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FULL-SCALE EVALUATION OF SO₂ CAPTURE INCREASE FOR A SEMI-DRY FGD
TECHNOLOGY

MOŽNOSTI ZVÝŠENÍ ÚČINNOSTI POLOSUCHÉ TECHNOLOGIE ODSÍŘENÍ

Abstract

The paper is focused on examination of a possibility of increase of current semi-dry FGD technology SO₂ capture ratio for two 130 t/h PC boilers that burn a blend of lignite and hard coal. The FGD unit has been designed to reach SO₂ emission limit 1350 mg/Nm³, the aim of the work is to verify reaching SO₂ emission targets 500 and 200 mg/Nm³. The examination consisted of experiments with the goal to determine real correlation of SO₂ capture ratio with Ca/S and various differences of temperature in absorber and dew point. Based on these correlations, solvent consumption for the new emission targets was obtained. Second objective was evaluation of solvent consumption for the case of future substitution of recent coal blend by a new blend of lignite and hard coal. Experiments using recent fuel have been carried out in a long-time range in full scale operation, resulting in quantification of correlation of Ca/S and temperature difference with the SO₂ capture ratio.

Abstrakt

Príspevek sa zaoberá možnosťou zvýšiť účinnosť u stávajúcej technológie polosuchého odsírenia pro kotle spalujúcej smes čierneho a hnedého uhli o výkonu 2x130 t/h, ktorá bola projektovaná pro dosažení emisního limitu SO₂ 1350 mg/Nm³, aby bylo možné dosáhnout úrovně koncentrace SO₂ ve spalínách 500, resp. 200 mg/Nm³. Cílem bylo experimentálně stanovit křivky závislosti účinnosti odsírení na poměru Ca/S a různé difference teploty v absorberu a teploty rosného bodu, na základě kterých by bylo možné stanovit provozní podmínky odsírení pro tyto nižší emisní limity, a stanovit spotřebu aditiva pro dosažení těchto limitů. Dalším cílem bylo stanovit spotřebu aditiva pro náhradu stávající směsi dvou uhli směsí jinou. Experimenty se stávající uhelnou směsí byly provedeny dlouhodobě v plném měřítku při různých provozních režimech odsírení, výsledkem je kvantifikace vlivu přebytku Ca/S a teplotní difference na účinnost odsírení.

Keywords

semi-dry FGD; SO₂ capture ratio; coal combustion; emission limit

1 INTRODUCTION

Recent years are in the scope of strengthening of emission limits for various pollutants, including sulfur dioxide. The first stage of reducing the emission limits is determined by current national legislation [1] that has set new emission limits from 1. 1. 2016 for sources > 50 MWt and from 1. 1. 2018 for sources < 50 MWt. However, the emission limits strengthening goes beyond the national legislation. A new Industrial Emission Directive (IED) [2] has been recently adopted and the new emission limits following BAT shall be implemented into the national legislation by 2021. This of

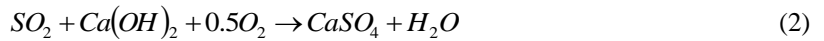
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course brings significant demands on energy sources operators, who are launching various attempts to improve performance of recent technologies rather than decide new investments. This is specifically valid for flue gas desulphurization (FGD) units that have been designed for certain SO₂ capture ratio and still have some possibility to go beyond the designed values. Such an example is presented in this paper, concerning experimental verification of SO₂ capture increase for a semi-dry FGD technology in a PC fired boiler.

2 SEMI-DRY FGD

The semi-dry FGD technology is commonly used as a “middle” way in SO₂ capture from flue gas, among the direct additive technology for FBC boilers and the wet scrubbing FGD for large scale and high sulfur fuels. The semi-dry FGD is typically used for medium size boilers combusting low to medium sulfur containing coal [3]. The technology typically consists of a spray absorber, where a solution of calcium hydroxide (so-called “lime milk”) is used for SO₂ capture. The reaction mechanism is as follows:



The resulting product is a mixture of CaSO₃ and CaSO₄ hydrates, so it cannot be further used and must be treated as a waste [4].

The SO₂ capture ratio is affected by two main parameters – the Ca/S ratio, defined as mol of Ca in the additive per mol of S in coal, and temperature difference between actual temperature in the spray absorber and the dew point of the flue gas in the absorber, further marked as Δt_{AD}. Alternatively, one can express the conditions in the absorber by relative humidity. Generally, a smaller difference between the temperatures improves the SO₂ capture ratio; however, the limitation is that condensation must not take place [5], [6]. An idea can be given by the following Figure 1, which shows correlation of SO₂ capture ratio with relative humidity in the absorber and three different Ca/S ratios.

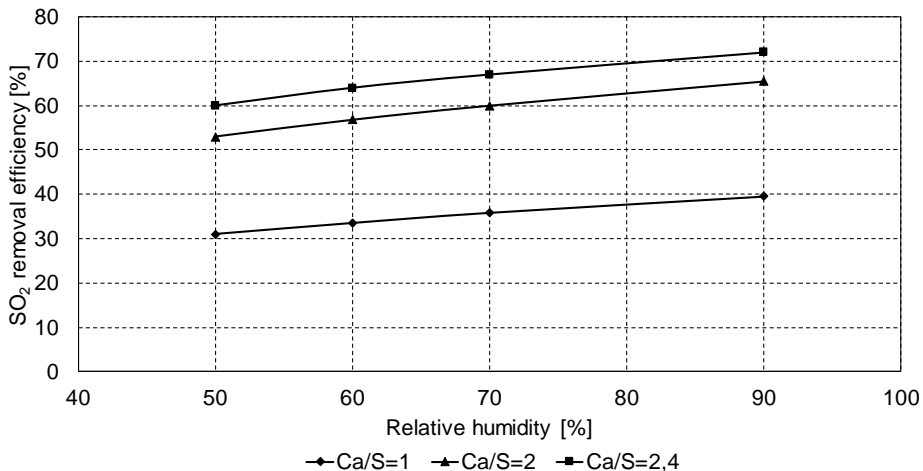


Fig. 1 Correlation of SO₂ capture ratio with Ca/S and relative humidity, reproduced from [7]

The correlation of sorbent stoichiometry expressed as the molar Ca/S ratio and SO₂ capture ratio can be approximated by following equation [8]:

$$\eta = 1 - \exp^{-K \cdot (Ca/S)} \quad (4)$$

The common problem of the Equation 4 is knowledge of K , w which must be usually obtained experimentally, since it depends on various parameters, mostly on sorbent properties, conditions in the spray absorber and its design as well as on fuel and flue gas properties. As long as the K is known for a certain temperature difference, estimation of SO_2 capture ratio with change of Ca/S can be made.

3 EXPERIMENTAL

The aim of the experiments was to evaluate current state of operation of a semi-dry FGD (delivered by ABB Fläkt in 1998) that has been designed for SO_2 capture for two 130 t/h PC boilers originally designed for lignite combustion, now burning a coal blend (70 % of lignite + 30 % of hard coal). This FGD unit is now reaching emission target 1350 mg/Nm^3 , which means the SO_2 capture ratio about 55 % for this sort of coal blend. However, due to the facts mentioned above, it is required to reach emission limit 500 and in further future possibly down to 200 mg/Nm^3 . For that purpose, a series of long-time duration experiments has been carried out, changing the Ca/S ratio and temperature difference in the spray absorber with aim to verify new limits attainability and evaluate sorbent consumption.

3.1 Current operation conditions of the semi-dry FGD unit

At the boiler load 130 t/h, typical operation parameters of the FGD unit are summarized in following Table 1. Flue gas flow and inlet water flow values are referenced to 1 kg of burned fuel. Some of the data is directly measured, typically temperatures, concentrations and pressures. Other data is calculated from material and energy balance of the boiler, based on measured boiler operation parameters.

Tab. 1 Operation parameters of the semi-dry FGD unit

Parameter	Value	Unit
Flue gas temperature inlet	165,3	°C
Temperature in the spray absorber	83,3	°C
Temperature of lime milk	20	°C
Pressure in the spray absorber	99,91	kPa
Flue gas flow inlet	7,836	$\text{Nm}^3/\text{kg}_{\text{fuel}}$
Flue gas flow outlet	8,777 *)	$\text{Nm}^3/\text{kg}_{\text{fuel}}$
Water vapor partial pressure	13,3	kPa
Dew point	51,5	°C
SO_2 inlet	3051	mg/Nm^3 , 6 % $\text{O}_{2\text{ref}}$
SO_2 outlet	1354	mg/Nm^3 , 6 % $\text{O}_{2\text{ref}}$
O_2 inlet	8,99	% vol.
O_2 outlet	9,80	% vol.
$\text{Ca}(\text{OH})_2$ inlet	478	kg/h
Water inlet	0,336	$\text{kg}/\text{kg}_{\text{fuel}}$

*) the outlet flue gas flow includes evaporated water from the sorbent and false air intake, evaluated on the basis of oxygen concentration difference between inlet and outlet of the absorber

The most problematic was obtaining consumption of the sorbent $\text{Ca}(\text{OH})_2$ that is not directly measured in the process. This value in Table 1 was obtained on the basis of knowledge of lime milk preparation process, where is separately measured flow of CaO and water into the feed tank, and

knowledge of dry matter fraction in the final lime milk 19,4 %. Important boiler and fuel parameters are summarized in Table 2.

Tab. 2 Boiler and fuel parameters

Parameter	Value	Unit
Boiler load	130	t/h
Efficiency	90,1	%
Fuel consumption	22,88	t/h
LHV	15,93	MJ/kg
A ^d	28,82	%
W ^r	23,84	%
S ^{daf}	1,83	%

Based on the data in tables 1 and 2, following major FGD parameters can be obtained:

- molar Ca/S ratio: 1,52 mol/mol
- temperature difference Δt_{AD} : 32,1 °C

3.2 Experiments at target SO₂ concentration 500 and 200 mg/Nm³

The experiments were carried out during standard operation of the boiler and the FGD unit. The control system of the FGD unit was modified to be able to keep the desired SO₂ concentrations by allowing the operator to manually set the amount of injected sorbent (i.e. change the Ca/S ratio) and to change temperature in the spray absorber by adjusting flow of injected water. Duration of the experiment at the target SO₂ concentration 500 mg/Nm³ took four days and the target 200 mg/Nm³ took eight days. The second phase with the lower emission target included measurement at two different Δt_{AD} . This was achieved by operating the spray absorber at two different temperatures – 82 and 77°C. The required temperature was controlled by flow of water inlet into the absorber. In the identification of the FGD operation, described in the chapter 3.1, the partial pressure of water vapor and the dew point were calculated based on material and energy balance. In the experimental phase, the calculation was validated by experimental determination of the dew point, using wet and dry bulb measurement at the inlet and outlet of the FGD spray absorber. For this purpose, a K-type thermocouple wrapped in a fabric cover saturated in distilled water was prepared. As the final wet-bulb temperature was considered a mean value of the stable section of the time series measured, as shown in the following figure.

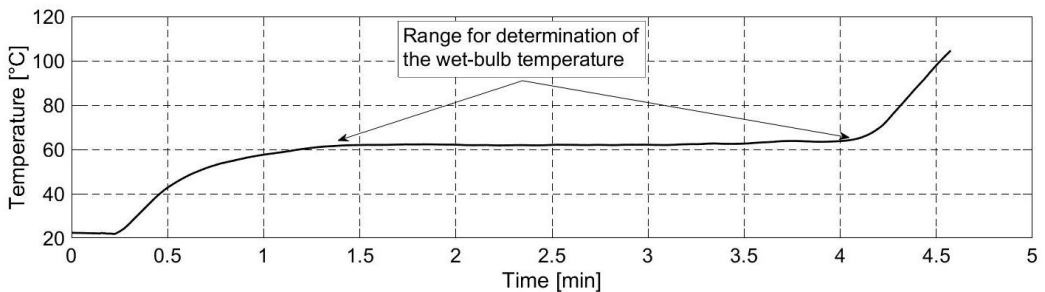


Fig. 2 Record of wet-bulb temperature

The dew point was determined by the following procedure. First, a saturated pressure of water vapor using the measured wet-bulb temperature was obtained, based on Antoine's equation:

$$\ln(p_w^0) = A - \frac{B}{(t_{Bw} + 273.15) + C} \quad (5)$$

with A = 16,2886, B = 3816,44 and C = -46,13 [9]. A second step was calculation of partial pressure of water vapor from the dry and wet-bulb temperatures, using equation [10]:

$$p_w = p_w^0 - A \cdot (t_A - t_{Bw}) \cdot p \quad (6)$$

Finally, the dew point is obtained using p_w calculated by the equation (6) back in the equation (5). A correlation for sulfuric acid increase of the dew point has not been taken into account.

4 RESULTS AND DISCUSSION

4.1 Dew point validation

Successful validation of the dew point calculation using the wet and dry-bulb measurement is the key point for reliability of overall desulfurization balance in the spray absorber. Overview of the calculation and measurement of the dew point is summarized in the table 3.

Tab. 3 Validation of the dew point

Parameter	Unit	Absorber inlet	Absorber outlet
wet-bulb temperature	°C	52,8	53,5
dry-bulb temperature	°C	164,0	82,1
p_w^0	kPa	14,14	14,50
p_w	kPa	6,9	12,60
dew point - measured	°C	38,7	50,4
dew point - calculated	°C	42,5	49,6
dew point difference		+ 9,8 %	-1,6 %

It is important to notice that the difference in dew point calculated from the material and energy balance and measured value is very good, and thus the calculated value can be considered as validated. The larger difference between measurement and calculation at the inlet to the absorber may be caused at the wet-bulb measurement by possible dissolving of flue gas components (particularly SO₂) in the distilled water saturated in the thermocouple wrapping, which can affect the rate and temperature of evaporation. Nevertheless, more important for the absorber balance is the outlet dew point, where is only 1,6 % relative difference between measurement and calculation.

4.2 Desulfurization performance

Following table shows overall results as daily averages, including average Ca/S ratio, SO₂ capture ratio and temperature difference between dew point and temperature of the spray absorber.

Tab. 4 Experimental results

	Day	Ca/S [mol/mol]	SO ₂ capture [%]	Δt_{AD} [°C]
SO ₂ target 500 mg/Nm ³	1	2,00	80,8	34,1
	2	2,09	78,9	34,3
	3	1,87	83,0	33,9
	4	2,28	83,2	32,9

SO ₂ target 200 mg/Nm ³ , Δt_{AD} as in normal operation	5	2,82	93,4	33,5
	6	2,50	93,4	33,3
	7	2,82	93,1	34
	8	2,73	91,9	33,3
SO ₂ target 200 mg/Nm ³ , Δt_{AD} lowered	9	2,34	90,4	26,2
	10	2,40	91,9	26,3
	11	2,69	91,9	26,6
	12	2,65	93,5	26,7
Normal operation at 1350 mg/Nm ³	13	0,76	61,4	25,9
	14	0,69	58,7	27,1
	15	0,84	46,9	31,4
	16	0,87	47,2	34,1
	17	0,94	46,7	34,8
	18	0,98	48,3	34,6

Besides the effect of Ca/S change, the results show significant effect of the Δt_{AD} on the SO₂ capture ratio. In the table 3 for the SO₂ target 200 mg/Nm³, the Ca/S ratio is in average 2,72 for average $\Delta t_{AD} = 33,5$ °C, whereas for average $\Delta t_{AD} = 26,5$ °C the necessary Ca/S ratio is 2,50 to reach the same SO₂ capture ratio. Based on this data, the correlation of Ca/S and SO₂ capture ratio for both temperature differences can be constructed, using equation 4. This is shown in following figure 3. The values of K of the equation 4 for mean values of Δt_{AD} are shown in table 4.

Tab. 4 K values of the equation 4

Δt_{AD} [°C]	K [-]
33,5	0,90
26,5	1,19

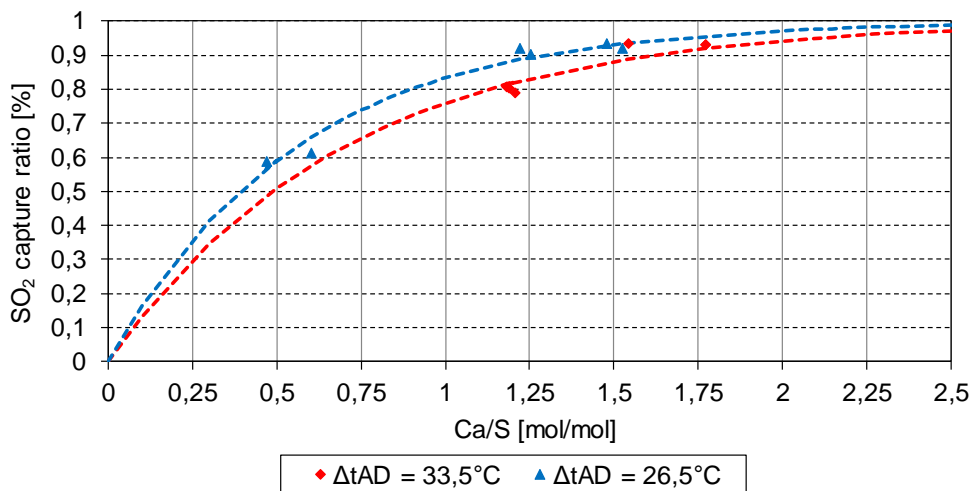


Fig. 3 Correlation of SO₂ capture ratio with Ca/S

It is important to notice that the positive effect of decreasing the Δt_{AD} is significant at lower SO_2 capture ratios. For the coal specified above, it is particularly important for reaching the emission target 500 mg/Nm^3 , corresponding to about 60 % SO_2 capture ratio. At this point, decrease of the Δt_{AD} by 7°C increases the SO_2 capture ratio by 10 per cent points, i.e. by almost 15 % relative. When this ratio is higher, the benefit from lowering the Δt_{AD} is much less significant and for ratio $> 95 \%$ the effect almost fades away, as can be seen from the figure 3.

In the following table 5 are compared measured and calculated Ca/S ratios for two daily values within the campaign with 200 mg/Nm^3 emission target. Necessity of this validation is certain inaccuracy of the equation 4 in the region of high SO_2 capture ratios, typically above 90 %. In this region, relatively high change of Ca/S has only a small effect on change of the SO_2 capture. The table 5 shows measured values of Ca/S and calculated values of the Ca/S by equation (4) using K from the table 4. For each Δt_{AD} are taken averages of day5-8 and day 9-12 of the experiment respectively.

Tab. 5 Measured and calculated Ca/S ratios

Δt_{AD} [$^\circ\text{C}$]	Ca/S [mol/mol]	SO_2 capture [%]	Ca/S by eq. 4 [mol/mol]	difference
26,5	2,34	92	2,13	- 9 %
33,5	2,82	93	2,95	+ 4,6 %

The table 5 shows that the validation gives generally less than 10 % difference, which is considered as satisfactory. It also shows that the Ca/S ratio is for a given SO_2 capture underestimated in the case of smaller Δt_{AD} , when applying the equation 4.

Increasing of the Ca/S ratio causes an increase of unreacted free Ca in the solid product from the spray absorber and fabric filter. At each emission target, including standard operation, was analyzed a mean sample for free Ca (as CaO) in the solid residue from the FGD. This is shown in following figure.

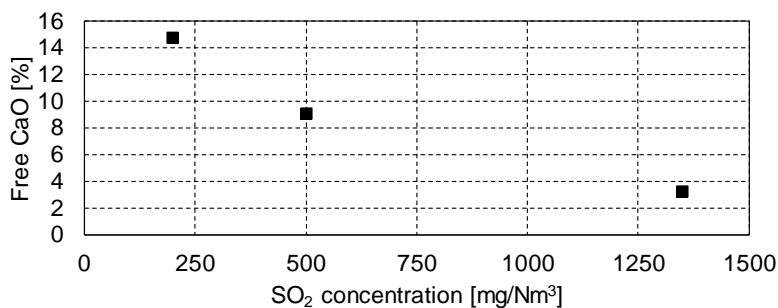


Fig. 4 Free Ca as CaO in the solids from FGD

It is also important to mention a few observations from the experiments at the SO_2 emission target 200 mg/Nm^3 . It is possible to reach this target, which corresponds to the SO_2 capture ratio $>90 \%$, even if this specific semi-dry FGD has been designed to 75 % capture. However, it is not possible to fully and continuously keep this emission target, particularly due to the fact, that there is a low flexibility of the technology to react on changes in SO_2 concentration in the flue gas and flue gas flow. The limitation is mainly in a large pre-prepared volume of the lime milk, thus not allowing a flexible change of the $Ca(OH)_2$ concentration. Second limitation is given by figure 3, where only small change in SO_2 capture ratio requires a large change of Ca/S in the region $>90 \%$. The SO_2 concentration record over the whole period of the experiment is shown in following figure.

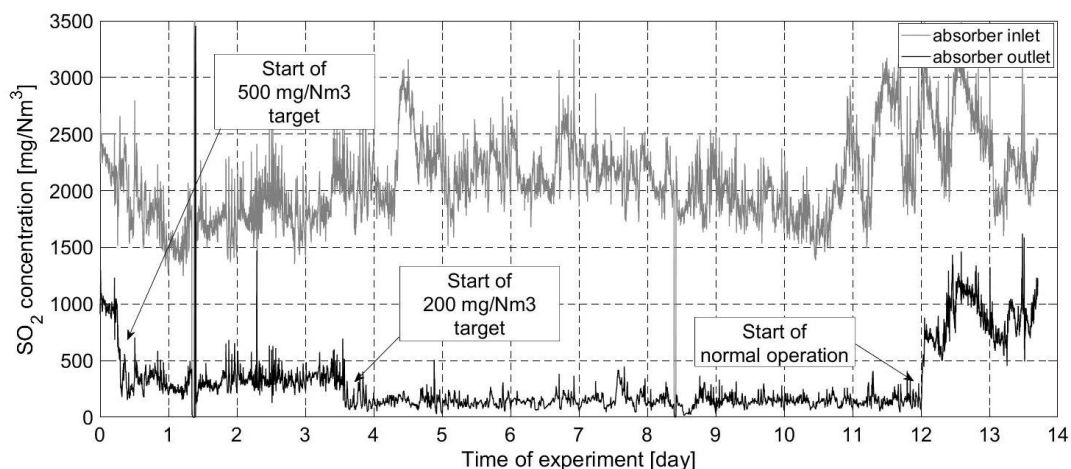


Fig. 5 Time series of the SO₂ concentration

4.3 Sorbent consumption for a different coal blend

The equation 4, validated by the experiments, can be now used for estimation of sorbent consumption in the case of fuel change for reaching required SO₂ emission targets. In the following table is shown composition of the new coal blend along with the original one.

Tab. 6 Original and new fuel parameters

Parameter	Original fuel (Tab. 2)	New fuel	Unit
LHV	15,93	17,15	MJ/kg
A ^d	28,82	20,98	%
W ^r	23,84	24,39	%
S ^{daf}	1,82	1,44	%

Considering the new fuel composition with a lower S content, the FGD inlet SO₂ concentration in the flue gas at 6 % O₂ content is calculated to 2440 mg/Nm³. The balance of the sorbent consumption is based on spray absorber temperature 82 and 77°C, corresponding to these temperatures at the experiments for SO₂ emission target 200 mg/Nm³. Four different operation points were evaluated for various target SO₂ concentrations – see following table 7.

Tab. 7 Calculation of Ca/S for new coal blend

SO ₂ target [mg/Nm ³]	Required SO ₂ capture ratio [%]	Ca/S at 82°C in absorber [mol/mol]	Ca/S at 77°C in absorber [mol/mol]
1350	44,7	0,66	0,50
500	79,5	1,76	1,33
250	89,8	2,53	1,91
200	91,8	2,77	2,10

5 CONCLUSION

Full scale and longtime duration experiments with a semi-dry FGD have validated theoretical considerations concerning relationship between stoichiometry of the sorbent and SO₂ capture ratio

(Ca/S), and shown a possibility of the semi-dry FGD system to operate at significantly higher SO₂ capture ratios, than originally designed. The experiments have also proven a significant effect of setting the operating temperature of the spray absorber, which changes the Δt_{AD} – difference between absorber temperature and the dew point. About 7°C Δt_{AD} is able to improve SO₂ capture by about 10 percent points. This effect has been quantified and used for calculation of sorbent consumption for a different fuel, than used in the experiments.

The experiments have also identified weak points, that need to be taken into consideration. At the required capture ratio >90 %, the semi-dry FGD is less flexible to follow changes in flue gas flow and SO₂ concentration, in principle due to flat characteristics of the SO₂ capture-Ca/S correlation in this region, which cannot be modified. Second point is impossibility to change flexibly the concentration of the lime milk. Obvious technical limitations for this system being operated beyond the design limit is overloading of lime milk preparation line as well as higher loads on transportation of FGD solid products.

LIST OF SYMBOLS

A ^d – ash content in dry sample	[%]
A (in eq. 6) – psychrometric constant: 662.10 ⁻⁶	[1/K]
Ca/S – Ca to S stoichiometric ratio	[mol/mol]
K – constant of eq. 4	[1]
LHV – lower heating value	[MJ/kg]
p _w – partial pressure of water vapour	[kPa]
p _w ⁰ – saturated partial pressure of water vapour	[kPa]
p – total pressure	[kPa]
S ^{daf} – sulphur content in dry-ash-free sample	[%]
Δt_{AD} – dry-bulb temperature and dew point difference	[°C]
t _A – dry-bulb temperature	[°C]
t _{Bw} – wet-bulb temperature	[°C]
W ^r – water content in raw sample	[%]
η – SO ₂ capture ratio	[1]

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