

EXPERIMENTS ON ADDITIVE DESULPHURISATION BY SODIUM BICARBONATE IN COAL-FUEL BOILERS

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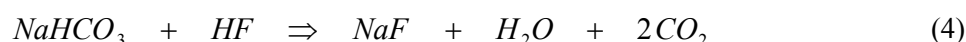
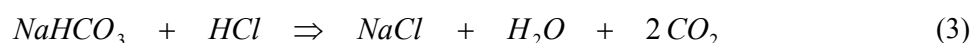
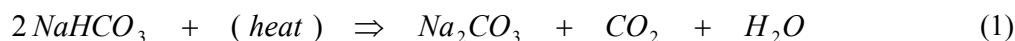
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This paper describes experiments on the application of sodium bicarbonate desulphurisation in the coal-fuel boiler. The boiler has been in operation for several years now and it has reliably fulfilled the original assignment to reduce SO₂ emissions from the value of 1200 - 1500 mg/Nm³ to 400 mg/Nm³. Higher desulphurisation efficiency is determined only by the ratio of Na/S sorbent dosage. The resulting product of desulphurisation is stored together with fly ash in underground mines, and has no influence on the groundwater. Positive experience of the tests and boiler operation lies in higher reactivity of sodium and sulphur as compared with conventional methods based on limestone. Within the scope of the secondary measures of elimination of sulphur oxides in combustion products, an experimental dry-method desulphurisation of combustion products was performed by blasting an agent containing sodium bicarbonate NaHCO₃ (99.6 %) into the flue ways before the electrostatic precipitator in a coal-fuel furnace with the steam output of 220 t/h.

Keywords: combustion, desulphurisation, pulverised, bicarbonate

1. INTRODUCTION

Calcium-based methods have a limited use of the desulphurisation product. Gypsum as calcium sulphate CaSO₄ is essentially hazardous waste and requires a special storage mode. In this situation the use of additive desulphurisation and other chemical compounds is better than calcium. Desulphurisation by sodium bicarbonate includes a process of thermal activation triggered by sodium bicarbonate interaction with hot combustion products. Sodium bicarbonate is at this stage immediately transformed into carbonate. Carbonate is very porous and has a large specific surface. The surface of newly generated carbonates is a very good sorbent of heavy metals and PCDD/F. The desulphurisation process can be described by the following equations:



Sodium bicarbonate is a hygroscopic substance and it tends to paste when fine ground (it is supplied as coarse grained and then ground to the required grain size immediately before dosing).

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Advantages: High desulphurisation efficiency, possible elimination of nitrogen oxides (only chemical consideration), financially and technically undemanding application of sodium bicarbonate (Halstead and Raask, 1969; Joutsenoja, 1998).

Disadvantages: High costs connected with the use of sodium bicarbonate (the price of the agent), deposition of sodium sulphate (Na_2SO_4) based products of desulphurisation (the largest and financially the most costly part).

The principle of the whole method of elimination of sulphur oxides (Szeliga et al., 2008) from combustion products is blasting ground sodium bicarbonate to the flue way before the two-stage electrostatic fly ash precipitator (the blasting location is shown in Fig. 1) with subsequent measurement of gaseous emissions and combustion product flow. The measurement of gaseous emissions was performed behind the flue exhauster as well as before the NaHCO_3 based agent inlet (see Fig. 1), that is at the outlet of the combustion gases from the furnace. Desulphurisation tests carried out at the furnace steam outputs of 110 t/h, 160 t/h, and 180 t/h, with the use of two types of the input fuel, i.e. black coal and a mixture of black coal and shed coal. Individual tests are described in Table 1.

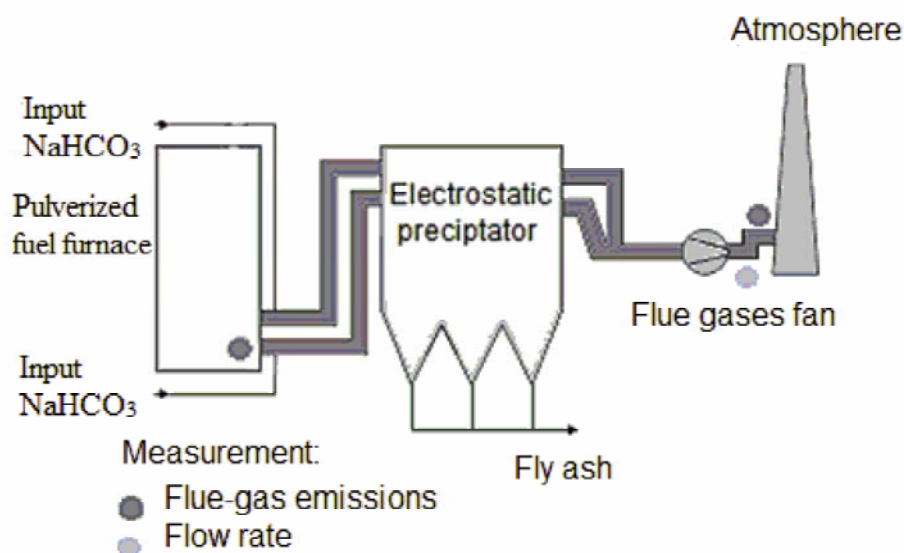


Fig. 1. NaHCO_3 unit

Table 1. List of desulphurisation tests

Date	Furnace output [t/h]	Fuel	Combustion product flow [Nm^3/h]
10.10.	110	pulverised fuel	152 100
11.10.	110	pulverised fuel + shed coal	145 616
15.10.	180	pulverised fuel + shed coal	271 944
16.10.	180	pulverised fuel + shed coal	269 495
17.10.	180	pulverised fuel + shed coal	261 538
18.10.	160	pulverised fuel + shed coal	220 991
19.10.	180	pulverised fuel + shed coal	274 244
22.10.	180	pulverised fuel + shed coal	258 106
23.10.	180	pulverised fuel + shed coal	265 112

The experimental desulphurisation tests were carried out at a pulverised-fuel furnace with a liquid slag chamber and with the steam output of 220 t/h and the nominal output of 161 MW. The temperature ranged from 165 to 195 °C. The SO₂ emissions represent min. 550 mg/Nm³, max. 1000 mg/Nm³, and the average concentration amounted to 650 mg/Nm³. The average concentration of SO₂ during the experimental tests was 747 mg/Nm³. The measurement methods and workplace equipments conforms to current requirements for chemical diagnostic methods. The research team is a part of accredited testing laboratory staff (CZ no. 1588).

Black coal was used in a one-day desulphurisation test only. During the remaining 9 days of tests a mixture consisting of black coal and shed coal was used. The chemical analyses of black coal and shed coal are stated in Table 2 and Table 3.

Table 2. Black coal parameters

Name	Marking	Value
Calorific value	[MJ/kg]	23.0
Ash content	[%]	14
Sulphur content	[%]	0.3 – 0.5
Water content	[%]	8 -10

Table 3. Black coal / shed coal mix parameters

Name	Marking	Value
Calorific value	[MJ/kg]	18.0
Ash content	[%]	44 - 46
Combustible volatile share	[%]	31 - 34
Ash softening temperature	[°C]	1 300
Ash fusing point	[°C]	1 445
Ash flow point	[°C]	1 505
Sulphur content	[%]	0.3 – 0.5
Water content	[%]	6 - 10

The dry method of elimination of sulphur oxides from the combustion products in the furnace with the maximum steam output of 220 t/h, was carried out with the use of a sodium bicarbonate (NaHCO₃) based agent. The agent contained 99.6 % of sodium bicarbonate and its specific weight was 1.1 – 1.3 kg/dm³. The NaHCO₃ based agent was supplied to the test site in 1 ton transport bags and it was then ground to the required grain size of $d_{90} \leq 20 \mu\text{m}$ using an experimental grinding unit with the rated output of 30 kW. The main objective of the experimental desulphurisation method (Galos et al., 2003) was to demonstrate that it is possible to eliminate SO₂ concentrations in combustion products and maintain the residual content of SO₂ below 200 mg/ mg/Nm³ with the use of other than the established methods based on exploitation of lime. The procedure of reduction of concentration of SO₂ in combustion gases was assigned in three theoretical levels of desulphurisation efficiency, 20 %, 40 %, 60 % and the maximum volume possible with regard to the maximum possible output of the mobile grinding unit. The experimental desulphurisation tests were carried out in the steam output levels of 110 t/h, 160 t/h, and 180 t/h in order to provide simulation of an actual operation. The duration of the experiment was 9 days and it was performed in the conditions of steady operation. The volume of the agent necessary to achieve the required desulphurisation efficiency was calculated in accordance with the stoichiometric balance (i.e. the known concentration of SO₂ in the raw combustion products,

theoretical efficiency, and the stoichiometric ratio of $2 \text{ NaHCO}_3/\text{SO}_2$ plus the final expert assessment. Continuous measurement of the SO_2 outlet gaseous emissions was conducted during each desulphurisation test including fly ash sampling from the right and the left section of the electrostatic separator. The samples were supplied for chemical analyses.

2. EXPERIMENTAL TESTS

The first desulphurisation test was conducted at the steam output level of 110 t/h within a two-day period. The aim of the desulphurisation tests was to achieve the theoretical efficiency of 20 %, 40 %, and 60 %. The initial fuel was black coal and for the remaining part of the test, which was carried out at the output level of 110 t/h, a mixture of black coal and shed coal was used. The development and the results of the two-day tests are presented in Table 4 and Fig. 2.

The concentration of SO_2 emissions was measured before and after the point of sorbent dosage. The flue gases pass through an electrostatic precipitator, where the ash from the boiler and reacted sorbent are captured in a form of sodium sulphate. After cleaning, the flue gases flow into the fan, where they are thoroughly mixed for analysis of the gaseous samples. The sampling site was located at the outlet of the flue gas fan, before entering the chimney. Measurements were carried out by the continuous analysers Hartmann Braun, Uras and Magnox based on the absorption principle in the infrared radiation. The measurement accuracy is determined by the type of device and the monitored gas. In general it can be stated that the accuracy of the SO_2 measurements by the continuous measurement analysers with calibration gas mixtures is around $\pm 3\%$ of calibrated span. Measurements were controlled by means of operating instruments and other independent analysers. The SO_2 concentration is determined before desulphurisation by means of combustible sulphur content in the fuel and it can not be changed. The sulphur concentration at the outlet was measured by means of two instruments. Each measurement method is burdened with a certain error. In the case of measuring the concentration of SO_2 sample after condensation it is slightly acidic. Passage of the fine fraction to the sample may affect the measured values. These changes are not essential.

Table 4. Results of desulphurisation of combustion gases – 110 t/h steam output

Date	Test No.	Desulphurisation target value	Flow rate NaHCO_3 [kg/h]	SO_2 [mg/ Nm^3]	HCl [mg/ Nm^3]	Capture [mg/ Nm^3] SO_2	Actual SO_2 [%]
10.10.	1	0%	0	704	60	0	0%
	2	20%	100	539	22	165	23%
	3	40%	180	411	12	293	42%
	4	60%	280	312	7	392	56%
11.10.	5	0%	0	728	63	0	0%
	6	20%	105	517	14	211	29%
	7	40%	195	399	6	329	45%
	8	60%	285	303	4	425	58%
	9	0%	0	739	50	0	0%
	10	20%	100	552	15	187	25%
	11	40%	185	452	7	287	39%
	12	60%	300	318	3	421	57%

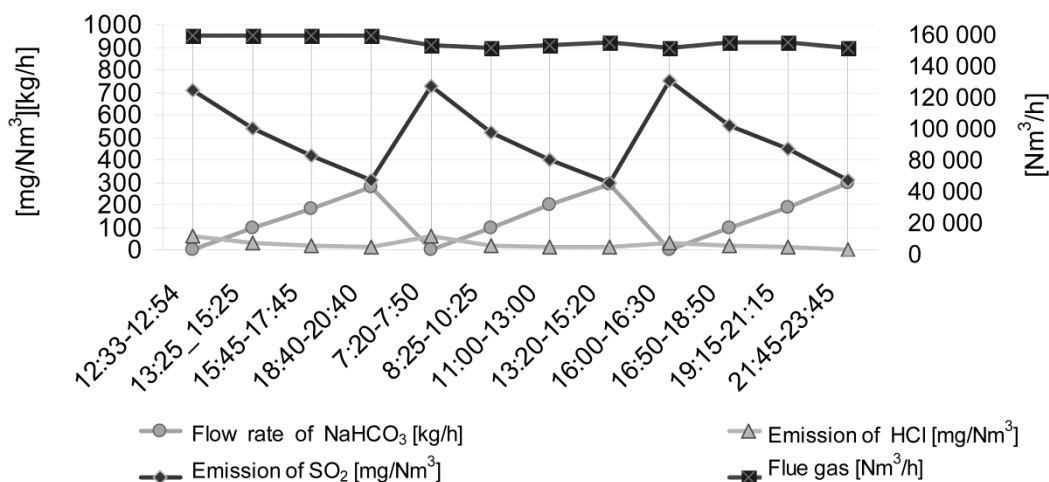


Fig. 2. Desulphurisation test results – 110 t/h

During the experiment the steam output of the furnace was increased to 160 t/h and a test was carried out with the goal to achieve the theoretical desulphurisation efficiency of 60%. The fuel used was a mixture of black coal and shed coal. The development and the results of the one-day desulphurisation test are presented in Table 5. and Fig. 3.

Table 5. Results of desulphurisation of combustion gases – 110 t/h steam output

Date	Test No.	Desulphurisation target value	Flow rate NaHCO ₃ [kg/h]	SO ₂ concent. [mg/ Nm ³]	HCl [mg/ Nm ³]	Capture [mg/ Nm ³ SO ₂]	Actual elim. SO ₂ [%]
18.10.	25	0%	0	780	58	0	0%
	26	60%	530	284	1	496	98%
	27	60%	523	302	1	478	98%

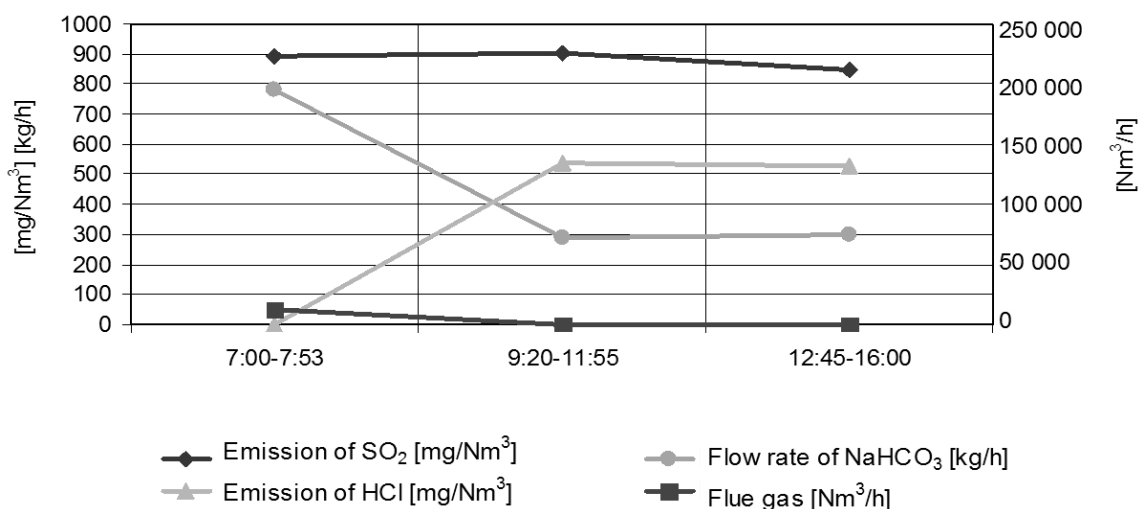


Fig. 3. Desulphurisation test results – 160 t/h

The experimental desulphurisation tests were further conducted at an increased steam output of 180 t/h. This test was performed with the maximum volume of the NaHCO₃ based agent. It was limited by the design and the maximum possible output of the mobile grinding unit. The tests at the steam output level had the longest time flow and were carried out over a six-day period. The fuel was a mixture of black coal and shed coal. The aim of the desulphurisation tests, apart from the already mentioned maximum volume of agent blasting, was to reach the theoretical efficiency amounting to 20 %, 40 %, and 60 %. The development and the results of the one day desulphurisation test are presented in Table 6 and Fig. 4.

Table 6. Results of desulphurisation of combustion gases –180 t/h steam output

Date	Test No.	Desulphurisation target value	Flow rate NaHCO ₃ [kg/h]	SO ₂ [mg/Nm ³]	HCl [mg/ Nm ³]	Capture [mg/ Nm ³] SO ₂	Actual elim. SO ₂ [%]
15.10.	13	0%	0	724	60	0	0%
	14	60%	453	263	0	461	64%
	15	60%	453	339	2	385	53%
16.10. - 17.10.	16	0%	0	715	53	0	0%
	18	20%	150	554	8	161	23%
	19	40%	297	392	2	323	45%
	17	20%	150	535	9	180	25%
	20	0%	0	746	62	0	0%
	21	40%	300	438	3	308	41%
	22	60%	476	338	2	408	55%
17.10.	20	0%	0	746	62	0	0%
	23	max	1015	145	2	601	81%
	24	max	1206	106	2	640	86%
19.10.	28	0%	0	780	57	0	0%
	29	40%	340	454	3	326	42%
	30	60%	548	323	1	457	59%
22.10.	31	0%	0	813	53	0	0%
	32	60%	496	307	1	506	62%
23.10.	33	0%	0	747	52	0	0%
	34	40%	280	426	2	321	43%

3. DISCUSSION

The main objective of the experimental desulphurisation tests was reduction of concentrations of sulphur oxides below the value of 200 mg/Nm³ by dosing the sodium bicarbonate (NaHCO₃) based agent into the flue ways, i.e. performing the dry additive method by a different chemical agent than is the commonly established lime CaCO₃ (Lindner and Wall, 1990; Meij et al., 1984). The initial part of the tests was performed at the steam output level of 110 t/h within a two-day period and with the theoretically determined efficiency of 20 %, 40 %, and 60 %.

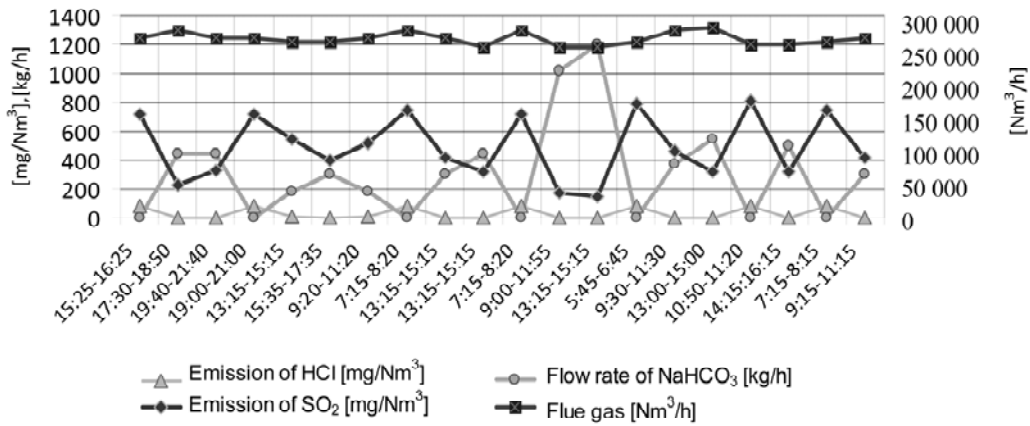


Fig. 4. Desulphurisation test results– 180 t/h

With the 148 858 Nm³/h average flow rate of the combustion products at the 110 t/h furnace output level, and with the 724 mg/Nm³ average concentration of sulphur dioxide in the combustion products, the reference consumption of the sodium bicarbonate based agent needed to meet the 200 mg/Nm³ emission limit was ca 439 kg/h. The reference stoichiometric ratio 2Na/S equals to the value of 1.55. The value of the reference stoichiometric ratio 2Na/S was determined on the basis of calculated and experimentally recorded figures. The longest period and the number of tests were conducted within the framework of the desulphurisation test at the 180 t/h steam output level. At the 180 t/h steam output level, with the 270 000 Nm³/h average flow rate, the average concentration of sulphur dioxide in combustion products amounting to 760 mg/Nm³, the reference consumption of the sodium bicarbonate based agent needed to meet the 200 mg/m³ emission limit was ca 780 kg/h (Fig. 5). The reference stoichiometric ratio 2Na/S equals to the value of 1.47.

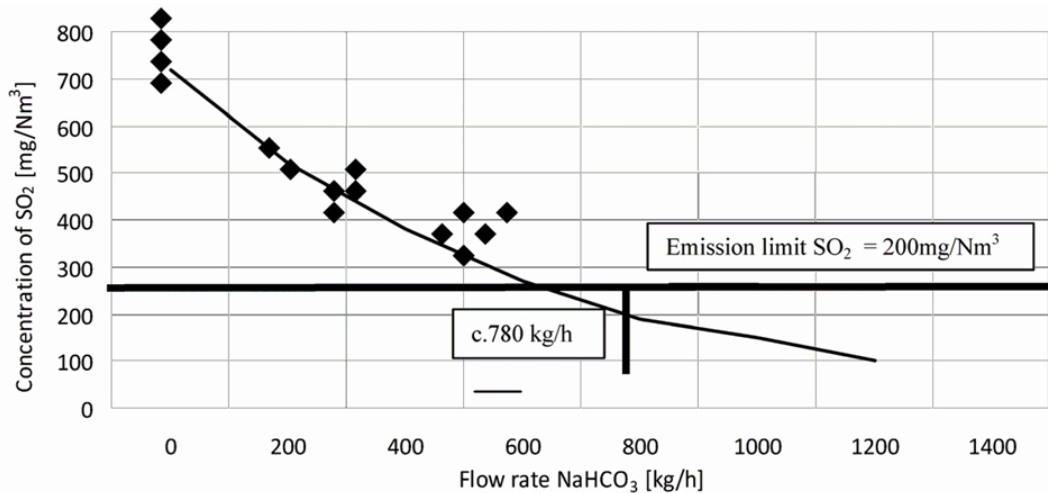


Fig. 5. Reduction of SO₂ in dependence on the NaHCO₃ flow – 180 t/h

The value of the reference stoichiometric ratio 2 Na/S was determined on the basis of calculated and experimentally recorded figures presented in Fig.6. The conclusions are presented in Fig. 6, which shows the dependency of the desulphurisation level on the stoichiometric ratio 2 Na/S. The final output of the experimental testing is recorded in the reference Fig. 7, which shows the dependency of the desulphurisation level on the stoichiometric ratio of all methods used in the Czech Republic, i.e. the dry method, the semi-dry method and the wet lime-cleaning method and the new method described in the article. The diagram includes the calculated values of dependency of the desulphurisation level on the stoichiometric ratio 2 Na/S, i.e. the results of the dry-way desulphurisation using the sodium

bicarbonate based agent. The possible ways of increasing desulphurisation efficiency with the sodium bicarbonate based agent may be summarise in the following points:

- The fine grain-size is a factor which enhances desulphurisation efficiency.
- Elimination of the friction losses in the transportation piping from the grinder to the agent blasting point to the lowest value possible.
- The blasting with flanges may be improved in order to achieve a better blending effect of the gaseous and the solid parts.
- A very significant factor influencing the acquired desulphurisation efficiency is the extension of the agent reaction time, and consequently possible adjustments of electrostatic fly-ash separator parameters.

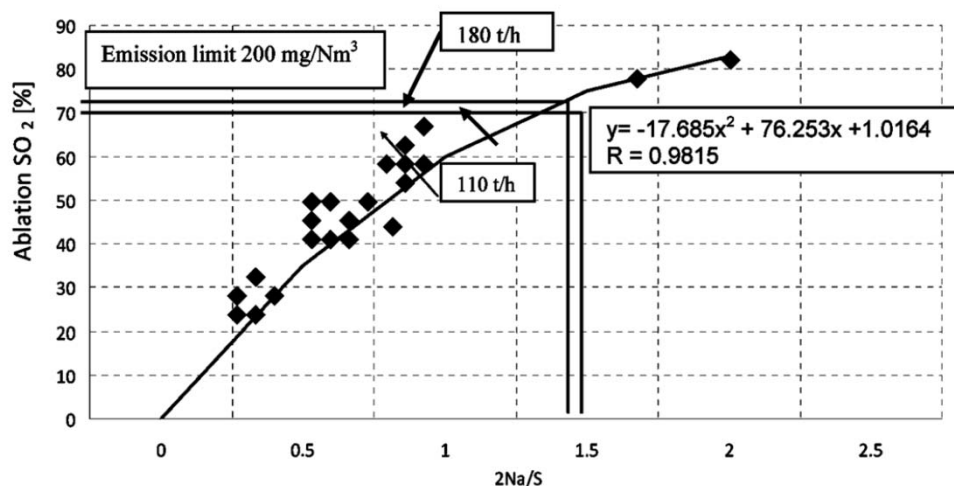


Fig. 6. The dependency of the level of desulphurisation on the stoichiometric ratio 2 Na/S

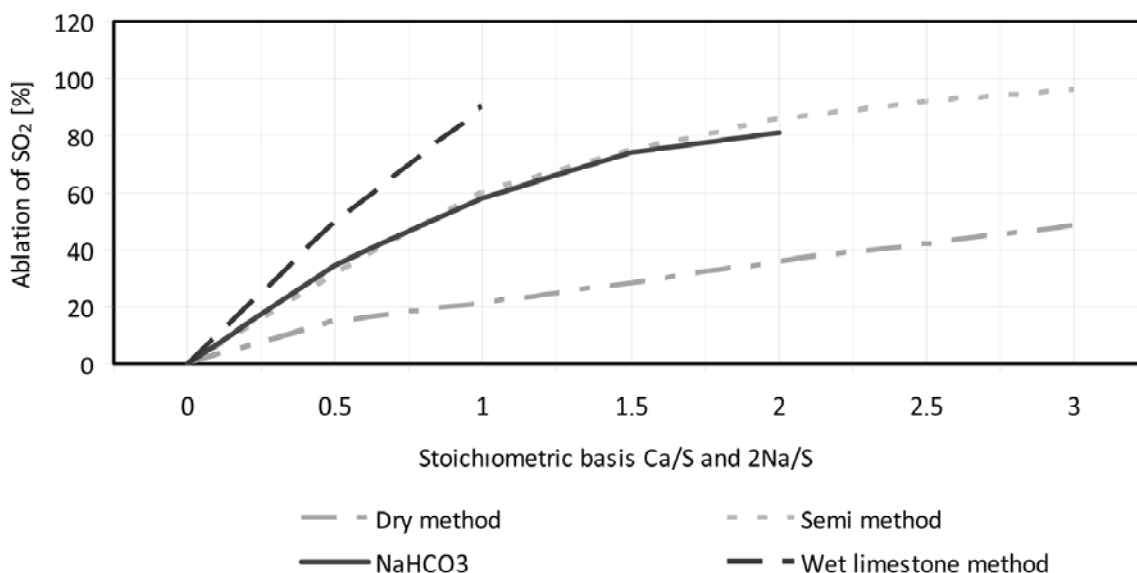


Fig. 7. The dependency of the level of desulphurisation on the stoichiometric ratio for individual methods and the new method by sodium bicarbonate described in the article

Dust emissions are determined by the particulate filter quality at the output of the boiler. In the case of the measured boiler the value guaranteed by the manufacturer of electrostatic filters is 100 mg/ Nm³.

During operation, the current value reaches 40-50 mg/ Nm³. In the case of sodium bicarbonate application, an increase in the flow of solids in the filter is negligible without measurable effect (separation efficiency of 99.95%). When using sodium bicarbonate, there are no serious corrosion problems. Basically, the flue gas tract operates only above the dew point. Utilisation of the desulphurisation product is limited and in the long term it is appropriate to store the product in underground coal mines.

During the desulphurisation process carbon dioxide is created. With regard to coal combustion this amount is negligible and does not affect significantly the total production of CO₂. Similar problems are encountered in the calcium desulphurisation processes. The sodium bicarbonate desulphurisation process was promoted and introduced by the company SOLVAY in the Czech Republic. The first tests were carried out in the melting boiler Třebovice power plant. The presented method is applied in the Kolín power plant.

4. EVALUATION

The critical place of the desulphurisation technology (Galos et al., 2003; Meij et al., 1984) with the use of sodium bicarbonate dosing is represented by the resulting properties of the fly ash. Primarily, it is the concentration of sodium ions Na⁺ and sulphate ions SO₄²⁻. A high concentration of salts in the leach does not allow its deposit to be regularly fly-ash dumped.

due to the dissolved matters and possible pollution of underground waters. The final concentrations of the dissolved matter which are influenced by quite high solubility of the final products with the sodium sulphate content may be critical also from the ecotoxicity viewpoint (Maier et al., 1990). Desulphurisation processes are currently drawing much attention. Calcium-based methods have a limited use of final products. The methods based on sodium require storing the final product in discarded mines, where there is no danger of underground water contamination. The method described in the article is simple and fast to implement.

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