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Siderite precipitation using by-product red gypsum for CO_2 sequestration

Omeid Rahmani[a,b,*]

[a] Department of Petroleum Engineering, Mahabad Branch, Islamic Azad University, Mahabad 59135-433, Iran
[b] Department of Natural Resources Engineering and Management, School of Science and Engineering, University of Kurdistan Hewlêr (UKH), Erbil, Kurdistan Region, Iraq

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ABSTRACT

In this research, the feasibility of CO_2 mineral carbonation by the use of by-product red gypsum (RG obtained from Huntsman Tioxide, Terengganu, Malaysia) to form iron carbonate ($FeCO_3$) was evaluated. Toward this aim, the wide-range conditions of key procedure variables such as reaction temperature, reaction time, and CO_2 pressure on the rate of mineral carbonation were studied. In addition, preliminary analyses on red gypsum were carried out to determine its physical and chemical characteristics. The feasibility of direct carbonation of RG to form $FeCO_3$ was assessed at different CO_2 pressures of 1 to 70 bar and different reaction temperatures of 25 to 200 °C to discover the effects of the key functions on overall direct carbonation. In general, increasing CO_2 pressure to 10 bar was found to increase the overall $FeCO_3$ purity and carbonation efficiency to 97% and 98%, respectively. Moreover, the reaction temperature affected the conversion rate at two different functions. First, $FeCO_3$ purity and its carbonation efficiency increased to the maximum values when the reaction temperature increased to 150 °C, and then they were slightly decreased to 91% and 92%, respectively, with increase of temperature to 200 °C. The results also showed that the maximum product purity is achieved at optimum reaction time of 150 min.

1. Introduction

Since the industrial revolution, the levels of greenhouse gases (GHGs) and carbon dioxide (CO_2) in the atmosphere have greatly increased [1–5]. Increasing anthropogenic GHGs concentration [6], especially CO_2 highlights the importance of carbon dioxide sequestration methods. In this regard, identifying industrial scale solutions to minimize the atmospheric CO_2 concentration has recently received significant attention [7–10]. CO_2 mineral carbonation is one of the current technologies for reducing atmospheric CO_2 concentration that involves the process by which CO_2 is eliminated from the atmosphere and is sequestrated as formed stable minerals.

Red gypsum (RG) is one of the industrial wastes that has received attention for CO_2 mineral carbonation purposes [3–5,11]. Red gypsum is generated by producing titanium dioxide (TiO_2) from ilmenite ($FeTiO_3$) ores containing about 54% TiO_2. $TiO_2$is extracted from $FeTiO_3$through stepwise procedures. The first procedure is the chemical reaction of $FeTiO_3$with sulfuric acid (H_2SO_4) to digest the ore and produce titanyl sulfate ($TiOSO_4$) and iron sulfate ($FeSO_4$). The second procedure is the clarification of produced liquor through solid separation. This is followed by the hydrolyzation of the liquor by steam for TiO_2 precipitation. The last procedure is to remove the impurities from the hydrated TiO_2 through washing with water. The neutralization of the spent H_2SO_4 during TiO_2 extraction with limestone and lime results in by-product red gypsum (Eqs. (1) and (2)). Afterwards, the red gypsum is filtered and separated from water, with the water then being recycled in the process. This industrial waste is disposed of in landfill areas (e.g. Huntsman Tioxide, Terengganu in Malaysia) or left as stacks close to the TiO_2 industry.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.\ 2H_2O \qquad (1)$$

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4 \qquad (2)$$

The carbonation reaction of RG is not yet fully detailed and the overall process requires more experimental research before it can be implemented on a large scale. The published data regarding the CO_2 mineral carbonation of red gypsum focuses on the production of calcite ($CaCO_3$) from RG [3–5], where the RG contains 32.2% CaO and ~29% Fe_2O_3. In this study, the optimization of carbonation reaction is geared toward iron carbonate ($FeCO_3$) production since the RG contains a significant amount of Fe.

2. Materials and methods

2.1. Materials

In this research, RG (Fig. 1a), was collected from the Huntsman

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* Corresponding author at: Department of Petroleum Engineering, Mahabad Branch, Islamic Azad University, Mahabad 59135-433, Iran.
E-mail addresses: omeid.rahmani@iau-mahabad.ac.ir, omeidrahmani@gmail.com.

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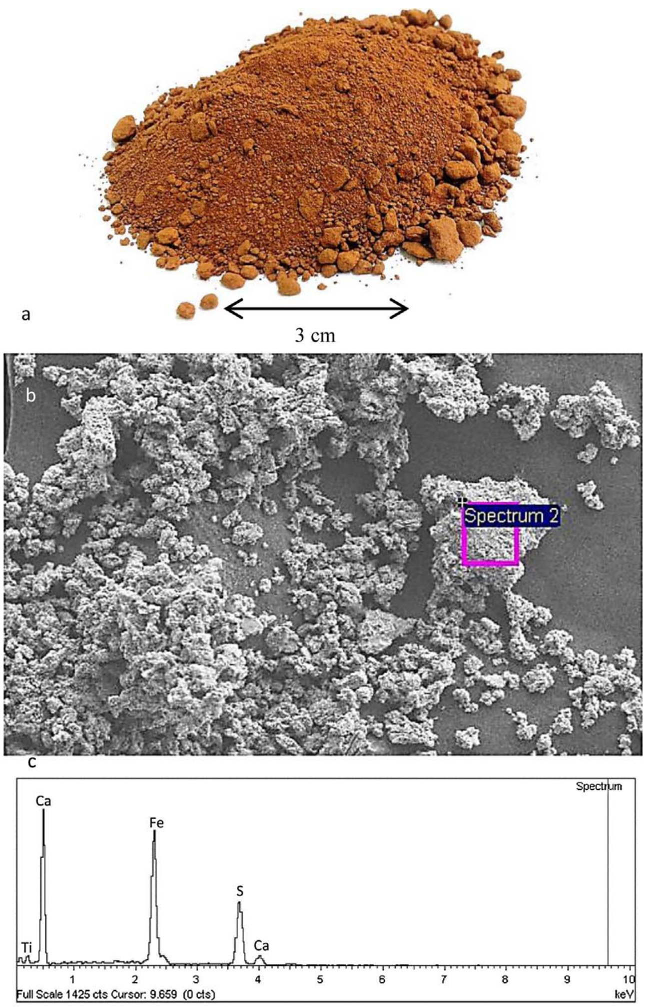

d. ZAF method quantitative analysis
Fitting coefficient: 0.8466
Processing option: all elements analyzed (normalized)
Number of iterations: 2

Element	Standard	Weight (%)
C	$CaCO_3$	6.45
O	SiO_2	14.63
S	FeS_2	18.09
Ca	Wollastonite	32.33
Fe	Fe	28.47

Fig. 1. The fresh sample of red gypsum (a), FESEM photomicrograph (b) illustrated different forms with EDX analysis (c) and ZAF method quantitative analysis (d).

Tioxide Landfill, Malaysia. Field emission scanning electron microscopy (FESEM-SU8200 JSM-6701F, Hitachi, Japan) was applied to generate high-resolution photomicrographs of the samples' morphology. The analysis was performed at 2.2 nm (1 kV) and 1 nm (15 kV) probe current, which is suitable to show nanoparticle size. Required samples for FESEM analysis were measured less than 38 μm as powder form (by particle size distribution MASTERSIZER 2000, Malvern Instruments Ltd.) for better identification of particle shape (Fig. 1b). Evidence pertaining to the phase analysis and bulk mineralogy of red gypsum samples was collected using an X-ray diffraction (XRD, X'Pert-MPD Philips, Japan). Samples of RG (each equal to 1 g) were dried overnight in an oven (at 45 °C) and then introduced into the XRD machine at a scan speed of 1°/min from 5° to 70° under 40 kV/40 mA. Geochemical composition of RG samples was conducted by X-ray fluorescence (XRF, PW-1410 PANalytical, Almelo, the Netherlands) and inductively coupled plasma optical emission spectrometry (ICP-OES, SPS3000 Hitachi, Japan) in order to determine major and trace elements, respectively. Thermogravimetric analysis (TGA, Q500 TA Instruments) was used to measure the weight loss of RG samples. Determination of the chemical bound present in solid residues was carried out using Fourier transform infrared (FTIR, Nicolet™ iS™50, Thermo Fisher Scientific) spectroscopy.

2.2. Carbonation study

The feasibility of direct carbonation of RG with a relative particle size of less than 38 μm was evaluated at different CO_2 pressures and reaction temperatures. The effect of CO_2 pressure on direct carbonation of RG was investigated by operating with CO_2 pressures of 1 to 70 bar. A reaction temperature of 25 to 200 °C was applied to discover the effects of reaction temperature on overall direct carbonation. In these experiments, ammonium hydroxide (NH_4OH) with a concentration ranging from 0.1 to 4 M was used as a basic solution. According to Dri et al. [12], a lower solid to solution ratio is more favorable than higher ratios because effective agitation and contact between CO_2 and the raw material is facilitated at lower ratios. Therefore, the solid to liquid ratio (s/l) of 20% (10 g/50 mL) was used. All carbonation experiments were conducted in a 150 mL mini reactor assembly (M00011E210, Parker Autoclave Engineers) capable of withstanding a maximum pressure of 2900 psi (~204 bar) and a maximum temperature of 315 °C (600 °F). The AE mini O-ring self-sealing closure was designed specifically for low pressure and moderate temperature applications, where O-ring seals are permissible. The diameter of the vessel was designed to be up to 35 mm (~1.38 inches). Temperature and stirring speed control from the vessel were achieved through embedding a digital set controller. To measure the net volume (%) of inlet gas and control the flow rate of injected CO_2, a flow-meter regulator (HPT-GAR-398CR Hero) was installed to a carbon dioxide cylinder (with a purity of 99.9%, purchased from Malaysian Oxygen). The flow-meter was connected to the mini reactor through a hose of 6 mm diameter and 3 m length. The carbonation studies were completed by injecting CO_2 into the NH_4OH solution in the mini reactor (Fig. 2). At the end of each experiment, final products and solutions were analyzed using XRD, TGA, and ICP-OES for phase determination and carbonation efficiency.

2.3. Experimental optimizations

In this study, two sets of experimental optimizations were defined. The reaction time, as the first set of optimization, varied from 1 to 180 min. The second set of control experiments was designed to investigate the effect of ammonia solution concentration on $FeCO_3$ purity

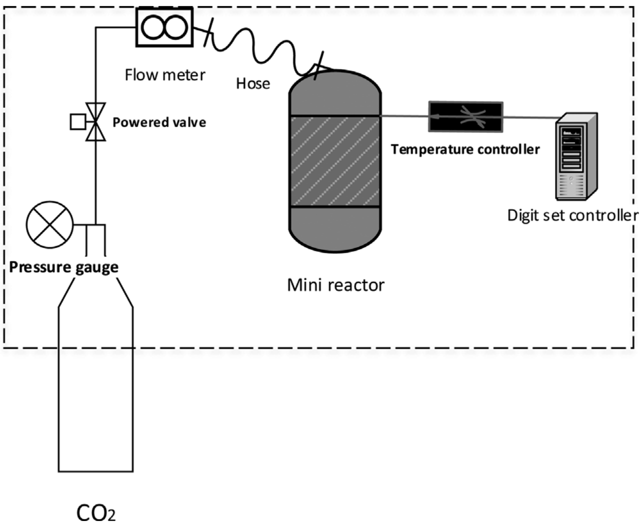

Fig. 2. A schematic diagram of experimental set-up.