Direct carbonation of red gypsum to produce solid carbonates

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ABSTRACT

This study focuses on direct mineral carbonation of waste gypsum, a by-product of titanium dioxide production industry and known as red gypsum. The red gypsum is a potential raw material for carbonation with carbon dioxide due to its high content of calcium. Before being used the red gypsum, it was characterized by MASTERSIZER 2000, XRD, and XRF analyses. The carbonation of red gypsum was carried out using a high pressure autoclave reactor. The reaction parameters such as CO_2 pressure, reaction temperature and red gypsum particle size were optimized to achieve the maximum yield and purity of calcium carbonate. The purity of calcium carbonate produced and the carbonation efficiency at different temperatures have also been investigated. Both the purity of the product and the efficiency of the reaction were increased when elevated CO_2 pressure and reduced particle size were used. They were increased initially with increasing temperature up to 200 °C, but dropped with further increase of temperature. The mineral carbonation technology by using red gypsum can potentially contribute to both reduction of CO_2 emission and remediation of environmental concern.

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1. Introduction

Industrial and structural development of many countries in the 21st century will increase energy demands by 57% of current world energy consumption by 2030. Most of the energy demand will be satisfied by fossil fuels. However, the combustion of fossil fuels for energy increases the net carbon dioxide (CO_2) concentration in the atmosphere. The concentration of the major component of greenhouse gases (GHGs) has increased sharply from 280 ppm in the 1750s to 398 ppm in 2013 due to the increase in fossil fuel consumption and human activities. The abnormal increase of CO_2 concentration in the atmosphere causes the increase of global temperature. Therefore, an increase in global temperature between 1.8 °C and 4 °C has been predicted by 2100 as the atmospheric CO_2 concentration is predicted to increase to 540–970 ppm [1,2].

Carbon capture and storage (CCS) is one of the proposed strategies for reducing world GHG emissions. Basic CCS methods consist of a series of post-combustion and pre-combustion steps to capture CO_2, including separation from other gases and sequestration. Electric power generation and hydrogen production plants use fossil fuels and release CO_2, which can be separated, transported, and finally stored by either injecting into the dead reservoirs or by using sequestration methods [3–8]. CCS methods are the best viable option to reduce atmospheric CO_2 concentration as a long-term technology. In fact, CCS can contribute

up to 15%— 55% of the cumulative global climate change mitigation effort by 2100 [9]. Some forms of CO_2 mitigation include forestation, geological storage, deep sea storage, and mineral carbonation [2].

Mineral carbonation is one of the CCS methods, which involve an exothermic chemical reaction between CO_2 and a metal–bearing oxide such as CaO, MgO, and/or iron oxides to form stable solid carbonates. Carbonation can take place either in situ or ex situ. In situ carbonation is the reaction of CO_2 with Mg and Ca minerals in underground where CO_2 is injected and ex situ carbonation is the same reaction which takes place above the ground in a chemical processing plant [10,11]. The CO_2 mineralization or mineral carbonation is an artificial rock weathering process, which was first proposed by Seifritz in 1990 [12], while the natural rock weathering is a geological time scale process. The energy state of mineral carbonate is 60 to 180 kJ/mol, which is lower than that of the energy state of CO_2 (400 kJ/mol). Therefore, mineral carbonation provides a permanent and leakage-free CO_2 disposal. In addition, the carbonate produced is environmentally benign and stable [13]. Several researchers investigated the well-known waste solids such as waste gypsum, waste ashes, waste cement, steelmaking slag and mining wastes for mineral carbonation [14–18].

By-product gypsum is an industrial waste that falls in several categories: flue gas desulfurization (FGD) gypsum, phosphogypsum, and titanogypsum. Titanogypsum is one of the most important industrial wastes that are produced from titanium dioxide manufacturing industry where ilmenite is used as a raw material. Titanium dioxide (TiO_2) pigment is manufactured through either the sulfate or the chloride-ilmenite process. The sulfate process involves digestion of ilmenite

(FeTiO$_3$) ore with sulfuric acid (H$_2$SO$_4$) to produce a cake, which is purified and calcined to produce TiO$_2$ pigment. Huntsman Tioxide is one of the world's largest producers of TiO$_2$ pigments. The capacity of its plant in Malaysia is about 56,000 metric tons per year [19].

The sulfate process generates sulfuric acid wastes, resulting in the need for expensive treatment by neutralization before being disposed of the wastes. This process leads to a gypsum by-product known as titanogypsum or also simply called red gypsum. Red gypsum waste is usually slurried with water and then pumped out of the TiO$_2$ pigment plant to nearby landfill site. Red gypsum contains mainly hydrated CaSO$_4$ (70% wt), Fe$_2$O$_3$ (30% wt), and very small amount of Al$_2$O$_3$ [20]. Red gypsum contains a considerable quantity of ferric floc, which limits its market in construction products, owing to the potential for iron staining after wetting. Red gypsum contains around 75% gypsum and 25% ferric floc by dry mass. Recycling of titanogypsum is limited by the high content of metallic impurities and radionuclides. Globally, Huntsman Tioxide produces over 1 million tonnes of gypsum each year. The total accumulation of red gypsum in Malaysia is about 400,000 tons per year [21].

In light of the above information, the aim of the present study is to evaluate the effectiveness of titanogypsum to be used as a source of Ca and Fe for carbon dioxide mineral sequestration. Re-using of this by-product not only manages the waste disposal but also helps reduce the depletion of natural gypsum. This new method is considered attractive and ecologically clean, since it has the potential to reduce two environmental problems simultaneously: management of hazardous industrial waste and GHGs emissions.

2. Materials and methods

2.1. Materials

Fresh red gypsum samples used in this study were obtained from landfill of Huntsman Tioxide, Kemaman, Terengganu, Malaysia. Ammonium hydroxide (NH$_4$OH) was purchased from Rankem. Research grade CO$_2$ (concentration of > 99.998 % was used without further purification) gas cylinder was purchased from Malaysian Oxygen.

2.2. 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 less than 45, 45–75, 75–100, 100–212, 212–300, 300–400, and 400–500 μm. The samples were stored under vacuum condition in a desiccator prior to analysis. A 1 M ammonia solution (NH$_4$OH) was prepared and used in all experiments.

2.3. Feedstock characterization

The characterization of raw red gypsum was performed by X-ray fluorescence (XRF) for quantifying major elements. 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. Particle size of red gypsum was analyzed using particle size analyzer model Malverrn Mastersizer 2000.

2.4. Carbonation experiments

A 100 mL high-pressure and high-temperature (HPHT) autoclave reactor was used for the carbonation experiments as shown in Fig. 1. The maximum operating pressure of autoclave reactor is 200 bar, and the maximum operating temperature is about 450 °C, respectively. A temperature controller controlled the furnace temperature. CO$_2$ gas was injected into the reactor from CO$_2$ cylinder using stainless steel tubing.
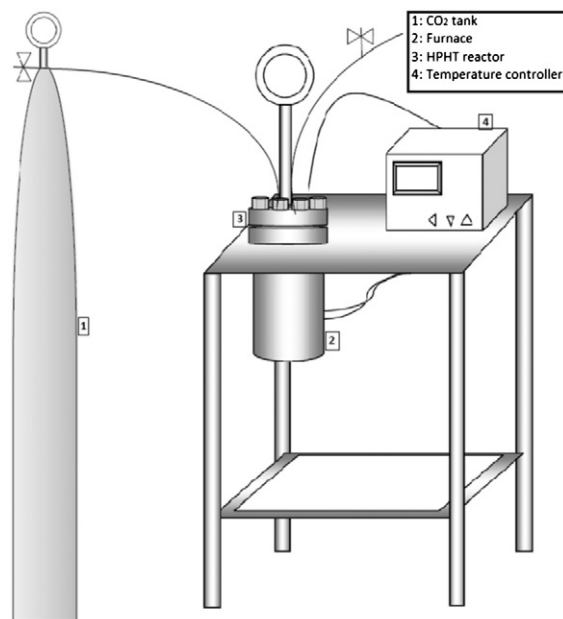

Fig. 1. Schematic diagram of HPHT autoclave reactor.

After material preparation, a 10 g of red gypsum with specific average particle size was weighed and poured into the reactor and then 50 mL of 1 M NH$_4$OH was added into the reactor. The mixture was stirred continuously using a magnetic stirrer at 1000 rpm for about 5 min. The reactor was then sealed air tightly and flashed with CO$_2$ in order to replace any air inside the reactor. Then it was pressurized by injecting CO$_2$ to a desired operating pressure and heated up to the desired temperature using a small tube furnace. At the stabilized reaction temperature, the reaction was allowed to take place for about 60 min for each experiment. During reaction, CO$_2$ gas was consumed by the reaction from the liquid phase. To keep the constant concentration of CO$_2$ in the liquid phase, the pressure was maintained constant in the autoclave reactor. In this study, we used a special gas regulator having 1–70 bar outlet gas pressure. The outlet of the regulator was directly connected to the autoclave reactor, and the CO$_2$ gas was continuously supplied into the reactor to make up the CO$_2$ consumed by the reaction [22]. Finally, carbonation product was collected, dried overnight at 105 °C, and further analyzed using TGA and XRD.

After drying the products, each sample was analyzed with XRD for phase detection. The purity of produced carbonates was also measured using thermogravimetric analysis. Since red gypsum contains significant amount of Ca and Fe, we examined the possibility of producing both calcium carbonate (CaCO$_3$) and iron carbonate (FeCO$_3$). The purity of FeCO$_3$ and CaCO$_3$ was calculated using Eq. (1), while the metal content in the red gypsum and the carbonation efficiency were calculated using Eqs. (2) and (3).

$$P_{XCO_3}(\%) = \frac{\Delta W(\%) \times MW_{XCO_3}}{MW_{CO_2}} \tag{1}$$

$$X \text{ mass in } XCO_3 = \Delta W(\%) \times \frac{MW_X}{MW_{CO_2}} \times \text{mass of solid residue} \tag{2}$$

$$\text{Carbonation efficiency } (\%) = \frac{X \text{ mass in } XCO_3 - X \text{ mass in reaction mixture}}{X \text{ total mass in feeding material}} \times 100 \tag{3}$$

In these equations, P stands for product purity, X is either calcium or iron in red gypsum, ΔW is the sample weight loss from TGA, and MW