Formation and decomposition of siderite for CO$_2$ treatment

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Abstract. In this research work, we studied the conditions for formation and decomposition of siderite FeCO$_3$ from hematite Fe$_2$O$_3$ along with carbon dioxide CO$_2$ at suitable thermodynamic conditions. As reductant agents were used mixtures of two elements, metallic iron and graphite. Best levels of carbonation were found in mixtures with bigger amounts of metallic iron. It was demonstrated that CO$_2$ capture capacity by hematite depends of temperature, CO$_2$ pressure, and reaction time. Temperatures between 100 and 150°C, pressures between 10 and 30bar and reaction times between 1 and 4h were adjusted for analyse the carbonation behaviour; siderite formation was improved by increases of these three variables. There was no carbonation without water in the mixtures, due to kinetic limitations. CO$_2$ capture capacity was calculated from Rietveld refinement results. Using vacuum system and Dielectric Barrier Discharge, DBD plasma, the siderite was decomposed at 300°C, and 320°C respectively. Techniques as X-ray diffraction, and surface area analysis were employed to study the material.

1. Introduction
Carbon dioxide CO$_2$ is a pollutant gas and the main cause of global warming with contribution close to 65%, reaching over 30,000 million metric tons in 2010, which has allowed generated high levels of CO$_2$ atmospheric concentration, around 400ppm in 2015 [1,2]. The CO$_2$ emissions have been increased in the last decades due to mainly generation energy, the manufacture of products at industrial level, fuel combustion and rainforest burning. Some agreements between countries have been subscript and although have helped to develop technologies and strategies to reduce the global warming, however these are still away to be a real solution [3,4]. Among others possible solutions are exchange from coal to renewable energy sources, improvements in energy efficiency in the combustion of fossil fuel, and replacement of raw material for waste materials rich in CaO. Amine in chemical absorption, is the mature technology mainly used in industrial processes, which has the disadvantage of high spend of energy for regeneration; physical adsorption can be implemented using different substances as zeolites or activated carbon but depends strongly of material features as pore size which increases the cost; membranes, cryogenics and micro algal are new promisors options, but are still in laboratory scale [5-7].

A very interesting technology to capture CO$_2$ that has gained interest in researches is use metal oxides that along with CO$_2$ at determined conditions of pressure and temperature can generate carbonates by mean of exothermic reaction. After that, those carbonates are heated in order to liberate the CO$_2$ and hence, metal oxides are regenerated inside an endothermic reaction [4,8,9]. Iron oxides are a good candidate to capture CO$_2$ in steel or non-steel industries; iron oxides or iron ore become
iron carbonate and can be regenerated at temperatures around 400°C [10] in order to be used in new cycle carbonation- calcination until active sites of material disappear.

Here, it is presented a study about some conditions of pressure, temperature and reaction time for carbonation of mixtures from hematite, iron and graphite; there were studied these materials because hematite is the iron oxide most frequently found inside iron ore, besides iron and graphite are materials available and employed in industrial processes as steel industry.

2. Methods and experimentation

The carbonation reaction was carried out using a closed cylindrical vessel of length 1.25 inches and internal diameter of 0.35 inches; inside this vessel were added 0.25g of hematite (99.945% metal basis) mixed with metallic iron (Good Fellow, 99% purity, <60mm) and graphite powder (Alfa Aesar, crystalline - 325 mesh, 99% in different molar radios. Approximately 0.15ml of water was added to the vessel wall to improve the kinetics of carbonation reaction. High purity CO₂ gas (99.99% purity, Airgas) was introduced into the system at desired pressures. Before the experiments, CO₂ gas was flushed three times to ensure an inert atmosphere inside the cylindrical vessel. After the desired reaction time for each experiment, the system was cooled by environment. The CO₂ sorption capacity was calculated for all experiments, using the results generated in Rietveld refinement from XRD patterns. The calcination temperature of FeCO₃ and the generated products were analysed by mean of two methods, heating the sample in vacuum environment and plasma generated in a dielectric barrier discharge configuration, using Argon atmosphere; to get vacuum was used a pump Franklin Electric MOD 1101006418, 0.5HP, 1725rpm, and to get plasma was used a power supply operating at 12Kv and 18KHz.

The product characterization was performed using X-ray powder diffraction method. Bruker GADDS/D8 is equipped with Apex Smart CCD Detector and direct-drive rotating anode. The MacSci rotating anode (Molybdenum) operates with a 50kV generator and 20mA current. X-ray beam size can vary from 50 to 300μm. The usual collection time is 1200s. An isothermal gas adsorption was employed to quantify internal surface areas of the reactant powder particles; this information is needed to get the N₂ adsorption–desorption isotherm. Micromeritics Tristar II 3020 (surface area and porosimetry analyser instrument) was used with N₂ as the adsorptive gas at 77K (liquid nitrogen bath). The samples were first degassed under 200°C using a N₂ gas flow for 2h to remove the moisture and other absorbed gases before analysis.

3. Results

3.1. Iron oxide carbonation

Siderite (JCPDS #00-083–1764) was identified as product of carbonation reaction at different conditions. Figure 1 shows the XRD pattern as result of the carbonation reaction using hematite, iron and graphite in equimolar proportion at 30bar CO₂ pressure, 150°C and 4 hours of time reaction; here, experiments performed without water did not present carbonation, due to kinetics limitations. Based on [11] water on the surface of hematite facilitates the reaction with CO₂, which results to the formation of CO₃²⁻ and H⁺ ions. Free Fe⁺² ions can further react with CO₃²⁻ to form FeCO₃.

Additionally, keeping constant the molar amount of hematite, there were used different molar radios between metallic iron and graphite in order to identify the best conditions for CO₂ capture. Table 1 presents the values for CO₂ capture capacity of the different mixtures at 100°C, 30bar and 2h.

According the values of CO₂ capture capacity, better results are accomplished using bigger amounts of metallic iron; this is due to graphite has lower activation energy. The best CO₂ capture capacity of the mixture is obtained using only metallic iron, reaching 6.3636mmolCO₂/gsorbent, which is translated to 45.74% of conversion.
Figure 1. XRD pattern in siderite formation at 30bar CO$_2$ pressure, 150°C and 4 hours using hematite, iron and graphite in equimolar proportion.

Table 1. CO$_2$ capture capacity of several mixtures of hematite, iron and graphite at 30bar CO$_2$ pressure, 100°C and 2 hours.

| Molar Ratio (Fe/C) | CO$_2$ capture capacity (mmolCO$_2$/gsorbent) |
|-------------------|---------------------------------------------|
| 1:0               | 6.3636                                      |
| 0.75:0.25         | 5.8752                                      |
| 0.5:0.5           | 5.1834                                      |
| 0.25:0.75         | 2.9087                                      |
| 0:1               | 0.0987                                      |

3.2. Dependence of temperature, pressure, reaction time

It has been demonstrated that factors as temperature, pressure and time reaction influence strongly the carbonation of metallic oxides [8,12,13]. Table 2 shows several values for CO$_2$ capture capacity at different conditions, keeping equimolar radios between hematite, iron and graphite.

Table 2. CO$_2$ capture capacity at different combined effects of pressure, temperature and reaction time.

| Pressure (bar) | Temperature (°C) | Reaction time (h) | CO$_2$ capture capacity (mmolCO$_2$/gsorbent) |
|---------------|------------------|-------------------|---------------------------------------------|
| 10            | 100              | 2                 | 2.0978                                      |
| 20            | 100              | 2                 | 3.4759                                      |
| 20            | 150              | 1                 | 3.8902                                      |
| 20            | 150              | 4                 | 4.9882                                      |
| 30            | 100              | 4                 | 6.1751                                      |
| 30            | 150              | 4                 | 6.3347                                      |

It can be evidenced from Table 2 that with the increases of pressure, keeping constant the temperature and reaction time, CO$_2$ capture capacity by mixture increases; hence, with the enough CO$_2$ pressure, molecules can react with the solid mixture at suitable conditions to form FeCO$_3$. Longer
reaction times increase the CO$_2$ capture regardless of conditions of pressure and temperature. Increase the temperature allows CO$_2$ molecules diffuse easier into the pores of hematite, iron and graphite and these CO$_2$ molecules are trapped in order to react with the mixture to form FeCO$_3$.

3.3 Thermal regeneration and recyclability

The decomposition temperature and generated products were studied from the sample processed in carbonation, it means at 30bar of CO$_2$ pressure, 150°C and 4h. As explained above, two methods were used to calcination, vacuum and plasma. The XRD patterns obtained from the decomposed samples are shown in Figure 2 and Figure 3, for vacuum and plasma respectively. Siderite was completely decomposed at 300°C in vacuum and at 320°C in plasma generated from 12Kv, 18KHz and electrical power delivered of 28w.

![Figure 2. XRD pattern of calcinated samples from vacuum.](image1)

![Figure 3. XRD pattern of calcinated samples from plasma.](image2)

According both XRD patterns, the calcinated products found are magnetite (JCPDS #00-089-2355), and hematite (JCPDS #00-033-0664). As can be inferred magnetite and hematite can be used along with carbon dioxide in a new cycle carbonation-calcination. Figure 4 depicts the N$_2$ adsorption–desorption isotherm curves for material calcinated in vacuum.

![Figure 4. N$_2$ adsorption-desorption isotherm curve for sample calcinated in vacuum.](image3)
This shape corresponds to type IV isotherms according to IUPAC classification. Mesoporous materials employed to capture gas, follow this typical isotherm curve; these kinds of patterns present hysteresis indicating the presence of slit-like pores.

4. Conclusions
Capture of carbon dioxide by hematite, iron and graphite was studied as an alternative to avoid emissions of this pollutant gas to atmosphere. Carbonation at different molar radios of metallic iron and graphite was analysed. Best levels of CO$_2$ capture capacity were found in mixtures where iron amount was higher. There was no carbonation in experiments without water, because water acts as an efficient catalyst, overcoming the kinetic limitations. Moreover, CO$_2$ capture capacity was calculated as a function of pressure, temperature and reaction time; longer reaction times, as well as higher pressures and temperatures favoured the CO$_2$ capture. Siderite decomposition temperature was identified by mean of two methods, heating the sample in vacuum environment and plasma created in a dielectric barrier configuration; this regard proposes plasma as a novel method for decompose the siderite; plasma has been used mainly for CO$_2$ treatment, transforming it in gases less harmful for global warming. There were identified magnetite and hematite as decomposition products. Calcinated material could be used in a new carbonation calcination cycle according its mesoporous feature.

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