SYNTHESIS PROPERTIES OF FECO3: UNDERSTANDING THE UNDERGROUND REACTIVE ROCK

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Abstract

Combatting anthropogenic CO2 emissions is one of the humanities considerable challenges, and carbon capture and storage (CCS) technologies are one of the tools that has been proposed for this. FeCO3 is attracting attention as it has been proposed to be a potential storage unit for CO2 injection in underground basaltic rock. Through mineral carbonation, dissolved CO2 reacts with underground reactive divalent metal-containing rock. However, the properties of FeCO3 is not well understood, and optimal permanent storage hinges on knowledge of the properties of the reactive species. We investigate the influence of synthesis parameters through a variation study, such as temperature, synthesis duration, and pressure. We then investigate the material properties, where the crystal structure and crystalline domains size is examined through XRD, thermal degradation stability with TGA and particle size with SEM. Through this investigation, a fundamental understanding of FeCO3 was gained, which will enhance the understanding of underground storage in reactive basaltic rock.

Keywords: CCS, Divalent metal carbonates, physiochemical investigation

1. Introduction

Man-made climate change is currently the most significant challenge we face as humanity. A possible mitigation strategy gaining popularity is capturing CO2 through direct air capture and storing it for future use. Recently, a large-scale pilot experiment on Iceland performed a successful project, where CO2 was captured and injected into reactive basaltic rock [1]. These rocks consist of Mg, Ca, and Fe. It is essential to understand the different processes occurring to optimize the efficiency of the storage procedure. Calcium carbonation is a well-investigated system. However, to optimize efficiency, it is essential to create knowledge on the carbonation of Fe and Mg. Currently, there exists conflicting evidence on the properties of FeCO3 [2]. No joint agreement on the colour of the synthesis product can be reached, and the solubility limit is also a debated topic [2]. FeCO3 can either be used synthetically or as extracted from underground, in the form of siderite. Other species (Mg, Ca) can be incorporated into the crystal lattice as an extracted material, affecting its properties. To investigate

synthetic FeCO3, it must be consistently the same synthesis product with identical properties when synthesized across the globe. As FeCO3 reacts readily with the oxygen in the atmosphere, it is not commercially available. Therefore, to ensure that researchers investigate the same product, knowledge must exist of the influence of various synthesis variables.

This study uses a patented synthesis method, utilizing an anoxic environment provided by a glovebox. We explore the synthesis parameter-space to investigate the influence of temperature, synthesis duration, and temperature on FeCO3 physiochemical properties. By probing the microscopic properties through XRD, macro properties through SEM, and couple these with the thermal stability through TGA, we create a correlation between synthesis parameters and what happens in the nm, μm, and mm scale.

2. Methods

2.1 Materials

FeCl2·4H2O, NaHCO3, and Na2HCO3 were obtained from Sigma-Aldrich without purification. Stock solutions of FeCl2·4H2O, NaHCO3, and Na2HCO3 were prepared with degassed with N2 ultra-pure Milli-Q water. The oxygen concentration was acquired with a multimeter (Hach Lange, HQ40D) connected to dissolved oxygen (DO) sensor (Hach Lange, LDO101).

2.2 FeCO₃ synthesis

The FeCO3 synthesis was prepared in a glovebox (MBRaun) with an anoxic environment. The atmosphere inside the glovebox was via catalyst to trap oxygen species and water.

FeCl2·4H2O and NaHCO3/Na2CO3 were mixed in a Fe/CO2 ratio of 1:4 in a titanium piston cylinder. The piston-cylinder was taken out of the glovebox, pressurized and placed in an oven at a constant temperature. The reaction was terminated by extracting the cylinder. After transferring the cool piston to the glovebox, the supernatant was decanted. FeCO3 was washed. FeCO3 was let to dry in the glovebox for two to three days. The adjustable synthesis variables are summarized in Table 1.

Table 1. Parameters for the FeCO₃ synthesis. T=Temperature, P=pressure, R=reaction time

Fe/CO$_2$	T (°C)	P (Bar)	R (h)
1:4	130	10	24
1:4	80	10	24
1:4	25	10	24
1:4	130	1	24
1:4	130	5	24
1:4	130	15	24
1:4	130	10	4
1:4	130	10	6
1:4	130	10	12
1:4	130	10	24
1:4	130	10	72
1:4	130	10	96

2.3 Sample characterization

2.3.1 X-ray powder diffraction

The crystal structure of FeCO3 was determined by x-ray powder diffraction (XRPD) at room temperature. The powder diffraction patterns were collected with a Huber G670 powder diffractometer in the 2θ range 3 to 100° in steps of 0.005° using CuKα1 radiation (λ = 1.54056 Å) for 10 min. The data were collected in transmission mode from a rotating flat plate sample inclined 45° relative to the primary beam.

Crystalline sizes were determined from the diffractograms via the Scherrer equation. To obtain the sizes through the Scherrer equation, the diffractograms were fitted to Gaussian first order models from which the FWHM was determined.

2.3.2 Scanning electron microscopy

Scanning electron microscopy (SEM) images have been acquired in a FEI QEISCAN with an acceleration voltage of 20 kV under a high vacuum. Samples were transported in an airtight environment from the glovebox to the SEM. During transfer to the SEM environment, the samples were exposed to less than 1 minute atmospheric conditions. The images were analysed in ImageJ and Gwyddion to obtain the particle sizes. Size distributions were obtained by measuring the diameter of more than 400 particles on each set of data.

2.3.3 Thermogravimetric analysis

Decomposition of FeCO₃ was performed using thermogravimetric analysis (TGA) (TA Instruments, Discovery TGA). The measurements were conducted in a nitrogen atmosphere and in the temperature range 27 to 900 °C with a temperature rate of 10 °C/min.
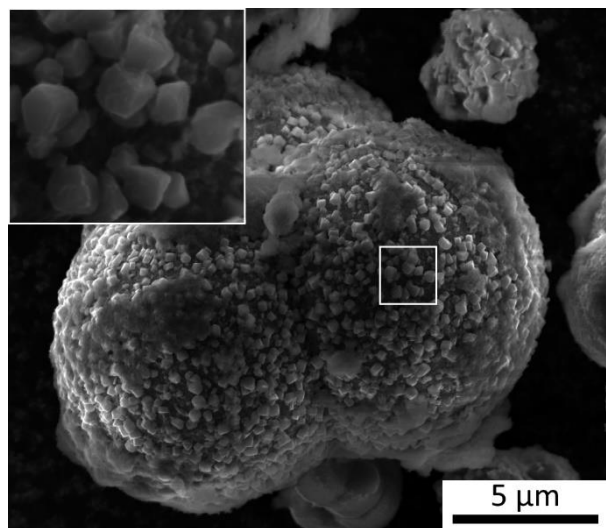
3. Results and Discussion

Figure 1. SEM image of FeCO₃

FeCO3 is known to have a rhombohedral crystal shape associated with that of carbonate crystals. In this work, we observed a hierarchical growth where rhombohedral crystals grow on larger aggregates. The larger particles act as a nucleation centre for the rhombohedral FeCO3 crystals, see Figure 1. These spherical particles were previously reported as amorphous FeCO3 (AFC). In our study, the particles were analysed utilizing TEM. It was shown that these particles exhibit crystallinity and can therefore not be AFC. In the following, this terminology will be used throughout. From Figure 2-2, the diameter of the large particle has been referred to as the particle size. At the same time, the individual crystallites are called either by crystallite size or by scattering coherence length. The crystallite sizes and particles sizes are

measured as a function of synthesis parameters, as presented in the following sections.

3.1 Microstructure

The size of the crystalline domains was estimated based on the Scherrer equation. The result can be seen in Figure 2-1. From these sizes, it can readily be concluded that the synthesis temperature and duration affect the resulting crystallite domain size. It should be noted that the synthesis performed for shorter than 24 h and below a temperature of 130 °C all have a crystalline domain size smaller than 3.5 Å. The pressure does not influence the crystallite size, and all synthesis resulted in crystallite size larger than 3.5 Å.

3.2 Macrostructure

The particle size was measured through a statistical analysis of SEM images. From this investigation, it was shown how there was a correlation between the macro properties of the particles and the synthesis parameters.

Particle sizes increased as both temperature, duration and pressure were increased. The most significant increase between process parameters is the pressure. Here the particle diameter is shown to increase from 3 μm to 7.5 μm from 1 bar to 15 bar respectively.

3.3 Influence of micro and macro on the thermal stability

Through TGA, the thermal properties of each product from the different synthesis was determined, see Figure 2-3. From the TGA results, two characteristic degradation paths could be estimated. One with only one steep slope, with a total mass loss of 36 % occurring at 350 °C. This was in agreement with previous observations on FeCO3. This behaviour was shared for the particles with a crystalline size large than 3.3 Å. This included the ones synthesized for longer than 24 h, at 130 °C and was observed for all pressure. The weight loss of ~36 % would agree with a decarbonisation through the following reaction:
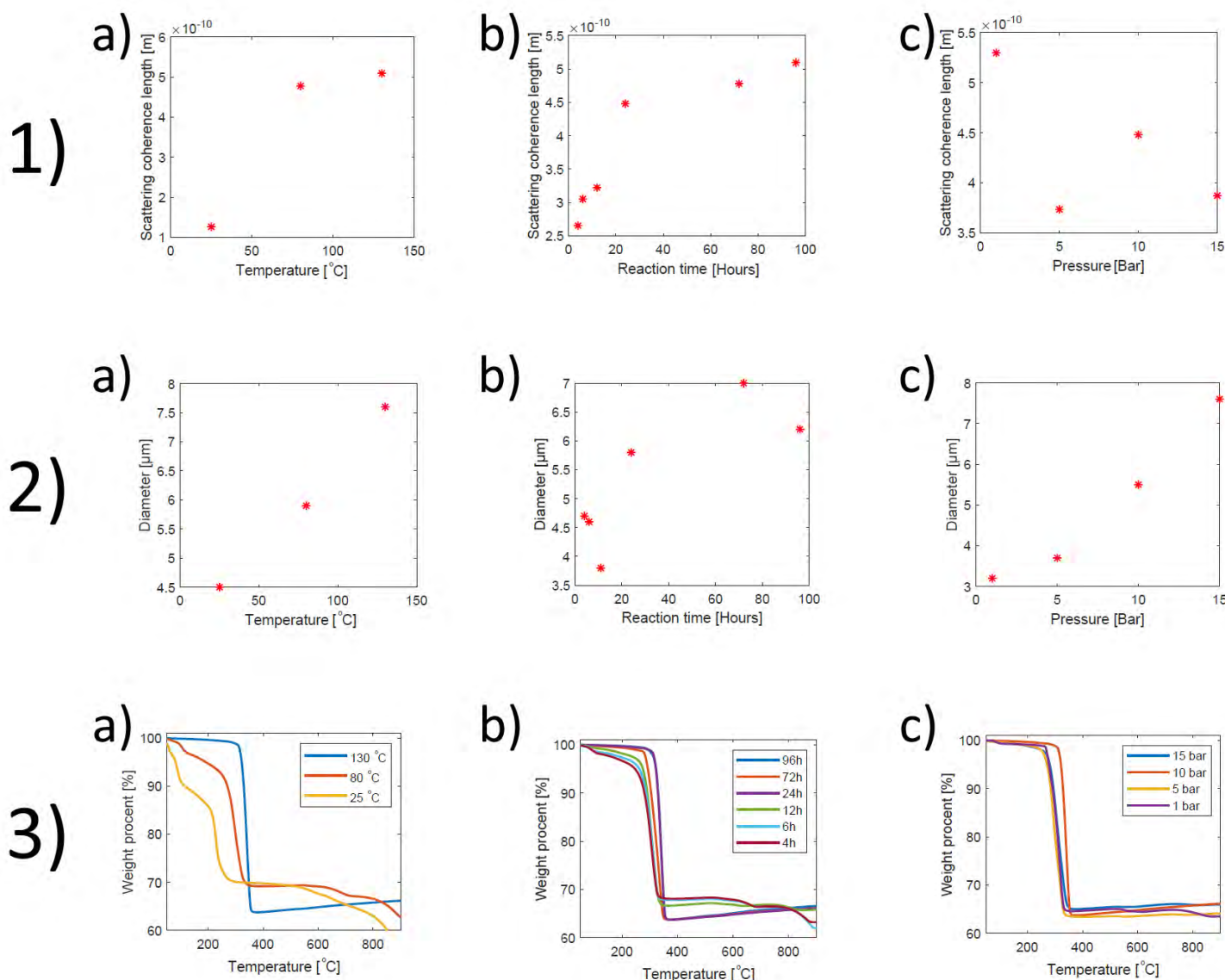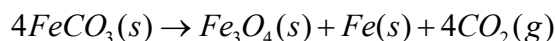

Figure 2. Physiochemical properties of FeCO3. a), b) and c) denotes a change in synthesis temperature, reaction duration or pressure. 1) The Scattering coherence length. 2) The particle diameter. 3) Thermogravimetric analysis

$$4FeCO_3(s) \rightarrow Fe_3O_4(s) + Fe(s) + 4CO_2(g)$$

The second degradation path had a gradual mass loss observed from 100 °C to 350 °C, and above 350 °C, there was a total mass loss of 32%. After 350 °C several weight losses are observed at 340, 600, and 800 °C. This was seen for particles with a crystallite size smaller than 3.3 Å. This indicates a critical crystalline size, under which there is a change of degradation path. The weight loss of 32 % can be explained by the reaction presented below

$$6FeCO_3(s) \rightarrow 2Fe_3O_4(s) + C(s) + 5CO_2(g) \quad (1)$$
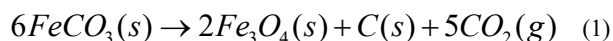
3. Conclusion and future implications

The main findings of this work can be summarized as follows:

- There exists a correlation between synthesis duration and temperature with the micro properties of FeCO3. Longer synthesis and higher temperatures lead to large crystallite domains. However, the crystallite domain size is invariant with synthesis pressure.

- Macrosize (the particle diameter), increase with an increase in all synthesis variables

- The thermal degradation of FeCO3 is not dependent on macro size, while it is heavily affected by the micro properties. Crystalline domains larger than 3.3 Å all exhibit a sharp weight loss at 350 °C, while smaller domains show a gradual weight loss.

These findings show the importance of accurately knowing the variables under which the synthesis was performed. All products would be characterized as FeCO3 through XRD. However, by a closer analysis, it became evident that the physiochemical properties were greatly dependent on the synthesis. As Fe constitutes a significant part basaltic rock, and FeCO3 is one of the product formed upon CO2 injection it becomes apparent that mapping the parameter space of the synthesis is of utmost importance.

Acknowledgements

References

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