

PARAMETERS AFFECTING EFFICIENCY OF FLUE GAS DESULFURIZATION SYSTEM USING WET LIMESTONE METHOD

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Abstract: Efficiency of Flue Gas Desulfurization System (FGD) is affected by numerous technical parameters like: proper fuel preparation, quantity and quality of fuel, combustion conditions in furnace chamber, quality of flue gas corresponding to the operating conditions of FGD system, design quantity and quality of flue gas at the inlet of FGD system, design quantity and quality of used sorbent, design quantity and quality of process water. The FGD system shall meet the required parameters of particulate emission, quantity of used media and quality of products for the whole variation range of flue gas volumetric stream. The paper outlines the effect of sorbent properties (physical properties and chemical constitution, particle-size distribution, content of CaCO_3 and alkaline oxides (MgO , K_2O , Na_2O and contaminating substances, e.g. aluminosilicates) on efficiency of FGD system using wet limestone method.

Keywords: limestone, reactivity, limestone sorbents.

Introduction

Coal combustion is the predominating way of heat energy generation in Poland, which causes atmospheric emission of particulates and gaseous pollutants including also sulphur dioxide. For this reason, coal-fired power generation units are under obligation to observe the sulphur dioxide emission standards specified in European Commission Directive [3] ((introduced into Polish legislation by the Regulation of the Minister of Environmental Protection [17]. Thus, the flue gas desulfurization systems need to be erected. Within the years 2000-2012, SO_2 emission in Poland was reduced from 1,511 kMg/year to 974 kMg/year [15], i.e. over 35%. The highest share in emission reduction was achieved by commercial power industry (over 54% [9]). The history of reducing SO_2 emission to atmosphere by application of FGD systems dates back to the nineteen thirties. Modernization of power generating sector, application of FGD systems in pulverized-fuel fired furnaces and construction of fluidized bed boilers allowed for reducing SO_2 emission to atmosphere from c. 4 million Mg/year to almost 2 million Mg/year [10, 20].

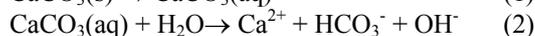
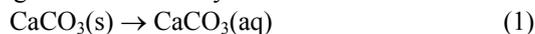
Wet limestone method of flue gas desulfurization

Taking into account a wide variety of FGD systems as concerns their capacities, kind of combusted fuel, local conditions, etc., it is difficult to point out a single and universal desulfurization technology which could be applied in any case. Selection of optimum technology for power generation flue gas desulfurization must be

preceded by analysis of the following criteria [4]: quantity and composition of flue gas, required efficiency of desulfurization, whether FGD system could be installed, capital expenditure, operating costs, types of waste products and their potential utilization.

Among high efficiency FGD methods, the most widespread is the wet limestone one. A ground limestone is the reagent of the method, while synthetic gypsum with functional qualities [7] is the final product of desulfurization.

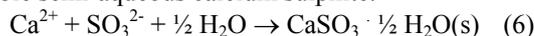
Wet limestone method consists in contacting the flue gas with aqueous limestone suspension in vertical spray reactor (absorber). When calcium carbonate is fed into a tank, its dissociation takes place in water to the degree resulting from its solubility:



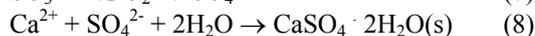
In the absorption zone of the absorber, SO_2 is dissolved in water



Sulphite anion connects with calcium cation to create insoluble semi-aqueous calcium sulphite.



Upon oxidation the sulphite anion to sulphate anion, a second insoluble product of gas desulfurization is created – synthetic gypsum.



Due to chemical reactions (7) and (8), the calcium cations are removed from the solution, which – according

to the solubility product – causes further dissolution of calcium carbonate. Additional oxygenation $\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ causes its conversion to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which – upon precipitation from the solution – subjects to processing to become the final product of flue gas desulfurization called the reagent gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The parameters characterizing the spray absorbers

The spray absorbers are characterized by the following parameters [1, 14]:

- velocity of flue gas phase in the absorber, ($w_g \approx 2\div 4.5$ m/s),
- rate of volumetric stream of sprayed absorption suspension to volumetric stream of gases subjecting to desulfurization, ($L/G \approx 5\div 60$ dm³/m³),
- height of absorption zone in the absorber,
- number of spraying levels in the absorber, ($n \approx 3\div 5$),
- spraying pressure of absorption suspension, ($\Delta p_r \approx 0.06\text{-}0.1$ MPa),
- pH value of absorption suspension, ($\text{pH} \approx 4.6\text{-}5.5$),
- SO₂ concentration in gaseous phase at absorber inlet,
- contact time for flue gas and absorption liquid,
- retention time for suspension in retention tank, (5÷10 min).

Depending on the way in which liquid phase contacts with gaseous phase in the unit, the following absorber types are distinguished: spray absorbers, shelf absorbers, with fixed and movable outfit, barbotage (bubbling) units, Venturi absorbers, and others. Considering the column arrangement, absorbers can be classified as horizontal and vertical units. On the grounds of the flow direction of the liquid phase with respect of gaseous phase, the absorbers can be divided to: concurrent flow, counter flow and cross flow scrubbers [11, 19].

The highest efficiency of flue gas desulphurization is achieved when appropriate hydrodynamic conditions and mass exchange requirements are met in vertical counter flow spray scrubbers. Horizontal spray absorbers in full industrial scale are the least examined and known units as concerns the mass penetration velocity and pressure losses of gaseous phase. Spray units most often used for flue gas desulfurization are the vertical columns because they require less land area for erection and are better comprehended as concerns phase movement hydrodynamics and kinetics of heat and mass penetration [5].

Technological aspects affecting efficiency of FGD system operating according to wet limestone method

Efficiency of FGD system depends on numerous technical parameters of the process media in use, which includes but is not limited to [4]: proper treatment of fuel, design quantity and quality of fuel (e.g. calorific value, content of sulphur and combustible fraction), combustion conditions in furnace chamber, quality of flue gas corresponding to the operating conditions of FGD system, design quantity and quality of flue gas at the inlet to FGD system (volumetric stream of flue gas,

temperature and pressure of flue gas, dust level and the contents of SO₂, SO₃, HCl, HF and O₂, design quantity and quality of used sorbent (physical properties and chemical constitution, grain size distribution, content of CaCO₃, content of contaminating substances, e.g. aluminosilicates, reactivity characteristics), design quantity and quality of process water (content of chlorides and suspension). The FGD installation should, for the whole range of volumetric stream of flue gas, meet all the quantitative/qualitative parameters of particulate and gaseous emissions, quantity of media used and quality of products.

Excessive volumetric stream of flue gas, change of fuel to other than the design one, thus other SO₂ content than designed upstream the absorber would cause strong reduction of desulfurization efficiency which could cause that the emission standards [17] are no longer maintained, consequently the reduction of productivity. High concentration of dust in flue gas at the inlet to FGD system adversely affects operation of the installation, causes technological problems in the absorber, and could cause worse quality of gypsum.

Calcium sorbents used in FGD installations

The most numerous group of reagents used in FGD installations are those based on calcium compounds. About 90% of Polish FGD installations in power industry use calcium sorbents [13]. This is due to their availability, low purchase costs and ease of utilizing the final product - synthetic gypsum (it refers to the wet desulfurization method). The calcium sorbents include:

- in dry desulfurization methods – ground burnt lime and limestone,
- in semi-dry desulfurization methods – hydrated lime and ground burnt lime,
- in wet desulfurization methods – ground limestone, ground burnt lime and chalk.

Various requirements are demanded from the sorbent in respect of its purity and chemical constitution depending on the method used to treat the power industry flue gases. In dry method, the sufficient purity level of limestone is 90-93% CaCO₃ [2, 18], in fluid bed furnaces - 85% [12] and wet limestone method – min. 95% [6].

The wet method of FGD requires the highest capital expenditure, ensures high efficiency of desulfurization (90-99%) [7] % and production of synthetic gypsum which is used in building materials industry.

Research part

While the FGD installation in ground limestone suspension is to be designed, at first you should assume some pH value of the suspension in the reservoir/reactor. Such procedure is based on experience and results from incomplete knowledge of physical/chemical properties of the reagent as it is so far not specifically fixed.

Prior to starting with implementation of the process project, it is advisable – in order to avoid errors and expensive corrections of operating conditions of FGD system – to proceed with not too expensive procedure of

sampling the limestone from well-known suppliers. The samples should be tested to determine their chemical constitution and grindability.

Results of such testing improve accuracy of designing the SO₂ absorption process in spray unit, owing to which the FGD installation would be more effective. It would allow to meet increasingly stringent standards for SO₂ emission to atmosphere, while operating and supervising personnel of the installation could enable to adapt system operation to varying technical parameters of the limestone supplied.

Chemical analysis of ground reagent intended for use in FGD process is to determine the following contents: CaO, MgO, Al₂O₃, Fe₂O₃, K₂O, Na₂O, SO₃ and CO₂, SiO₂, and also organic carbon. Moreover, determinations are made of particles insoluble in hydrochloric acid, sorbent reactivity and contents of metals [18].

In testing made in Research and Teaching Department of Atmosphere Protection, I-15 of Wrocław University of Technology, there were used fifteen samples of crushed but not ground burnt lime or ground burned lime, fine-grained and coarse-grained sorbent (ground down in lime plant) and ground in dry mills to lime powder for FGD processes with dry, semi-dry and wet methods. Samples were made available by five domestic limestone plants.

Laboratory testing of limestone aiming at determining its usability in FGD, especially with wet limestone method consist, first and foremost, in determining: physical

properties and chemical constitution, degree of milling (grain size distribution), reactivity with respect to sulphur dioxide and water dissolution ratio.

Analysis of physical properties and chemical constitution of limestone samples

Physical properties and chemical constitution of reagent (ground limestone) used in FGD with wet limestone method is of great importance for process efficiency, its evaluation and for balance calculation of each FGD installation. It is determined in accordance with the standard [16].

Chemical constitution of tested limestone samples was carried out in Chemical Laboratory of Multi-Element Analyses, Wrocław University of Technology. The results of testing expressed as CaCO₃ fractions and total fractions of contaminating substances in samples of limestone are shown in tab. 1. These results are characterised by coverage factor $k = 2$, which means that they are at the level of confidence 95%.

On the basis of chemical constitution of limestone samples under testing, it was found that they differ widely as concerns the content of individual constituents, especially CaCO₃ content (69.02 - 95%) and total fraction of contaminating substances, namely Fe₂O₃ + K₂O + SO₃ + Na₂O + MgO + Al₂O₃ + SiO₂ + NR + Humidity (1.23 - 10.52%).

Tab. 1. Fractions of calcium carbonate and total fractions of remaining substances in limestone samples under testing.

Limestone sample	Fractions CaCO ₃	Total fractions of contaminating substances (Fe ₂ O ₃ + K ₂ O + SO ₃ + Na ₂ O + MgO + Al ₂ O ₃ + SiO ₂ + NR + Humidity)
	% mas	%
2	82,63	10,52
3	90,32	8,20
4	86,77	7,48
5	69,02	8,58
6	93,90	2,37
7	95,70	1,79
8	80,67	2,21
9	94,02	4,09
10	89,65	6,21
12	92,22	1,67
13	94,22	2,59
14	70,60	3,99
15	94,16	1,27
16	92,57	2,92
18	94,57	4,09

Grain size distribution of ground reagent

The size analysis illustrating accumulated distribution of particles was made with Malvern laser meter of particle size (laser diffractometer). A polydispersion laser method was used with dry attachment where atmospheric air was used as a diluent. The measuring range of the lens was 300 mm, and the laser beam length

2.40 mm. We also determined: (i) average diameters of particles which cumulative fractions are 10, 50 and 90% of the volume of weighted particles $D(v, 0,1)$, $D(v, 0,5)$, $D(v, 0,9)$; (ii) average diameter of weighted volume $D[4,3]$, (iii) specific surface S.S.A. and (iv) average diameter of weighted surface $D[3,2]$. Summary of data on size analysis for samples of limestone is given in tab. 2.

Tab. 2. Summary of data on size analysis for samples of limestone.

Limestone sample	D(v,01)	D[4,3]	D(v,05)	S.A.A.	D[3,2]	D(v,09)
2	2,91	39,46	13,96	0,2992	7,775	116,76
3	2,98	30,60	15,00	0,2913	7,96	81,,08
4	2,23	38,76	14,04	0,3740	6,20	107,09
5	2,39	26,73	8,75	0,4038	5,74	43,51
6	3,09	25,36	13,58	0,2963	7,83	52,19
7	12,34	249,94	224,96	0,0795	29,16	506,04
8	131,58	279,93	258,68	0,0186	124,37	466,72
9	11,95	583,57	537,18	0,0656	35,37	1255,62
10	3,04	54,71	29,44	0,2547	9,10	142,37
12	2,32	30,53	10,35	0,3593	6,45	39,64
13	2,56	40,58	9,17	0,3669	6,32	132,20
14	2,36	28,77	8,11	0,4179	5,55	57,47
15	4,05	431,99	314,52	0,1566	14,81	1076,42
16	8,25	612,38	490,33	0,0858	27,03	1450,37
18	2,66	34,35	11,76	0,3329	6,97	102,88

Limestone reactivity

Reactivity of limestone powder is determined by pH-static titration with sulphuric acid at pH = 5.2 and at temperature of 50°C. The volume of used acid during 60-minute test necessary to maintain constant pH value of 5.2 is converted to percentage of reacted ground limestone, and the result is compared with reference diagram. The conversion of limestone particles after some determined time (e.g. each 1 minute) is calculated according to formula (9) and the results are placed in the graph versus time (Fig. 1).

$$R = \frac{V_{H_2SO_4} \cdot c_{MH_2SO_4} \cdot M_{CaCO_3}}{1000 \cdot m} \cdot 100\% \quad (9)$$

where:

R - percentage of reacted particles of limestone sample, %,

V_{H₂SO₄} - volume of used sulphuric acid, cm³,

c_{MH₂SO₄} - molar concentration of sulphuric acid,

M_{CaCO₃} - molar mass of calcium carbonate, g/mol,

m - test portion from limestone sample, g.

The curve obtained should lie, in the diagram (Fig. 1.) within scheduled area of reactivity (above the lower limit of reactivity).

In domestic laboratories, the analysis of limestone powder reactivity is carried out according to Austrian Energy instruction.

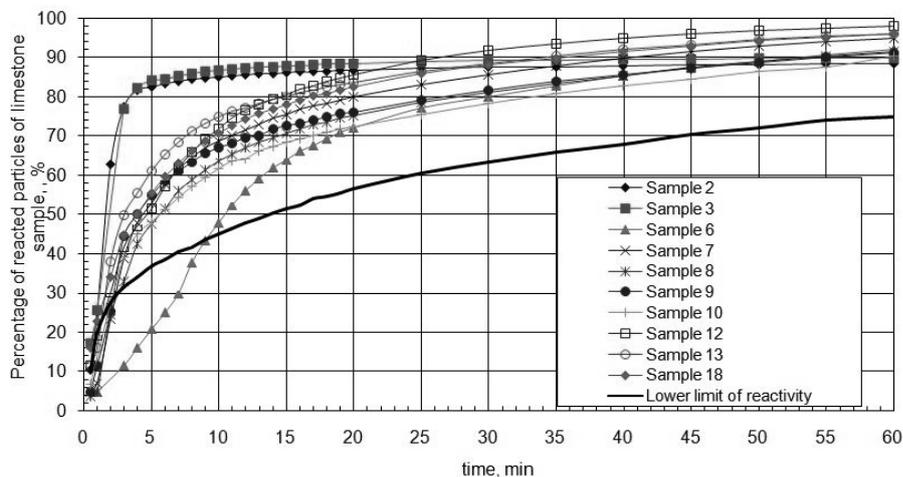


Fig. 1. Reactivity of limestone samples under testing (2...18 samples of limestone particles).

Dissolution rate of limestone powder

Examinations were run in the Research and Teaching Department of Atmosphere Protection, Institute of Environmental Protection Engineering, Wrocław University of Technology. Testing included effect of limestone grinding degree, excess of CaCO_3 in

absorption suspension in respect to SO_2 in gaseous phase at absorber inlet, suspension retention time in the reservoir and other variable parameters on the pH value of absorption suspension and on efficiency of gaseous phase desulfurization. A scheme of testing stand is shown in Fig. 2.

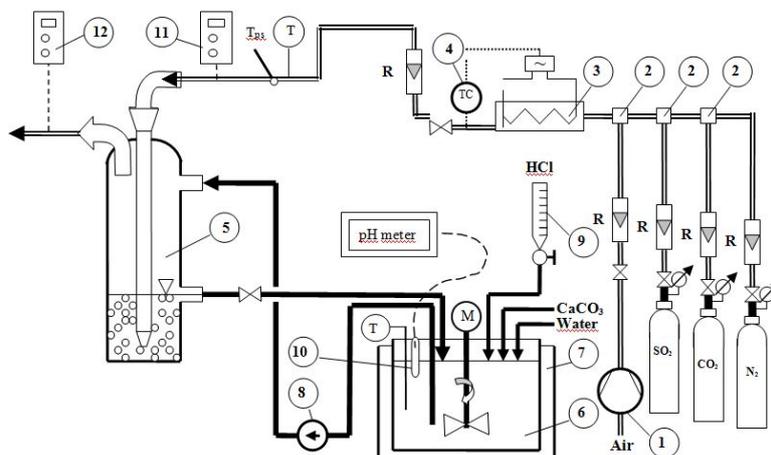


Fig. 2. Scheme of testing stand: 1 – blower, 2 – mixer, 3 – electric heater, 4 – thermostat, 5 – absorption reactor, 6 – reservoir of absorption suspension, 7 – water bath, 8 - peristaltic pump, 9 – batcher of additives, e.g. HCl, 10 -pH metering electrode, 11, 12 – analyzer, type Dioxor II, manufactured by Bacharach, M- mechanical mixer, T- thermometer, R – rotameter.

The conditions prevailing during testing the efficiency of gaseous phase desulfurization in water suspension of limestone substances:

- atmospheric pressure: 1010 - 1020 hPa,
- ambient temperature around installation: 290-299 K,
- absorption suspension temperature: 318- 343 K,
- relative humidity of air around installation: 53.0 – 66.0%,
- concentration of absorption suspension (ground limestone): c. 1% by weight,
- concentration of SO_2 in gaseous phase at inlet to scrubber: 1,100 – 1,999 ppm,
- volumetric stream of gaseous phase fed to bubbling washer: $G = 60 \text{ dm}^3/\text{h}$,
- volumetric stream of suspension fed to the washer: $L = 18.0 \text{ dm}^3/\text{h}$,
- temperature of absorption suspension in the washer: 323 K,
- range of variation of initial pH value of absorption suspension: 8.16 – 7.51,
- range of variation of final pH value of absorption suspension: 1.98 – 1.66,
- duration of absorption process in bubbling washer: 55 – 251 minutes,
- minimum efficiency of gaseous phase desulfurization in absorption suspension: 77-96.15%.

Efficiency of gaseous phase desulfurization versus duration of absorption process in bubbling washer (reactor) for 6 fractions of the limestone no.7 sample is

shown in fig. 3-5.

On the grounds of all results from examining the effect of limestone size reduction on initial pH value of absorption suspension and pH value and efficiency of desulfurization of gaseous phase after specific time, one can note that after the same time of desulfurization duration, the finest fractions feature the highest efficiency of SO_2 removal from gaseous phase and the lowest reduction of pH value.

The coarsest fractions are marked by the highest reduction of pH value and exhibit the lowest efficiency of SO_2 removal from gaseous phase.

Basing on results of examinations of the effect of limestone kind on pH value and efficiency of SO_2 removal from gaseous phase after specific duration of desulfurization, it can be seen that in case of six fractions examined, the limestone kinds exhibit, after the same time of the process, various efficiency of SO_2 removal from gaseous phase and different pH value of absorption suspension circulating in the circuit of suspension retention reservoir and bubbling washer adopted to reactor for SO_2 absorption process. The initial pH value of absorption suspension in each experiment of SO_2 absorption is relatively high. This results in high efficiency of gaseous phase desulphurization. Then, with continued process of SO_2 absorption, reduction of pH value is observed, however the desulfurization efficiency is still high. Increased efficiency of desulfurization could be reached by using sorbents of finer particles.

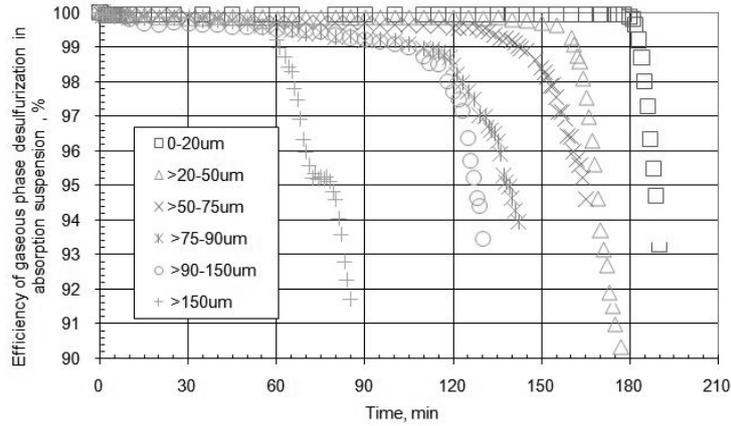


Fig. 3. Efficiency of gaseous phase desulfurization in absorption suspension versus duration of SO₂ absorption process in bubbling washer (sample 7).

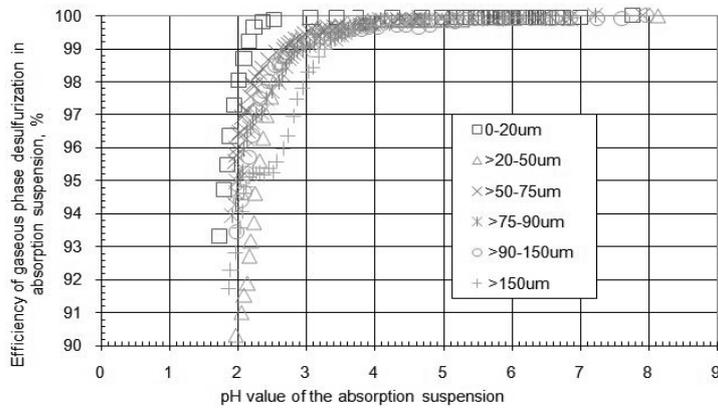


Fig. 4. Efficiency of gaseous phase desulfurization in absorption suspension versus pH value of the absorption suspension (sample 7).

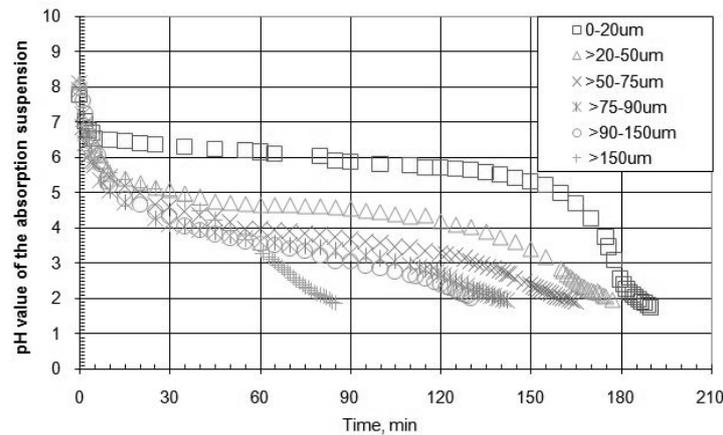


Fig. 5. pH value of absorption suspension versus duration of SO₂ absorption process in bubbling washer (sample 7).

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Conclusions

The quality of flue gas desulfurization process and reduction of SO₂ emission to atmosphere, so as to meet the admissible levels, i.e. consistent with national and EU standards in force, depends largely from physical properties and chemical constitution of the reagents in use.

When process and operating parameters of FGD system are properly selected, the flue gas can be purified with wet method at the efficiency of 95% or even higher than 99% when the excess reagent ratio with respect to the SO₂ content in flue gas is maintained within 1.02 - 1.05 [8].

When reactivity value is known, optimum limestone reagent can be selected as concerns its usefulness in FGD technology with wet limestone method at the stage of process design and during everyday operation of the installation.

The research work run in Research and Teaching Department of Atmosphere Protection, I-15, Wrocław University of Technology, dealt with 15 samples of reagents used in flue gas desulfurization with dry, semi-dry and wet methods.

The physical properties and chemical constitution of the reagent (ground limestone) used in wet method FGD process are of great influence on FGD process efficiency and the range of balance and process calculations for each FGD system. Efficiency of desulfurization process is to a large degree, or even – as some say – decisively, dependent on the fineness of the limestone.

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