



# Evaluation of limestones for the purposes of desulphurisation during the fluid combustion of brown coal

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## HIGHLIGHTS

- ▶ Limestone with lower calcium content desulphurises better than limestone with higher.
- ▶ A limestone fraction with particles <0.04 mm contains the smallest amount of CaO.
- ▶ Ballast materials contained in the smallest fractions deactivate limestone calcines.
- ▶ The selection of the limestone should correspond to the character of the brown coal.

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## ABSTRACT

Laboratory tests of the reactivity of two limestones used for desulphurization of fluidized bed boilers showed that the desulphurization capacity of their calcinates do not yet correspond to routinely applied opinions on the absolute content of CaO in the limestone. Limestone with lower CaO content desulphurised the combustion gas more. This was caused by the fact that the desulphurization reactions of combustion gas are significantly negatively affected by the reaction of CaO with ballast oxides of ash and limestone. The amount of ballast oxides in both limestones rises along with the decrease of the particle size. When choosing proper limestone for the given power equipment it is necessary to respect these side effects. It is useful to pre-select and optimise the distribution the limestone particles according to the nature of the burnt coal. Thereby it is possible to reduce the consumption while complying with the SO<sub>2</sub> emission limits.

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## 1. Introduction

The largest amount of gaseous pollutants emitted into the atmosphere by industrial anthropogenous activity (besides agriculture) comes from fossil-fuel combustion. The flue gas created can be characterised as a gaseous mixture polluted by solid materials (fly-ash, soot, etc.) which contains particularly carbon dioxide, oxygen, water vapour, sulphur dioxide and nitrogen oxides. Sulphur dioxide as one of the main components negatively affecting the biosphere is usually considered at the same time as an indicator of atmospheric pollution. The sulphur dioxide generated from power stations and rating plants amounted to almost 200 million tonnes every year in 2007 [1]. There have been two major processes up to now: the wet-type scrubbing process, which is most commonly used (90%), and the dry or semidry scrubbing process [2].

The knowledge so far connected with the desulphurisation of circulation fluidised-bed boilers burning brown coals testifies that

it is necessary to conduct an optimisation of the limestone selection for the individual brown coals exploited, namely regardless of their calcium oxide content.

In this article, brown coal from the Jiří Quarry (Sokolov Brown-Coal Basin) and limestone samples from the Čertovy schody and Štramberk quarries were considered.

The actual evaluation was based on the testing of limestone samples after they were mixed with brown-coal samples and subsequent calcination of the mixture at a temperature of 850 °C. The mixtures of ash and calcinated limestone were evaluated by testing the relative reactivity in a laboratory fluid reactor.

It was clearly shown that the clayish components of the coal and the limestone impurities comprise crystalline compounds with the limestone calcine at temperatures typical for fluidised-bed boilers, which are a cause of the hindered access of the SO<sub>2</sub> to the surface of the particle of the CaO created through calcination [3]. The CaO particles created through calcination from the limestone then capture sulphur dioxide very insufficiently and are deposited in tips in the form of so-called free CaO. The revealed undesirable reaction mechanisms associated with covering the

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CaO surface in connection with the obligations to maintain the emission limits and flows then lead to increased limestone consumption.

## 2. Dry desulphurisation

The principle of the technology of the desulphurisation of the boiler flue gas with the dry limestone method lies in the injection of a mixture of air and finely ground limestone into the combustion area of the boiler or in the addition of ground limestone into coal. In the desulphurisation process, mainly reactions [4,5] take place:



Limestone calcination (1) generally takes place at temperatures of 800–900 °C; the reaction between the created CaO and SO<sub>2</sub> (2) occurs at more significant speeds between 600 and 1000 °C. The product of the reaction besides unreacted CaO is calcium sulphate; calcium sulphite is not thermostable at temperatures above 600 °C and disproportionates according to the reaction:



where calcium sulphide (CaS) further oxidises to CaSO<sub>4</sub>. The injection of limestone up to temperatures higher than 1050 °C is not appropriate with respect to the deactivation of the calcine created (so-called overfiring) as a consequence of a change of the porous structure.

From the chemical perspective, the reaction between CaO and SO<sub>2</sub> is a 'solid material – gas' heterogeneous reaction [6]. The initial stage of the reaction can be expressed as a reaction of the first order, i.e. proportional to SO<sub>2</sub> concentration. In the capture of SO<sub>2</sub>, a CaSO<sub>4</sub> layer first forms on the surface of the calcinated particle; it causes the remaining share of SO<sub>2</sub> to reach the particles by diffusion through this layer [7–10].

With granulation boilers, the time dwell of the particle in the band of the optimal temperatures for the reaction of CaCO<sub>3</sub> (or CaO) + SO<sub>2</sub> (i.e. 1100–600 °C) is very short and depending on the efficiency of the boiler fluctuates between 2 and 6 s. It therefore is not possible in a realistic arrangement using this technology to reach a high level of desulphurisation with a stoichiometrically bearable amount of limestone [11].

With the fluid combustion of coals, the dwell of the particles of limestone in the fluid layer is excessively long and can reach on average ca several hundred to a thousand seconds [12]. During this period of contact, at the optimal temperature of fuel combustion (800–850 °C), when the limestone calcination is followed by sulphation, also the diffusion of SO<sub>2</sub> through the layer of CaSO<sub>4</sub> can therefore be applied more significantly. Calcinate sulphation is also partially supported by the character of the fluid process, in which a partial attrition of the surface of the particles of the CaSO<sub>4</sub> created occurs and with that an acceleration of SO<sub>2</sub> diffusion to the surface of free CaO inside the grain.

Since the mass flow of the particles many times exceeds the flue-gas mass, the temperature in the boiler practically does not change. The heat-transfer surfaces are adjusted so as to maintain a temperature in the layer of 810–870 °C. According to the knowledge theoretically preferred so far, the particle size should not exceed 600 μm with a median size of 150–200 μm [13,14].

## 3. Experimental

### 3.1. Apparatus

The laboratory apparatus used for testing the samples of the calcines of the limestones with coal is depicted in Fig. 1.

The reactor itself was constructed of two concentrated quartz pipes connected by ground joint. The upper removable part of the reactor was equipped with a narrower tube closed by a frit, in which a sample was placed in a stationary bed. The thermoelement for monitoring the temperature was placed in the quartz filler in the lower part ensuring the heating of the entering standard gas with SO<sub>2</sub>. Having been filled with sorbent, the reactor of 41 cm long with diameter 2 cm and volume 128.7 ml was placed in the electrically warmed kiln. Its supply tubes were heated with resistance heating to 105 °C with the aim of avoiding the condensation of possible water vapours contained in the gas mixture.

After heating the reactor to the desired temperature (while letting inert nitrogen flow through the reactor), the prepared mixture of model combustion gas was released into the reactor and subsequently went through a layer of sorbent.

The SO<sub>2</sub> mass captured by the sorbent was determined by a calculation from the measured data by following formula:

$$M_{\text{SO}_2} = (C_{\text{SO}_2} - C_{1,\text{SO}_2}) * Q * t \quad (4)$$

where  $M_{\text{SO}_2}$  is the amount of SO<sub>2</sub> absorbed by tested sorbent (mg);  $C_{\text{SO}_2}$  is the concentration of SO<sub>2</sub> in model gas (mg l<sup>-1</sup>);  $C_{1,\text{SO}_2}$  is the concentration of SO<sub>2</sub> in outgoing gas (mg l<sup>-1</sup>);  $Q$  is the flow rate of model gas (l h<sup>-1</sup>);  $t$  is the time of reaching the required concentration, (h).

The data gained in this way were considered as basic for the evaluation of the relative reactivity of the sorbents. Increase of catchment of the SO<sub>2</sub> mass when the limestone with higher relative dynamic absorption capacity was substituted with worse limestone was calculated with following formula:

$$\Delta m_{\text{SO}_2} = (c_{\text{SO}_2(1)} - c_{\text{SO}_2(2)}) * 1000 \text{ g}^{-1} \quad (5)$$

where  $\Delta m_{\text{SO}_2}$  is the increase of SO<sub>2</sub> absorption due to substitution for better sorbent (g kg<sup>-1</sup>);  $c_{\text{SO}_2(1)}$  is the relative dynamic adsorption capacity for SO<sub>2</sub> limestone (1) (mg g<sup>-1</sup>);  $c_{\text{SO}_2(2)}$  is the relative dynamic adsorption capacity for SO<sub>2</sub> limestone (2) (mg g<sup>-1</sup>);  $g$  weight of the followed limestone (3 g); 1000 is conversion to 1 kg.

Increase of the volume of desulphurised combustion gas when the limestone with higher relative dynamic absorption capacity was substituted with worse limestone was calculated with following formula:

$$\Delta V_{\text{fg}} = \Delta m_{\text{SO}_2} * 1000 \text{ g}^{-1} \quad (6)$$

where  $\Delta V_{\text{fg}}$  is the increase of volume of desulphurised combustion gas due to substitution with better sorbent (m<sup>3</sup>);  $\Delta m_{\text{SO}_2}$  is the increase of SO<sub>2</sub> absorption due to substitution for better sorbent (g kg<sup>-1</sup>);  $g$  is the selected model mass of SO<sub>2</sub> absorbed (5000 mg m<sup>-3</sup>).

The gas that had gone through the layer of tested material was cooled after leaving the reactor and analysed by the SO<sub>2</sub> Servomex Xentra 4900 continual analyser, which simultaneously monitored also the entry concentration of SO<sub>2</sub> and oxygen.

### 3.2. Materials

#### 3.2.1. Coal samples

For the purposes of this work, four samples of coal were taken in the Jiří Quarry directly at the individual wheel excavators. The overview of them with labels following the deposition in the quarry is shown in Table 1.

The actual evaluation was based on the testing of the chemisorption activities of the limestone samples with a particle size of 0.3–0.6 mm after their mixture with the cited types of coals and subsequent calcination at a temperature of 850 °C, where the individual coals were, before mixing with the limestones of the listed particle sizes, first dried and then ground in an agate bowl.

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