was used for adjusting the reaction temperature at desired temperature. A magnetic stirrer was used for providing 1000 rpm agitation. During reaction, the acid was vaporized and to reflux the acid, a tap water cooled condenser was used. When the reaction conditions were stabilized, 10 g of red gypsum was added into the solution. The reaction was continued until the desired time and then the reactor was kept for a while at room temperature to be stabilized under ambient condition. The mixture was then filtered and the solution phase was sent to analyze by ICP-OES for the determination of dissolution efficiency.

2.4. FT-IR analysis of solid residues after filtration

After dissolution experiments and filtration, the solid residues were collected, dried over night at 105 °C and used to analyze by FT-IR spectrometer. The FT-IR analysis was carried out in the mid-infrared region from 4000 cm^{-1} to 500 cm^{-1} using a Bruker Tensor 27 spectrometer. Each analysis was carried out under ambient air condition using KBr as a diluent.

2.5. Kinetic analysis

Performing an effective mineral carbonation process requires comprehensive understating of the dissolution kinetics. In a solid–liquid reaction, the reaction rate is controlled by one of the following steps: diffusion through the fluid film, diffusion through the ash (or solid
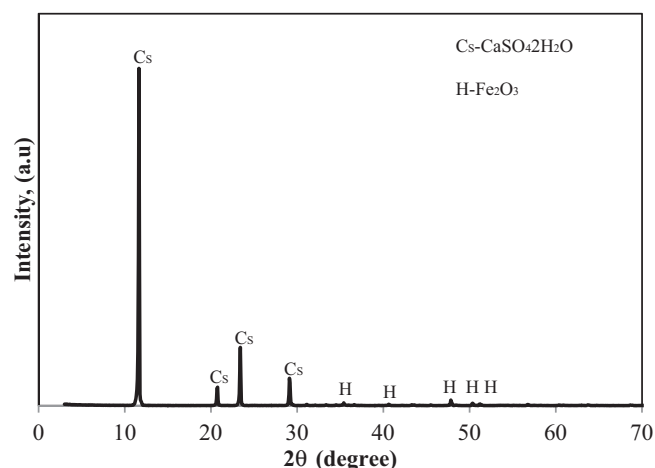

Fig. 1. Red gypsum dissolution experiment set up.

Fig. 2. X-ray diffraction of bulk red gypsum.