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Enrichment of Limestone Used in the Desulphurisation of Fluidised-Bed-Boiler Flue Gases

Buryan Petr (ID) **and Tomas Hlincik** (ID)

Department of Gaseous and Solid Fuels and Air Protection, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic

Correspondence should be addressed to Buryan Petr; buryanp@vscht.cz

In this work, we analysed the impact of adding several previously untested Sorbacal calcium-based substances to the raw limestone that is currently used for dry desulphurisation of brown-coal fluidised-bed boilers. Our focus was to examine whether these additives could potentially improve the limestone SO_2 adsorption capacity. The main criterion was the time period for which each enriched limestone was able to keep its desulphurisation ability, i.e., time for which the SO_2 concentration in the heated model flue gas was kept below $200\,mg/m^3$ (current legal limit for the technology in our scope). The analysis showed that the limestone desulphurisation ability increased when 20% of Sorbacal SP was added to the calcined limestone. The overall desulphurisation capacity of this enriched mass was even higher than what would be proportional to the isolated capacity of the additive itself. On the other hand, the enrichment of raw limestone with Sorbacal H 90 proved to be unpromising for the technology of brown-coal fluidised-bed boilers as the fine particles of the additive were carried away, and fluidised bed was inhomogeneous with ducts forming in it.

1. Introduction

Tightening of emission limits has recently put strong pressure on fluidised bed boiler operators. For example, the current SO_2 emissions limit for the technology in our scope—fluidised-bed boilers with the rated total power output of over 100 MW—is $200\,mg\,SO_2/m^3$ (6 vol. % of O_2, dry flue gases) (collection of laws of the CR). In effect, the boiler operators started to search for available substances that would improve the desulphurisation ability of their current desulphurisation technologies. One of the research areas are additives that would improve the desulphurisation capacity of limestone that is commonly used as adsorption agent during the dry limestone method [1].

The aim of the work we present here was to determine potential suitability of Sorbacals, a family of previously untested calcium-based substances currently used for neutralisation of acidic compounds, to improve flue-gas desulphurisation in the circulating fluidised boilers. Our core focus was to determine the impact of adding Sorbacals into the limestone that is already used in flue-gas desulphurisation of boilers burning brown coal with power output of more than 100 MW.

The efficiency of desulphurisation of flue gas coming from fluidised bed boilers burning brown coal (as well as methods of its improvement) has already been subject of several studies in the past. The imperfections of flue-gas desulphurisation were originally ascribed to the nonstandard capacity of the boilers, to unsuitable operating modes, to improper distribution of coal and limestone particles dosed into the boiler furnace, etc. Operating conditions of fluidised bed boilers which exhibited insufficient flue-gas desulphurisation characteristics has been focus of research described, e.g., in [2–5]. One important finding of the research [6, 7] is that also using limestone with higher content of calcium carbonate for flue-gas desulphurisation can lead to worse results (when compared to application of limestone with lower calcium carbonate content). The analyses have confirmed that the insufficient flue-gas desulphurisation can often result from the reactions of calcination-produced CaO with oxides of the ballast components of coal

and limestones and also from formation of a number of crystalline compounds on the surface of the limestone grains that block the access of SO_2 to limestone [7–10].

It should also be noted that, unfortunately, current efforts to replace fossil fuels with various types of biomass with the aim of reducing CO_2 emissions further decrease the desulphurisation efficiency [7, 8]. This happens mainly due to the presence of various oxides in the biomass (e.g., $CaO.SiO_2$, $2CaO.SiO_2$, $CaO.SiO_2.Al_2O_3$, or $CaO.SiO_2.Al_2O_3.Fe_2O_3$) that further limit limestone desulphurisation capacity by creating the abovementioned crystalline compounds on its surphace. All of this brings even more motivation to search for methods to improve the fluidised-bed-boiler desulphurisation efficiency. Adding various additives to the main desulphurisation agent is definitely one of potential ways forward (e.g., [11, 12]). Partially motivated by our previous work [13], we focused here on adding Sorbacals, substances originally produced for the purpose of acidic pollutants neutralisation.

Sorbacals are substances obtained by thermal processing of limestone resulting in highly porous hydrated lime. The principle of the processing is hydration of calcined limestone during which the limestone carbonates are thermally transformed (among other products) into hydroxides outside the desulphurisation technology. We tested two of these Sorbacal substances [14]: Sorbacal H90 and Sorbacal SP. Sorbacal H90, sometimes referred to as "lime milk" (as a 20% suspension), are slaked lime $(Ca(OH)_2)$ designed for neutralisation of acidic pollutants. Sorbacal SP [14] is a white slaked lime produced mainly for flue gas cleaning. Specifically designed for DSI applications, Sorbacal SP is characterized by increased ability to remove acidic flue gas components when applied in dry and combined technologies, namely, due to its large specific surface area (typically 40 m^2/g, BET) and high porous volume (typically 0.20 cm^3/g, BJH). The adsorption capacity of Sorbacals during the desulphurisation process of flue gases in the temperature range of 110–130°C is discussed in detail in [13].

The main assumption that we wanted to test in this study was that adding Sorbacal into limestone can bring improvement of limestone-based desulphurisation efficiency. Dosage of the Sorbacal substances straight into the area with temperature of 850°C should improve efficiency of limestone-based desulphurisation while not invoking chemical processes that may negatively affect the reactivity of the mixtures of Sorbacals and limestone. We also expect differences in impact of the two Sorbacal additives. Sorbacal H 90 shows higher hydroxide content (lower share of hydroxide compared to oxide) in comparison to Sorbacal SP. This means that under the given reaction conditions, we can—theoretically—expect lower desulphurisation capabilities of H 90 due to higher calcium hydroxide content. It can be assumed that part of its hydroxide will react with other components than SO_2, e.g., with carbonates that will then be further calcined to the oxides.
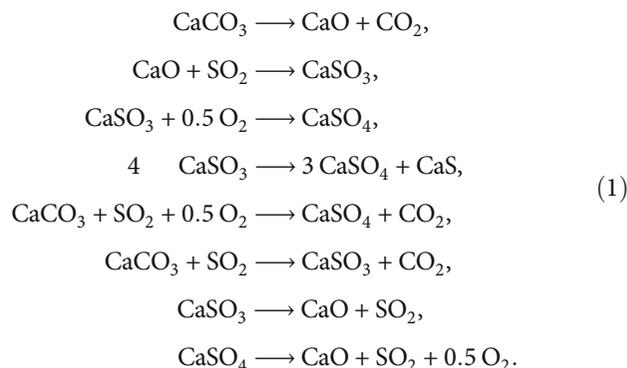
2. Flue-Gas Desulphurisation

The main goal of desulphurisation of flue gas coming from brown coal burning fluidised-bed boilers is the fluid adsorp-

tion of SO_2 from the released gases. The most frequent method is injecting limestone directly into the fluidised bed of the boilers where SO_2 adsorption takes place at high temperature. The temperature in the fluidised bed is almost constant, and its value depends on the optimum temperature of the flue-gas desulphurisation process (790–850°C) [1]. Apart from the limestone, several technologies use other substances, e.g., lime mud $(CaCO_3)$ or $Ca(OH)_2$ that come from technological processes [7] or are by-products of various dolomite applications [15].

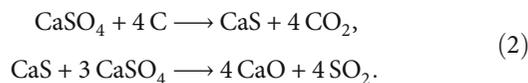The usual limestone particle size ranges between 100 and 800 μm, depending on the type of fluidised-bed furnace. The mean dwell time of these desulphurisation agent particles in the fluidised bed is up to one thousand seconds (ca 16.7 minutes). SO_2 is usually adsorbed throughout most of this period. This is partly due to the fact that $CaSO_4$ penetrates into the centre of the grains and also because the surface of the particles in the fluidised bed is continuously abraded. This enables SO_2 better access to the previously covered parts of the particles. The main causes of the abrasion are mutual contact of the limestone particles, contact with incinerated coal, combusts, desulphurisation products, or contact with the lining of the combustion chamber.

Usually, the following reactions occur during the reaction of SO_2 with limestone at high temperatures [7, 10, 16–18]:

$$\begin{aligned} CaCO_3 &\longrightarrow CaO + CO_2, \\ CaO + SO_2 &\longrightarrow CaSO_3, \\ CaSO_3 + 0.5\,O_2 &\longrightarrow CaSO_4, \\ 4\quad CaSO_3 &\longrightarrow 3\,CaSO_4 + CaS, \\ CaCO_3 + SO_2 + 0.5\,O_2 &\longrightarrow CaSO_4 + CO_2, \\ CaCO_3 + SO_2 &\longrightarrow CaSO_3 + CO_2, \\ CaSO_3 &\longrightarrow CaO + SO_2, \\ CaSO_4 &\longrightarrow CaO + SO_2 + 0.5\,O_2. \end{aligned} \tag{1}$$

Unfortunately, the desulphurisation efficiency of the limestone is often decreased by formations of a number of crystalline compounds on the surface of the limestone grains. This crystalline layer then encapsulates free CaO and SO_2 can never reach it [2, 6]. This is often influenced by the elemental and oxide composition of the limestone leading to reactions between CaO and certain oxides, in particular, SiO_2, Al_2O_3, and Fe_2O_3 [8, 13, 19–21]. This is behaviour that can be expected especially for Sorbacal H90 (due to its chemical composition).

Another example of disruptive process that negatively affect the desulphurisation is described in [22, 23] and is described by the sequence of the following reactions:

$$\begin{aligned} CaSO_4 + 4\,C &\longrightarrow CaS + 4\,CO_2, \\ CaS + 3\,CaSO_4 &\longrightarrow 4\,CaO + 4\,SO_2. \end{aligned} \tag{2}$$

This sequence can take place during the recirculation of captured particles from the flow of flue gases containing

unburnt carbon and $CaSO_4$ into the furnace with a change in oxidising and reducing atmosphere. In effect, the mechanism allows undesirable rerelease of the captured SO_2.

3. Experiment Set-Up

In our work, we studied the impact of Sorbacal additives on the desulphurisation ability of raw limestone that is currently used for the desulphurisation of flue gases from fluidised-bed boilers. For this purpose, we used three calcium-based substances obtained from the limestone quarry of Vápenka Čertovy schody (Czech Republic): raw limestone (type dr. 5), Sorbacal SP, and Sorbacal H90. Eight samples/sample mixtures were compiled out of these base substances and placed into a heated quartz reactor to compare their reactivity with SO_2. We prepared and heated model flue gas and determined the desulphurisation capacity of each sample by measuring SO_2 concentration in the gas after it was blown through the reactor. The desulphurisation capacity of the sample was defined as the length of the time period for which each sample was able to keep its desulphurisation ability. The moment when this ability is lost was defined as the moment when the SO_2 concentration in the exiting flue gas grows above the presently valid emission limit for boilers with power output of more than 100 MW, i.e., 200 mg/m^3 at 6 vol. % of oxygen in dry-flue gases.

Our experiment was designed to be carried out in 3 phases. First, we measured desulphurisation capacity of the raw limestone that is currently used as desulphurisation agent (without any additive). Then, we analysed the capacity of both Sorbacal substances (without any raw limestone presence), and eventually, we focused on the behaviour of the Sorbacal-limestone mixtures to assess impact of adding Sorbacal to the raw limestone.

3.1. The Apparatus. The experimental apparatus we used to assess the desulphurisation capacity of our samples was quartz reactor placed in an electrically heated furnace. During our previous work (e.g. [7]), we have proven that this set-up is a very good model of fluidised-bed boiler. Scheme of the apparatus is in Figure 1 [7]. After placing the sample into the reactor, we blew heated model flue gas through the reactor for a period of up to 350 minutes and measured the SO_2 concentration in the exiting gas. We focused mainly on determining the time period for which each sample was able to keep its desulphurisation ability (defined as time until the SO_2 concentration grew over the limit of 200 mg/m^3—see above).

The reactor itself consisted of two quartz tubes connected by a ground joint that was placed in an electrically heated furnace. The upper, removable, part of the reactor was equipped with a narrower tube closed by a frit that contained the monitored sample. Since the diameter of the frit was smaller than the diameter of the reactor internal-tube, the expanding section of the reactor tube was filled with crushed quartz (grain size of 0.5–1 mm). Small quartz tubules were fused to both quartz tubes so that we could collect and analyse the gas before in enters the reaction bed with the adsorbent sample and also after it leaves it. The bottom half of the reactor, where the reaction gas was heated, was filled with crushed quartz with a grain size of 5–7 mm. The temperature in the reactor was measured using a thermocouple placed in a blind quartz capillary in the middle of the reactor. In this way, the thermocouple measured the temperature of the gas in close proximity to the part of the apparatus where the sample was placed.

The gas exiting the reactor was driven to the analyser through a bubbler bottle that functioned as a hydraulic closure. Two pressure bottles were attached to the model apparatus, one with nitrogen and one with our model flue-gas mixture. These flue gases model mixture we used for the experiment had the following composition: 6850 mg of SO_2/m^3, 7 vol. % of O_2, 13 vol. % of CO_2, with the rest being N_2.

3.2. The Sample Base. In this work, we used three base substances for measurement samples—raw limestone (type dr. 5), Sorbacal SP, and Sorbacal H 90 (all from the Lhoist S.A. company, branch Vápenka Čertovy schody, a.s.):

(1) *Limestone Sample.* Raw limestone mineral extracted in the area of Loděnice, Devon Barandien [24]

(2) *Sorbacal SP* [25]. Slaked lime specially modified for the purification of flue gases, characterized by an increased ability to remove acidic components from flue gases when used in dry and combined technologies, specifically designed for DSI applications; its qualities make the material significantly more effective for acid gas removal than standard hydrates: the surface area (BET) of the material is over 40 m^2/g (two times higher than standard hydrated lime) and pore volume (BJH) more than 0.2 ml/g (compare to 0.08 cm^3/g for standard hydrated lime)

(3) *Sorbacal H 90* [14]. This is a standard quicklime product ($Ca(OH)_2$) designed for neutralisation of acidic pollutants, sometimes referred to as "lime milk" (as a 20% suspension); it is often used as economical and effective solution to a number of problems, such as wastewater treatment, flue-gas purification, solid-waste disposal, and drinking or process water treatment; it appears as a white, dry, ready-to-use powder and can be used directly in dry processes with or without recycling; the surface area (BET) of the material is over 20 m^2/g and pore volume (BJH) ca 0.1 ml/g

The general characteristics of the base substances are provided in Table 1(a) (chemical composition) and Table 1(b) (particle sizes). The adsorption capacity of both Sorbacals during the desulphurisation of flue gases in the temperature range of 110–130°C is discussed in [13]. Both Sorbacals were produced on purpose for this experiment by controlled activation after calcination and grinding of the calcined product of that limestone.

The chemical composition of the base raw substances as well as substances calcined at 850°C from which test samples were taken/compiled was determined by the sequential
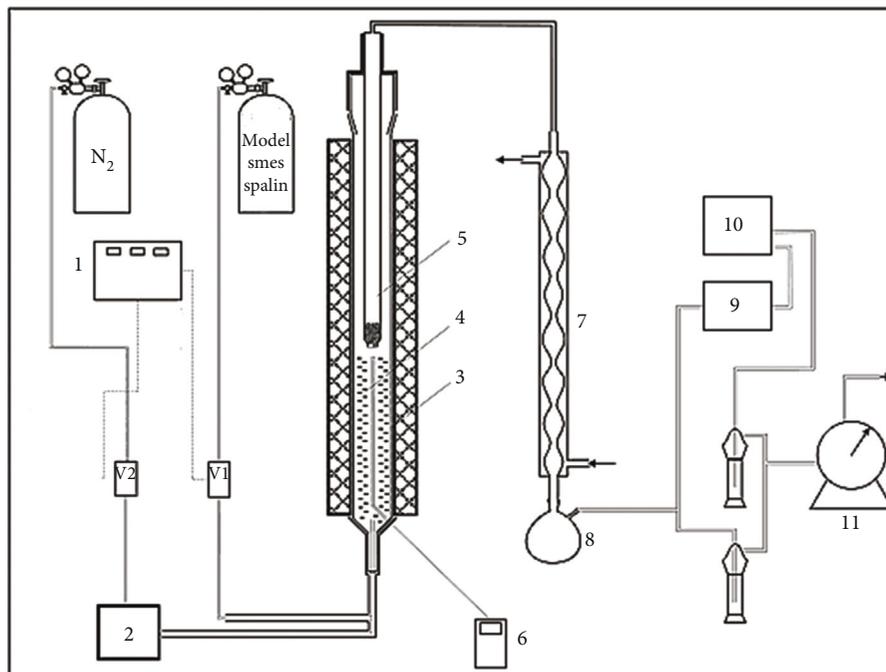
FIGURE 1: Experimental apparatus. 1—control unit, 2—analyser, 3—reactor, 4—crushed quartz, 5—quartz reactor with the sample, 6—thermometer, 7—water cooler, 8—condensate trap, 9—cooling unit, 10—analyser, 11—gasometer, V1 and V2—control valves.

TABLE 1

(a) Characteristics of analysed samples [wt. %]—basic composition

Parameter	Substance A: limestone	Substance B: Sorbacal SP	Substance C: Sorbacal H90
$CaCO_3$	98.98		
$MgCO_3$	0.86		
$Ca(OH)_2$		92.96	97.20
CaO, total	55.43	73.50	74.81
CO_2	44.20	2.83	0.98

(b) Characteristics of analysed samples [wt. %]—particle sizes

Particle size	Substance A: limestone	Substance B: Sorbacal SP	Substance C: Sorbacal H90
>1.00 mm	90,3	88,7	0,1
>0.63 mm	7,3	7,7	11,36
>0.20 mm	0,4	0,1	51,7
>0.09 mm	2,0	2,5	22,40

wavelength-dispersive X-ray fluorescence spectrometer ARL 9400 XP equipped with an X-ray lamp with a 4GN Rh anode with a 75 μm-thick Be end window. The intensities of the spectral lines of the elements were measured in vacuum by the WinXRF program. The combinations of the settings of the generator-reflector-sight-crystals-detectors were opti-mised for the 79 measured elements with the time of 6 s/ele-ment. Detected intensities were eventually processed by the

Uniquant 4 program (without the need to measure the stan-dards). Detailed data are provided in Tables 2(a) and 2(b).

Both tables show that all of the three substances had a relatively high CaO content—the highest appeared in the case of Sorbacal H90. Both Sorbacals had approximately the same content of SiO_2. However, the Al_2O_3 content in individual samples was different. The lowest concentration was exhibited by Sorbacal SP and the highest by calcium car-bonate. Based on the elemental composition, we expect the desulphurisation capacity of Sorbacals to be better than that of raw limestone.

3.3. The Samples. From the three substances introduced above, we prepared and studied six samples and two mix-tures—see Table 3 for details.

Samples 1 and 4 represent examples of limestone that is currently used for desulphurisation. Samples 2, 3, 5, and 6 were prepared to see isolated behaviour of Sorbacals during desulphurisation. Mixtures A and B represent examples of limestone enriched with Sorbacal additive to see impact of this additive on the limestone behaviour. It should be noted that the weight of the mixtures after adding Sorbacal was 2.4 g, and we prepared the raw limestone sample 4 to match exactly this weight so as to allow for direct comparison.

The sorbents were sieved so as to obtain sample with grain size of 0.3–0.6 mm that respected the working condi-tions of the apparatus used in the experiments. Each sample was calcined to activate it for the upcoming desulfurization (the essence of calcination is decarboxylation of the carbon-ate). The calcination was performed in a muffle furnace at a temperature of 850°C for about 14 hours. Only the 2-gram sample charges were calcined (i.e., pure limestone, Sorbacal

(a) Detailed composition of base raw substances [wt. %]

Oxides	Substance A: limestone	Substance B: Sorbacal SP	Substance C: Sorbacal H90
CaO	70.70	80.20	81.20
MgO	0.374	0.533	0.573
SiO_2	0.138	0.071	0.080
Al_2O_3	0.091	0.036	0.050
Fe_2O_3	0.052	0.058	0.066
SrO	0.041	0.036	0.040
P_2O_5	0.037	0.017	0.017
SO_3	0.023	0.137	0.112
K_2O	0.018	0.008	0.011
MnO	0.007	0.011	0.013

(b) Detailed composition of calcined substances [wt. %, calcination at 850°C]

Oxides	Substance A: limestone	Substance B: Sorbacal SP	Substance C: Sorbacal H90
CaO	98.291	98.901	98.802
MgO	0.478	0.657	0.697
SiO_2	0.466	0.880	0.970
Al_2O_3	0.283	0.450	0.600
Fe_2O_3	0.191	0.720	0.820
SrO	0.039	0.450	0.490
P_2O_5	0.016	0.200	0.200
SO_3	0.029	0.169	0.136
K_2O	0.020	0.099	0.130
MnO	0.023	0.140	0.160

SP, and Sorbacal H90 only). No individual special calcination was performed with the mixtures—using only the noncalcined substrate in the mixtures was motivated by effort to model the impact of feeding the additive directly into the operating combustion chamber of the fluidised boiler (a situation we expect to be most practical should the additives be used in the normal operation of the boilers).

After removing the sample from the calcination furnace (and potentially mixing them with other desulphurisation components—see above), we planted it into the reactor in the apparatus. After all parts of the apparatus were properly connected, the entire appliance was thoroughly sealed. As the last step of apparatus initialisation, it was washed with nitrogen at a flow rate of 30 l/h. After this initialisation, the furnace was turned on set to 850°C and the experiment started. The output signal of the Servomex Xentra 4900 analyser monitoring the SO_2 concentration at the exit of the quartz reactor was transferred via a HyperTerminal to a computer, and the recording frequency was five seconds. Testo Easy Emission program was used for evaluation. The results of the measurements are provided in the results section in Figures 2–8.

4. Experiment Results

Results of our measurements are provided in Figures 2–7. The charts show the output concentrations of SO_2 from the fluidised bed versus time, given constant input concentration of SO_2 in the model gas. The curve dynamics shows "breakthrough" characteristics—it clearly reveals that concentration of SO_2 is low during the initial phase when there is enough free CaO available in the sample and sharply increases when the amount of free CaO is reduced.

Since the present limit for currently operated boilers with a power output of >100 MW is 200 mg/m^3 at 6 vol. % of oxygen in dry-flue gases, the data obtained were recalculated to respect these conditions.

We started the experiment with analysing behaviour of sole limestone—$CaCO_3$ (dr. 5). Figure 2 shows SO_2 concentration measured for sample 1 (2 g of $CaCO_3$ dr. 5) and sample 4 (2.4 g of $CaCO_3$ dr. 5). As expected, the desulphurisation capacity of sample 4 was better than that of sample 1 as sample 4 reached the emission limit after 125 minutes, whereas sample 1 reached this limit only after 105 minutes (i.e., the capacity of sample 4 is 19% higher). It should be emphasized here that this is consistent with the fact that sample 4 contained 20% more CaO than sample 1. The capacity grows linearly with increasing the mass of the agent.

Another importance of measuring the curve of sample 4 was also to obtain data for comparison of desulphurisation capacity with mixtures A and B (that were analysed further in our work). Its weight was the same as the weight of the mixtures (2.4 g), and we used the data as basic benchmark for analysis of additives' impact.

As a second step, we focused on measuring isolated behaviour of the additives—see Figures 3 and 4. Figure 3 shows results of adding sample 2 (2 g of Sorbacal SP). It is clear that sample 2 has much high adsorption capacity than the limestone samples, reaching the emission limit after 331 minutes. Hence, its use for the desulphurisation of fluidised-bed boilers seems to be quite promising. Of course, it should be noted that manufacturing of sample 2 is more complex than that of samples 1 or 4 as it is produced by limestone calcination followed by subsequent treatment with water.

Results of adding sample 3 (2 g of Sorbacal H 90) follow in Figure 4. The irregular course of the curve shows that this type of desulphurisation substance is not suitable for the selected apparatus. The reason for this irregular dynamic was that the fine particles of the calcined sample were carried away into higher parts of the apparatus during the experiment, and the fluidised bed was inhomogeneous, with ducts forming in it.

For better comparison, we have also carried out the SO_2 adsorption test on uncalcined Sorbacal additives—see Figure 5. Comparison of breakthrough time of calcined and noncalcined Sorbacal SP samples shows that the interval of the uncalcined sample (sample 5) is similar to the calcined one. On the other hand, for Sorbacal H90 (sample 6), we clearly see much different behaviour as the uncalcined sample reaches the breakthrough after 136 minutes without any irregular behaviour that was observed for the calcined version (see breakthrough curve of sample 3 on Figure 4).

TABLE 3: Description of studied samples.

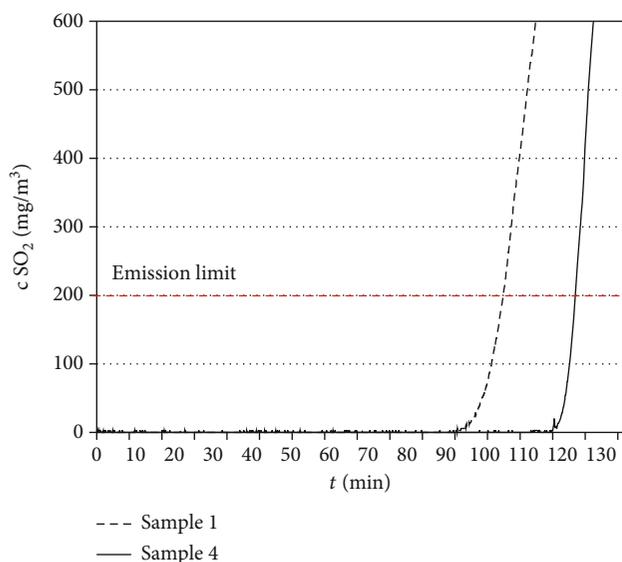| Sample ID	Sample composition	Sample preparation
Sample 1	2 g of $CaCO_3$ dr. 5	Weighed and subsequently calcined
Sample 2	2 g of Sorbacal SP	Weighed and subsequently calcined
Sample 3	2 g of Sorbacal H 90	Weighed and subsequently calcined
Sample 4	2.4 g of $CaCO_3$ dr. 5	Weighed and subsequently calcined (same as sample 1 but 20 wt. % more limestone)
Sample 5	2 g of Sorbacal SP	No calcination—weighed and inserted into the apparatus without calcination
Sample 6	2 g of Sorbacal H 90	No calcination—weighed and inserted into the apparatus without calcination
Mixture A	2 g of $CaCO_3$ dr. 5 + 20 wt. % of Sorbacal SP	$CaCO_3$ weighed and subsequently calcined, Sorbacal uncalcined
Mixture B	2 g of $CaCO_3$ dr. 5 + 20 wt. % Sorbacal H 90	$CaCO_3$ weighed and subsequently calcined, Sorbacal uncalcined

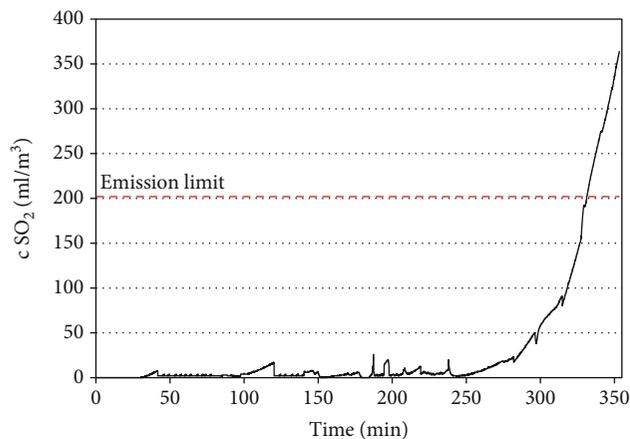FIGURE 2: The breakthrough curves of samples 1 and 4.

FIGURE 4: The breakthrough curve of sample 3.

FIGURE 3: The breakthrough curve of sample 2.

FIGURE 5: The evaluation and comparison of samples 5 and 6.

As our last step, we focused on assessing utilisation of Sorbacals as additives to the limestone. Figure 6 shows impact of the 20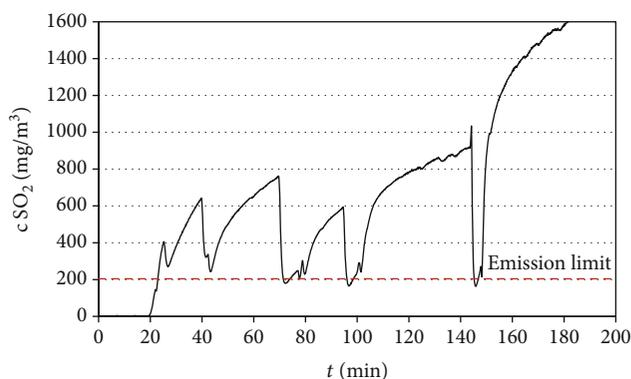 wt. % addition of Sorbacal SP to limestone (sample mixture A) compared to pure limestone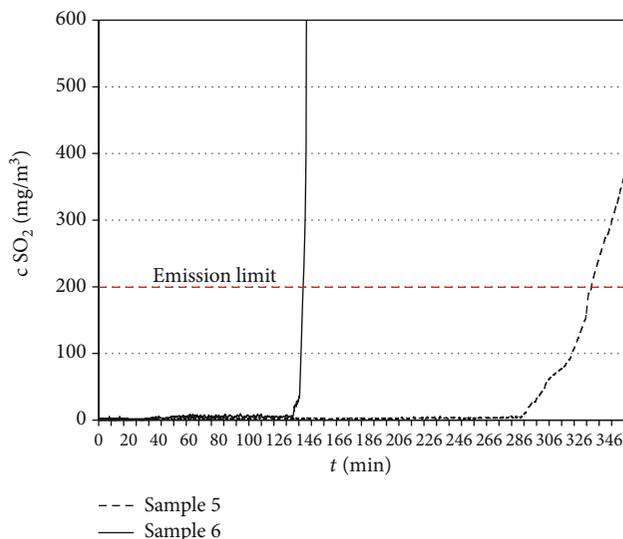 (sample 1). Mixture A clearly had better desulphurisation abilities than limestone from sample 1. The capacity increased by 81% (85 minutes), reaching the SO_2 limit after 190 minutes (vs. original 105 minutes). The 20% addition of Sorbacal SP
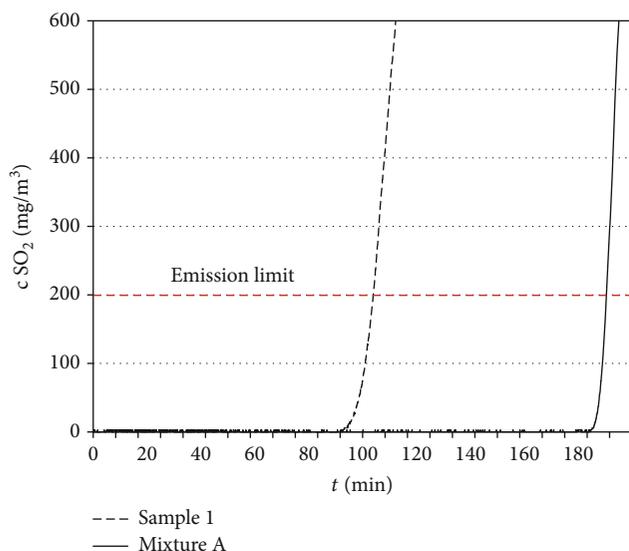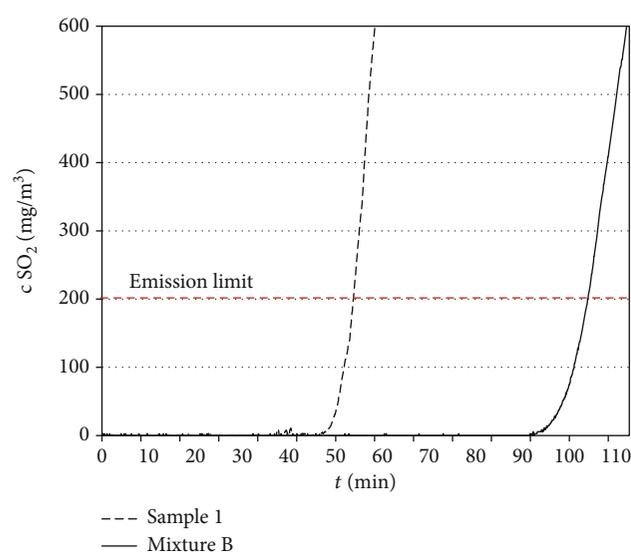
FIGURE 6: Comparison of mixture A with sample 1.

FIGURE 7: Comparison of mixture B with sample 1.

FIGURE 8: The evaluation and comparison of mixture A, mixture B, and sample 4.

TABLE 4: Time to reach the emission limit of 2.4 g samples [min.].

Sample	Time (min)
Mixture B	54
Sample 4	125
Mixture A	190

to limestone clearly significantly improved the desulphurisation capacity of the limestone. This increase was in our case even higher than proportional to the amount of Sorbacal SP added. The capacity of mixture A reached 190 minutes, i.e., it increased by 19 minutes (29%) more than the proportion of the isolated capacity of the additive used. The capacity of the added 0.4 g Sorbacal SP should be around 66 minutes (20% of 331 minutes, if we used proportional estimate based on the substance weight—see results of Sample 2), but the total capacity of the mixture increased by 85 minutes.

Eventually, we measured impact of adding Sorbacal H90 to the limestone (mixture B). Figure 7 shows that mixture B reached the emission limit already in 54 minutes. In comparison with sample 1 (pure limestone), the desulphurisation abilities were worse by 51%. Not only that the 20% addition of Sorbacal H90 did not improve the desulphurisa-
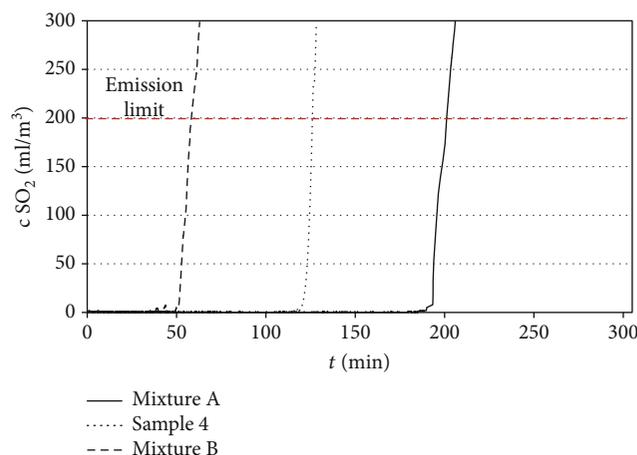
tion abilities of limestone but it made it worse. This behaviour can be attributed to the secondary reactions of calcium hydroxide with calcined limestone [8, 19, 20].

The overall summary of our experiments is provided in Table 4 and in Figure 8. Here, we show the comparison of the capacity of both mixtures and sample 4, all of which weighted 2.4 g. Quick analysis of the time necessary to reach the emission limit shows that the breakthrough times of SO_2 through the fluidised bed of the monitored samples occurred in the order: mixture B, sample 4, and mixture A. The desulphurisation capacity of mixture A (raw limestone + Sorbacal SP) was by 52% better than that of sample 4 (raw limestone of the same weight). On the other hand, mixture B (raw limestone + Sorbacal H90) exhibited significantly lower desulphurisation capacity than any other sample.

5. Discussion

All of the studied samples had a relatively high CaO content (see Table 2(a))—raw limestone (70.70 wt.% CaO content), Sorbacal SP (80.20% CaO content), and Sorbacal H90 (81.20% CaO content). Both Sorbacals had approximately the same content of SiO_2 (ca 0.075%). However, the Al_2O_3 content in individual samples was different. The lowest concentration was in Sorbacal SP (0.036%). Based on this elemental composition, we could expect that the best desulphurisation abilities should appear when both Sorbacals are used as desulphurisation agent. However, this was not proved by the data from our experiments (see Figure 4). The graphical representation of the breakthrough curves

clearly shows that the character of sample 3 (2 g of Sorbacal H 90) is not suitable for the assembled desulphurisation apparatus, mainly because of the size of the particles and their emission from the fluidised bed.

Comparison of samples created by the Sorbacal addition into limestone shows that the best desulphurisation abilities are exhibited by mixture A (2 g of $CaCO_3$ dr. 5 + 20 wt.% of Sorbacal SP). The 20% addition of Sorbacal SP led to increase of desulphurisation capacity of the basic limestone agent by 81%. The Sorbacal SP addition significantly improved the desulphurisation capacity of the limestone as the compound sample held the SO_2 below the limit for 190 minutes (vs. original 105 minutes). The increase was overproportional to the amount of Sorbacal substance added—the total increase of 85 minutes is 19 minutes (29%) more than what would be proportional to the capacity of the additive used, based on its weight.

On the other hand, the addition Sorbacal H90 did not bring satisfying results, and we cannot recommend to use this substance as limestone additive for desulphurisation. The reason of this behaviour is likely to be caused by specific composition and structure of Sorbacal H90. By replacing part of the limestone with Sorbacal H90, we are removing raw limestone while adding portion of calcium hydrates, i.e., a form of processed limestone that is unfortunately unsuitable for the desulphurisation process in this technology. An important part of the ongoing reactions in the production of H90 is the hydration of calcination of oxides, silicates, alginates, ferrites, and clinkers, where Ca^{2+} and OH^- ions are in the interlayers, eventually leading to formation of internal and external hydrates of CaO and SiO2, including $Ca(OH)_2$. Unlike Sorbacal SP, calcium hydroxide of H 90 can at given temperatures react to an increased extent with other flue gas components than SO_2 which adversely affects the desulfurization process. The hydration performed during the H90 production also has its adverse effect on the granulometry of the final desulfurization agent.

In addition, one of the side effects of different Sorbacal H90 structure was that the fine particles of H90 were carried into higher parts of the apparatus during the experiment and the fluidised bed got inhomogeneous. However, we do not assume that this behaviour of Sorbacal H90 can be attributed to the influence of the design of the apparatus. The apparatus was until now used in several studies of lignite flue-gas desulphurisation by the dry limestone method, and each time, fluidization was always very good, providing solid model of real large fluidised bed desulphurisation appliance, e.g., see [8, 19–21].

6. Conclusion

This study presents results of our work on the way to increase efficiency of the limestone-based desulphurisation of the flue gas from circulating brown coal-burning fluidised boilers through additives. Namely, we looked at impact of adding previously untested Sorbacal substances (CaO-based activated products prepared from quicklime) to the limestone that is already used for desulphurisation. Our comparison showed promising results for Sorbacal SP sorbent—a substance that contains more carbonate and less hydroxide than other products of the Sorbacal family.

In our work, we used three limestone-based substances from the quarry Čertovy schody (Czech Republic) as materials for the SO_2 sorption analysis. Our measurement focused not only on the desulphurisation capacity Sorbacals alone but we also analysed the limestone and the Sorbacal-limestone mixtures. The desulphurisation capacity was judged by the time period for which each sample was able to keep the SO_2 concentration in heated model flue gas below the present limit for currently operated boilers with a power output of more than 100 MW, i.e., 200 mg/m^3 at 6 vol. % of oxygen in dry-flue gases.

Our measurement of these breakthrough curves showed that the limestone desulphurisation abilities increased when Sorbacal SP was used as additive. The overall desulphurisation capacity of the enriched limestone mass was in our case even higher than what would be proportional to the isolated capacity of the additive itself.

Unfortunately, the enrichment of limestone with the other Sorbacal substance we used—Sorbacal H90—proved to be unpromising. This substance is not suitable for the selected apparatus as the capacity of this sorbent showed to be significantly lower than that of the raw limestone itself. This was caused by specific composition and structure of Sorbacal H90 resulting in the fine particles of Sorbacal H90 being carried into higher parts of the apparatus during the experiment and the fluidised bed getting inhomogeneous with ducts forming in it.

Data Availability

The data beyond what was presented in the article cannot be made available due to agreement with the sample-providing party.

Disclosure

The authors received no financial support for the research, authorship, and/or publication of this article.

Conflicts of Interest

The authors declare that there is no conflict of interest.

References

[1] J. Vejvoda, P. Machač, and P. Buryan, *Air Protection and Flue Gas Purification Technology*, VŠCHT Praha, 1980, ISBN 80-7080-517-X.

[2] P. Buryan, J. Vejvoda, J. Krátký, and L. Veverka, "A new method characterization limestones used in kettles with layer for desulfurization of combustions products," *Chemické listy*, vol. 102, no. 1, pp. 88–92, 2008.

[3] F. Gutiérrez, P. Ollero, A. Cabanillas, and J. Otero, "A technical pilot plant assessment of flue gas desulfurisation in a circulating fluidised bed," *Advances in Environmental Research*, vol. 7, no. 1, pp. 73–85, 2002.

[4] C. Sheng, M. Xu, J. Zhang, and Y. Xu, "Comparison of sulphur retention by coal ash in different types of combustors," *Fuel Processing Technology*, vol. 64, no. 1-3, pp. 1–11, 2000.

[5] P. Thy, B. Jenkins, S. Grundvig, R. Shiraki, and C. Lesher, "High temperature elemental losses and mineralogical changes in common biomass ashes," *Fuel*, vol. 85, no. 5-6, pp. 783–795, 2006.

[6] P. Buryan, J. Vejvoda, J. Krátký, and L. Veverka, "The causation of high consumption of limestone in coal fluidized bed boiler desulfurization," *Ceramics–Silikáty*, vol. 54, no. 1, pp. 85–88, 2010.

[7] T. Hlinčík and P. Buryan, "Use of technical lanoline from adjustment of sheep wool in desulfurization of fluidized-bed combustors," *Fuel Processing Technology*, vol. 92, no. 8, pp. 1475–1479, 2011.

[8] P. Buryan, "The negative effect of biomass co-combustion on desulfurization of combustion products from fluid steam generators," *Chemické listy*, vol. 108, no. 12, pp. 1162–1167, 2014.

[9] M. Hartman, O. Trnka, K. Svoboda, and V. Vesely, "Agglomeration of particles and defluidization phenomena in the fluid bed," *Chemické listy*, vol. 97, no. 10, pp. 942–948, 2003.

[10] Y. Suyadal, M. Erol, and H. Oguz, "Deactivation model for dry desulphurization of simulated flue gas with calcined limestone in a fluidized-bed reactor," *Fuel*, vol. 84, no. 12, pp. 1705–1712, 2005.

[11] E. Kakaras and D. Giannakopoulos, "Modeling of flue gas desulphurization using dry additives," *Chemical Engineering and Processing: Process Intensification*, vol. 34, no. 5, pp. 421–432, 1995.

[12] L. Lv, J. Yang, Z. Shen, Y. Zhou, and J. Lu, "Effect of additives on limestone reactivity in flue gas desulfurization," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 39, no. 2, pp. 166–171, 2017.

[13] T. Hlinčík and P. Buryan, "Evaluation of limestones for the purposes of desulphurisation during the fluid combustion of brown coal," *Fuel*, vol. 104, no. 2, pp. 208–215, 2013.

[14] Lhoist Group, "Sorbacal H and Sorbacal SP-Manufacturer's manual," 2019, May 2019. https://www.lhoist.com/us_en/market-segment/flue-gas-treatment-0.

[15] P. Buryan, "Use of waste dolomite from the production of glass beads from the desulphurisation of fluidised-bed boilers," *Chemické listy*, vol. 111, no. 4, pp. 333–337, 2017.

[16] A. Garea, J. R. Viguri, and A. Irabien, "Kinetics of flue gas desulphurization at low temperatures: fly ash/calcium (31) sorbent behaviour," *Chemical Engineering Science*, vol. 52, no. 5, pp. 715–732, 1997.

[17] A. H. Hattfield, "Investigation of reactivity of limestone for SO2 control," in *Dry limestone symposium injection process*, Gillbertswille, Kentucky, USA, June 1970.

[18] H. Nygaard, S. Kiil, J. E. Johnsson et al., "Full-scale measurements of SO_2 gas phase concentrations and slurry compositions in a wet flue gas desulphurisation spray absorber," *Fuel*, vol. 83, no. 9, pp. 1151–1164, 2004.

[19] P. Buryan, "The influence of alternative solid fuels on desulfurization of fluidized bed boilers," *Chemické listy*, vol. 109, no. 8, pp. 635–640, 2015.

[20] P. Buryan, "The effect of biomass on the compliance with emissions limits in fluidised bed boiler desulfurization," *Energy and Fuel*, vol. 31, no. 1, pp. 119–123, 2017.

[21] P. Buryan, "Formation of Incrustations during the Cocombustion of Biomass in Fluidised Bed Boilers," *Journal of Chemistry*, vol. 2019, 7 pages, 2019.

[22] R. Agnihotri, S. S. Chauk, S. K. Mahuli, and S. S. Fan, "Sorbent/ash reactivation for enhanced SO2Capture using a novel carbonation Technique," *Industrial and Engineering Chemistry Research*, vol. 38, no. 3, pp. 812–819, 1999.

[23] Y. Wu, J. F. Charland, E. J. Anthony, and L. Jia, "A Study on the reactivation of five fly ashes from commercial Circulating Fluidized Bed (CFB) boilers," *Energy & Fuels*, vol. 18, no. 3, pp. 830–834, 2004.

[24] J. Starý, P. Kavina, M. Vaněk, I. Sitenský, J. Kotková, and T. Hodková, *Mineral Resources of the CR*, Geofond Prague, 2009.

[25] Lhoist Group, "Dry powdered lime for acidic gas removal in coal fired power plant, Manufacturer's presentation," 2020, August 2020. http://bioxysorb.eu-projects.de/Portals/30/Dry%20powdered%20lime%20for%20acidic%20gas%20removal%20in%20coal%20fired%20power%20plant_LHOIST.pdf.