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Siderite decomposition at room temperature conditions for CO₂ **capture applications**

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Abstract

The decomposition of synthetic siderite (FeCO₃) in air atmosphere at room temperature conditions was studied. Siderite was formed by mechanochemical reaction of $Fe₃O₄$ and graphite at high CO₂ pressure in the presence of water. Kinetics of decomposition reaction was studied over period up to 9 days and it is shown that decomposition reaction obeys geometrical contraction solid-state reaction mechanism model. It was found that the water infuences not only the kinetics of siderite formation but also its stability. Siderite completely decomposes at ambient conditions yielding magnetite ($Fe₃O₄$) and hematite $(Fe₂O₃)$ which can reversibly re-absorb carbon dioxide.

Keywords Mechanochemical reaction · Room temperature decomposition · Kinetics of siderite decomposition · Efficient reversible absorbent of $CO₂$

Introduction

During the last two centuries and mainly the last several decades Earth has warmed as a result of increasing emissions of green-house efect gases to the atmosphere (Pannoccia et al. [2007;](#page-7-0) Cheng-Hsiu et al. [2012](#page-7-1)). These gases include carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydrofuorocarbons (HFC), perfuorocarbons (PFCs) and sulphur hexafluoride (SF_6) . Among of these, carbon dioxide is considered the main cause of global warming. Two major contributors to $CO₂$ emission are different sectors of industry which utilize fossil fuel and forest fres (Cheng-Hsiu et al. [2012](#page-7-1); Han et al. [2014;](#page-7-2) Kumar et al. [2015a;](#page-7-3) Merkel et al. 2009). It is predicted that by the year 2100 the $CO₂$ concentration in atmosphere could reach 570 ppm, causing further increase of global temperature, sea level rise and extinction of many living species (Yan et al. [2008](#page-8-0); Stewart and Hessami [2005](#page-7-5)).

Although most countries are aware of this situation, today there are no large-scale developments to predict that this problem is close to being solved. This, due to the high costs and in most cases, the technologies used has not been integrated to the expected level (Mora et al. [2019a\)](#page-7-6). Organizations as National Energy Technology Laboratory (NETL), are pursuing efforts of the governments, industrial sector and research community, which are focused on developing technologies to reduce emissions of $CO₂$, its separation and capture, and long-term storage (Figueroa et al. [2008\)](#page-7-7). Carbon dioxide capture and sequestration are promising technologies to reduce atmospheric concentration of $CO₂$.

Selection of technology for $CO₂$ capture in industrial sector depends on the type of plant and fue gas composition. For example in power generation, the possible configurations are pre-combustion capture, post-combustion capture, oxy-fuel combustion capture and chemical combustion capture, and each the gas stream to be treated has its specifc conditions of pressure, temperature and $CO₂$ concentration (Zaman and Lee [2013\)](#page-8-1).

The most studied methods to deal with $CO₂$ are chemical and physical absorption, adsorption, membrane separations, and several novel separation techniques (Pannoccia et al. [2007;](#page-7-0) Zaman and Lee [2013](#page-8-1)). Chemical absorption is the most mature technology, although it has important disadvantages as low $CO₂$ absorption capacity, thermal degradation

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and corrosive nature of the absorbents (Han et al. [2014](#page-7-2)). Amines, ammonia and potassium carbonate are mainly used in chemical absorption technology (Zaman and Lee [2013](#page-8-1); Bello and Idem [2005](#page-7-8); Cullinage and Rochelle [2004\)](#page-7-9). Microgel particles have been studied for enhancing of efficiency of amines (Yang et al. [2020](#page-8-2)). Physical absorption method uses solvents as Selexol, Rectisol, Fluor, Purisol and Sulfolane (Breckenridge et al. 2000) and operates more efficiently at low temperatures and high pressures (Zaman and Lee [2013](#page-8-1)). Although adsorption has not been commercialized yet, it has attracted a lot of attention because of low energy requirements for adsorbent regeneration and wide temperature range for operation (from room temperature up to $700 \degree C$) (Zaman and Lee [2013\)](#page-8-1). Adsorption can have physical or chemical nature. The regeneration of adsorbents is based on techniques using pressure, vacuum, hybrid vacuum–pressure and electricity methods (Zhang and Webley [2008](#page-8-3)). Membranes act as filters to separate $CO₂$ from other gas components. Although it has been shown that the membranes could offer advantages by reducing energy requirements and cost compared with amine technology, this technology is still at laboratory-scale level due to operational problems, contamination, and implementation on large sc (Stewart and Hessami [2005](#page-7-5)) ale at power plants applications (Folger [2013](#page-7-11)). Latest research works have revealed important improvements in membranes performance for $CO₂$ capture from coalbed methane (Zhang et al. [2010\)](#page-8-4) or using polymeric thin films (Xie et al. [2019;](#page-7-12) Han and Winston Ho [2018\)](#page-7-13). Cryogenics and micro algal are identifed as other novel separation techniques, which are being studied in preliminary phases (Song et al. [2019\)](#page-7-14).

Potential use for CO₂ capture of compounds as Mg_2SiO_4 , Mg_2VO_4 , and Mg_2GeO_4 is under study (Kang [2020\)](#page-7-15). Recently, carbonation of some metal oxides such as MgO, FeO, ZnO has been studied due to favourable thermodynamics of $CO₂$ absorption reaction and their abundance in nature (Kumar and Saxena [2014\)](#page-7-16). After carbonation the material (metal carbonate) is heated in order to released $CO₂$ and regenerate the oxide, which can be used in another cycle of carbonation/calcination (Salvador et al. [2003\)](#page-7-17).

Siderite has gained a remarkable interest among researchers because it is a suitable source of iron for industrial processes (Feng et al. [2011;](#page-7-18) Patterson [1994](#page-7-19)). Normally, natural siderite contains diferent amounts of Mg, Ca, Mn impurities (Gotor et al. [2000\)](#page-7-20). Solid solutions with carbonates of Mg and Mn exist in all range of concentrations, while a wide miscibility gap reported between carbonates of Fe and Ca (Mora et al. [2019a](#page-7-6)). Synthetic siderite can be obtained either by wet chemistry methods or at high temperature high pressure conditions by reactions of iron oxides, particularly $Fe₃O₄$ or $Fe₂O₃$ and carbon dioxide (Chai [1994;](#page-7-21) Das [2016](#page-7-22); Zhou [2011](#page-8-5)). These iron oxides have important use in blast furnace for steel fabrication.

There are several studies about mechanism of thermal decomposition of siderite which report $Fe₃O₄$, FeO, α -Fe₂O₃ and γ -Fe₂O₃ as major products of decomposition (Feng et al. [2011;](#page-7-18) Alkaç and Atalay [2008;](#page-7-23) Fosbøl et al. [2010](#page-7-24); Kumar et al. [2015b](#page-7-25)). Formation of specifc product depends on the atmosphere, chemical composition of the siderite sample (presence impurities), and synthesis history (Feng et al. [2011;](#page-7-18) Gotor et al. [2000;](#page-7-20) Alkaç and Atalay [2008;](#page-7-23) Fosbøl et al. [2010](#page-7-24)). Under flow of oxygen, oxidation occurs rapidly and $Fe₂O₃$ is formed while in inert atmosphere or vacuum $Fe₃O₄$ and FeO or $Fe₂O₃$ are detected at moderate (Feng et al. [2011](#page-7-18); Gotor et al. [2000](#page-7-20); Alkaç and Atalay [2008](#page-7-23)) and high temperatures (Gallagher and Warne [1981](#page-7-26)), respectively. Moreover, the temperatures of thermal decomposition of synthetic and natural samples of siderite are diferent. Decomposition temperature of synthetic siderite is approximately 200 K lower than that one of the natural sample (Gotor et al. [2000\)](#page-7-20).

This paper presents results on CO_2 capture using Fe_3O_4 as an absorbent. Siderite is a product of mechanochemical reaction between gaseous CO_2 and solid Fe_3O_4 . Effect of water on the chemical stability of siderite (carbon dioxide desorption properties) is studied. Reactions ([1\)](#page-1-0) and ([2\)](#page-1-1) correspond to the carbonation and decomposition reactions respectively, which were studied in this work.

$$
2Fe3O4(s) + C(s) + 5CO2(g) \rightarrow 6FeCO3(s)
$$
 (1)

$$
3FeCO_3(s) + 1/2O_2 \rightarrow Fe_3O_4(s) + 3CO_2(g)
$$
 (2)

Experimental

Planetary ball mill Retsch PM100 operating at 400 revolutions per minute was used to establish mechanochemical reaction between magnetite and carbon dioxide at room temperature and elevated CO_2 pressure (10–30 bar). Reaction vessel was a stainless-steel jar of 50 mL volume capable for holding up to 100 bar gas pressure. High purity $CO₂$ gas (Airgas, 99.999%) was loaded into the reactor at diferent pressures together with 3.00 g of magnetite (Alfa Aesar, nanopowder, 97%) and graphite (Alfa Aesar CD Graphite powder, crystalline, 325 mesh, 99%) mixture (molar ratio 2:1, according reaction [\(1](#page-1-0))). Water (3.0 ml) was added to the mixture of magnetite and graphite. The powder to balls (stainless steel) weight ratio was 2:27. Reactor was fushed several times with $CO₂$ gas to ensure a pure $CO₂$ atmosphere inside the reactor. Mechanochemical reaction was run for 36 h. Each 1 h milling interval was followed by half an hour cooling interval to avoid overheating of the sample, which can afect the stability of siderite.

Thermogravimetric analysis (TGA) and diferential scanning calorimetry (DSC) were conducted in a temperature range of 25–1000 °C using TA Instruments SDT Q600 instrument. Experiments were performed in air and Ar atmospheres with a heating rate of 10 °C/min.

Powder X-ray difraction patterns were collected using Bruker GADDS/D8 diffractometer equipped with Apex Smart CCD Detector and molybdenum rotating anode. Collected 2D difraction patterns were integrated using Fit2D software (Hammersley [1997\)](#page-7-27). Quantitative phase analysis of the samples was performed using Rietveld method and GSAS package (Toby [2001;](#page-7-28) Larson and Dreele [2004\)](#page-7-29). The $CO₂$ sorption capacity was calculated using the results generated by Rietveld refnement of XRD patterns. Surface area of the powders was measured using Brunauer–Emmett–Teller (BET) method and Micrometrics Tristar II 3020 instrument.

Results

Thermodynamic simulations in the system Fe₃O₄-C-CO₂

FACTSAGE software and the databases therein, FACT— F*A*C*T 5.0, SGPS—SGTE and SGSL (Bale et al. [2002\)](#page-7-30) were used for thermodynamic modelling in $Fe₃O₄-C-CO₂$ system. Figure [1](#page-2-0) shows the calculated equilibrium temperature as a function of $CO₂$ pressure in the system $Fe₃O₄-C-CO₂-H₂O$ with different amounts of water, according reaction ([1](#page-1-0)). The results indicate that the siderite formation is favored either by high $CO₂$ pressures at a constant temperature or by low temperatures at a constant $CO₂$ pressure (Mora et al. [2019a\)](#page-7-6). Moreover, results reveal that siderite stability depends strongly on water amount in the mixture. As can be seen, equilibrium temperature decreases

Fig. 1 Equilibrium temperature of siderite decomposition as a function of CO_2 pressure for the system Fe_3O_4 -C-CO₂-H₂O with different amounts of water

with the increasing amount of water, which suggests that the regeneration of material is possible at relatively low temperatures.

Siderite formation

Kinetics of iron (II) carbonate formation in mechanochemical reactions between magnetite or hematite and metallic iron as reducing agent was studied in (Mora et al. [2019a](#page-7-6)). Carbonation of iron ore in mechanochemical reactions was studied (Mora et al. [2019b\)](#page-7-31). It was shown that magnetite carbonation under mechanochemical activation can not be accomplished in the absence of water using graphite as reducing agent due to kinetics limitations. It was demonstrated that water acts as a catalyst in carbonation reactions promoting the formation of CO_3^2 ⁻ and H⁺ ions (Kumar et al. [2015a](#page-7-3)[, b\)](#page-7-25).

The XRD pattern of the reaction products after 36 h ball milling at 400 rpm and 30 bar $CO₂$ pressure is shown in Fig. [2](#page-2-1). XRD pattern reveals the presence of siderite (JCPDS # 00-029-0696) as the major phase and minor amount of unreacted magnetite. Amount of the siderite, which was obtained by the Rietveld refinemenet of XRD pattern, is 85.86% that is equivalent to 0.4829 g $CO₂/g$ sorbent absorption capacity and 78.82% of magnetite-to-siderite conversion.

Calculated lattice parameters of siderite are $a = b = 4.6638$ (3) Å and $c = 15.6744$ (7) Å, which are in good agreement published data (Mora et al. [2019a\)](#page-7-6). Average crystallite size of FeCO₃ after 36 h ball milling was estimated using Scherrer's formula and is equal to108 Å.

Fig. 2 XRD pattern of $Fe₃O₄ + C$ mixture after 36 h of ball milling (400 rpm) at 30 bar $CO₂$ pressure

Siderite decomposition

Siderite decomposition reactions were studied at room and high temperature (by TG/DCS) conditions. Figure [3](#page-3-0) shows the TG/DCS plots of the siderite in argon and air atmospheres.

Weight loss below 100 °C for both samples can be related mainly to the loss of water. As it is evident from DTG curves, highest rate of siderite decomposition is achieved at 263 °C and 343 °C in Ar and air atmospheres, respectively. Higher decomposition temperatures of siderite in air compared to inert atmosphere have been reported previously by others, e.g. (Mora et al. [2019a,](#page-7-6) [b;](#page-7-31) Alkaç and Atalay [2008](#page-7-23)). Moreover, these decomposition temperatures of the siderite obtained in the presence of water are lower than decomposition temperature of the siderite synthesized from magnetite and metallic iron by mechanochemical reaction at dry condition [367 \degree C and 407 \degree C in Ar and air atmospheres, respectively (Mora et al. [2019a](#page-7-6))].

Fig. 3 TG-DSC curves of siderite (formed in $Fe₃O₄+C$ reaction at 30 bar CO_2 pressure, 400 rpm, 36 h) in Ar (a) and air (b) atmospheres at 10 °C/min heating rate

Formation of non-stoichiometric wustite, FeO, is the frst step of siderite decomposition (Mora et al. [2019a](#page-7-6)), as follows:

$$
\text{FeCO}_3(\text{s}) \rightarrow \text{FeO}(\text{s}) + \text{CO}_2(\text{g}) \tag{3}
$$

Depending on experimental conditions, other products can form from FeO because of its instability below 563 °C (Ding et al. [1998](#page-7-32)). In inert atmosphere FeO disproportionate producing $Fe₃O₄$ and Fe:

$$
4FeO(s) \rightarrow Fe_3O_4(s) + Fe(s)
$$
\n(4)

In oxygen atmosphere, siderite is oxidized rapidly, yielding $Fe₃O₄$ according reaction ([2](#page-1-1)) and hematite as follows:

$$
4FeCO3(s) + O2(g) \rightarrow 2Fe2O3(s) + 4CO2(g)
$$
 (5)

At low oxygen partial pressure, $FeCO₃$ can decompose in the presence of the graphite buffer as follows:

$$
3FeCO_3(s) \rightarrow Fe_3O_4(s) + 3C(s) + 5/2O_2(g)
$$
 (6)

Thermogravimetry plot in Fig. [3a](#page-3-0), reveals that the release of CO₂ by siderite in Ar atmosphere, starts at relatively low temperature (close to 100 °C), presenting the maximum rate at 263 °C. According to TG plot, the total weight loss in the frst step of siderite decomposition is 20.3% calculated at corresponding temperature of 303 °C. As can be calculated from Fig. [3](#page-3-0)b, the experimental total weight loss in air atmosphere is 13.2%, taking account 343 °C as the fnal siderite decomposition temperature. This loss weight is less than the one in inert atmosphere, due to decomposition of $FeCO₃$ in air is accompanied by iron oxidation to $Fe₂O₃$ and $Fe₃O₄$ according to reactions (2) (2) and (5) (5) . (Weight loss in reactions ([3\)](#page-3-2) and ([5\)](#page-3-1) are 37.99% and 31.08% respectively).

In air atmosphere weight loss at higher temperatures with a maximum rate of loss at 550 °C can be related to the oxidation of unreacted carbon which was added to magnetite as a reducing agent. The same carbon acts as a reducing agent in inert atmosphere reducing iron oxides (Fe₂O₃ and Fe₃O₄) to FeO or even to elemental iron. These reduction reactions are accompanied by the weight loss above 900 °C in Ar atmosphere.

Prior to $CO₂$ release at high temperature, the hydrated material losses absorbed and bound water. Ball milling transfers kinetic energy to material leading to the generation of crystal defects such as vacancies, dislocations and grain boundaries (Ding et al. [1998;](#page-7-32) Kumar [2014](#page-7-33)). Moreover, the ball milling decreases the difusion distance (Gheisari et al. [2009\)](#page-7-34) and creates active sites on the surface of material increasing the surface area (Mora et al. [2019a,](#page-7-6) [b](#page-7-31)). These efects facilitate decomposition reaction by lowering the diffusion distance and enhancing the difusivity (Gheisari et al. [2009](#page-7-34)) in material.

Fig. 4 XRD pattern of decomposed siderite at 400 °C in air for 1 h

Fig. 5 XRD pattern of spontaneously decomposed siderite after 24 h exposure to air at room temperature

Figure [4](#page-4-0) shows the X-ray difraction pattern of the products of siderite decomposition in air at 400 °C. Magnetite and hematite are detected as decomposition product of siderite proving the discussed above decomposition reactions ([2\)](#page-1-1) and [\(5](#page-3-1)).

Siderite decomposition was also studied at room temperature conditions (20 °C) in air atmosphere. Material after carbonation reactions was grinded using mortar and pestle and left at room temperature in air for diferent periods of time. After 24 h exposure time amount of siderite in the sample decreased to 68.48% (see Fig. [5](#page-4-1) for XRD pattern of

192 4.88 216 0.77

Fig. 6 XRD pattern of spontaneously decomposed siderite (216 h decomposition time)

decomposition product), that is 17.38% reduction compared with initial siderite content after carbonation reaction. Magnetite concentration in the sample increased evidencing the decomposition of siderite at room temperature conditions according to reaction [\(2](#page-1-1)).

Changes in the composition of the siderite sample were studied for longer reaction times up to 216 h (9 days) by recording X-ray difraction patterns every 24 h. Table [1](#page-4-2) summarizes results of this study by showing weight fraction of undecomposed siderite in the sample.

As can be seen, after 216 h of spontaneous decomposition siderite in the sample has practically vanished. Figure [6](#page-4-3) shows XRD pattern of the sample after 216 h exposure to ambient atmosphere. This pattern reveals presence of hematite (JCPDS # 00-089-2810) that can be associated to magnetite oxidation according to reaction [\(7](#page-5-0)). Lack of reducing agent and intermediate products after capture $CO₂$ process reveals the suitable efficiency of carbonation reactions. Next

 Sorbent no treated Sorbent 2 h milled Sorbent after 4th cycle

Table 2 $CO2$ capture capacity of sorbent, reaction time to decompose the siderite and the extra substances added, in second, third and fourth cycles, in spontaneous decomposition of siderite from Fe_3O_4 -C-CO ₂ system	Cycle	Extra substances added	Siderite vield $(\%)$	$CO2$ capture capacity $(g CO2/g sorb-$ ent)	$FeCO3$ weight fraction in decomposed sample (216 h)
		Water, 3 ml	85.48	0.5237	0.62
	\mathbf{r}	Water, 3 ml	88.89	0.5446	0.43
	4	Water, 3 ml	91.27	0.5591	0.22

Table 3 Pore volume and surface area for initial mixture of magnetite and graphite after 2 h of ball milling and after fourth carbonationcalcination cycle

carbonation has high probability of success due to not only the compounds present in the decomposed sample are $Fe₂O₃$ and $Fe₃O₄$, but also the absorb properties of the material have improved as can be seen in "Porosity analysis and crystallite size".

$$
4 \,\text{Fe}_3\text{O}_4(s) + \text{O}_2(g) \to 6\text{Fe}_2\text{O}_3(s) \tag{7}
$$

Carbonation–decomposition cycles

Recyclability of the products of siderite decomposition at room temperature conditions in subsequent carbonation cycles was also studied. The kinetic limitation in the second carbonation cycle was reduced by adding a considerable amount of water (3.0 ml) per 3.00 g of regenerated iron oxides. Carbonation reaction was studied at 30 bar $CO₂$ pressure, 400 rpm and for 36 h. Table [2](#page-5-1) shows the extra substances added, siderite yield, $CO₂$ capture capacity of the sorbent and amount of undecomposed siderite after 216 h of exposure to room temperature condition in second, third and fourth cycles.

The results confrm that the regenerated iron oxides can be re-carbonated. Higher capture capacities are achieved with each subsequent carbonation cycle. After 216 h, absence of siderite is evident, which allows to conclude that siderite decomposition kinetic is enhanced by increasing ball milling (Criado et al. [1988](#page-7-35)). Here, longer ball milling time generates defects, lowers difusion distance and increases surface area, (Jagtap et al. [1992](#page-7-36)) (see Table [3\)](#page-5-2) ease capture and release of $CO₂$, as it was explained in "[Siderite](#page-3-3)" [decomposition"](#page-3-3).

Fig. 7 XRD patterns of initial mixture of initial magnetite and graphite mixture, after 2 h of milling and after of the fourth cycle

Porosity analysis and crystallite size

It has been demonstrated that carbonation of iron oxides is accelerated in the presence of water (Kumar et al. [2015b](#page-7-25); Mora et al. [2019b](#page-7-31)). Furthermore, high efficiency and high capacity of $CO₂$ capture by iron oxides and iron ore have been accomplished by mechanochemical reactions (Mora et al. [2019a](#page-7-6), [b](#page-7-31)). These results have been attributed among others to the surface properties of material. Table [3](#page-5-2) presents surface area and pore volume of initial mixture of magnetite and graphite, after 2 h of planetary ball milling and after the fourth cycle of carbonation-decomposition, evidencing that larger surface area and bigger pore volume which are gained by exposing the material to longer milling time allows to improve the sorbent properties.

Additionally, Fig. [7](#page-5-3) shows three XRD patterns of initial mixture, after 2 h of milling and after of the fourth cycle. Broadening of difraction peaks of magnetite during milling indicates about crystallite size reduction. Average crystallite sizes of magnetite in three samples are 112 Å, 78 Å and 45 Å respectively. These sizes are consistent with the reported in other works that synthesized iron carbonate from iron oxides by ball milling process (Mora et al. [2019a\)](#page-7-6).

Kinetic model of siderite decomposition

Kinetics of siderite decomposition at room conditions was studied. Figure [8](#page-6-0) plots the siderite conversion fraction as a function of time in frst and fourth decarbonation cycles. For the same reaction time, a slightly higher siderite conversion fraction is observed in fourth cycle that can be attributed to a longer total milling time with increasing carbonation/ decomposition cycle number. Siderite moves to lower energy expenses by increasing milling time (Kumar [2014](#page-7-33)).

Obtained kinetic data were ftted to diferent solid-state reaction mechanism models (Feng et al. [2011](#page-7-18); Gotor et al.

Fig. 8 Siderite conversion factor at room temperature conditions as a function of time in frst and fourth carbonation/decomposition cycles

[2000;](#page-7-20) Luo et al. [2016;](#page-7-37) Zakharov and Adonyi [1986](#page-8-6)). The best fit was obtained for geometrical contraction models, R2 and R3. Results of ftting are illustrated by Fig. [9.](#page-6-1) Geometrical contraction models assume that nucleation occurs rapidly on the surface of the crystal. The rate of reaction is controlled by the resulting reaction interface progress toward the center of the crystal. Depending on crystal shape, diferent mathematical models may be derived. In the current study we tested the contracting cylinder (R2) and the contracting sphere/cube (R3) models. As seen in Fig. [9,](#page-6-1) [R2](#page-2-1) model provides slightly better ft of experimental kinetic data compared with R3 model. Reaction constants for R2 and R3 models in frst and fourth decomposition cycles are provided in the Fig. [9](#page-6-1). It is worth noticing small increase of reaction constant in the fourth cycle decomposition reaction compared to the frst cycle reaction which can be attributed to particle size reduction and surface area increase.

Conclusion

Siderite was synthesized by mechanochemical reactions from magnetite and graphite at 30 bar $CO₂$ pressure, 400 rpm and 36 h of reaction time in the presence of water. Use of this reaction for carbon dioxide capture is suggested and discussed. Such a sorbent (magnetite and carbon mixture) has CO_2 capture capacity of 0.4829 g CO_2/g sorbent capacity that corresponds to 78.82% of theoretical conversion. It was found that synthesized $FeCO₃$ is unstable at room temperature conditions and ambient atmosphere. Complete decomposition takes around 9 days

Fig. 9 The integral reaction rate vs. time for siderite decomposition after frst (**a**) and fourth (**b**) carbonation cycle. The scattered plots represent the experimental points while the solid lines represent the

straight line ft for the contracting cylinder (red) and contracting sphere/cube (blue) solid state reaction mechanism models

yielding magnetite and hematite. The kinetics study shows that the decomposition reaction obeys geometrical contraction model. Cycling stability of the sorbent was tested in four carbonation–decomposition cycles and it was found that the sorbent $CO₂$ capacity increases with cycle number because of the reduction in the particle size, increase of the surface area and surface activation.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no confict of interest.

References

- Alkaç V, Atalay Ü (2008) Kinetics of thermal decomposition of Hekimhan-Deveci siderite ore samples. Int J Miner Process 87:120–128
- Bale C, Chartrand P, Degterov S, Eriksson G, Hack K, Ben Mahfoud K, Melancon J, Pelton A, Petersen S (2002) Factsage thermochemical software and databases. Calphad 26:189–228
- Bello V, Idem R (2005) Comprehensive study of the kinetics of the oxidative degradation of $CO₂$ loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during $CO₂$ absorption from flue gases. Ind Eng Chem Res 45:2569–2579
- Breckenridge W, Holiday A, Ong J O, Sharp C (2000) Use of SELEXOL process in coke gasifcation to ammonia project: In Proceedings ofthe Laurance Reid Gas Conditioning Conference. pp397-418
- Chai NAL (1994) Enthalpy of formation of siderite and its application in phase equilibrium calculation. Am Mineral 79:921–929
- Cheng-Hsiu Y, Huang C-H, Tan C-S (2012) A review of $CO₂$ capture by absorption and adsorption. Aerosol Air Qual Res 12:745–769
- Criado J, Gonzalez M, Macias M (1988) Infuence of grinding of both the stability and thermal decomposition mechanism of siderite. Thermochimica 135:219–223
- Cullinage T, Rochelle G (2004) Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. Chem Eng Sci 59:3619–3630
- Das S (2016) Temperature-induced phase and microstructural transformations in a synthesized iron carbonate (siderite) complex. Mater Des 92:189–199
- Ding J, Miao W, Pirault E, Street R, Mc Cormick P (1998) Structural evolution of Fe + Fe₂O₃ during mechanical milling. J Magn Magn Mater 177:933–934
- Feng Z, Yu Y, Liu G, Chen W (2011) Kinetics of the thermal decomposition of wangjiatan siderite. J Wuhan Univ Technol Matter 1:523–526
- Figueroa, Fout T, Plasynski S, Srivastava R (2008) Advances in CO₂ capture technology—the U.S. Department of Energy's Carbon Sequestration Program. Int J Greenhouse Gas Control 2:9–20
- Folger P (2013) Carbon capture: a technology assessment, de congressional research service report. University of Nebraska, Lincoln
- Fosbøl P, Thomsen K, Stenby H (2010) Review and recommended thermodynamic properties of $FeCO₃$. Corros Eng Sci Technol 45:114–135
- Gallagher P, Warne SJ (1981) Thermomagnetometry and thermal decomposition of siderite. Thermochimca 43:253–267
- Gheisari K, Javadpour S, Oh J, Ghafari M (2009) The efect of milling speed on the structural properties of mechanically alloyed Fe–45%Ni powders. J Alloy Compd 472:416–420
- Gotor F, Macías M, Ortega A, Criado J (2000) Comparative study of the kinetics of the thermal decomposition of synthetic and natural siderite samples. Phys Chem Minerals 27:495–503
- Hammersley AP (1997) FIT2D: an introduction and overview. European Synchrotron Radiation Facility Internal Report ESR-F97HA02T, 68-58.
- Han Y, Winston Ho W (2018) Recent advances in polymeric membranes for $CO₂$ capture. Chin J Chem Eng $26:2238-2254$
- Han K, Ahn CK, Su Lee M (2014) Performance of an ammoniabased $CO₂$ capture pilot facility in iron and steel industry. Int J Greenhouse Gas Control 27:239–246
- Jagtap S, Pande A, Gokarn A (1992) Kinetics of thermal decomposition of siderite: efect of particle size. Int J Miner Process 36:113–124
- Kang S (2020) First-principles evaluation of the potential of using Mg_2SiO_4 , Mg_2VO_4 , and Mg_2GeO_4 for CO_2 capture. J CO2 Utiliz 42:101293
- Kumar S (2014) The effect of elevated pressure, temperature and particles morphology on the carbon dioxide capture using zinc oxide. J CO2 Utiliz 8:60–66
- Kumar S, Saxena S (2014) A comparative study of $CO₂$ sorption properties for diferent oxides. Mater Renew Sustain Energy 3:1–15
- Kumar S, Saxena S, Drozd V, Durygin A (2015a) An experimental investigation of mesoporous MgO as a potential pre-combustion CO₂ sorbent. Mater Renew Sustain Energy 4-8
- Kumar S, Drozd V, Durygin A, Saxena S (2015b) Capturing CO₂ Emissions in the Iron Industries using a Magnetite-Iron Mixture. Energ Technol.<https://doi.org/10.1002/ente.201500451>
- Larson A, Von Dreele R (2004) General structure analysis system (GSAS). Los Alamos National Laboratory REport LAUR, pp 87–748
- Luo Y, Zhu D, Pan J, Zhou X (2016) Thermal decomposition behaviour and kinetics of Xinjiang siderite ore. Miner Process Extr Metall 125:17–25
- Merkel T, Lin H, Wei X, Baker R (2009) Power plant post-combustion carbon dioxide capture: an opportunity for membranes. J Membr Sci 359:126–139
- Mora E, Sarmiento A, Vera E, Drozd V, Durygin A, Chen J, Saxena S $(2019a)$ Iron oxides as efficient sorbents for $CO₂$ capture. J Market Res 8:2944–2956
- Mora E, Sarmiento A, Vera E, Drozd V, Durygin A, Chen J, Saxena S (2019b) Siderite formation by mechanochemical and thermo pressure processes for $CO₂$ capture using iron ore as initial sorbent. Procesess. <https://doi.org/10.3390/pr7100735>
- Pannoccia G, Puccini M, Seggiani M, Vitolo S (2007) Experimental and modeling studies on high-temperature capture of $CO₂$ using lithium zirconate based sorbents. Ind Eng Chem Res 46:6696–6706
- Patterson J (1994) A review of the effects of minerals in processing of Auatralian oil shales. Fuel 73:321–327
- Salvador C, Lu D, Anthony D, Abadanes J (2003) Enhancement of CaO for CO_2 capture in an FBC environment. Chem Eng J 96:187-196
- Song C, Liu V, Qi Y, Chen G (2019) Absorption-microalgae hybrid $CO₂$ capture and biotransformation strategy—a review. Int J Greenhouse Gas Control 88:109–117
- Stewart C, Hessami MA (2005) Study of methods of carbon dioxide capture and sequestration––the sustainability of a photosynthetic bioreactor approach. Energy Convers Manage 46:403–420
- Toby B (2001) EXPGUI, a graphical interface for GSAS. J Appl Cryst 34:210–221
- Xie V, Fu Q, Quiao G, Webley P (2019) Recent progress on fabrication methods of polymeric thin film gas separation membranes for $CO₂$ capture. J Membr Sci 572:38–60
- Yan H, Xu Z, Fan M, Bland A, Wright I (2008) Progress in carbon dioxide separation and capture: a review. J Environ Sci 20:14–27
- Yang Y, Xu X, Guo Y, Wood C (2020) Enhancing the $CO₂$ capture efficiency of amines by microgel particles. Int J Greenhouse Gas Control 103:103172
- Zakharov V, Adonyi Z (1986) Thermal decomposition kinetics of siderite. Thermochim Acta 102:101–107
- Zaman M, Lee JH (2013) Carbon capture from stationary power generation sources: a review of the current status of the technologies. Korean J Chem 30:1497–1526
- Zhang J, Webley P (2008) Cycle development and design for $CO₂$ capture from fue gas by vacuum swing adsorption. Environ Sci Technol 42:563–569
- Zhang N, Pan Z, Zhang Z, Zhang W, Zhang L, Baena-Moreno F, Lichtfouse E (2010) $CO₂$ capture from coalbed methane using membranes: a review. Environ Chem Lett 18:79–96
- Zhou GT (2011) Synthesis of siderite microspheres and their transformation to magnetite microspheres. Eur J Mineral. [https://doi.org/](https://doi.org/10.1127/0935-1221/2011/0023-2134) [10.1127/0935-1221/2011/0023-2134](https://doi.org/10.1127/0935-1221/2011/0023-2134)

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