

Experimental Investigation of Sulfation Phenomena in Calcium Looping Systems Integrated in Cement Plants

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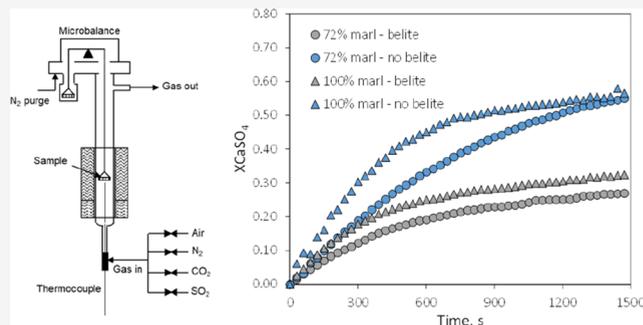
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ABSTRACT: The sulfation phenomena of raw meal materials involved in calcium looping (CaL) applications to capture CO₂ from cement plants are investigated. The effects on sulfur capture capacity and reaction rates of different raw meals, temperatures, SO₂ concentration, and degree of belite conversions have been investigated using a thermogravimetric analyzer. SO₂ is shown to react with both free CaO and CaO in belite. An apparent reaction order of 0.8 and activation energies of 20.9 and 34.7 kJ/mol were estimated for cases with no-belite and belite formations, respectively. Results indicate that CaL systems for CO₂ capture will also remove SO₂ emissions in cement plants.



INTRODUCTION

CO₂ capture technologies are recognized as essential to meet zero-emission targets for the cement industry by 2050.^{1–3} In recent years, calcium looping (CaL) is being confirmed as a very promising CO₂ capture technology for the cement production, especially when CaL systems are integrated in the production process.^{4–7} In such integrated CaL systems, there is a single oxy-fired calciner producing the calcined raw meal that is fed to the rotary kiln, where clinker is produced. Part of the calcined raw meal is directed to the carbonator, where the free and active CaO contained in the calcined raw meal will react with the CO₂ contained in the flue gases from the rotary kiln. The resulting carbonated solids are then separated from the CO₂-lean flue gases and returned to the oxy-fired calciner to recover the captured CO₂ in a high concentration form. Process details for integrated CaL systems can be found elsewhere.^{4–7}

Since CaCO₃ is the main component making up the raw meal of cement plants, the carbonator in CaL systems in cement plants will naturally work with high molar flow ratios of active CaO to CO₂ (F_0/F_{CO_2}). Such an F_0/F_{CO_2} ratio is known to lead to a high average activity of the sorbent (X_{ave}).⁸ However, when fresh raw meal is used as a CO₂ sorbent, the parallel reaction of belite formation decreases the value X_{ave} .^{9–11} Also, the presence of gas contaminants such as SO₂ will decrease and make an impact on X_{ave} as noted in an early paper by Li et al.,¹² where calcined raw meals are considered. On the other hand, different mathematical models have been developed for describing the sulfation phenomena of porous CaO under different conditions,^{13–18} and these models can be used as a basis to understand the sulfation of calcined raw

meals in CaL systems. However, there is great variability in the sulfation mechanism, apparent reaction orders (between 0.6 and 1), and activation energies (between 20 and 70 kJ/mol). In this context, the purpose of this work is to derive kinetic parameters of the sulfation reactions relevant for the calcined raw meals under operating conditions expected in the carbonator and calciner of CaL systems integrated in the cement plant. The chosen configuration is the highly integrated CaL system presented by De Lena et al. in ref 4 and being evaluated in the European project CLEANKER.⁵ The highly integrated CaL system differs from a standard Tail end CaL system (i) by the presence of a single calciner which has the dual function of regenerating the sorbent and preparing the material for the clinker burning phases in the rotary kiln and (ii) by the use of the raw meal as a CO₂ capture material in order to have a greater integration between the CO₂ capture process and the clinker production process. Such raw meals are typically composed by fine particles of CaO (dp_{50} in the range of 10–20 μm) and contain other calcium compounds (such as belite) with affinity for SO₂, for which there is currently a gap in information regarding the sulfation mechanism and reaction rates.

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EXPERIMENTAL SECTION

A schematic view of the thermogravimetric analyzer used in this work is shown in Figure 1, and it is described in detail

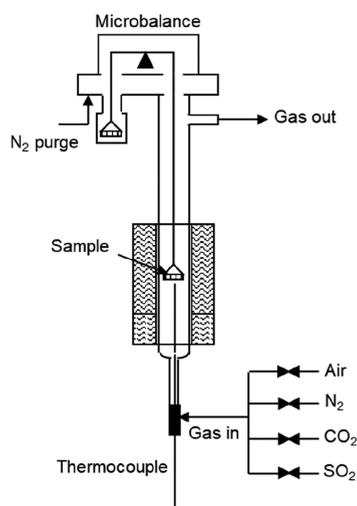


Figure 1. Schematic of the thermogravimetric analyzer used during experiments.

elsewhere.¹⁹ Briefly, the reactor consists of a mullite tube with a platinum-suspended basket in a double furnace system that works at different temperatures. The temperature and weight of the sample were continuously recorded on a computer by a thermocouple located near the basket. Commercial pressurized gas bottles were used to simulate the reaction atmosphere: CO₂ in air/N₂ and SO₂ in air.

The test procedure consisted of samples with an initial weight of about 2 mg (to avoid external mass diffusion effects) placed inside the basket of the thermogravimetric analyzer. The sample was first heated in air for the calcination step. Two calcination conditions were used regarding the kinetics of belite formation as the sorbents used in this work were previously studied.¹⁰ The first calcination condition was to heat up the sample in air atmosphere up to 800 °C and maintained for about 1 min to ensure total calcination and, at the same time, to avoid belite formation as much as possible. The second calcination condition was to carry out the calcination of the sample in air at 900 °C during 10 min, where it was estimated previously that the maximum possible amount of belite is formed.¹⁰ After this period of time, the sample was brought to the desired sulfation temperature and the atmosphere was switched to air containing SO₂. These operating conditions were maintained for 25 min. This procedure was performed for different sulfation temperatures (650, 800, 850, and 900 °C) and SO₂ concentrations (500–1000–1500–2000 ppm_{vol}). Finally, the impact of the nature and type of raw meal on sulfation was evaluated: two different raw meals were used, RM1 and RM2, whose compositions and particle size distributions are shown in Table 1 and Figure 2.

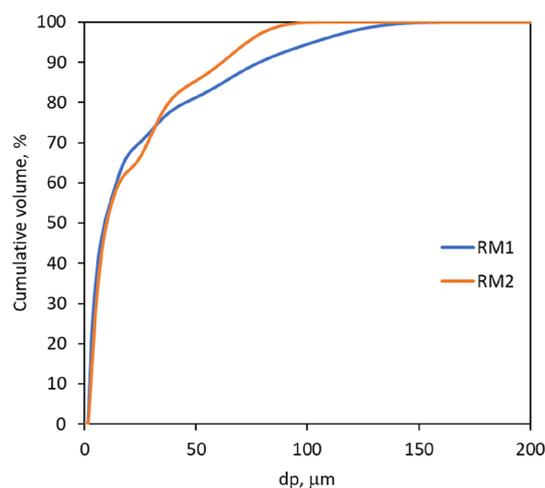


Figure 2. Particle size distributions of raw meals used.

As shown in Table 1, the chemical composition of both raw meals is similar. However, these two raw meals have been chosen because RM1 is composed mainly by a marl and RM2 is a mixture of 72%_{wt} of a marl and 28%_{wt} of a limestone (i.e., with almost one-third of CaCO₃ totally separated from the Si components at particle scale distances, and therefore, the reaction rate to form belite is slower than for a marl). The particle size distribution of RM2 shows three particle size ranges 0–20, 20–45, and 45–100 μm, whereas the particle size distribution of RM1 is more homogeneous in sizes. In spite of these differences, the average particle size of both materials is similar: 9 μm for RM1 and 10 μm for RM2.

The authors are aware of the inevitable approximation introduced in the experimental campaign by the use of a SO₂/air mixture which does not take into account the real composition of the flue gases in the two reactors. However, in the experiments under calcination conditions, it can be assured that the direct effect of other gases and other possible gas–solid reactions with CO₂ and steam will be negligible because these gases are not reactive with CaO at calcination temperatures above 900 °C.^{20–22} However, it is true that both CO₂ and steam are known to have an impact on sintering phenomena under calcination conditions. Such sintering alters the pore and surface structure of the Ca material and thus the sulfation rates. On the other hand, as far as carbonation conditions are concerned, the carbonation reaction can compete, in principle, with the sulfation reaction as it is a much faster reaction due to the 2–3 orders of magnitude larger concentrations of CO₂ with respect to the concentration of SO₂. However, it has been shown in previous studies with CaO that the sulfation of CaO can progress to similar or even higher Ca-conversion levels under carbonation conditions^{23–25} with respect to the sulfation of CaO. This is because the formation of CaSO₄ is thermodynamically favored with respect to CaCO₃.

Table 1. Chemical Composition of Raw Meals Used

raw meal	type	composition, % wt														
		CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	P ₂ O ₅	K ₂ O	TiO ₂	MnO	SrO	ZrO ₂	LOI	
RM1	100% marl	42.72	13.39	4.09	1.94	0.65	1.04	-	-	0.89	0.18	-	-	-	35.01	
RM2	72% marl 28% limestone	41.50	15.21	3.56	2.13	1.26	0.30	-	0.10	0.57	0.16	0.08	0.08	0.02	35.26	

RESULTS AND DISCUSSION

Figure 3 shows the evolution of the conversion of CaO in CaSO₄ (X_{CaSO_4}) for different temperatures, obtained using the raw meal RM2, considering an air flow with a SO₂ concentration of 500 ppm_{vol} at the thermogravimetric analyzer inlet for a calcination temperature of 800 °C (Figure 3a) and of 900 °C (Figure 3b).

The conversion of CaO in the raw meal to CaSO₄ (X_{CaSO_4}) is calculated through eq 1

$$X_{\text{CaSO}_4} = \frac{(W_t - W_{\text{calc}})}{80} \cdot \frac{56}{W_0 \times \frac{W_{\text{CaO}}}{56}} \quad (1)$$

where W_t is the weight during sulfation at time t , W_{calc} is the weight of calcined raw meal at sulfation temperature, W_0 is the weight of fresh raw meal, and W_{CaO} is the mass fraction of CaO in the fresh raw meal.

From the results shown in Figure 3, the presence of a fast initial period (kinetic stage) followed by a second period with a lower reaction rate during which X_{CaSO_4} tends to stabilize (diffusional stage) can be seen. Moreover, in both cases depicted in Figure 3, as the temperature increases, both the slope of the initial period and the final conversion of the material increase until 850 °C. This behavior is entirely analogous to what occurs for the sulfation of pure limestone.^{26,27} Moreover, the high Ca conversion achieved in the absence of belite (Figure 3a) is shown, in fact it is higher than 0.55 at all temperatures. These high conversions seem to indicate that the sulfation pattern tends to be a network or homogeneous sulfation pattern.²⁸ These sulfation patterns not only are favored by the small particle size related with these materials but also may be related with the fact that 65%_{wt} of CaO is in the marl where the structure is different to CaO in the calcite. Figure 3b shows how, in cases with high belite formation, calcination conditions affect both the slope of the initial period and the final conversion of the material. The latter is also related to the reaction between belite and sulphur to form CaSO₄, which is in fact known to occur in a temperature range between 550 and 1150 °C.²⁹ As mentioned above, increasing both the calcination temperature and time promotes the formation of belite. Belite formation during RM2 calcination at 900 °C was demonstrated experimentally and analyzed by Alonso et al.¹⁰ Exploiting the results and methodology in ref 10, it is also possible to demonstrate the simultaneous presence of the two reactions mentioned above. As proposed by Alonso et al.,¹⁰ the total amount of CaO converted to belite (X_B) can be calculated from eq 2.

$$X_B = 1 - \frac{X_{\text{carb}}}{X_{\text{max}}} \quad (2)$$

where X_{carb} is the carbonation conversion measured at the end of the carbonation period and X_{max} is the degree of carbonation that should be achieved if no belite is formed and, therefore, it is only function of the raw meal used. To measure the value of X_{max} the methodology described by Alonso et al.¹⁰ was followed: the raw meal was calcined at 800 °C for 1 min in air, cooled to 650 °C, and carbonated in an atmosphere consisting of 10%_{vol} of CO₂ and 90%_{vol} of air for 5 min, obtaining for RM2 an X_{max} of about 0.64. To determine the value of X_{carb} , a carbonation test (90% air and 10% CO₂, for 5 min) was conducted on a sample of approximately 2 mg of RM2 after it

was previously calcined in air for 10 min at 900 °C: an X_{carb} value of about 0.23 was found. Therefore, the fraction of belite formed is about 0.64; thus, the fraction of free CaO is about 0.36. As shown in Figure 3b, the final conversion of the material is always higher than 0.4 (except for the case at 650 °C); therefore, also the CaO in the belite participates together with free CaO to form CaSO₄. In order to confirm the only presence of CaSO₄ as a sulfated species, an XRD analysis was conducted on the sample from the 900 °C sulfation test (calcination at 900 °C) and is shown in Figure 4.

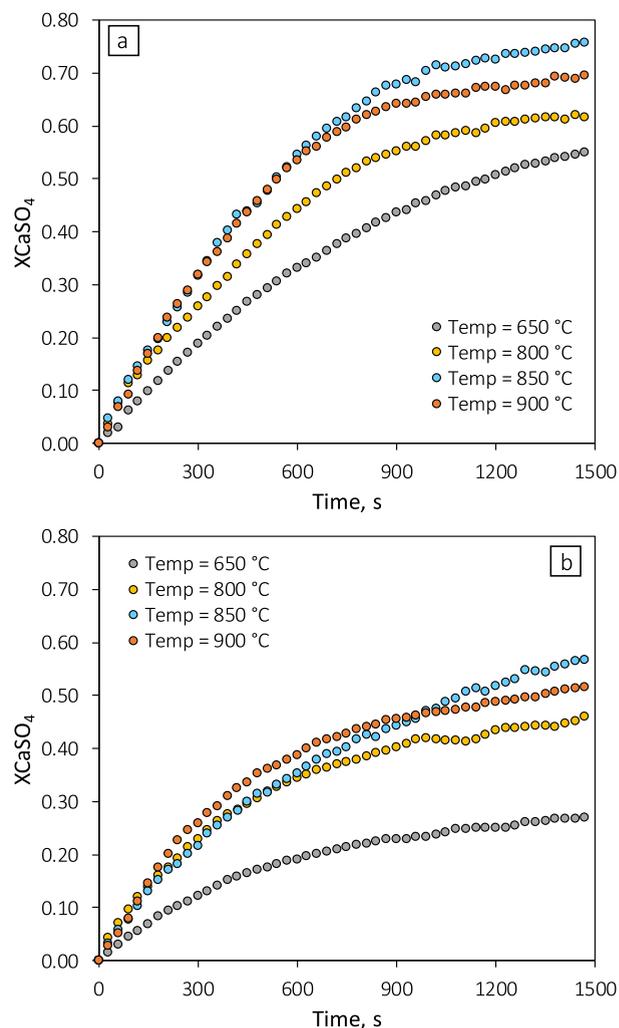


Figure 3. Effect of sulfation temperature on X_{CaSO_4} in the case with (a) calcination temperature of 800 °C and a time of calcination of 1 min, i.e. low belite formation case and (b) calcination temperature of 900 °C and calcination time of 10 min, i.e. high belite formation case (raw meal: RM2, SO₂: 500 ppm_{vol}).

Hence, the reaction rates observed in this second case are due to two simultaneous sulfation reactions. When the slopes and final conversions achieved under maximum belite formation and without the presence of belite are compared, it can be inferred that the sulfation reaction rate of belite should be slower than the reaction rate of CaO whenever it was (i.e., in the marl or in the lime). In addition, the final conversions achieved were lower than the conversions achieved under no presence of belite, probably by the increase in the diffusion resistance of SO₃ across the product layer.

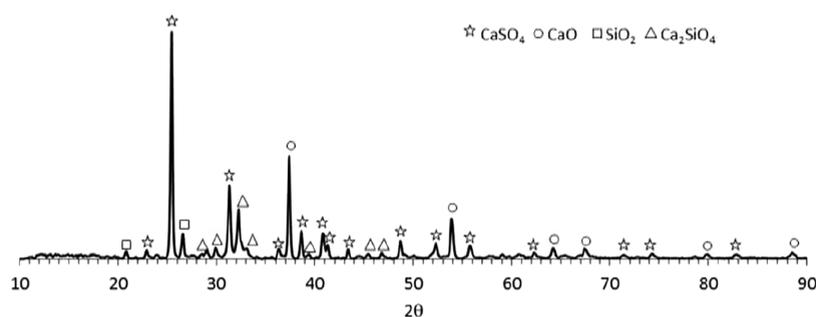


Figure 4. XRD spectra of sulfated calcined RM2 ($T_{\text{sulf}}: 900\text{ }^{\circ}\text{C}$, $\text{SO}_2: 500\text{ ppm}_{\text{vol}}$).

Figure 5 shows the time evolution of X_{CaSO_4} for RM2 for an operating temperature of $650\text{ }^{\circ}\text{C}$ and varying SO_2 concen-

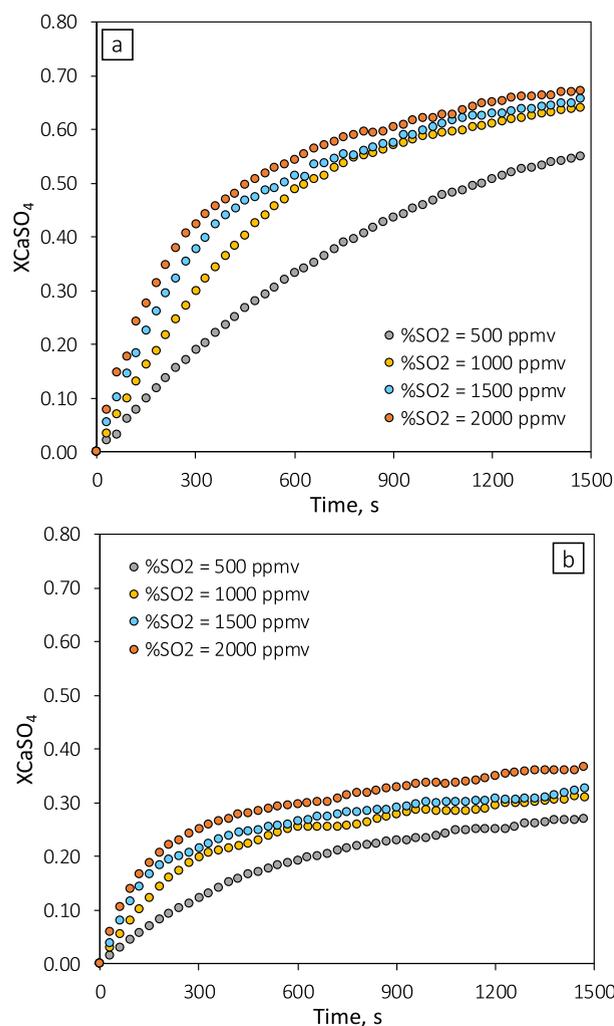


Figure 5. Effect of SO_2 concentration on X_{CaSO_4} in the case with (a) calcination temperature of $800\text{ }^{\circ}\text{C}$ and a time of calcination of 1 min and (b) calcination temperature of $900\text{ }^{\circ}\text{C}$ and a calcination time of 10 min (raw meal: RM2, $T_{\text{sulf}}: 650\text{ }^{\circ}\text{C}$).

tration (between 500 and $2000\text{ ppm}_{\text{vol}}$) in the inlet gas mixture. Also, for these tests, both calcination conditions described above are presented (Figure 5a calcination at $800\text{ }^{\circ}\text{C}$ and Figure 5b calcination at $900\text{ }^{\circ}\text{C}$).

As the SO_2 concentration increases, both the slope of the initial stage and the final conversion of the material increase,

similar to a pure limestone.^{14–17,30} Also in this case, as the temperature and calcination time increase, both the slope of the kinetic stage and the final conversion of the sorbent decrease. This behavior can also be attributed to the presence of belite in much the same way as described above.

The impact of the nature of the raw meal on sulfation was also evaluated, and RM2 was compared to RM1 composed of pure marl. As can be observed in Figure 6, where a comparison

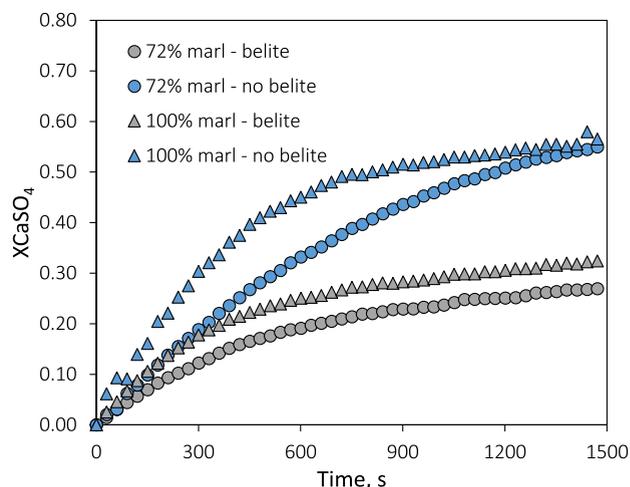


Figure 6. Comparison between X_{CaSO_4} for RM1 (triangles) and RM2 (circles) for both the calcination conditions considered in this work ($T_{\text{sulf}}: 650\text{ }^{\circ}\text{C}$, $\text{SO}_2: 500\text{ ppm}_{\text{vol}}$).

between these two raw meals is shown in the case of sulfation at $650\text{ }^{\circ}\text{C}$ and $500\text{ ppm}_{\text{vol}}$ of SO_2 , the reaction is strongly dependent on the nature of the raw meal itself, in terms of both the reaction rate in the kinetic stage and final conversion of the material.

RM1 has higher values for the slope of the initial period, compared to RM2, for both calcination conditions considered. This is may be because in RM1, all CaO is in the marl structure, whereas in RM2, only the 65% of CaO is in the marl and the remaining is in the calcined calcite form. It seems that the structures of calcined marls are wider-opened than the calcite and hence the diffusion of SO_2 to CaO is facilitated and the pore plugging effect is mostly prevented. The belite presence effect seems to be similar for both raw meals by decreasing the reaction rates in the initial stage. Although, the final conversion of RM1, compared to the results obtained for RM2, is higher for the case with the most severe calcination conditions.

As Figures 3, 5, and 6 show, raw meals can be an efficient SO_2 -sorbent material in both reactors of the CaL system.

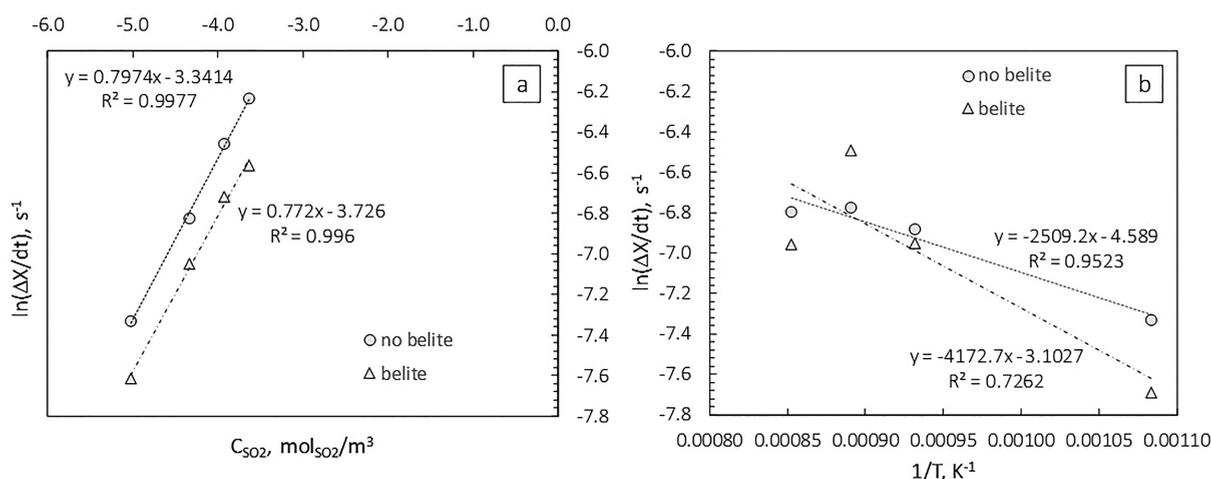


Figure 7. (a) Maximum reaction rate vs SO_2 concentration and (b) maximum reaction rate vs $1/\text{temperature}$ for minimum belite formation (circles) and maximum belite formation (triangles).

Although the generated CaSO_4 cannot be regenerated under the operating conditions of the reactors, the large Ca/S ratio and low number of carbonation–calcination cycles expected would turn both the entrained flow reactors into efficient SO_2 abatement systems, as is the case in other CaL systems.³¹

By analyzing the maximum sulfation rate ($\Delta X/\Delta t$) for the initial period (up to reaction times of 200 s), an apparent reaction order of raw meal sulfation can be determined for the two calcination conditions considered in this work. In Figure 7a, $\Delta X/\Delta t$ is represented against the SO_2 concentration and a good linearity can be observed. In particular, the apparent reaction order for raw meal sulfation is 0.8 and is independent of the presence of belite (and therefore of the temperature and calcination time), as depicted in Figure 7a. Moreover, this value is perfectly in line with the values found in the literature for pure limestone (between 0.6 and 1).^{14–17,30,32}

The activation energy of the kinetic stage (E_{act}) was estimated for both conditions (i.e., without belite and in the presence of belite), as shown in Figure 7b, where $\Delta X/\Delta t$ is represented against $1/T$. In the case of no belite formation, an E_{act} of about 20.9 kJ/mol is obtained, which is similar to the E_{act} values for a pure limestone.^{30,32,33} Instead, in the case of maximum belite formation, the E_{act} of the sulfation reaction increases slightly and is about 34.7 kJ/mol but in the same range of values reported for limestones.^{14,30,31,34,35} Figure 7b shows a scattering of the experimental data for the case with belite, resulting in an R^2 of about 0.73. This is due to the fact that these are natural materials, containing mixtures of components and subject to secondary reactions, and under such conditions, such scattering of data is inevitable.

Whereas this raw material is typically used in entrained flow reactors, the period of greatest interest is the kinetic stage. In fact, the raw meal has been recently proposed as a CO_2 sorbent for the CaL technology applied to cement plants. In this context, the residence time of the raw meal in the various reactors is of the order of magnitude of tens of seconds. Therefore, to estimate X_{CaSO_4} , it is possible to use a simple equation of the type of

$$X_{\text{CaSO}_4}(t) = A \cdot \exp\left(-\frac{E_{\text{act}}}{RT}\right) \cdot C_{\text{SO}_2}^{\alpha} \cdot t \quad (3)$$

where α is the apparent reaction order, T is the temperature (in K), C_{SO_2} is the SO_2 concentration (in ppm_{vol}), t is the time

(in seconds), R is the universal gas constant, and A is the pre-exponential factor which best fits the experimental data. The A values obtained are 16.8 and 4.4 s^{-1} for cases without belite formation and with belite formation, respectively.

CONCLUSIONS

In this work, the sulfation of raw meal was analyzed considering two different calcination conditions. It has been experimentally verified that the operating conditions under which calcination takes place deeply influence X_{CaSO_4} in terms of both maximum conversion and reaction rate in the kinetic stage. This is mainly due to the formation of belite during calcination. In particular, it was observed that:

- if calcination occurs at relatively low temperatures and for short times, belite formation is minimized and raw meal sulfation follows a network or homogeneous sulfation patterns that maximize the CaO utilization
- if calcination occurs at elevated temperatures and for long times, belite formation is maximized and raw meal sulfation shows both lower final conversion and kinetic period slope than in the case without belite formation.

It has also been experimentally observed that not only free CaO but also CaO present in belite reacts with sulfur to form CaSO_4 . The reaction between belite and sulfur should be at a lower reaction rate than the reaction rate of CaO that causes the decrease in the overall reaction rates measured and the final CaO conversion. In addition, the calcined marl structures seem to be wider-opened than the structure of some calcites, facilitating the reaction between SO_2 and CaO and translating into higher reaction rates.

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Notes

The authors declare no competing financial interest.

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