



Porous apatites as novel high temperature sorbents for carbon dioxide

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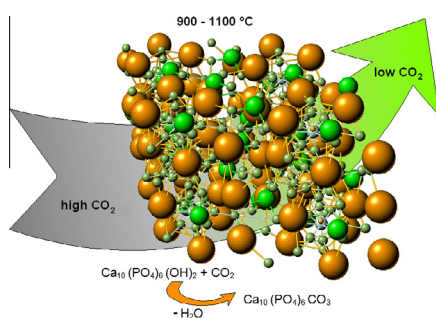
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HIGHLIGHTS

- Synthetic hydroxyapatite as potential new material for CO₂ capture at temperature higher than that of CaO based sorbents.
- No appreciable decay of the absorbing activity upon several cycles.
- The temperature of pre-treatment of porous granules impacts on sorption capacity.
- CO₂ carrying capacity very close to theoretical limit of 2.6% by mass.
- Lower heat for regeneration in comparison with CaCO₃ sorbents.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 February 2014

Received in revised form 5 May 2014

Accepted 7 May 2014

Available online 24 May 2014

Keywords:

Apatite

Solid porous sorbent

CO₂ capture

CO₂ carrying capacity

ABSTRACT

Synthetic hydroxy-apatite was tested as a potential new material for CO₂ capture at high temperature, over the operation limit of CaO-based sorbents. Some porous granules of hydroxy-apatite were prepared *ad hoc*. They were shown to absorb CO₂ upon dehydroxylation in the very high temperature range of 900–1200 °C, resulting in A-type carbonated apatite. No appreciable decay of the absorbing capacity was observed with a higher number of absorbing–desorbing cycles, differently from what happens in a conventional chemical sorbent, e.g. calcined natural calcium carbonate. The CO₂ carrying capacity was maximum at 1000–1100 °C and very close to the theoretical limit of 2.6% by mass. The macro-granule porosity network appeared to be effective in making the sites available for CO₂ capture. At first glance, the process appeared to be chemically controlled. The pre-treatment temperature of the porous granules also had an impact on the sorption capacity. As a first proof of concept, the results obtained by thermogravimetric analysis, and supported by FTIR and XRD analysis, were confirmed by tests carried out in a laboratory-scale reactor, operated as a fixed bed.

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1. Introduction

In the next decades the exploitation of fossil resources will continue and is expected to increase [1] until other options and concepts (e.g. solar energy, clean/safe nuclear energy, biorefinery, etc.) have been fully demonstrated and implemented worldwide. In order to mitigate the impact of fossil energy on pollution and

greenhouse effect, the current technologies must be improved to become less harmful for the environment and more sustainable (zero emissions). The capture and the sequestration of the CO₂ generated from the conversion of fossil fuels are being investigated as effective measures to reduce greenhouse gas emissions [2]. Nonetheless, the feasibility of a closed cycle of power generation and carbon dioxide separation and sequestration has not been fully demonstrated yet. As far as the capture step is concerned, different options are available: dry or wet chemical absorption [3], physical adsorption [4], and separation by means of membranes [5]. Behind

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Nomenclature

Acronyms

BET	Brunauer–Emmet–Teller
CA	carbonated-apatite
ESEM	environmental scanning electron microscopy
HA	hydroxy-apatite
NS	natural sorbent
OA	oxy-apatite
TG	thermo-gravimetric

Symbols

C	CO ₂ carrying capacity, –
c _p	Specific heat, kJ mol ⁻¹ K
C _{CO₂}	CO ₂ concentration, % vol.
K _{eq}	Chemical equilibrium constant, –

G	Gibbs free energy, kJ mol ⁻¹
H	enthalpy, kJ mol ⁻¹
M _s	mass of sorbent, g
M _w	molecular weight, g/mol
Q	molar flow rate, mol/s
T	temperature, K
Y _{CO₂}	partial pressure of CO ₂ , –
Y _{H₂O}	partial pressure of H ₂ O, –
t	time, s

Greek symbols

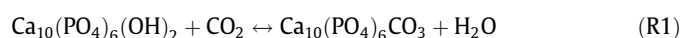
ΔG _r ⁰	Standard Gibbs free energy variation
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the implementation of state-of-the-art technologies, some innovative concepts are under investigation including the synthesis of new materials, for instance MOF-HKUST-1 [6], as well as enzyme-based bio-chemical processes [2].

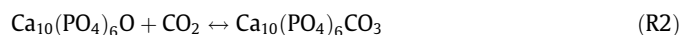
When sorbents are used in granular or structured forms, the keys to an effective process are a high superficial area and a well-developed open porosity. The application to a typical continuous process also requires the sorbent to be mechanically resistant, regenerable and easily available. In addition, a suitable CO₂ sorbent should also maintain its absorbing capacity and structural properties over several absorbing–desorbing cycles. Unfortunately, sorbents derived from natural limestone lose their reactivity over a number of reaction cycles with carbon dioxide and their capacity of CO₂ uptake decays [7].

Hydroxy-apatite (HA) is an inorganic material containing calcium and phosphorus, having chemical formula Ca₁₀(PO₄)₆(OH)₂. HA is the most common apatite, also available in natural reserves as the hydroxylated form of oxy-apatite (OA), with formula Ca₁₀(PO₄)₆O. Carbonated apatite (CA) is generated by the substitution of the hydroxyl group, leading to Ca₁₀(PO₄)₆CO₃. Since it is the main constituent of the bone tissue in vertebrates [8], hydroxy-apatite is mainly used in the biomedical field. For this reason it has been extensively studied in the form of powder and of porous aggregates or constructs to develop new synthetic functional materials. Some previous research on the conversion of stoichiometric hydroxy-apatite into carbonated apatite or on the direct synthesis of substitutes has shown that carbonate ions can be substituted at both the phosphate and the hydroxyl sites in the HA lattice, generating type B and type A carbonated hydroxy-apatite, respectively [9–13]. The two types of substitution can occur simultaneously in the apatite lattice, especially if they are prepared through wet based synthesis; the powder synthesis and the thermal treatment can be controlled so as to selectively favor one of the two types of carbonation. The thermal treatment in different atmospheres has also been investigated [9,10,12–14], with a focus on CO₂ gas, mainly in order to avoid or limit the B-type de-carbonation and/or improve the densification of the material at temperatures lower than the conventional value. A-type carbonate-substituted apatite is commonly prepared by heating stoichiometric HA in a CO₂ atmosphere at temperatures of 800–1000 °C for long times [10,12–14].

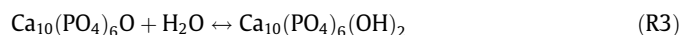
This finding has opened up new perspectives on the use of hydroxy-apatite for high-temperature carbon capture via reversible chemical Reaction (R1):



The parallel path via oxy-apatite is also possible, as expressed by Reaction (R2):



In turn, the hydroxylation Reaction (R3) is linearly dependent upon Reactions (R1) and (R2)



This article reports on the use of apatites as new sorbents for the high-temperature uptake of CO₂, under conditions where other materials, like CaO, are ineffective. The results in terms of CO₂ carrying capacity – experimentally obtained in a TG apparatus and a fixed bed reactor – are reported, discussed and compared with a classical CaO based sorbent, i.e. quick lime derived from natural limestone. Some speculations about apatite being used for CO₂ separation are also presented.

2. Materials and methods

A commercial hydroxy-apatite powder (Riedel de Haen) was used as a starting material to produce porous HA macrogranules having sizes in the range 400–600 μm, using a wet based granulation process. To prepare the HA granules, an aqueous solution with 1% polyethylene glycol was sprayed on a powder layer using a solid/solution weight ratio 1:1. The wet powder particles were agglomerated into granules by rolling and rotational movements. The granules were oven-dried, then calcined at 850 °C for 1 h, and sieved (between 400 and 600 μm).

For comparison purposes, a ground natural calcium carbonate (“Massicci” limestone from Italy) coded NS, natural sorbent, in this paper was also used. Some calcined granules of the same size range were prepared. This limestone had already been investigated as sorbent for CO₂ and SO₂ in fluidized bed at moderately high temperatures [15,16].

Calcination in Ar at 850 °C was carried out for both materials before the experiments.

The morphological and microstructural characterisation of the materials was performed by environmental scanning electron microscopy ESEM (Quanta 200 FEI). The specimens were made conductive before the analysis using a sputter-coater (Assing sputter coater Polaron Equipment Limited) with an Au target.

X-ray diffraction analysis (Bruker D8 Advance Bruker-Karlsruhe) was used for crystallographic evaluations. Fourier transformed infrared (FTIR) spectroscopy (Thermo Nicolet-Avatar 320 FT-IR) was performed to prove carbonate substitution. The pellet-specimen was prepared by cold pressing a mixture of the powder with KBr using a ratio 1:100 by mass; the air spectrum, detected immediately before the specimen analysis, was automatically subtracted from the specimen spectrum. The pore size distribution in the range 0.0058–100 μm was analyzed by mercury

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