

LIMESTONE IN FLUE GAS DESULPHURISATION IN OXYGEN-ENRICHED ATMOSPHERES. PART II: THE EFFECT OF CO₂ ON DIRECT LIMESTONE SULPHATION

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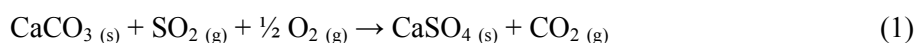
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The article presents tests carried out on three selected samples of limestone originating from three commercially exploited deposits. The tests of sorbents included desulphurisation in different atmospheres and a physicochemical analysis of desulphurisation products. The aim of the tests was to determine desulphurisation efficiency and conversion degree as dependent on the concentration of O₂ and CO₂.

Keywords: limestone, direct sulphation, conversion degree, desulphurization efficiency

1. INTRODUCTION

Limestone is a sorbent that is most commonly used in processes of dry flue gas desulphurisation in power plants equipped with circulatory fluidized-bed boilers. The dry flue gas desulphurisation process involves feeding of dry sorbent to the boiler's combustion chamber. If the partial pressure of CO₂ in the system is lower than the equilibrium pressure of limestone decomposition, direct limestone sulphation reactions will occur; If, on the other hand, the system CO₂ partial pressure is higher than the equilibrium pressure of limestone decomposition, the process of direct limestone sulphation will take place in the boiler. This type of reaction is represented by the equation below (Guilin Hu et al., 2007):



Direct sulphation is influenced by many factors. As reported in the literature, out of these factors, temperature should be distinguished, as it has a significant effect on the limestone conversion degree. The sulphation degree increases with temperature (Chuanmin Chen et al., 2006). An important role is also played by the effect of temperature on the sinterability of the sorbent surface, which may have a considerable effect of reducing the sorbent specific surface. This, however, does not need to imply the loss of microporosity (Guilin Hu et al., 2006).

The product layer that forms in a direct sulphating process is porous and brittle. The pore size increases with an increasing temperature. Changes in the pore structure with changes in temperature have a significant influence both on the sulphation reaction and on the product layer (Guilin Hu et al., 2006).

Direct sulphating is also affected by combustion gases, such as CO₂, SO₂ and O₂. The rate of the reaction and limestone transformation increases with the increase in SO₂ concentration. Figure 1 represents the process of direct sulphating as dependent on the concentration of SO₂ in a mixture of

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synthetic gases (Chuanmin Chen et al., 2006). An increase in SO_2 concentration accelerates the diffusion of SO_2 into limestone pores, thus speeding up the liberation of CO from sorbent particles (Spartions and Vayenas, 1991).

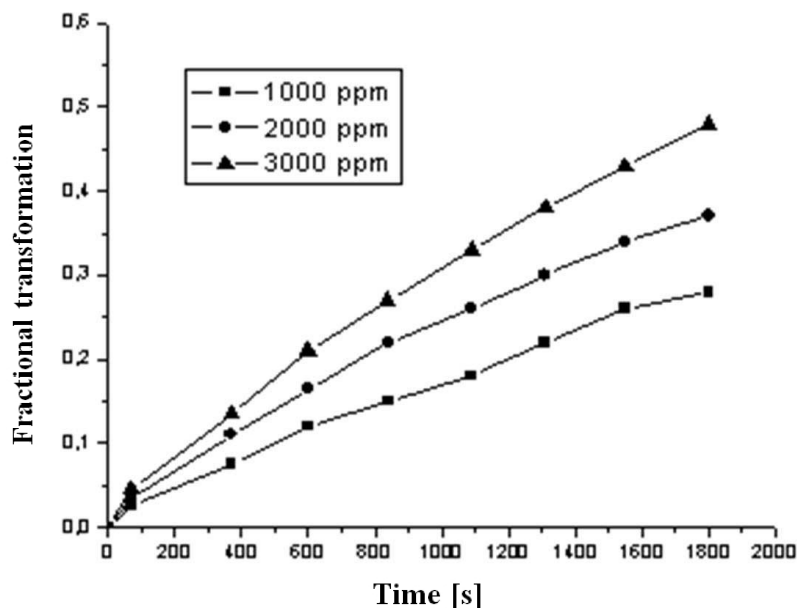


Fig. 1. Effect of SO_2 concentration for the transformation of CaCO_3 into CaSO_4 during direct sulphation of limestone (Chuanmin Chen et al., 2006)

An increased CO_2 concentration slows down direct sulphation. A lower sulphation rate at a higher CO_2 concentration is associated with slower diffusion of the CO_2 released from limestone particles (Guilin Hu et al., 2006; Ulerich et al., 1980).

The pressure system has also a significant influence on direct sulphation. In systems with an increased pressure, this reaction might be considerably inhibited. This implies that the rate of diffusion through the sorbent layer is lower in a higher pressure system (Guilin Hu et al., 2006).

Limestones differ reactivity, which results from the differences in their geological age that translates into the structure and morphology of sorbents, as well as their chemical composition, which ultimately shapes their sorption properties (Szymanek, 2008).

The effectiveness of direct sulphation can be improved by using additives, including alkaline metal salts. An improvement of sulphation effectiveness by additions is associated with the capability to enhance ion mobility in the sorbent solid phase (Guilin Hu et al., 2007; Fuertes and Fernandez, 1996). Also an addition of MgCO_3 can have an effect of considerably increasing direct sulphation rate. This addition is distinguished by a lower decomposition temperature, a higher equilibrium pressure value and a larger specific surface compared to CaCO_3 (Guilin Hu et al., 2007; Zevenhoven et al., 1998).

2. METHODOLOGY

Three limestone samples selected previously, derived from three commercially exploited deposits, were subjected to testing.

Physicochemical examinations of limestones after desulphurization were carried out using the following testing methodologies:

- Calcium content determination – by a volumetric method with EDTA – which involves compleximetric titration of calcium with a standard disodium versenate solution in the presence of Patton and Reeder's indicator, after prior dissolving of the sample in a diluted hydrochloric acid solution. Any possible effect of interfering cations (Fe, Al) is removed by an addition of triethanolamine.
- Determination of carbonates (CO₂) – by a gravimetric method – which involves acidimetric titration of the excess of the standard hydrochloric acid solution, added to the sample solution to decompose carbonates, with a standard NaOH solution in the presence of the orange indicator.
- Determination of sulphate sulphur (S_{SO₄}) content by the gravimetric method. The principle behind this method involves precipitation of sulphates in the form of barium sulphate using barium chloride in an acid medium and then gravimetric determination of the sulphate contents.
- Determination of free calcium oxide (CaO_{free}) by the volumetric method. The principle of this method relies on the extraction of free calcium oxide using ethylene glycol in a water-free medium and titration of leachate ions with hydrochloric acid.
- Determination of Mg content by the optical emission spectrometry method. The principle of this method relies on pressure microwave mineralisation of a test weighed sample in the system of concentrated mineral acids (HCl, HNO₃, HF). In the obtained mineralizates, the intensity of emitted radiation of a wavelength characteristic of a given element is measured by the optical emission spectrometry technique with excitation in inductively coupled argon plasma (ICP-OES).
- Determination of the pH reaction by the electrometric method. The method involves the measurement of the electromotive force (EMF) of the cell composed of the measuring electrode and the reference electrode, both being immersed in the test solution. The measured potential is proportional to hydrogen ion concentration, that is to the pH. 1% suspensions which were subjected to the tests.
- Identification of phase composition by the infrared spectroscopy (FTIR) method. The sample spectrum was obtained by the Attenuated Total Reflection (ATR) method. Thus obtained reflection spectra were compared with the reference material spectrum. The spectrometer's software makes it possible to compare a sample spectrum with the reference spectrum and to determine the extent in which the spectrum under examination is consistent with the standard spectrum (qualitative analysis).

The desulphurisation test was carried out on a laboratory stand as shown in Figure 2. The main component of the test stand was an electric furnace with a quartz column placed in it.

Calcium carbonate and the model gas containing sulphur dioxide, oxygen and carbon dioxide were fed to the column. The reaction chamber temperature was 850°C and it was maintained at a constant level for the duration of the experiment. The flow of sulphur dioxide was controlled using a double control system consisting of a regulator coupled with a rotameter, and a mass flow controller. The flow of the remaining gases was controlled and regulated using regulators and rotameters. Concentrations of individual gas components at the column outlet were also measured using a FTIR type flue gas analyser.

The conversion degree X was determined based on variations in sulphur dioxide concentration during the test and the initial concentration, as well as the amount of calcium oxide fed to the reaction column. Calcium oxide from the limestone was assayed in a chemical analysis prior to the test. The calculation was made following the equation below.

$$X = \frac{V_s \cdot R \cdot T}{w \cdot P} \int_0^t (C_0 - C_f) dt \quad (2)$$

Desulphurisation efficiency was calculated from the obtained average SO₂ concentration in the flue gas and the calculated SO₂ concentration, assuming 100% conversion of S to SO₂.

$$\eta = \frac{C_{TSO_2} - C_{SO_2}}{C_{TSO_2}} \quad (3)$$

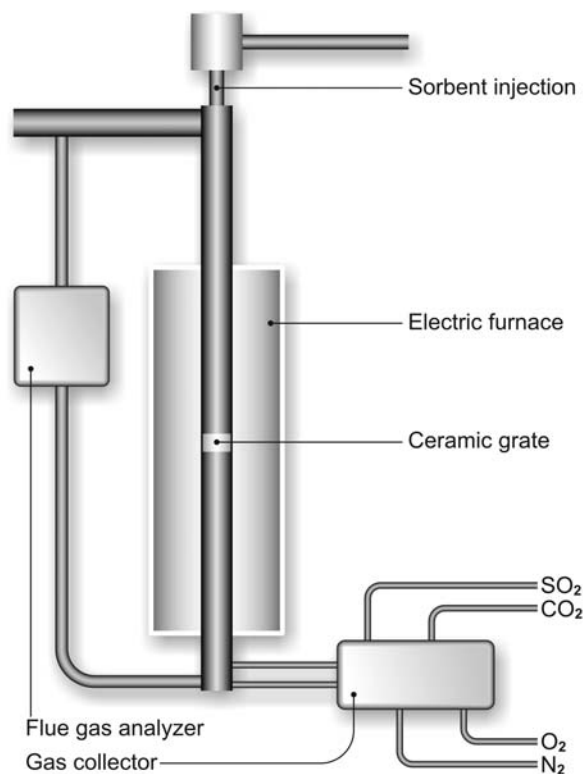


Fig. 2. Reactivity test stand

3. ANALYSIS OF THE OBTAINED RESULTS

3.1. Desulphurisation tests

The tests were carried out following the adopted methodology, and the results are presented in the successive figures. A mixture of gases in the model flue gas stream was used, while using, respectively: 20%, 40%, 60% and 80% of CO₂.

Figure 3 represents the variations in SO₂ concentration with time when feeding the sorbent to the reactor chamber. As the sorbent, limestone originating from the Jurassic geological period was used. Figure 4 shows the relationship of SO₂ concentration variation with time with sorbent originating from the Tertiary geological period. Figure 5 represents the relationship of SO₂ concentration variation with sorbent originating from the Viséan age.

Table 1 summarises the obtained flue gas desulphurisation efficiencies for all the sorbents at a CO₂ concentration of 80% and 20%, respectively.

Based on the carried out tests, a full relationship between desulphurisation efficiency and flue gas CO₂ concentration was positively found. The lowest value was obtained for a CO₂ content of 80%, which amounted to 29.5% (Sorbent I), 19.4% (Sorbent II) and 27.1% (Sorbent III); while the highest value was obtained for 20% CO₂, amounting to 74.7 (Sorbent I), 93% (Sorbent II) and 74.5 (Sorbent III). The best desulphurisation efficiency was exhibited by Sorbent II.

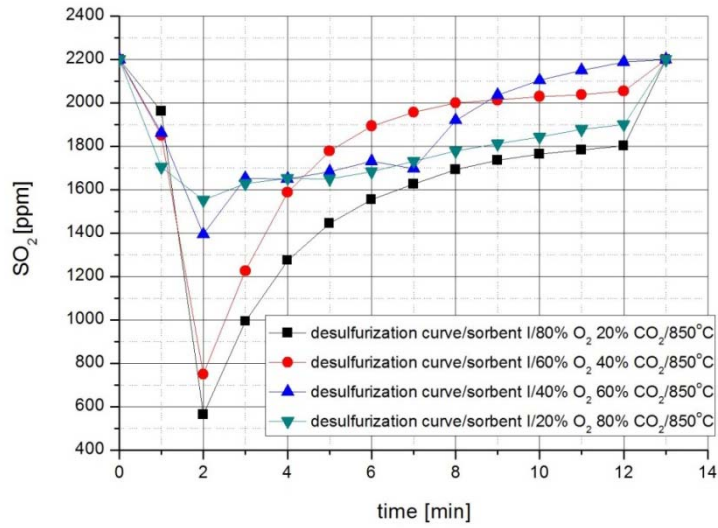


Fig. 3. Variations in SO₂ concentration as a function of model gas composition for Sorbent I

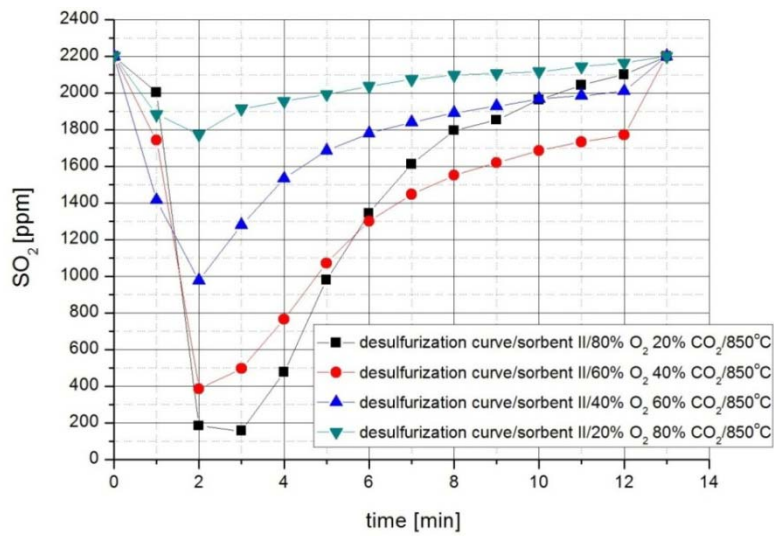


Fig. 4. Variations in SO₂ concentration as a function of model gas composition for Sorbent II

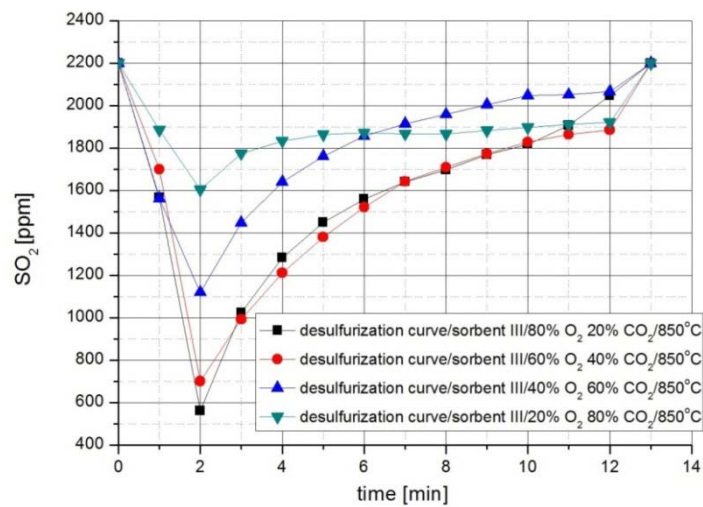


Fig. 5. Variations in SO₂ concentration as a function of model gas composition for Sorbent III

Table 1. Desulphurization efficiency

Flue gas desulfurisation efficiency [%]			
	SORBENT I	SORBENT II	SORBENT III
80% CO ₂	29.5	19.4	27.1
20% CO ₂	74.7	93	74.5

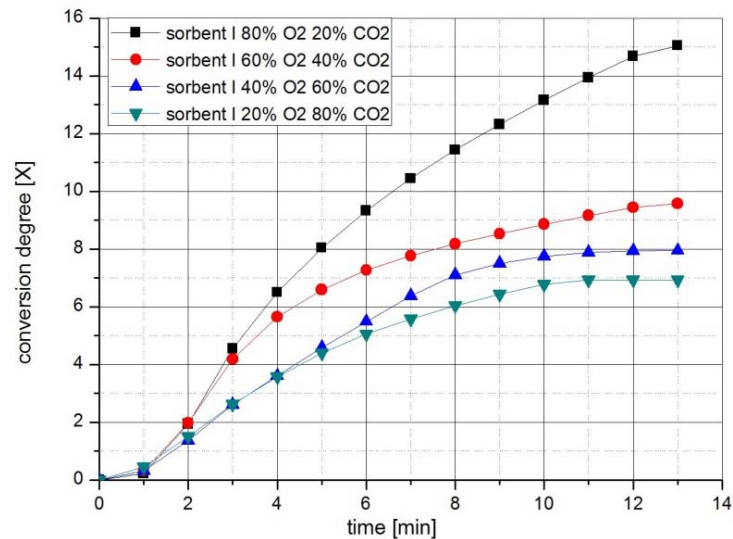


Fig. 6. Variations of the conversion degree as a function of CO₂ concentration in the model gas mixture for Sorbent I

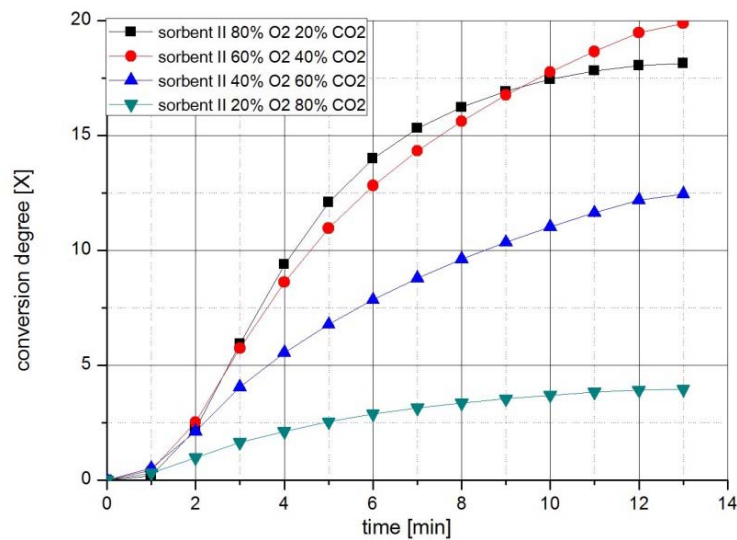


Fig. 7. Variations of the conversion degree as a function of CO₂ concentration in the model gas mixture for Sorbent II

The subsequent figures illustrate the variation of the conversion degree X with time for the three tested sorbents. Figure 6 shows Sorbent I. Figure 7 illustrates the above-mentioned relationships for Sorbent II. Figure 8 shows the variations of the conversion degree for Sorbent III.

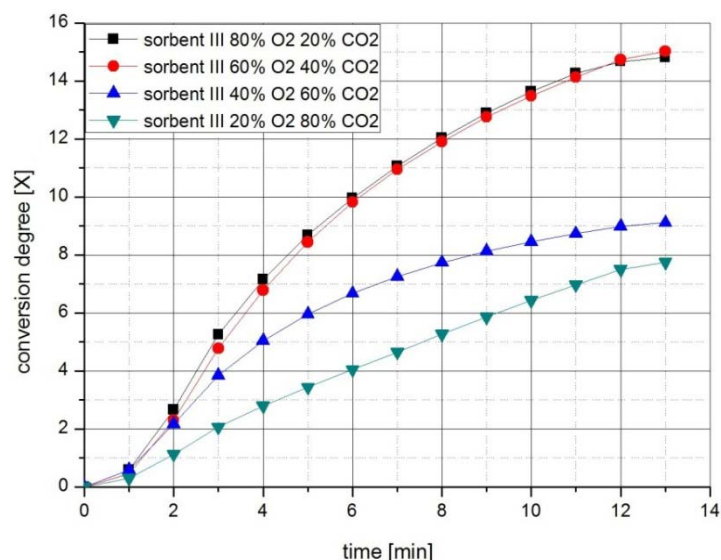


Fig. 8. Variations of the conversion degree as a function of CO₂ concentration in the model gas mixture for Sorbent III

It was found in the performed tests that the conversion degree decreases with the increase in CO₂ concentration from 15% at 20% CO₂ to 6.9% at 80% CO₂ for Sorbent I; from 18% at 20% CO₂ to 3.9% at 80% CO₂ for Sorbent II; and from 15% at 20% CO₂ to 7.7% at 80% CO₂ for Sorbent III.

3.2. Physicochemical analysis of the used sorbent

The physicochemical examinations included the evaluation of desulphurisation products based on the results of chemical composition analysis and the identification of the phase composition by the infrared spectroscopy (FTIR) technique.

Table 2 shows the chemical composition analysis results for the flue gas desulphurisation products.

Table 2. Chemical composition analysis results

Determined parameter	Desulphurisation product tested		
	Sorbent I	Sorbent II	Sorbent III
Ca content, [%]	38.5	34.5	36.4
SO ₄ content, [%]	6.41	19.2	12.4
CO ₂ content, [%]	37.0	32.0	33.2
Mg content, [%]	0.15	0.12	0.32
CaO _{free} content, [%]	1.48	3.29	0.14
1% suspension pH	11.65	11.8	10.0

The chemical composition analysis results shown above indicate differences in the composition of desulphurisation products. The used sorbents differ in the contents of both calcium, sulphates and carbonates. The presence of magnesium compounds, as well as free calcium oxide, has a little effect on

the phase composition of the desulphurisation products. As a result of reaction between calcium carbonate and sulphur oxides, calcium sulphate forms following desulphurization. Its molar mass of 136.14 g/mol is higher than that of calcium carbonate (100.09 g/mol), which has the effect of reducing the total calcium content of calcium carbonate – calcium sulphate mixtures with increasing sulphate content, and it is the relationship that occurs in the examined desulphurisation products. The magnesium present in the analysed samples occurs probably in the form of sulphates, which has little effect on the calcium sulphate content.

In each of the evaluated desulphurisation products the presence of free calcium oxide was identified, as confirmed also by the results of the 1% suspension pH measurement. The highest alkalinity is exhibited by Sorbent II ($pH = 11.8$), which is also confirmed by the highest free calcium oxide content. The remaining samples are also characterised by high alkalinity: Sorbent I – $pH = 11.65$ at a free calcium oxide content of $\text{CaO}_{\text{free}} = 1.48$; and Sorbent III with a slightly lower reaction of $pH = 10.0$ at a free calcium oxide content of $\text{CaO}_{\text{free}} = 0.14$.

By converting the chemical analysis results, the phase composition of the investigated desulphurisation products can be assumed, as shown in Table 3.

Table 3. Approximate phase composition of the desulphurisation products

Probable chemical substance	Contents [wt%]		
	Sorbent I	Sorbent II	Sorbent III
CaSO_4	8.23	26.52	15.75
CaCO_3	84.0	72.7	75.5
MgSO_4	0.75	0.6	1.6
CaO	1.48	3.26	0.14

4. CONCLUSIONS

On the basis of the flue gas desulphurization tests out, as well on the physicochemical analysis of the sorbents and the desulphurisation products, the following has been found:

- With an increase of CO_2 concentration the conversion degree decreases from 18 at 20% CO_2 to 3.9 at 80% CO_2 .
- An increase of CO_2 concentration in the flue gas influences the flue gas desulphurisation efficiency. The lowest value obtained for 80% CO_2 was 19.4%, whereas the highest value obtained for 20% CO_2 was 93%.
- The evaluation of the three desulphurisation products showed that the used sorbents have different abilities to bond sulphur oxides in desulphurisation conducted in an oxygen-enriched atmosphere. The highest sulphur oxide removal potential was exhibited by Sorbent II, whereas Sorbent I was the least efficient, containing a three times lower calcium sulphate content compared to the product of desulphurisation with Sorbent II. All the samples were characterised by high alkalinity. The highest free calcium content occurred in Sorbent II, which probably had also an effect on its high desulphurisation ability.

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SYMBOLS

C_o	initial SO ₂ concentration in the model gas mixture, kmol m ⁻³
C_{SO_2}	average SO ₂ concentration in the flue gas, mg/Nm ³
C_t	SO ₂ concentration in time t, kmol m ⁻³
C_{TSO_2}	SO ₂ concentration in the flue gas assuming the 100% conversion of S to SO ₂ , mg/Nm ³
P	pressure in the reactor, Pa
R	gas constant, Pa m ³ kmol ⁻¹ K ⁻¹
t	reaction time, s
T	temperature, K
V_s	molar velocity of gas flowing through the reactor, kmol s ⁻¹
w	number of calcium moles fed to the reactor, kmol
X	molar Ca conversion degree, %

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