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# Insights into High Temperature Sorbents for Carbon Dioxide

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This article reports on an experimental research dealing with the use of solid sorbents for $CO_2$ uptake from gaseous stream at high temperature. Hydroxyl-apatite and strontium carbonate have been adopted as starting materials for preparing a regenerable sorbent, upon calcination. Both sorbents have been characterized in TG tests with an alternating atmosphere of $CO_2$/Ar and Ar, accomplishing steps of carbonatation and calcination/regeneration at temperature over 900 °C. The apatite based sorbent maintained its capability of $CO_2$ absorption for several cycles, whilst the Sr based sorbent exhibited a quick decay of its capability due to changes of the micro-structure. The $CO_2$ carrying capacity after conditioning reached stable values of around 3% and 5% for apatite and strontium sorbents, respectively. TG curves were worked out in order to obtain kinetic data for both carbonatation and calcination, showing that apatite is slightly more reactive than strontium sorbent. The TG tests were also complemented by a fixed bed experiment aimed at demonstrating the feasibility of apatite regeneration with steam.

## 1. Introduction

Besides other methods, solid chemical sorbents can be effectively used for capturing $CO_2$ originated from fossil sources at relatively high temperature (Figueroa et al., 2008). These materials should have high and accessible superficial area, apart from being regenerable and mechanical resistant. In addition, the absorbing capacity and structural properties must be maintained over several absorbing-desorbing cycles. Oxides of alkaline and alkaline earth metals are very effective as absorbing materials for $CO_2$ at high temperature. Lithium based sorbents promoted with potassium carbonate were successfully developed and used up to 580 °C (Puccini et al., 2013). In most cases, Ca oxide from limestone calcination is selected as sorbent, having a theoretically $CO_2$ carrying capacity up to 78% by mass of the calcined material. Unfortunately, a loss of reactivity occurs upon repetition of carbonatation/calcination cycles (Blamey et al., 2010). Furthermore, CaO based sorbents can be used in a limited temperature interval, between 700 and 800 °C, at atmospheric pressure. In some cases, for instance the pre-combustion removal of $CO_2$ from syngas produced by entrained flow gasification, the possibility to carry out $CO_2$ capture without cooling the gas could result beneficial for the whole process optimization (Miccio et al., 2014).This option demands the availability of effective sorbents up to 1200 °C.

Hydroxyl-apatite or oxy-apatite can be considered as a potential sorbent for $CO_2$ in the very high temperature range 900-1200 °C. Apatites are the main constituent of bones in vertebrates, so they can be relatively cheap if recovered and processed. The reaction with $CO_2$ leads to generation of A-type carbonated apatite. The process was tested and characterized in the temperature range 900-1100 °C in both TG and fixed bed equipment by Landi et al. (2014).

Strontium oxide SrO can be another substance able to chemically absorb $CO_2$, forming $SrCO_3$, in a temperature range over than that of the homologous CaO. Strontium carbonate occurs in nature as the mineral strontianite that after milling has the appearance of a white or grey powder. By high temperature

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calcination, it gives rise to the oxide, having temperature of fusion of 2430 °C. In addition, the theoretical $CO_2$ absorbing capacity (43%) is higher than that of hydroxyapatite (4%).

This paper reports on new insights on the utilization of both apatite and strontium oxide as $CO_2$ sorbents for very high temperature. Results in terms of $CO_2$ carrying capacity and kinetic data are presented and discussed for both adsorbing and desorbing steps along with the outcomes of some trials aimed at sorbent regeneration by treatment with steam.

## 2. Experimental

Thermal analysis has been carried out in a STA 449 Jupiter Netzsch equipment in order to explore the $CO_2$ absorbing/desorbing behaviors of the sorbents under controlled conditions. Different atmospheres of $CO_2$/Ar for the absorbing steps and pure Ar for the desorbing steps were used at temperatures in the range 800-1200 °C and a total flow rate of 40 ml/min. The sample weight was in the range 50-100 mg.

Some tests were performed in a fixed bed reactor at high temperature with a stream of Ar or Ar/$CO_2$ mixture, the detailed description of the equipment and technique being available elsewhere (Landi et al., 2014).

A commercial hydroxyl-apatite powder (Riedel de Haen) was used as starting material to produce porous HA macro-granules having sizes in the range 400-600 μm, following a wet based granulation process.

Commercial Strontium Carbonate (Merck Technipure) powder was also used in TG tests.

## 3. Results

### 3.1 Results with the apatite sorbent

TG tests were performed with apatite samples of around 50 mg at different temperature (T) and two partial pressure of $CO_2$ ($P_{CO2}$) during the carbonatation step, i.e. 0.2 and 0.5. A typical diagram of the weight variation obtained at T=1000 °C and $P_{CO2}$=0.5 is shown in Figure 1-A.

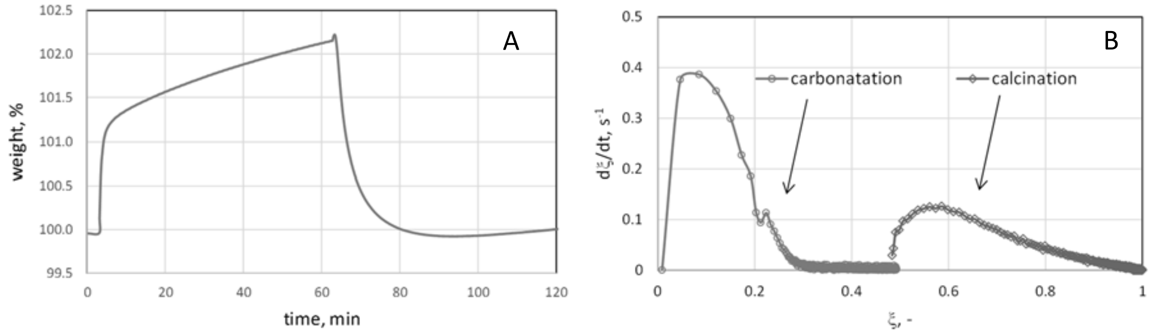

*Figure 1: TG weight variation of an apatite sample for one step of carbonatation and calcination (panel A); reaction rate versus conversion degree during carbonatation and calcination steps (panel B) $P_{CO2}$=0.5 and T=1000 °C*

The results were worked out in order to have kinetic parameters. The conversion degree ξ was evaluated on the basis of the weight change for carbonatation and calcination steps according to Eq(1) and Eq(2), respectively:

$$\xi_{carb} = \frac{W - W_0}{\Delta W_{\text{th}}} \tag{1}$$

$$\xi_{calc} = 1 - \frac{W - W_0}{\Delta W_{\text{th}}} \tag{2}$$

where $W$ is the current weight, $W_0$ the initial weight of the calcined sample and $\Delta W_{th}$ the theoretical mass change at full conversion. The conversion rate was computed as the time derivative of ξ. The dependence of the reaction rate on the conversion degree is shown in Figure 1-B for the data reported in the panel A of the same figure. A maximum of dξ/dt occurred at early stages of both carbonatation and calcination, when reactive sites were largely available. The shift toward right of the calcination data is due to the partial conversion occurred during the previous step of carbonatation, meaning that calcination starts at ξ>0.

The results confirmed the values obtained by Landi et al. (2014) with maximum effectiveness at 1100 °C, achieving 3% of $CO_2$ carrying capacity at $P_{CO2}$=0.5, for cycles of 20+20 min.

### 3.2 Results with the SrO based sorbent

A first test in the TG equipment (Figure 2) at increasing temperature from 800 to 1200 °C revealed that the maximum reactivity of $SrCO_3$ toward calcination and carbonatation was over 1000 °C, lower temperatures being ineffective as shown in Figure 2 up to time 400 min. Thus, two levels of the temperature were chosen for the quantitative assessment of the $CO_2$ carrying capacity, i.e. 1100 and 1200 °C.

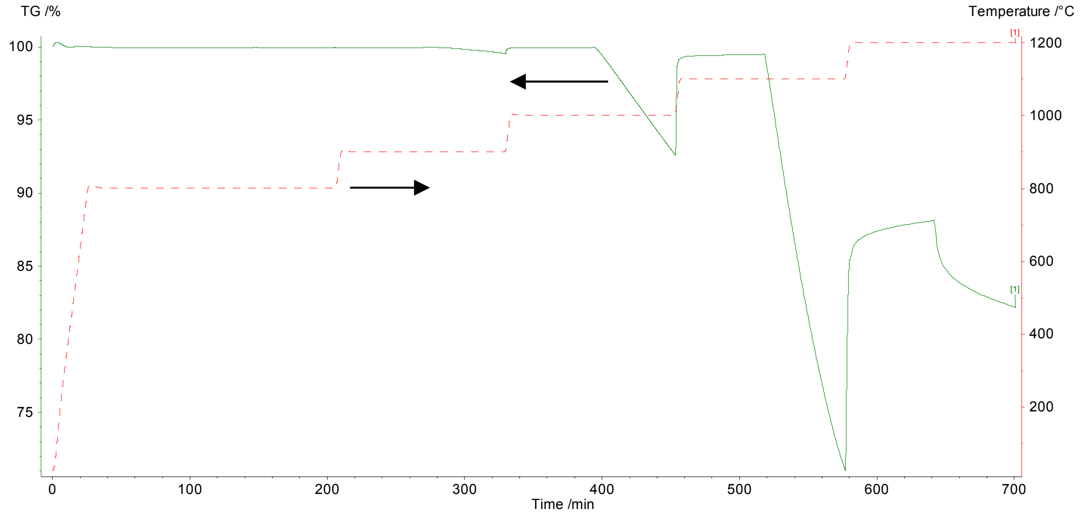

*Figure 2: TG weight variation of a $SrCO_3$ sample for steps of calcination and carbonatation (50% $CO_2$) in the temperature range 800-1200 °C*

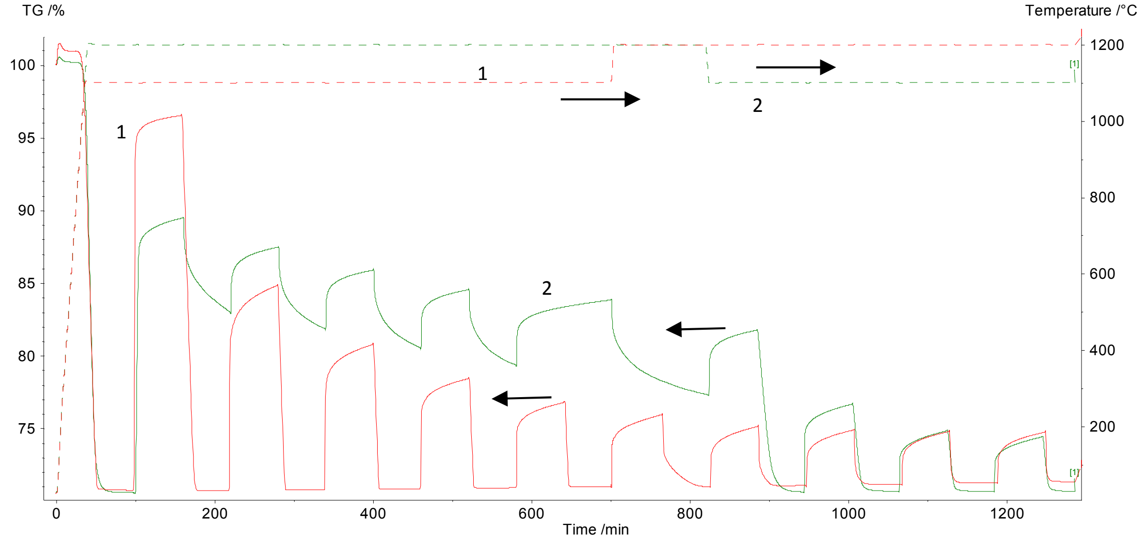

*Figure 3: TG weight variation of a $SrCO_3$ sample for steps of calcination and carbonatation (50% $CO_2$) at temperature of 1100 and 1200 °C (curve 1) and of 1200 and 1100 °C (curve 2)*

The diagram of isothermal weight variation obtained for a $SrCO_3$ sample in the TG equipment is shown in Figure 3. Five steps of calcination followed by carbonatation in a mixture of Ar (50%) - $CO_2$ (50%) were carried out at both temperatures (1100 and 1200 °C). The first weight loss was very close to the theoretical value 29.8%, indicating complete calcination of the sample. Upon the next step of carbonatation not full conversion to $SrCO_3$ occurred, the weight gain being 26.0%. The sorbent reactivity further decreased during the other cycles, achieving a value of weight loss/gain equal to 6.9% after 5 cycles at 1100 °C. During the other five cycles performed at 1200 °C the performance of the sorbent was slightly worsened, achieving a stable final value of 3.9% with respect to initial mass of $SrCO_3$. In a parallel test with inversion of the temperature levels (firstly 1200 °C and secondly 1100 °C) the final $CO_2$ capture capacity was practically the same, but a very different response was observed during first steps, indicating a promoting effect of the high temperature on the deactivation that could be attributed to closing the open porosity and sintering. This finding is supported by the

SEM analysis of the material before and after the cycling test (Figure 4). The starting agglomerate, formed by sub-micronic particles (Figure 4a), becomes less porous after the thermal treatment at 1200 °C (Figure 4b), becoming less permeable to $CO_2$.

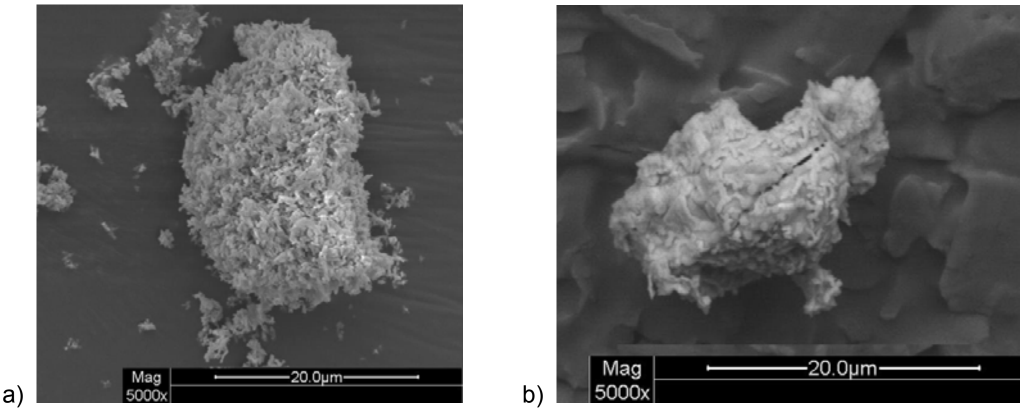

*Figure 4: SEM images of the Sr based material before (a) and after (b) the TG cycling test at 1200 °C*

### 3.3 Steam regeneration of the apatite sorbent

A test of steam regeneration of carbonate-apatite (CA) has been carried out in a fixed bed reactor following a procedure similar to that described by Landi et al. (2014), but accomplishing the calcination by flowing steam instead of Ar. Two carbonatation steps, intercalated by a regeneration, were carried out at 900 °C and $P_{CO2}=0.4$. During regeneration, distilled water was pumped into the reactor at a rate of 0.94 ml/min and the gas exiting the reactor was fed into a beaker containing a saturated solution of barium hydroxide, giving rise to precipitation of barium carbonate in presence of $CO_2$.

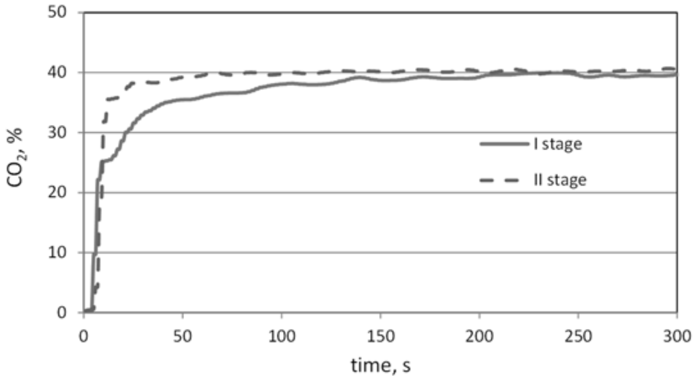

*Figure 5: breakthrough curves of the $CO_2$ concentration for Ar regenerated apatite (I stage) and steam regenerated apatite (II stage). Fixed bed reactor, T= 900 °C, $P_{CO2}=0.4$*

Figure 5 shows the breakthrough curves of both carbonatation tests before and after steam regeneration. The comparison between the curves indicates that the steam regenerated apatite was less effective than that calcined in Ar. By integrating over the time the $CO_2$ concentration profile (Landi et al., 2014), the total amount of captured $CO_2$ resulted equal to 570 and 170 mg for argon and steam regeneration, respectively. On the whole, the test demonstrated that the sorbent regeneration is feasible also in $H_2O$ atmosphere, with clear advantages in order to obtain a final $CO_2$ pure stream upon steam condensation. The presence of precipitated barium-carbonate in the trap downstream the reactor confirms the release of carbon dioxide during the steam regeneration. Furthermore, FTIR analyses on steam regenerated and carbonated samples revealed the presence of typical signals of hydroxyl groups in substitution of the carbonated groups. Figure 6 shows the comparison of the FTIR spectra obtained for the two samples. The spectrum of the regenerated sample exhibits strong signs of the presence of structural OH groups, such as the stretching peak at 3600 $cm^{-1}$ and the bending peak located at 630 $cm^{-1}$. However, the spectrum also shows the presence of residual groups of type A carbonate, indicated by the pair of stretching peaks at wave number 1460+1540 $cm^{-1}$ and the bending peak at 880 $cm^{-1}$, indicating that only partial conversion to hydroxyl-apatite occurred.

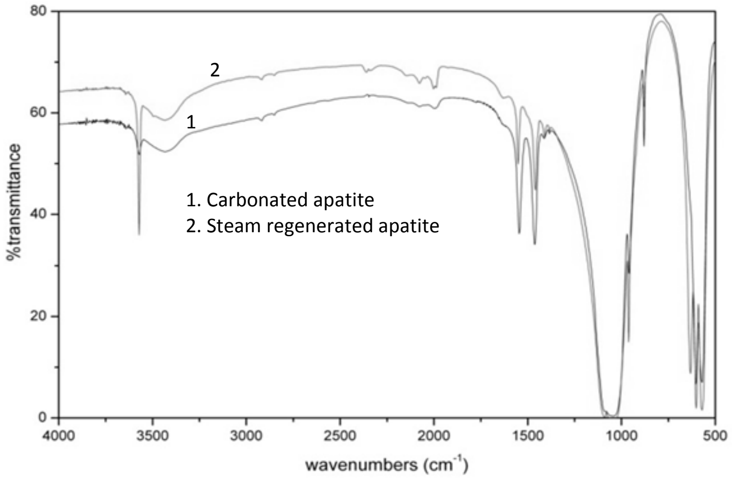

*Figure 6: FTIR spectra of carbonated apatite (curve 1) and steam regenerated apatite (curve 2)*

## 4. Discussion

Figure 7 displays the curves of thermodynamic stability at atmospheric pressure for $CaCO_3$, $SrCO_3$ and carbonate-apatite (CA). For $CaCO_3$ and $SrCO_3$ the computations were made by using CEA software tool (Gordon and McBride, 1994), whilst the data reported by Landi et al. (2014) were used for CA. It was assumed an initial system composed by one mole of Ar and one mole of carbonated species, or $CO_2$ in other words. Figure 7 provides the possible operating conditions of a carbonatation/calcination process for $CO_2$ capture. $SrCO_3$ is more stable and should allow operation in a very high temperature range (e.g. 1000-1150 °C).

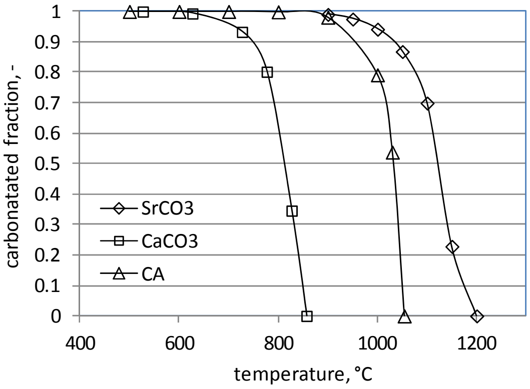

*Figure 7: fraction of the carbonated form versus temperature as resulting from thermodynamic equilibrium computation (equimolar system of $CO_2$ and Ar)*

A kinetic equation can be proposed for the dependence on $P_{CO2}$ and $T$ of the dimensionless reaction rate $r$=dξ/dt, following a classical Arrhenius approach (Senneca et al., 2002).

$$\frac{d\xi}{dt} = A \exp\left(-\frac{E}{RT}\right) {P_{co2}}^{n} \tag{3}$$

Table 1 reports the maximum values of $r$ versus $P_{CO2}$ and $T$, for both apatite and SrO sorbents during carbonatation and calcination. The elaboration was made for the steps where same conversion degree were achieved (e.g. last cycles in Fig. 3)

For apatite carbonatation, an increase of $r$ with $T$ occurs up to 1050 °C, afterwards the approaching chemical equilibrium (Figure 7) has a detrimental effect on $r$. Concerning calcination, there is a steady increase of r in the whole range of T, with exception of the point 1100 °C $P_{CO2}$=0.2 probably because of the limited conversion degree during the carbonatation. Excluding the point at 1100 °C, the interpolation of the data leads to the following values:

$n=1$, $E/R_{carb}$=11000K and $E/R_{calc}$=11500K.

For the Sr based sorbent, the calcination is much more faster at 1200 °C, whilst the carbonatation is slower at 1200 than 1100 °C for the same above reported reason, i.e. approaching chemical equilibrium (Figure 7).
It is worth noting that Table 1 reports the maximum reaction rate during carbonatation/calcination, whilst *r* changes with the conversion degree during each stage, as clearly shown in Figure 1B for example.

*Table 1: Maximum reaction rate as function of T and $P_{CO2}$*

| | Apatite | | | | SrO | |
|---|---|---|---|---|---|---|
| | Carbonatation | | Calcination | | Carbonatation | Calcination |
| | dξ/dt*, $min^{-1}$ | dξ/dt*, $min^{-1}$ | dξ/dt*, $min^{-1}$ | dξ/dt*, $min^{-1}$ | dξ/dt*, $min^{-1}$ | dξ/dt*, $min^{-1}$ |
| T, °C | $P_{CO2}$=0.2 | $P_{CO2}$=0.5 | $P_{CO2}$=0.2 | $P_{CO2}$=0.5 | $P_{CO2}$=0.5 | $P_{CO2}$=0.5 |
| 900 | 0.08999 | 0.101649 | 0.040780 | 0.061659 | | |
| 950 | 0.17418 | | 0.063869 | | | |
| 1000 | 0.28242 | 0.386707 | 0.087371 | 0.12634 | | |
| 1050 | 0.25920 | 0.385817 | 0.119732 | 0.171424 | | |
| 1100 | 0.27451 | 0.409248 | 0.104187 | 0.18187 | 0.197684 | 0.020258 |
| 1200 | | | | | 0.080441 | 0.088297 |

* maximum value during a test

## 5. Conclusions

The $CO_2$ uptake at very high temperature (900-1100 °C) was accomplished with both apatite and strontium based sorbents, although rather low $CO_2$ carrying capacity was achieved (less than 10% by mass).
The apatite based sorbent maintained its capability of $CO_2$ absorption (3%) for several cycles, whilst the Sr based sorbent exhibited a quick decay of its capability down to 5% due to changes of the micro-structure.
From a preliminary kinetic study, the carbonatation is faster for apatite than SrO and its rate is limited for both sorbents when chemical equilibrium is approached at higher temperatures.
The apatite sorbent can be regenerated in $H_2O$ atmosphere, as demonstrated in a test in fixed bed reactor at 900 °C, confirmed by FTIR analysis of the recovered sample.
Further investigations are needed in order to limit the detrimental effects of repeated cycles on the sorbent reactivity, in particular for the strontium sorbent, as well as to produce a complete set of kinetic data.

### Acknowledgements

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