THE CAUSATION OF HIGH LIMESTONE CONSUMPTION
IN COAL DESULFURIZATION FLUIDIZED BED BOILER

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Laboratory research of the reactivity of limestone used for desulfurization of coal fluidized bed boilers have shown that reactivity of CaO after limestone calcination process in boiler is significantly influenced by reactions of CaO with SiO_2, Al_2O_3 and Fe_2O_3 contained in ash. The reaction products do not react with SO_2 and consumption of limestone should be extremely high. Quantity and composition of the formed compounds influence of surface of CaO produced from limestone at high temperatures. It is useful to take into account the influence of the compounds coming from coal and limestone found in laboratory tests.

INTRODUCTION

Limestone addition to combustion chamber of coal fluidized bed boilers (FBB) is used for SO_2 removal from flue gas. Much struggle has been devoted to process optimizing. Unfortunately, comparison of results differs in sorption capacities of various limestones that were added to the same combusted coal. This discrepancies are usually explained by operation conditions in FBB or reactivity of limestone as result of the content of $CaCO_3$ and $MgCO_3$, size of crystals in original limestone, the surface CaO produced during the calcination and particle size of limestone before its injected to FBB [1], [2], [3].

This article links to finding concerning the influence of SiO_2, Al_2O_3 and Fe_2O_3 contained as impurities in limestone and coal ash discussed in articles [8], [9], [10], preferentially from the point of view of unfavorable reactions of CaO with inorganic oxides that decrease the reactivity to SO_2.

For combustion of brown coal in existing FBB there is emission limit value set to 500 mg/m^3 (standard condition, 6 % O_2, dry bases). For new FBB exceeding thermal input greater than 100 MW set to 200 mg/m^3 only. To meet these values may cause difficulties at usual stoichiometry ratio $CaCO_3 : SO_2 = 2 - 3$ [8], [9], [10].

At desulfurization the flue gas in FBB take place following reactions [3]:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$\Delta H^0(298) = +178{,}5 \text{ kJ.mol}^{-1} \tag{1}$$

$$CaO + SO_2 + 0{,}5\ O_2 \rightarrow CaSO_4$$
$$\Delta H^0(298) = -502{,}2 \text{ kJ.mol}^{-1} \tag{2}$$
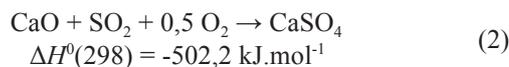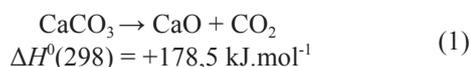
Limestone calcination takes place in the range 800-900 ^{o}C, nevertheless Reaction (2) already beginning at temperatures greater than 600 ^{o}C in two stages [2]. The first reaction is the chemical absorption of SO_2 on surface CaO:

$$CaO + SO_2 \rightarrow CaSO_3$$
$$\Delta H^0(298) = -227{,}5 \text{ kJ.mol}^{-1} \tag{2a}$$
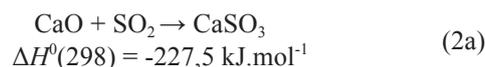
This reaction is followed by quick oxidation to the sulfite to sulfate. $CaSO_3$ at temperature over 600 °C is not stable and disproportionable by reaction:

$$CaSO_3 + 0.5\ O_2 \rightarrow CaSO_4$$
$$\Delta H^0(298) = -274{,}7 \text{ kJ.mol}^{-1} \tag{2b}$$
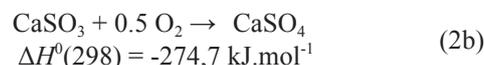
$CaSO_4$ formed in the porous structure of particles limits the income SO_2 to inside of the particles. Chemical reaction becomes controlled by diffusion of SO_2 through the formed $CaSO_4$ and a great portion of CaO inside particles remains free. Free CaO contained in ash is removed in fabric filters (or electrostatic precipitators) as fly ash or as the bottom ash from the bottom of FBB. Free CaO in ash negatively influences the degree of desulfurizatin. Free CaO forms with air humidity $Ca(OH)_2$ and makes troubles during transportation to ash utilization or disposal [9].

Calcination of limestone over 1050°C leads to dead burned lime and porous structure of particles sinters (so called overburning of limestone) [4].

Limestone reactivity evaluation were devoted numerous research works. Limestone is usually dissolved in different acids (HCl, adipic acid) and rate of dissolution in measured. Such methods are useful in wet limestone process, in which SO_2 is absorbed in limestone slurry at 60 °C. Fluidized bed combustion takes place at 800-850 °C. Measurements the single limestone at such temperatures in laboratory gives great absorption of SO_2, nevertheless in contact with coal in is substantially decreased [4]. It obvious that CaO can react with SiO_2 and Al_2O_3 in coal at temperature greater than 800 °C and limits inlet of SO_2 to the limestone particle. Our effort was concentrated to find changes developed by possible side reactions.

EXPERIMENTAL

Relative reactivity measurement

Sorption capacities of limestones calcinates, or mixtures of limestones and coal have been studied in quartz reactor (Figure 1) composed of two quartz tubes connected with spherical-ground quartz joint. Upper removing part was furnished by narrower tube in which was insert tested sample on supported on quartz frit. Flue gas simulated gas mixture [SO_2–air–CO_2–H_2O (g)] was heated to desired reaction temperature in lower part of the tube filling. The temperature of gas mixture was measured by Pt-Rh thermocouple. The reactor was inserted into an electrically heated kiln. The upper part of the tubes outside of the reactor was heated to 105 ºC to prevent condensation of H_2O vapor from the gas mixture.

After heating to desired temperatures 3 g the limestone particle tested (fraction 0.3-0.6 mm) were inserted and standard gas mixture 0.3 % of volume SO_2, 13 % CO_2, 7 % O_2 and N_2 was introduced. Servomex Xentra analyzer using two channels SO_2 detectors continuously monitored flow rate of the gas. The content of O_2 was measured by one channel cell [8].

Samples for comparison reactivity of tested limestones alone and mixtures of coal with limestones (26 g coal and 3 g $CaCO_3$) in described apparatus were prepared in laboratory kiln at temperature 850 °C.

XRD powder diffraction

Samples (26 g coal and 2 g limestone tested) were tested after calcination in laboratory kiln at 850°C by XRD powder analysis.

For crystalline phase determination XRD-diffractometer X´Pert PANalytical X´Pert PRO (PANalytical, The Netherlands), Cu tube was used. System consists of goniometr, PC computer for data collection and evaluation with database PDF-2 on CD ROM containing approximately 130 000 experimental and calculated powder patterns. The curved graphite monochromatic, fixed slits and scintillation counter are available to improve the measured patterns. Commercial software HighScore (PANalytical) is available for data evaluation, search-match and profile fitting. Quantitative and qualitative phase analysis, Rietvelt analysis, and measurement of lattice parameters, thin film measurement, crystalline size determination is possible.

RESULTS AND DISCUSSION

Reactivity of limestone with coal in calcination process

The samples of limestone were tested in mentioned laboratory apparatus using dry simulated flue gas at the temperature range 750-950°C in stationary bed. Results showed the temperature optimum of 850 °C. Results of this experiment substantially differ from desulfurization of flue gas in industrial FBB with output 256 MW_e [7], [8]. Similar results were gained in laboratory tests using simulated gas mixture containing 8300 mg/m^3 SO_2 and
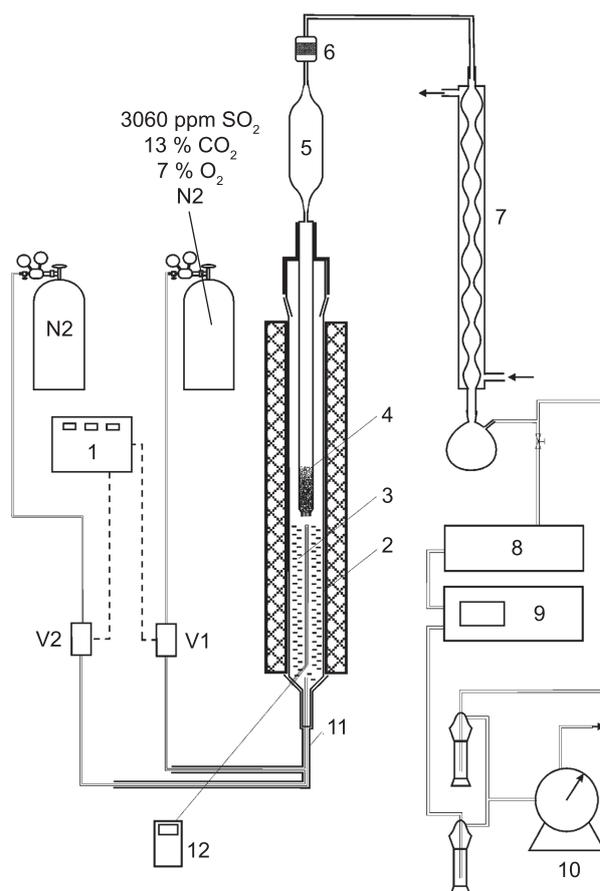
Figure 1. Limestone reactivity testing apparatus; 1 - Central loop processor, 2 - Quartz reactor, 3 - Quartz fill, 4 - Sample tested tube, 5 - Dust separator, 6 - Filter, 7 - Water cooler, 8 - Refrigerator, 9 - Analyzer, 10 - Gas meter, 11 - Reactor heating, 1 - Thermometer.

15 % of water vapor or after calcination with addition of ash achieved by combustion coal Bílina mining area in separate kiln at 850°C.

To understand the differences between laboratory tests and full scale FBB, a mixture of coal with limestone (10 % limestone, fraction 0.3-0.6 mm and 90 % coal) was heated in laboratory kiln in air at 850 °C. Products of the calcinations were tested on SO_2 absorption in laboratory reactor. Result of SO_2 absorption tests of the alone limestone and limestone after mutual calcinations with coal was compared.

Results of SO_2 reactivity measurements can be seen in Figure 2. The single limestone can absorb substantially higher quantity of SO_2 than the same limestone after calcinations with coal. The most obvious differences are evident for Čížkovice limestone. The Čížkovice chalky limestone contains impurities such as SiO_2, Al_2O_3 and Fe_2O_3. In spire of lower $CaCO_3$ content (app. 72 %) single Čížkovice was able to absorb greater quantity of SO_2 than pure calcites (Lahošť, Čertovy schody, $CaCO_3$ content greater than 95 %).
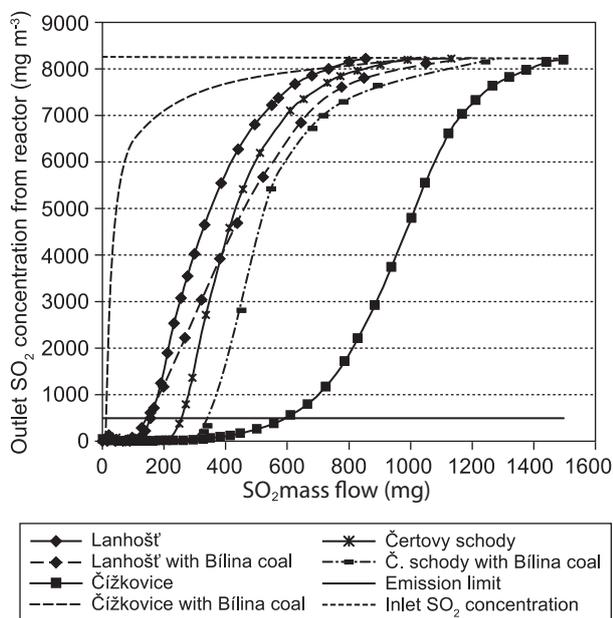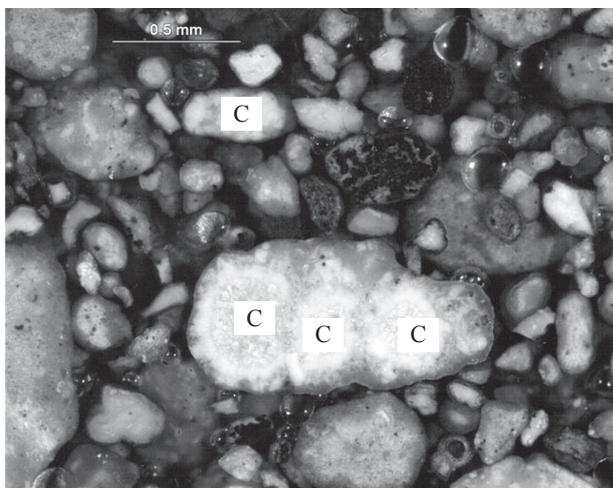
Comparison of SO_2 absorption curves for Lahošť or Čertovy schody calcites with Čížkovice chalk in the Figure 2 proved that SO_2 reactivity of Čížkovice calk is substantially greater than of both tested calcites.

This finding led to conclusion that Čížkovice limestone with coal can react at temperatures over 800 °C not only with impurities in limestones (metal oxides), but also with clays coming from coal and forming alumosilicates. Surface of CaO particles is blocked by alumosilicates and income of SO_2 through porous structure to CaO is significantly limited. Sintered structure of bottom ash particle is shown in the Figure 3.

In order to understand the above conclusion further experiments were carried out. Calcinated limestone with in advanced prepared ash of lignite Bílina deposit (90 % coal and 10 % limestone) were used. The tests were carried out at temperature 900 °C. Results of XRD analyses proved crystal phases containing CaO and oxides coming from impurities in limestones and from waste and shale or coal. Those findings were later confirmed in samples of bottom ash and filter ash taken from full scale FBB.

Influence of the content of ash and clays in coal on crystal phases formation in the calcination products

In order to prove existence of formation crystal phases in the mixture of limestones with coal-clays the different standards of typical clays were tested; clays from Mořina deposit, cypris clay from Družba and pure kaolin. Calcinations were out at temperature 900 °C in laboratory kiln (67 % limestone and 33 % of mentioned clays). Results of XRD analyses are presented in Table 1.

Figure 2. Reactivity of limestones with SO_2 after combustion at 850 °C.

Figure 3. Particle of bottom ash (C = rest of CaO not to take part on the desulphurization).
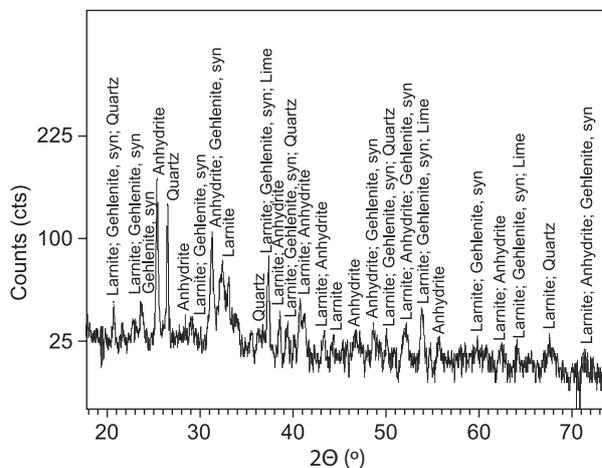
Figure 4. XRD pattern of the bottom ash.

RTG diffraction enables to identify particular of crystals nevertheless is not able to find amorphous phase and the share of crystals on total quantity of analyzed substances.

The crystal phases proved by XRD prevent probably the incomes of SO_2 to the particles containing free CaO and restrict in such way the formation of $CaSO_4$.

Results of XRD-analysis are presented in Figure 4.

CONCLUSION

Reactivity tests of selected limestones used for FGD fluidized in bed boilers proved that reactivity of limestone to FGD in fluidized bed at temperatures 850-900 °C is significantly influenced by reactions of CaO with oxides contained in ash, especially SiO_2, Al_2O_3 and Fe_2O_3.

Products of reactions formed in this way (Figure 5) negatively influence surface structure of CaO particles (formed from $CaCO_3$ in kiln) in such way that they do not react sufficiently with SO_2. Therefore greater consumption of natural limestone is demanded to comply emission limit legislation.

For projection of new FGD boiler it is useful to make laboratory test to find if the selected coal with limestone do not form products blinding surface of CaO particles and in such way economize of limestone consumption.

References

1. Borgward R. H: Environ. Sci. Technol. *4*, 363 (1970).
2. Borgward R. H., Harvey D. R.: Environ Sci. Technol. *6*, 350 (1972).
3. Vejvoda J., Hrnčíř J.: Ochrana ovzduší *10*, 139 (1974).
4. Borgward R. H.: AIChE Journal *31*, 101(1985).
5. Ar I., Dogu G.: Chem. Eng. J. *83*, 1321 (2001).
6. Khinast J., Krammer G. C., Brunner C., Staudinger G.: Chem. Eng. Sci. *13*, 2198 (1996).
7. Buryan P., Vejvoda J., Chalupa P., Maryška M., Krátký J., Veverka L.: Understanding of causation problems with desulfurization fluidized bed boilers, Conference *Boilers and Energetic Plants* 2006*, section IV, F018, Ed. AVO Brno 2006 (Czech).*
8. Buryan P., Vejvoda J., Krátký J., Veverka L.: Chemické listy *102*, 188 (2008).
9. Buryan P., Vejvoda J., Chalupa P., Maryška M., Krátký J., Veverka L.: Chemické listy *102*, 188 (2008).
10. Buryan P., Vejvoda J., Chalupa P., Maryška M., Krátký J., Veverka L.: Desulfurization of fluidized bed boilers, Conference *Air Protection 2005*, pp. 37-43, Ed. Congress management Bratislava, Štrbské Pleso (Slovakia), 2006.

Figure 5. Proposed reactions of limestone in FBB; C - CaO, S - SiO_2, A - Al_2O_3, F - Fe_2O_3.

Table 1. Phase composition of samples after calcination (wt.%).

Sample Composition	Albite $Na_{0,84}Ca_{0,16}Al_{1,16}Si_{2,84}O_8$	Andalusite $Al_2(SiO_4)O$	Anortite $CaAl_2Si_2O_8$	Garnet $Ca_3Al_2Si_3O_{12}$	Gehlenite $Ca_2Al(AlSiO_7)$	Nacrit $Al_2Si_2O_5(OH)_4$	Larnite Ca_2SiO_4
CIZ							
CO+CIZ	13	-	-	10	10	-	14
CIZ+CY	-	13	23	-	6	-	31
CIZ+KA	10	-	12	6	12	-	31
CIZ+MO	-	16	-	7	9	-	35
CS							
CO+VCS	13	-	-	13	12	-	-
CS+CY	-	-	18	16	5	-	29
CS+KA	-	-	-	17	16	-	36
CS+MO	-	-	-	19	8	5	25
STR							
CO+STR	11	-	-	-	13	-	21
LAH							
CO+LAH	12	-	-	-	10	-	26
LAH+CY	-	-	18	15	4	6	25
LAH+KA	-	-	-	30	20	-	-
LAH+MO	-	-	-	27	12	-	-

Limestones quarries - (CIZ - Čížkovice, STR – Štramberk, LAH – Lahošť, CS – Čertovy schody), Coal (CO) or clays coming from Mořina (MO), cypris clay (CY) or kaolin (KA) deposits