

COMPARISON OF LIMESTONE ADSORPTION REACTIVITY DURING DESULFURISATION OF FLUE GAS FROM CO-COMBUSTION OF LIGNITE AND WOODCHIPS IN FLUIDISED-BED BOILERS

Petr Buryan

Department of Gas, Coke and Air Protection, University of Chemistry and Technology, Prague, Technická 5, 166 28, Praha 6, e-mail: buryanp@vscht.cz

Research presented in this article proves that woodchips addition significantly negatively influences limestone-based flue gas desulfurization process. This work focuses on the reduction of the adsorption reactivity of two types of calcined limestone that were used for capturing sulfur dioxide from flue gases originating from woodchips and brown-coal co-combustion in a fluidized-bed combustor.

Keywords: limestone, woodchips, fluidized-bed combustor, co-combustion, desulfurization

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1. Introduction

Sulfur dioxide emission reduction is achieved by feeding limestone into a fluidized bed combustor. It should be noted that the presence of lignite ash materials and limestone impurities play an important role on the desulfurization reactivity of limestone. Therefore, when selecting limestone the effect of the aforementioned substances should be taken into account. Among the possible side reactions of particular importance are the unfavorable reactions of silicon, aluminum, and iron oxides with the calcium oxide formed due to calcination under the real conditions in the combustor [1-3]. In our previous works was established that similar reactions take place during flue gas desulfurization when co-combusting various biomasses and lignite. As a result the surface CaO will be covered by compounds resulting from calcination [4-10]. In Figure 1 the sequence of particular minerals formation is depicted [8].

Currently attempting to reduce greenhouse gas emissions fossil fuels are being replaced with biomass. As a result the negative effects arising from the presence of various oxides becomes of crucial importance when using limestone. In fact in these cases increase in the consumption of limestone used for flue gases desulfurization is noted. Additionally it also results in increased energy consumption connected with limestone disintegration, transportation, storage, etc. Therefore, it is necessary to carefully choose both the proper limestone and ideal ratio of the combusting components in order to reduce limestone consumption.

The main focus of this study is to provide the foundations that will help to select the most suitable limestone for different expected ratios of the materials co-combusted with biomass i.e. of woodchips as well as ash composition formed during combustion.

2. Experimental part

2.1. Composition of the analyzed raw materials

The complex comparison of the desulfurization characteristics focused on the typical raw materials used in power plants in the Czech Republic. A series of biomass-related experiments were carried out. In this work the experimental results from lignite combustion by Sokolská uhelná company (U) are presented. The specific data were acquired from woodchips-lignite co-combustion, while using limestone from Čertovy schody (CS) and Štramberk (STR) quarries for desulfurization. The selected size of the limestone grains was 0.3-0.6 mm. This size range was selected considering the fluidization conditions (optically checked) in the laboratory apparatus – see Figure 2 [1, 2, 4]. In Tables 1 – 4 monitored raw material parameters are listed.

In Table 3 can be observed that the content of oxides that deposit on limestone particles and that are formed by the substances present in the combustion area (e.g. gehlenite, kernite, aluminum calcium silicates, ferrite, etc. [8]) is not insignificant.

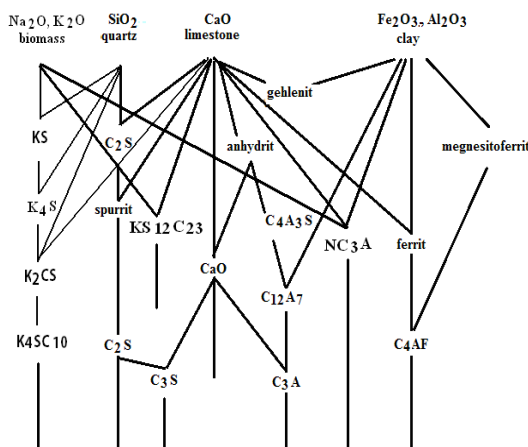


Figure 1: Formation of particular minerals, C - CaO, S - SiO₂, A - Al₂O₃, K - K₂O, N - Na₂O, spurrite - 2(2CaO·SiO₂) CaCO₃, magnesitoferrite - MgCO₃ enriched Fe₂O₃, gehlenite - 2CaOAl(Al_{1,22}Si_{0,78}O_{0,78})(OH)_{0,22}

Table 1 Parameters of the monitored lignite and biomass - % wt.

Parameter	Lignite	Woodchips
W ^a	35.61	1.22
A ^d	26.59	14.83
V ^a	39.17	67.23
Q _s [MJ/kg]	20.79	17.00
Element		
N ^d	0.51	0.83
C ^d	48.37	42.64
H ^d	5.28	5.13
S _{sp} ^d	1.55	0.10

Note: *. The content of the combustible sulfur, d .. dry, a .. anal. sample

Table 2 Contents of sulfur forms in the dry lignite

Sample	Total	Sulfate	Pyritic	Organic
Lignite	2.16	0.21	0.79	1.16

Note: the investigated lignite did not contain the sulfide sulfur

Table 3 Composition of lignite and woodchips ash (% wt)

Oxide	Lignite	Woodchips
Na ₂ O	1.05	0.59
MgO	1.02	4.18
Al ₂ O ₃	32.28	7.61
SiO ₂	47.01	39.56
P ₂ O ₅	0.28	3.51
SO ₃	3.68	2.29
K ₂ O	1.67	9.35
CaO	2.97	25.70
TiO ₂	1.73	0.67
MnO	0.06	2.50
Fe ₂ O ₃	7.84	3.70
SrO	0.06	0.06
Cl	-	0.51

Table 4 Limestone composition - % wt

Oxide	ŠTR	ČS
Na ₂ O	0.09	0.15
MgO	0.78	0.78
Al ₂ O ₃	0.50	0.87
SiO ₂	1.68	2.17
P ₂ O ₅	0.20	0.15
SO ₃	0.09	0.07
K ₂ O	0.06	0.11
CaO	96.20	95.20
TiO ₂	0.04	0.06
MnO	-	0.03
Fe ₂ O ₃	0.27	0.32
ZnO	0.1	-
SrO	0.04	0.06
Cl	0.02	0.03

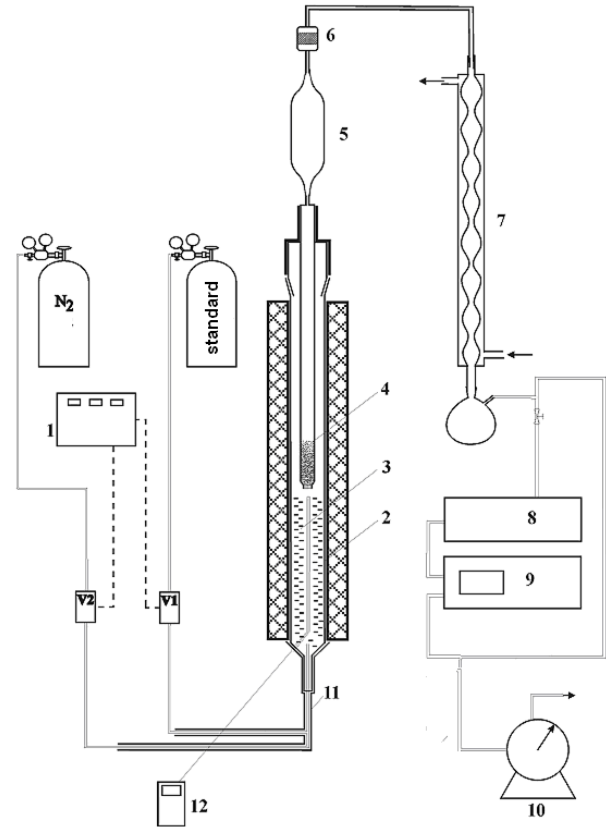


Figure 2: Apparatus scheme

1 – control unit, 2 – silicious reactor, 3 – silicious infill, 4 – reactor (inner diameter 1,7 cm, length 42 cm) with sample and with frit, 5 – flow speed inhibitor, 6 - filter, 7 – water cooler, 8 – cooling aggregate, 9 - analyzer, 10 - gasometer, 11 - heating, 12 - thermometer, V1,V2 – governors

2.2. Examination of biomass impact on the adsorption capacity of calcined limestone

The comparison of the adsorption capacity of both calcined limestones during lignite and woodchips co-combustion was monitored by breakthrough curves of standard model gas. The standard model gas had a composition similar to that flue gas generated from lignite combustion at 850 °C after flowing through a fluidized bed of calcined limestone. The model gas composition was the following: 13% CO₂, 6% O₂ and 6860 mg SO₂m⁻³ and balance N₂.

In the first part of the study the mixture to undergo calcination consisted of the same mass ratio of lignite to limestone and mixtures where 10% and 20% of the lignite mass was added as woodchips.

In the mixture used for the second part 5% and 10% of the lignite energetic content was replaced by woodchips. The required limestone quantity was also adjusted. In Table 5 the exact mixtures characteristics are given. Calcination process was performed in an external oven at 850 °C in the presence of air.

Table 5: Composition of the monitored mixtures –mass concentration

Sample	Lignite [g]	Limestone [g]	Biomass [g]	Biomass addition
1	20.0	4.0		
2	20.0	4.0	2.0	10 % lignite weight
3	20.0	4.0	4.0	20 % lignite weight
4	19.0	3.8	1.2	5 % lignite energetic content
5	18.0	3.6	2.4	10 % lignite energetic content
A		ČS		
B		ŠTR		

The basic criterion for comparison of the particular laboratory results was the time that passed from the moment of model gas input into the reactor until output sulfur dioxide concentration reached 400 mg SO₂m⁻³. The selected value is the current SO₂ emission limit for fluidized bed-boilers with power output over 100MW [11].

Another evaluated criterion was the quantity of SO₂ captured by the sorbent for constant concentration of input gas from the beginning of the experimental tests until the monitored concentration was reached. The quantity of SO₂ captured was calculated by the following formula:

$$M_{SO_2} = (C_{SO_2} - C_{1,SO_2}) \cdot Q \cdot t \quad (1)$$

where: M_{SO₂} quantity of SO₂ captured by tested sorbent, [mg];
 C_{SO₂} concentration of SO₂ in model gas, [mg.l⁻¹];
 C_{1,SO₂} concentration of SO₂ in output gas, [mg.l⁻¹];
 Q model gas flow, [l.h⁻¹];
 t time to achieve a required concentration, [h].

The quantity of sulfur captured by limestone during the calcination process of the mixture with lignite is not taken into account.

Experimental data that capture the effect of the addition of various quantities of woodchips (biomass) into the monitored mixtures of lignite and limestone are summarized in the Tables 6 – 13. In these tables are listed the time needed to achieve the emission limit, the quantity of SO₂ captured by calcination and the quantity of the captured SO₂ normalized to 1kg of raw limestone.

To simplify the comparison of all particular additives the experimental results were compiled in the form of the so-called breakthrough curves depicted in Figures 3 – 11.

These breakthrough curves give the relation between the times needed to reach 400 mg/m³ SO₂ concentration and the SO₂ concentration in output flue gas from the fluidized bed reactor.

Initially a comparison of the mixtures of calcined limestone and lignite without the addition of woodchips was carried out. The obtained data are listed in Table 5, for the breakthrough curves see Figure 3.

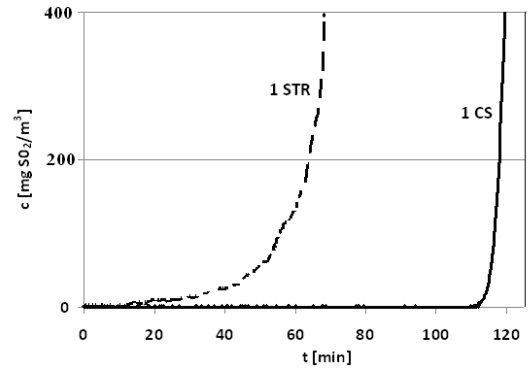


Figure 3: The desulfurization capacity of limestone mixture comparison

Table 6: Comparison of limestone adsorption characteristic in when achieving emission limit

Sample	Time to achieve the emission limit [min]	Total SO ₂ capture [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
1 CS	119.6	547.0	136.7
1 STR	68.5	311.5	77.9

Figure 3 SO₂ concentrations at output from the reactor heated at 850 °C with CS limestone calcines and STR obtained in the presence of lignite are depicted. From Figure 3 can be observed that the adsorption reactivity of CS limestone calcine is significantly higher (compared to STR limestone). The desired emission limit was achieved after approximately 2 hours. In contrast, the STR limestone calcine desulfurization ability to achieve the emission limit was 43% worse.

Data acquired from the laboratory monitoring of individual limestone and lignite mixtures to which the woodchips equivalent to 10% wt. lignite at temperature 850°C was added are depicted in Table 7 and graphically in Figure 4. The breakthrough curves depicted in Figure 4 and data in Table 7 are similar to those of mixtures without woodchips addition. Adsorption when using CS limestone calcine has almost 16% better desulfurization capacity compared to STR limestone. The time needed to achieve the emission limit were 93 minutes and 79 minutes for CS limestone and STR limestone, respectively.

The results obtained at 850 °C for the mixture of particular limestone and lignite after woodchips was added to the amount of 20% wt of lignite, are depicted in Table 8 and graphically shown in Figure 5.

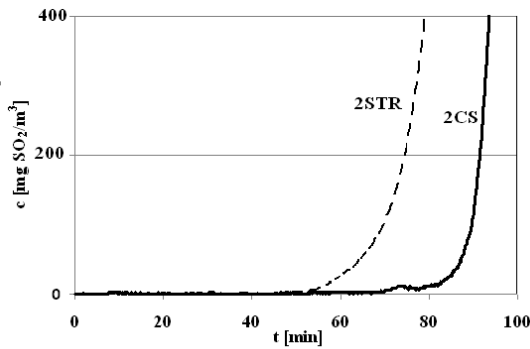


Figure 4: Impact of addition of 10% wt. woodchips on desulfurization capacity of limestone

Table 7: The time needed and total SO₂ captured to achieve the emission limit after replacing 10% wt lignite with woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
2CS	93.4	426.9	106.7
2 STR	79.0	360.1	90.0

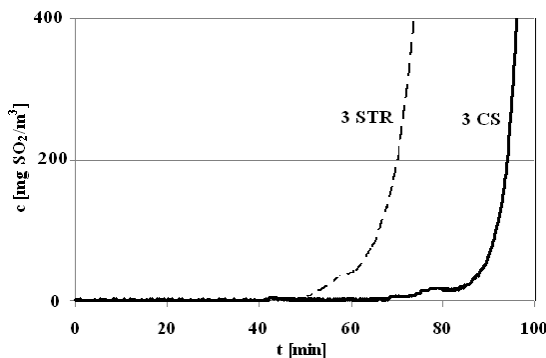


Figure 5: Impact of 20% wt. woodchips addition on the desulfurization capacity of limestone.

Table 8 The time needed and total SO₂ captured to achieve the emission limit after replacing 20 wt.% lignite with woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
3 CS	96.1	439.4	109.8
3 STR	73.7	336.0	84.0

From the acquired results a higher efficacy in the SO₂ capture rate when using CS limestone, approximately by 23%, can be observed. The time needed to achieve the emission limit was 96 minutes during when

using CS limestone and 74 minutes when using STR limestone.

Experimental tests were performed also at 850 °C by continuous monitoring of the mixtures limestone and lignite into which 5% of lignite was replaced by woodchips. The results are given in Table 9 and graphically compared in Figure 6.

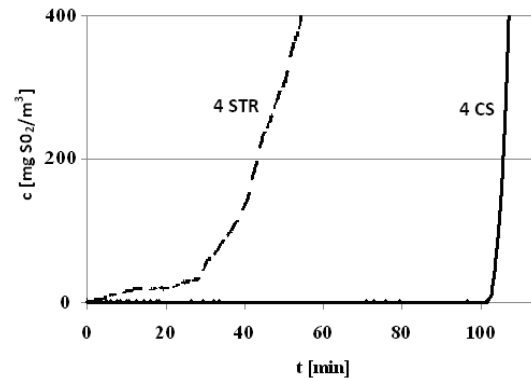


Figure 6: Impact of 5% lignite replacement with woodchips on the desulfurization capacity of limestone

Table 9: The time needed and total SO₂ captured to achieve the emission limit after replacing 5 % wt. lignite with woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
4 CS	107.1	489.9	128.9
4 STR	54.7	247.0	65.0

In Figure 6 the SO₂ breakthrough curves when using lignite and limestone mixtures after the addition of woodchips at 5% of lignite energetic content are depicted. After the addition of woodchips, a significant time reduction to achieve the emission limit in the flue gas for both limestones is observed. The time needed to achieve the emission limit when using CS limestone was approximately 107 minutes. When using STR limestone was 55 minutes which means 49.6% lower desulfurization capacity compared to CSR limestone.

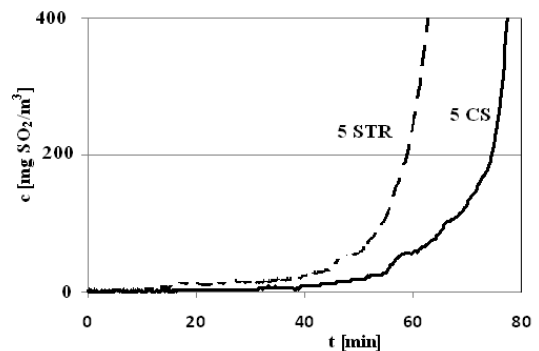


Figure 7: Impact of 10% lignite replacement with woodchips on the desulfurization capacity of limestone.

Table 10: The time needed and total SO₂ captured to achieve the emission limit after replacing 10% wt. lignite by with woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
5 CS	77.3	352.2	97.8
4 STR	62.8	286.0	79.4

In Figure 7 the SO₂ breakthrough curves comparing the adsorption capacity of lignite, limestone and woodchips mixtures after replacing 10% wt. lignite with woodchips are depicted. It is obvious from Figure 7 that limestone calcine from STR quarry has lower desulfurization efficiency (ca by 19%) compared to CS limestone calcine. The time needed to achieve the emission limit was 77 minutes when using CS and 63 minutes for STR limestone.

The summary data presented in Tables 5 – 10 and in Figures 3 – 7 were processed so that the results for CS and STR limestone are shown separately.

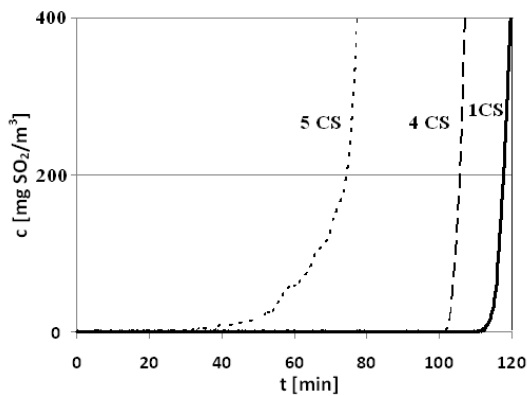


Figure 8: The breakthrough curves of lignite and CS limestone mixtures and after the replacement of 5% and 10% of the energetic content of lignite by woodchips.

Table 11: The time needed and total SO₂ captured to achieve the emission limit when using CS limestone mixture and after replacing 5% and 10% wt lignite by with woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
1 CS	119.6	547.0	136.7
4 CS	107.1	489.9	128.9
5 CS	77.3	352.2	97.8

In Figure 8 the SO₂ breakthrough curves and in Table 11 the assembled data are depicted. A decrease on CS limestone adsorption reactivity is observed. This behavior was observed after replacing 5% and 10% energetic content of lignite with woodchips. It is obvi-

ous from Figure 8 that the highest desulfurization efficacy has lignite and CS limestone mixture without woodchips addition. With a slightly worse time needed to achieve the emission limit (by less than 11%) comes the mixture where 5 % lignite was replaced by woodchips. The shortest desulfurization time needed to achieve 400 mg of SO₂ in this case was observed for the mixture where 10% lignite was replaced by woodchips (deterioration by ca 35%). Regarding the adsorption capacity the result after the decrease reached 71.5%.

Other breakthrough curves depicted in the Figure 9 and data in the Table 12 clearly summarize the reactivity of STR limestone depending on the quantity of lignite replacement by biomass monitored in ČEZ power plants. In Figure 9 a comparison of desulfurization activity among pure lignite and the mixtures of lignite and biomass in which 5% and 10% of lignite energetic content was replaced by woodchips is depicted.

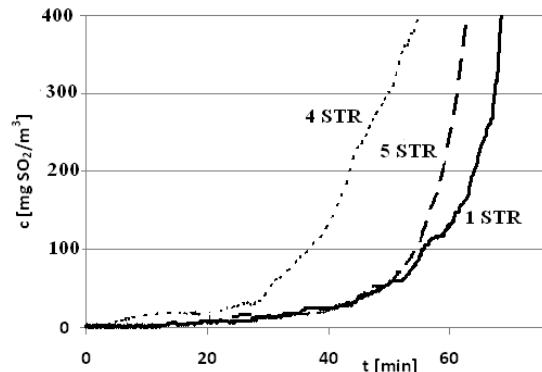


Figure 9: The breakthrough curves of lignite and STR limestone mixtures and after the replacement of 5% and 10% of the energetic content of lignite by woodchips

Table 12: The time needed and total SO₂ captured to achieve the emission limit when using STR limestone mixture and after replacing 5 wt% and 10 wt% lignite by with woodchips.

Sample	Time to achieve emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
1 STR	68,5	311.5	77.9
4 STR	54,7	247.0	65.0
5 STR	62,8	286.0	79.4

Referring to the Figure 9 can be stated that the highest desulfurization efficacy occurs for pure lignite and STR calcine mixture. The reaction with the mixture took place with only a slightly shorter time difference to achieve the emission limit. It should be noted that instead of 10% only 8% of lignite was replaced with woodchips. Desulfurization time when using the mixture containing 5% woodchips was over 20% shorter. On the contrary the adsorption capacity of calcine prepared by replacing 10% lignite energetic content with

woodchips increased by more than 1.5 g SO₂/ kg limestone.

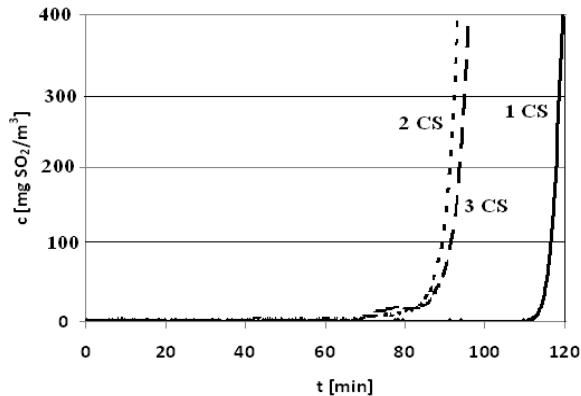


Figure 10: The breakthrough curves of lignite and CS limestone mixtures and after the addition of 10 and 20% wt. of woodchips

Table 13: The time needed and total SO₂ captured to achieve the emission limit when using STR limestone mixture and after adding 10% wt. and 20% wt. woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
1 CS	119.6	547.0	136.7
2 CS	93.4	426.9	106.7
3 CS	96.1	439.4	109.8

The breakthrough curves of SO₂ concentration in Figure 10 show the CS limestone reactivity for three different mixtures. Number 1 consists of limestone and lignite mixture, number 2 is the mixture where 10 % of lignite mass was added as woodchips and number 3 is the mixture where 20 % of lignite mass was added as woodchips. Based on the experimental results the highest desulfurization efficacy was observed for the mixture of lignite and limestone calcined without woodchips. Other breakthrough curves of the mixtures with the woodchips have comparable behavior and their desulfurization capacity is similar. Compared to the activity of pure lignite with limestone CS, the desulfurization time to achieve the emission limit for the mixture containing 20% woodchips is shorter by almost 20%, while for 10% woodchips addition even by 22%.

The intersection curves in Figure 11 and the data depicted in Table 14 show STR limestone reactivity for three sample mixtures. The activity of the sample containing only lignite, and also for the samples containing lignite with 10 and 20 % wt. woodchips addition are depicted. The best behavior was observed for the mixture containing 10% woodchips. The second one needing only 7% shorter time to achieve the emission limit was the mixture containing 20% woodchips. The last one needing 13% shorter time to reach the emission

limit was the mixture containing lignite and STR limestone.

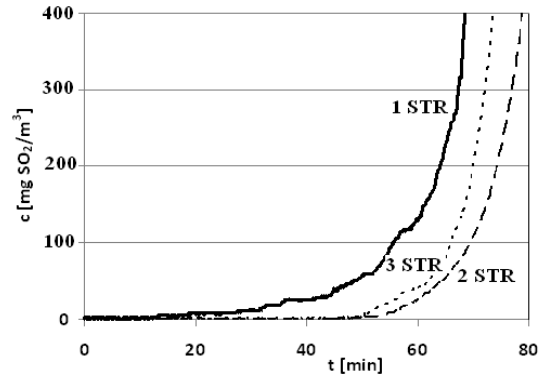


Figure 11: The breakthrough curves of lignite and STR limestone mixtures and mixtures after the addition of 10 and 20% wt. woodchips

Table 14: The time needed and total SO₂ captured to achieve the emission limit when using CS limestone mixture and after adding 10% wt. and 20% wt. woodchips

Sample	Time to achieve the emission limit [min]	Total SO ₂ captured [mg]	SO ₂ capture rate in relation to limestone - kg [g SO ₂ /kg limestone]
1 STR	68.5	311.5	77.9
2 STR	79.0	360.1	90.0
3 STR	73.7	336.0	84.0

The total adsorption capacity base on the ability to capture SO₂ at 850 °C, i.e. relative limestone reactivity is summarized in Table 15. In Table 15 the differences between SO₂ adsorption under the given conditions related to CS limestone sorption as well as increase in limestone consumption compared to CS limestone consumption without woodchips addition under the corresponding adsorption conditions are listed.

Table 15: Total limestone adsorption capacity comparison once the emission limit was reached

Specification	Adsorption robustness [g SO ₂ /kg limestone]	Difference [g SO ₂ /kg limestone]	Consumption increase [kg limestone]
1 CS	136.75	0	0
4 CS	128.93	-7.82	6.1
3 CS	109.85	-26.9	24.5
2 CS	106.73	-30.02	28.1
5 CS	97.84	38.91	39.8
2 STR	90.03	-46.72	51.9
3 STR	84.00	-52.75	62.8
5 STR	79.44	-57.31	72.1
1 STR	77.88	-58.87	75.6
4 STR	65.01	-71.74	110.4

Table 15 clearly shows better results for CS limestone usage even when performing woodchips co-combustion compared to STR limestone. For any ratio of lignite to limestone to woodchips, the application of CS limestone is more convenient than STR limestone. For example, in the experiments with only with limestone can be observed that the difference in adsorption capacity is over 43%. CS limestone capture rate is 136.75 g SO₂/kg limestone and STR limestone capture only 77.88 g SO₂/kg limestone. The entire comparison confirms that higher CaO is not the only indicator for higher desulfurization efficacy.

Based on the experiments presented in this paper when considering the suitable ratio of lignite to limestone to biomass for co-combustion in a fluidized-bed combustor, the most suitable mixture appears to be the one where 5% of the energetic value of lignite was replaced with woodchips. SO₂ capture rate in this case was 128.93 g SO₂/kg limestone which is 94% efficacy of sample without woodchips. Other experiments with addition of 10% and 20% lignite weight showed capture rate efficacy around 79% of the SO₂ captured when using CS limestone without woodchips addition.

This model study focused only on standard gases with SO₂. Effects related to the catalytic reduction of nitrogen oxides in the flue gases and tar influence on flue gas desulfurization were not monitored.

3. Conclusion

In this work adsorption reactivity of two limestone types – limestone from Čertovy schody and limestone from Štrambersk quarries was compared. In all cases, the laboratory experiments showed a higher adsorption capacity of limestone originating from Čertovy schody, regardless of the fact that limestone from Štrambersk has a higher CaO content. The difference in SO₂ capture rate reached in one comparison even 43%. The comparison confirms that higher CaO is not the only indicator for higher desulfurization efficacy.

The results for Čertovy schody limestone proved in all cases that desulfurization efficacy of fluidized-bed boilers flue gases is worse after the addition of biomass during calcination. On the other hand, for the Štrambersk limestone the adsorption capacity increased after woodchips addition (except for one case).

Taking into consideration the current technological conditions the utilization of Čertovy schody limestone instead of Štrambersk limestone at any ratio with biomass leads to significant cost decrease. This means that limestone consumption decreases as well as energy on its alternation, transportation, storage, etc. Additionally, there is also clear decrease in the quantity of the resulting stored energetic side products.

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