

Morphological analysis of sulfated Ca-based sorbents under conditions corresponding to oxy-fuel fluidized bed combustion

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ABSTRACT

The use of Ca-based sorbents in circulating fluidized beds (CFB) allows the in-situ desulfurization in oxy-fuel combustion processes. The sulfation process involves important changes in the sorbent morphology, which could vary depending on the operating conditions and be different to those observed in conventional air combustion. This work analyzes the morphological variations observed during limestone and dolomite sulfation at typical oxy-fuel combustion conditions (high CO₂ concentration, higher temperatures than in air combustion) in CFB combustors (long reaction times). Sulfated samples prepared in a thermogravimetric analyzer were analyzed by Scanning Electron Microscope (SEM). The space limitations due to the higher molar volume of CaSO₄ compared to CaO in the external surface of the particles make that the CaSO₄ product layer trend to grow outwards to form a honeycomb-shaped structure. This structure appeared for limestone at both calcining and non-calcining conditions. A strong effect of the CaSO₄ sintering phenomenon was observed at temperatures above 950 °C. Moreover, the honeycomb structure was never observed working with dolomite in spite of the high sulfation conversions reached with this sorbent.

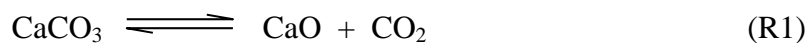
keywords: CO₂ capture, oxy-fuel combustion, fluidized bed, Ca-based sorbent, desulfurization.

1. INTRODUCTION

Oxy-fuel combustion is a carbon capture technological option which consists of burning the fuel with a mix of pure oxygen and a CO₂-rich recycled flue gas. In this way, the flue gas leaving the combustor is mainly composed of CO₂ and H₂O and thus a highly CO₂ concentrated stream can be obtained after steam condensation in order to be subsequently transported and stored.

There are two types of boilers to burn coal in oxy-fuel mode: Pulverized Coal (PC) and Fluidized Bed (FB) combustors [1]. In oxy-fuel combustion, SO₂ is a pollutant gas to take into consideration before CO₂ transport and storage. In the process of SO₂ removing, an additional unit is needed in PC boilers. However, in FB combustors the desulfurization process may be directly performed inside the boiler by supplying a Ca-based sorbent, this aspect being a relevant advantage compared to PC. The limestone, mainly composed of CaCO₃, is currently one of the most used Ca-based sorbent in entire world to perform the desulfurization process due to its low cost and its high availability.

According to the equilibrium diagram of CaCO₃ calcination reaction (R1) [2], which is represented in Fig. 1, the temperature and CO₂ partial pressure are important operating variables to define the behavior of the limestone. In conventional air combustion conditions, the CO₂ concentration generated from coal combustion is relatively low (about 15 vol.%) and thus the limestone sulfation is always performed in calcining conditions (R2) [3,4]. However, in oxy-fuel combustion conditions, the CO₂ concentration existing in the boiler is much higher, ranging from 65 to 90 vol.%, and therefore the limestone may operate in calcining (R2) or non-calcining conditions (R3) [5, 6].



One of the limiting characteristic of the limestone as Ca-based sorbent is its level of sulfation which seldom reaches full conversion. This means it is not possible to make use of the whole particle since the blockage of the outer pores occurs as CaSO_4 is forming. It must be considered that the molar volume of CaSO_4 is higher than that of the initial reactant, that is, CaCO_3 or CaO .

In previous studies on sulfation of Ca-based sorbents performed by the research group at oxy-fuel conditions in a thermogravimetric analyzer (TGA) [7] and in a batch FB reactor [8], it has been observed that the highest sulfation conversions are achieved in calcining conditions and the sulfation reaction is carried out in two steps, the former being faster than the latter. The first one is controlled by the diffusion of the reactant gas through the porous system of the particle until the blockage of the external pores is produced, and the second one by the diffusion of the reactant gas through the product layer according to the shrinking core model [9]. Several researchers [10, 11] found that the residual activity of the limestone, that is, the second reaction step, plays an important role in the sulfation process at long reaction times which are typical of the circulating fluidized bed combustors (CFBC). Therefore, the study of the evolution of the product layer formed during the sulfation process could be a key aspect to have an insight into the sulfation process.

On the other hand, at oxy-fuel operating conditions, an optimum temperature with respect to sulfur retention was found to be about 900-925 °C corresponding to calcining conditions [12]. Operating temperatures above 925 °C led to a decrease in the sulfur retention values. This fact suggests that the limestone particles undergo a loss of reactivity due to the sintering phenomena associated with the reactant solid [13], CaO or CaCO_3 , or the product layer, CaSO_4 . Anthony and Granatstein [14] reported another explanation based on the possibility of CaSO_4 decomposition at high temperatures, leading to a release of SO_2 and lower sulfur retention values. Those results were corroborated by de las Obras-Loscertales et al., (2014) during the operation in a continuous oxy-fuel bubbling FB combustor.

Most of the research studies about morphological properties of sulfated Ca-based sorbents have been carried out under conventional combustion conditions [11, 15, 16]. However, as a consequence of the

very different conditions (regarding gas composition and temperature) existing in the oxy-fuel boiler, different morphological properties in the sorbents could be expected.

The main novelty of this work is focused on studying the morphological variations of the Ca-based sorbents during sulfation at oxy-fuel combustion conditions; especially the evolution with time of the external product layer of CaSO_4 at different operating conditions. For this purpose, sulfated sorbent samples obtained in a TGA were analyzed by the Scanning Electronic Microscope (SEM) technique.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used as calcium sorbent for the SEM analysis were two Spanish Ca-based sorbents, one limestone and one dolomite, in a narrow particle size interval between 0.1 and 0.2 mm. The sorbents were dry. The limestone used is mainly composed of CaCO_3 , whereas the dolomite is characterized by presenting a Ca/Mg molar ratio close to one ($\text{Ca/Mg} = 1.1$).

Since Ca-based sorbents can be used for the sulfur retention in calcining or non-calcining conditions, it is essential to know the main physical properties of raw and calcined sorbent. Table 1 shows the chemical composition and the physical properties of the sorbents used. Chemical composition was determined by inductively coupled plasma (ICP) analysis. Apparent density and porosity were determined by Helium pycnometry and mercury intrusion, respectively. As can be seen, these properties undergo great changes depending on whether the sorbent is raw, semi-calcined (dolomite case) or calcined. These variations are related to the different molar volume of the compounds (MgCO_3 or MgO and CaCO_3 or CaO). In all the cases, raw sorbents presented a high crystallization level which involves low porosity. During the calcination stage the sorbents develop a high porosity because the CaO molar volume is lower than that of CaCO_3 . Later, the porosity decreased during sulfation process because the CaSO_4 presented a higher molar volume than the CaO .

2.2. Characterization methodology

The sulfated sorbent samples were prepared in a TGA, Setaram TGC-85 type, described elsewhere [7]. The sample holder was a wire mesh platinum basket (8 mm diameter, 2 mm height). The reacting gas mixture containing SO₂, CO₂, O₂ and N₂, was controlled by specific electronic mass-flow controllers and it was introduced at the bottom of the reaction tube. In calcining conditions, the sorbents underwent two stages, calcination and sulfation, whereas in non-calcining conditions the sulfation was carried out over the raw sorbent. For each run, 30 mg of sample was put into the basket and rapidly introduced into the TGA reactor at the desired temperature and gas composition (N₂+CO₂+O₂). SO₂ was introduced after weight stabilization of calcined or non-calcined sample. The total gas flow was 10 lN/h to assure that neither external mass transfer nor inter-particle diffusion were affecting the sulfation reaction rate. The interval of temperature ranged from 800 to 975 °C, the CO₂ concentration from 15 to 80 vol.%, and the O₂ concentration from 4 to 40 vol.%. The SO₂ concentration was kept constant at 3000 vppm in all tests.

The sulfation conversion of the sorbents along time in both calcining ($X_{s,cal}$) and non-calcining conditions ($X_{s,non-cal}$) was calculated from the sample mass variation registered by the TGA as follow:

$$X_{s,cal}(t) = \frac{W(t) - W_{CaO}}{W_{CaSO_4} - W_{CaO}} \quad (1)$$

$$X_{s,non-cal}(t) = \frac{W(t) - W_{CaCO_3}}{W_{CaSO_4} - W_{CaCO_3}} \quad (2)$$

being $W(t)$ the mass of the sample at each time, W_{CaO} the initial mass of CaO, W_{CaCO_3} the initial mass of CaCO₃, and W_{CaSO_4} the mass of the sample assuming total conversion to CaSO₄.

The sulfated samples were kept in a desiccator to avoid hydration before analysis.

To analyse the internal section of the particles, particles were embedded in epoxy resin, cured overnight, cut and polished before SEM characterization. The morphology of the sorbents was analysed in a Scanning Electron Microscope (SEM) ISI- DS – 130 coupled to an ultra-thin window PGT Prism detector for energy dispersive X-ray (EDX).

3. RESULTS AND DISCUSSION

The effect of temperature (from 800 to 975 °C), CO₂ concentration (from 15 to 80 vol.%), and reaction times (15 min to 24 hours) on the sulfation process were analysed in a TGA to cover the possible conditions existing in a oxy-fuel FB combustor [17]. To follow the evolution with time of the CaSO₄ product layer, samples sulphated at different reaction times were obtained.

3.1. Effect of reaction time on product layer

The mean residence time of solids in CFBCs is an intrinsic variable of this type of boilers which can range up to 10-20 hours for particles just above 200 µm [18]. In addition, it has been demonstrated that the residual activity of the sorbent after blocking the outer pores during the sulfation process may be significant [7, 10, 11]. Therefore, it is expected that an increased residence time of the solids leads to higher sulfur retention values.

To get an insight into the evolution of the CaSO₄ product layer with respect to the residence time of the solids in the combustor, sulfated samples at different reaction times were prepared in the TGA and analyzed by SEM technique. These samples correspond to the points represented in the sulfation conversion curves showed in Fig. 2 for limestone and dolomite under calcining and non-calcining conditions. Figs 3 and 4 illustrate the evolution of the external and internal surface of sulfated particles of Granicarb limestone at different reaction times, both in calcining and non-calcining conditions, respectively.

Fig. 3A shows how the structure of the limestone is being closed during the first step of the sulfation reaction and therefore for short reaction times, 15 minutes, the product layer of CaSO₄ is not well defined because the external pores are not completely blocked. Subsequently in next picture (Fig. 3B) it can be seen that the CaSO₄ product layer has plugged the external pores and has completely covered the outer part of the particle indicating that the second reaction step has already started. This second step is characterized by producing a decrease in the sorbent reactivity whose sulfation pattern corresponds to the Shrinking Core Model (SCM) [9]. Likewise, the change of the mechanism of

reaction, between first and second step, can be graphically identified with the change in the slope of the sulfation curve obtained in TGA tests (see Fig. 2). Subsequently, as the sulfation reaction is proceeding, a continuous increase in the thickness of the CaSO_4 product layer and in the grain size of CaSO_4 were observed (Fig. 3C). So, for long reaction times, the thickness of the product layer might reach values near the radius of the limestone particle as it is shown in Fig. 3D. In addition, in this picture, two different structures of CaSO_4 product layer were observed.

The first one, corresponding to the inner part, was composed of small CaSO_4 crystals. The second one, corresponding to the outer part, was composed of CaSO_4 crystals with honeycomb-shaped structure. The space limitations as a consequence of the higher molar volume of CaSO_4 compared to CaO in the external surface of the particles make that the CaSO_4 product layer tend to grow outwards to form this honeycomb-shaped structure. Moreover, making a comparison between CaO and CaSO_4 grains, a significant increase in the grain size is observed during the sulfation stage not only due to the different molar volume but also to the agglomeration or coalescence of several grains.

In non-calcining conditions (see Fig. 4), the CaCO_3 grains are not well-distinguished in the inner part of the particle and exhibited a more compact appearance. However, some similarities with respect to the calcining conditions were observed, i.e. the sulfation pattern coincided with the SCM and an external honeycomb-shaped CaSO_4 product layer was developed. It should be remarked that this structure is formed at shorter reaction times as a consequence of the higher space limitations in the external layer of the limestone particles.

Hajaligol et al. [19] and Snow et al. [20] reported that the CO_2 released outside from direct sulfation reaction was capable of creating preferential ways which provided higher porosity and high sulfation conversion. Nevertheless, based on the SEM images taken in this work, negligible differences in the CaSO_4 product layer between calcining and non-calcining conditions were detected.

Regarding unreacted core at calcining conditions, previous studies found that CaO sintering produced important variations in sorbent structure [21]. This phenomenon affects sorbent reactivity especially in those processes where the time scales of sorbent decomposition and reaction are similar, e.g., the

calcination–sulfation in furnace sorbent injection processes (particle sizes below 80 μm and short reaction times, below minutes) [22]. In non-calcining conditions, de Diego et al. [23] observed that CaCO_3 sintering affected reaction rate during sulfidation at typical gasification conditions and particle sizes used in FB, but no relevant changes were observed in the morphological analysis of the particles. In a similar way, the morphological analysis of the unreacted core carried out in this work revealed negligible variations in the internal structure of the sorbent during long sulfation times despite their possible effect on reactivity.

In addition, the morphological changes suffered by dolomite in the product layer were masked due to the existence of MgO which provide an extra porosity to the particle (MgO behaves as inert solid during the sulfation process) (see Fig. 5). Previous studies demonstrated that dolomites are able to reach high sulfation conversions, near 1 with respect to Ca content, both in calcining and non-calcining conditions during oxyfuel combustion in fluidized beds [24], as observed in Fig. 3. The no space limitation as a consequence of the extra porosity avoided the honeycomb-shaped structure formation at any operating condition, even at high sulfation conversion. This characteristic was also maintained at semi-calcining conditions ($\text{CaCO}_3\text{-MgO}$).

3.2. Effect of temperature on the product layer

As stated above, temperature is an important variable in the sulfation process because depending on the CO_2 partial pressure used, the limestone will be sulfated under calcining or non-calcining conditions. This variable will highly affect the sulfation level reached by the sorbent. In addition, temperature may have a direct influence on morphological and structural properties of the sorbent.

To analyze the influence of the sintering phenomenon in the CaSO_4 product layer, several samples sulfated at different temperatures at long reaction times (24 hours) were studied. The SEM images of the external surface are shown in Fig. 6. Considering the high sulfation level of the particles, negligible differences for samples sulfated at temperatures below 900 $^\circ\text{C}$ and typical honeycomb-shape structure at the external layer were detected. This structure undergoes a slight change from 900

to 950 °C but the most relevant change was observed in the sulfated sorbent at 975 °C. Some researchers [25-27] found that high temperatures led to the sintering phenomenon of the sorbents decreasing their sulfation capacity. Therefore, this effect seems to be one of those responsible for decreasing the sorbent sulfation conversion at temperatures above 900 °C obtained in TGA [7]. However, Anthony and Granatstein, [14] and de las Obras-Loscertales et al. [24] reported that the existence of reducing conditions in localized parts of the bed are capable of producing the reverse sulfation reaction at high temperatures during operation in FB combustors. This phenomenon together with the sorbent sintering could be responsible for the optimum temperature found during the sulfur retention in oxy-fuel FB combustors, 900-925 °C (see Fig. 6).

Finally, it must be considered that the morphology of the calcium sulfate layer and the conversion degree can be modified by attrition phenomena [28, 29] and the presence of fuel-ashes [14] under real FB combustion conditions.

3.3. Effect of CO₂ concentration on the product layer.

Oxy-fuel combustion is based on burning the fuel with a mix of oxygen and a CO₂-rich recirculated flue gas stream in order to control the operating temperature in the combustor. Therefore, the CO₂ concentration is a key factor to be considered in the process when comparing with conventional air combustion process. As it was stated, Ca-based sorbent may operate under calcining or non-calcining conditions. Nevertheless, there is no an agreement with respect to the effect of CO₂ concentration on sulfation reaction. Some researchers found that the sulfation conversion was higher under non-calcining than under calcining conditions [19, 20]. They argued that the CaSO₄ product layer formed under non-calcining conditions was more porous than in calcining conditions due to the CO₂ flow released during the direct sulfation reaction (R3). However, Hu et al. [30] disagreed with this assumption since they consider that porosity is unlikely to be created from a diffusional flow of CO₂. Likewise, other authors [31-33] have observed that high CO₂ partial pressures reduce the sulfation reaction rate under certain operating conditions.

To analyze the influence of the CO₂ partial pressure on the CaSO₄ layer formed around the particles, SEM photographs of highly sulfated limestone at different CO₂ concentrations (15, 65 and 80 vol.%) were studied, which corresponded to both non-calcining and calcining conditions. As can be seen in Fig. 7, the outer surface of the particles exhibits similar structure and is not affected by the concentration of CO₂ at each specific condition, calcining or non-calcining. These results corroborated previous studies carried out by the research group [7, 8] where it was found that the main effect of CO₂ concentration on the sulfation process was associated with the fact of defining calcining or non-calcining conditions. An increase in CO₂ concentration shifted the temperature of CaCO₃ decomposition to higher values. However, once calcining or non-calcining conditions were reached, the effect of CO₂ could be considered negligible.

4. CONCLUSIONS

Morphological characterization of two Ca-based sorbents, one limestone and one dolomite, during the sulfation process was carried out at conditions kind of oxy-fuel CFB combustion. A TGA was employed to obtain the sulfated samples. The sorbent structure and the evolution of CaSO₄ product layer were analyzed by SEM-EDX technique.

Two different structures of CaSO₄ product layer were observed during limestone sulfation. The first one, corresponding to the inner part of particles, was composed of small CaSO₄ crystals. In contrast, the space limitations as a consequence of the higher molar volume of CaSO₄ compared to CaO in the external surface of the particles make that the CaSO₄ product layer trend to grow outwards to form a honeycomb-shaped structure. This structure was observed both in calcining and non-calcining conditions.

The honeycomb-shaped structure was never found during dolomite sulfation because the extra porosity developed during MgCO₃ calcination lead to the lack of space limitations. In this case, high sulfation conversions were reached in semi-calcining (CaCO₃-MgO) and calcining (MgO.CaO) conditions.

The morphological changes in the sulfated particles were analyzed in the whole range of temperatures from 850 to 975 °C. The honeycomb-shaped structure was observed at all temperatures, except to 975 °C, as a consequence of the severe sintering effect observed at values above 950 °C.

Eventually, the external surface of limestone particles was not affected by the CO₂ concentration in both calcining and non-calcining conditions.

Acknowledgment

This work has been supported by The Spanish Ministry of Science and Innovation (MICINN, Project: CTQ2008-05399/PPQ) and by the European Regional Development Fund (ERDF). M. de las Obras-Loscertales thanks to MICINN for the F.P.I. fellowship and A. Rufas to CSIC for the JAE fellowship.

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TABLES AND FIGURES

Table 1. Chemical analysis and physical properties of the sorbents.

| | Limestone | Dolomite |
|--|-----------|--------------|
| | Granicarb | Sierra Arcos |
| Composition (% wt) | | |
| CaCO ₃ | 97.1 | 52.5 |
| MgCO ₃ | 0.2 | 40.5 |
| Na ₂ O | 1.1 | <0.1 |
| SiO ₂ | <0.1 | 3.8 |
| Al ₂ O ₃ | <0.1 | 1.7 |
| Fe ₂ O ₃ | <0.1 | 0.6 |
| Apparent density (kg/m³) | | |
| Raw (CaCO ₃) | 2573 | 2512 |
| Semi-calcined (CaCO ₃ ·MgO)* | | 1912 |
| Calcined (CaO)** | 1578 | 1454 |
| Porosity (%) | | |
| Raw (CaCO ₃) | 3.7 | 9.5 |
| Semi-calcined (CaCO ₃ ·MgO)* | | 30.6 |
| Calcined (CaO)** | 49.0 | 51.7 |

* Calcined in CO₂ atmosphere at 850 °C during 10 minutes.

** Calcined in N₂ atmosphere at 900 °C during 10 minutes

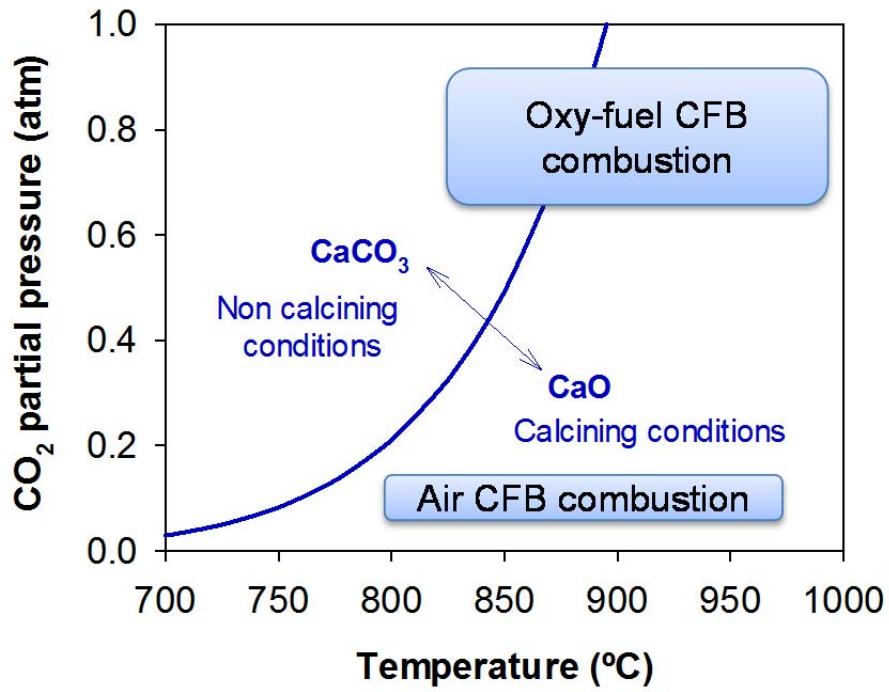


Fig. 1. Thermodynamic equilibrium curve of CaCO₃ calcination

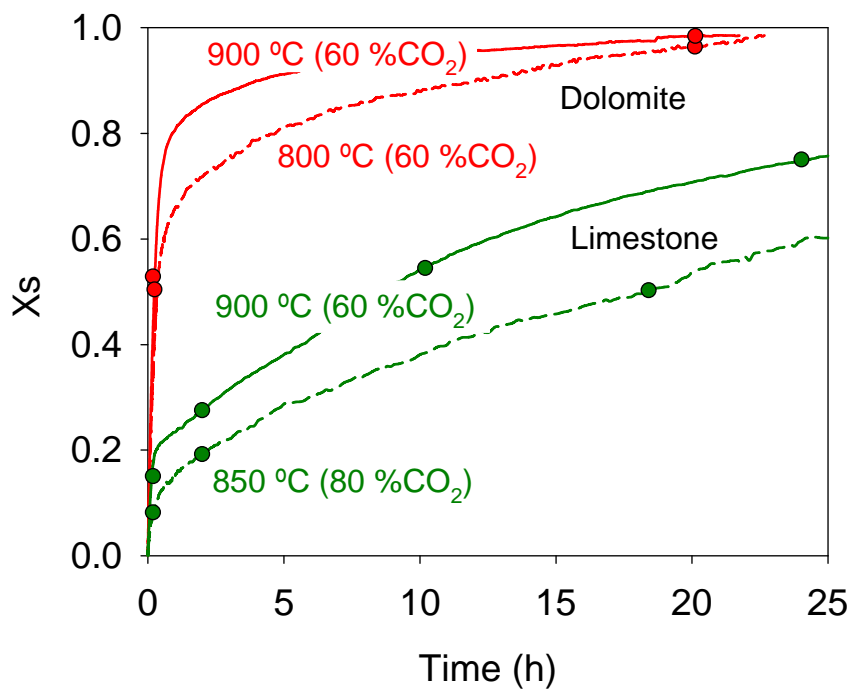


Fig. 2. Sulfation conversion curves in TGA. Symbols represent sulfated samples used for SEM characterization. — calcining and --- non-calcining conditions. SO₂=3000 vppm. dp=0.1-0.2 mm.

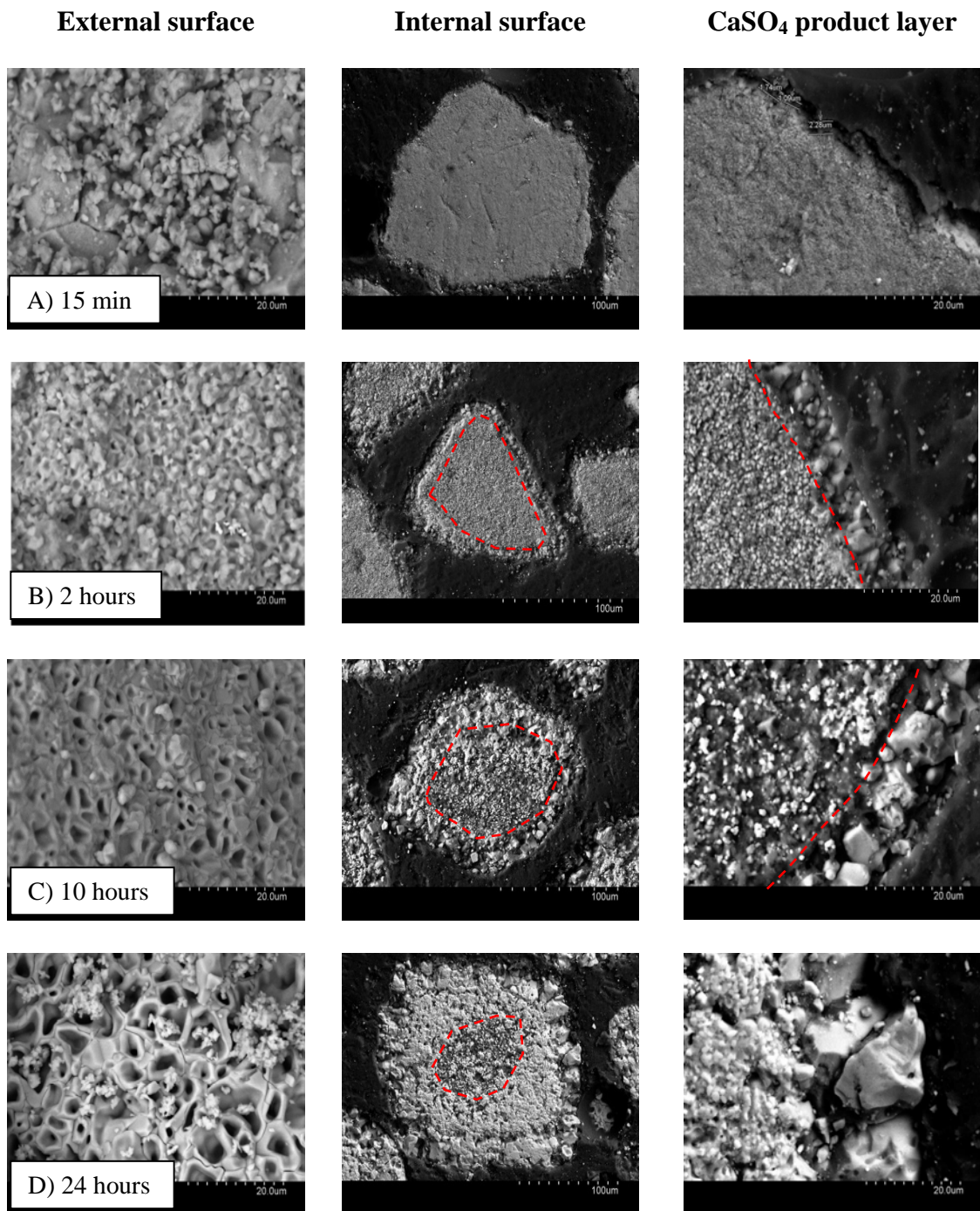


Fig. 3. SEM images of external and internal surface of Granicarb limestone in calcining conditions at different reaction times. 900 °C, 60% CO₂, 3000 ppm SO₂, dp= 0.1-0.2 mm.

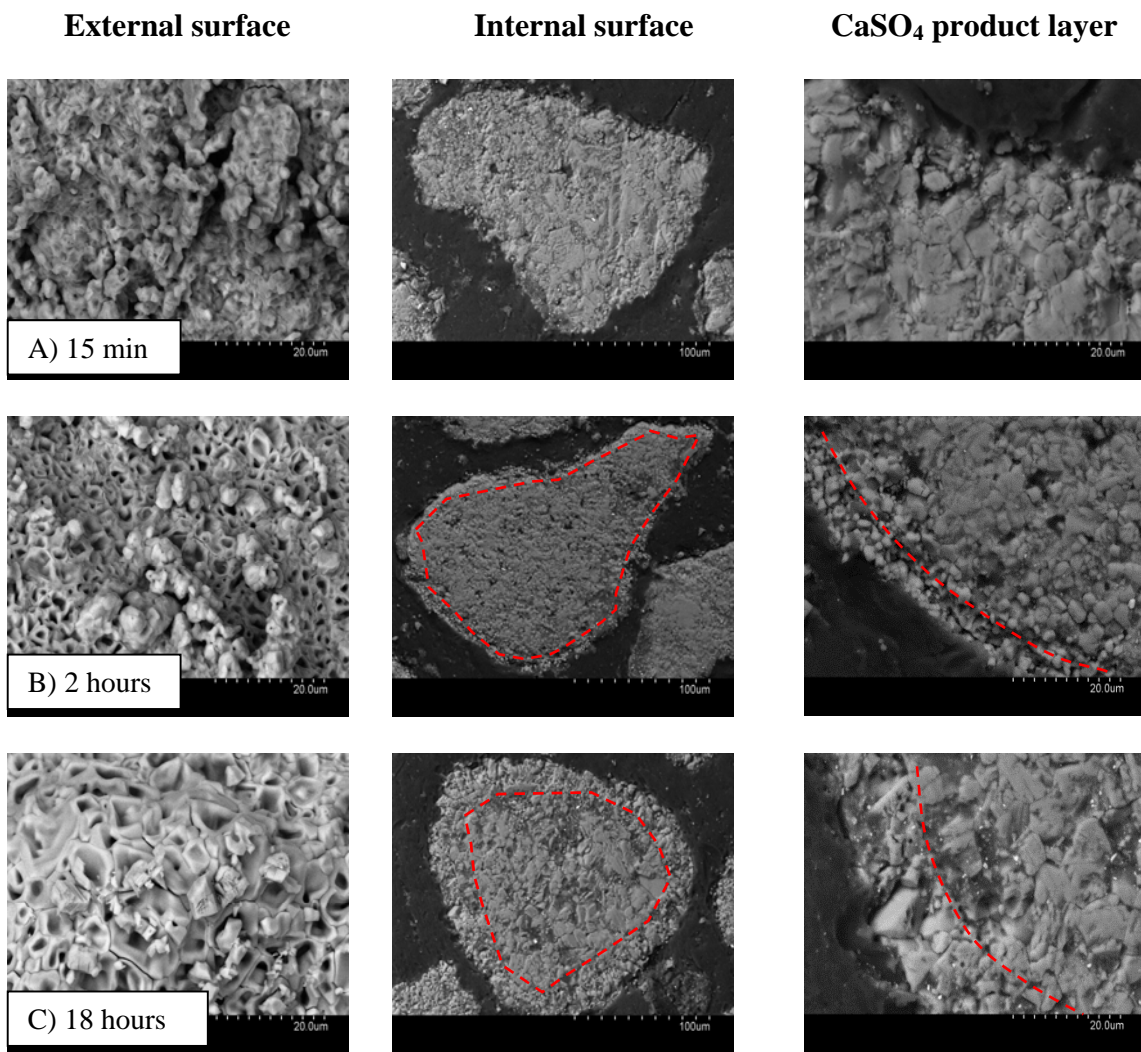


Fig. 4. SEM images of the external and internal surface of Granicarb limestone in non-calcining conditions at different reaction times. 850 °C, 80% CO₂, 3000 ppm SO₂, dp= 0.1-0.2 mm.

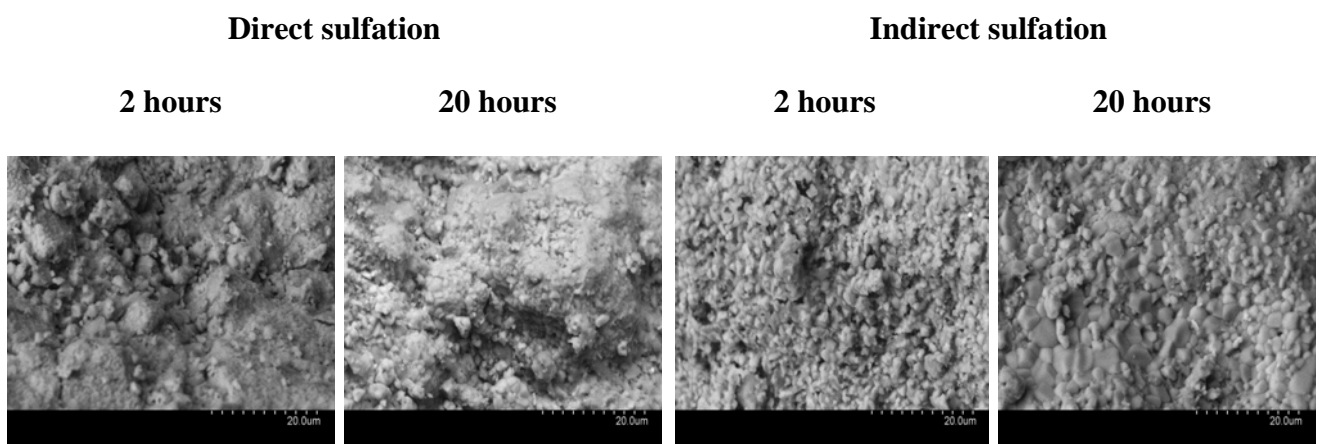


Fig. 5. SEM images of external CaSO_4 product layer of Sierra de Arcos dolomite at different reaction times. 60% CO_2 , 3000 ppm SO_2 , $d_p = 0.1\text{-}0.2$ mm. Direct sulfation (800°C) and indirect sulfation (900°C).

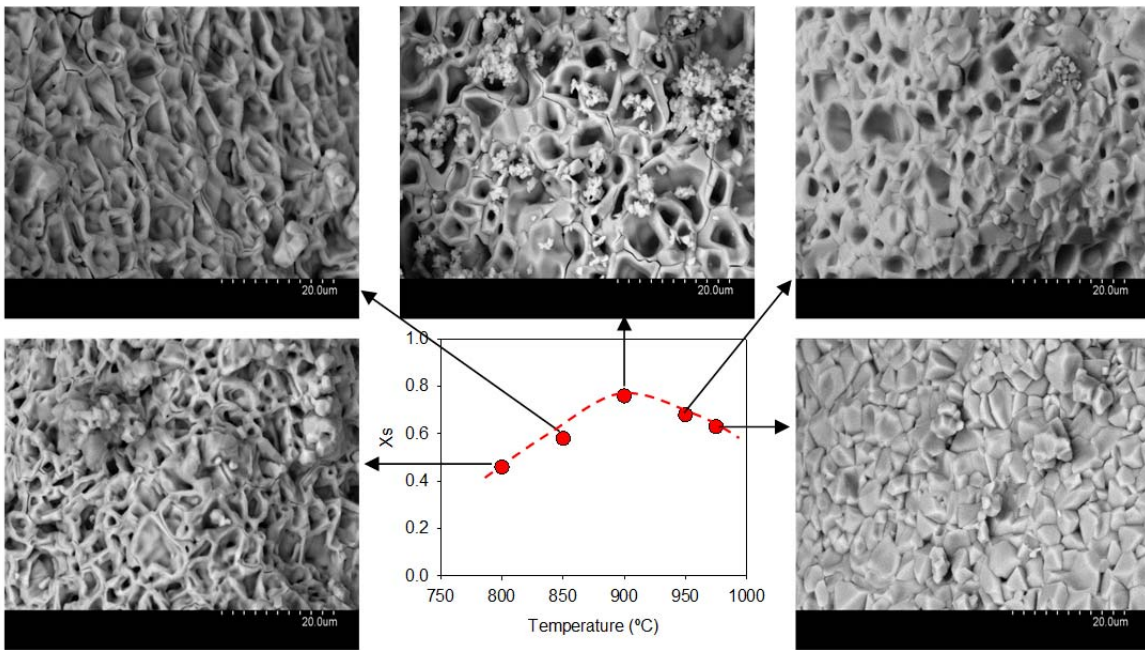


Fig. 6. SEM images of external surface of Granicarb limestone sulfated at different temperatures for 24 hours. 60% CO₂, 3000 ppm SO₂, dp= 0.1-0.2 mm.

Indirect sulfation

Direct sulfation

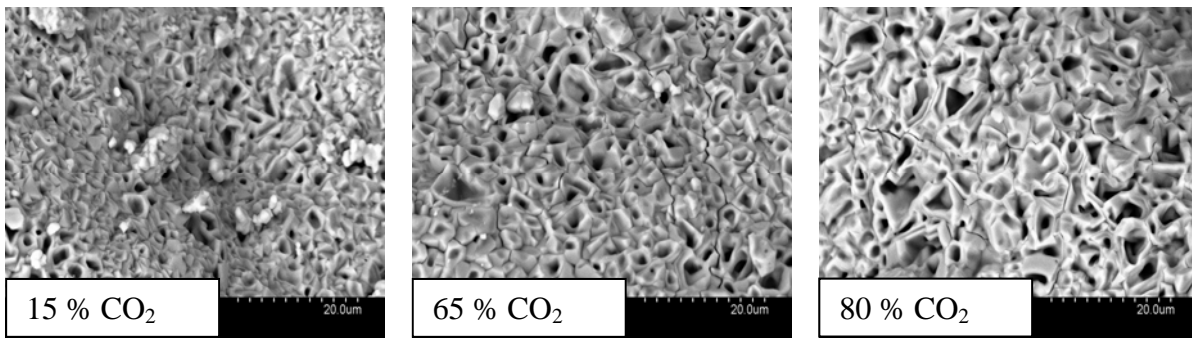


Fig. 7. SEM images of the external surface of Granicarb sulfated limestone for 24 hours at different CO₂ concentrations. 850 °C, 3000 ppm SO₂, dp= 0.1-0.2 mm.