

MICHAŁ GŁOMBA*, ELŻBIETA SZMIGIELSKA*

IMPACT OF LIMESTONE GRINDING DEGREE ON THE VOLUME OF THE ABSORPTION SUSPENSION TANK IN FLUE GAS DESULPHURIZATION SYSTEMS

The impact of the reagent (limestone) grinding degree, of its dissolution rate and pH of the absorption suspension used in flue gas desulfurization systems on the working volume of the reactor tank in the flue gas SO₂ absorption unit has been discussed. A correlation equation, defining the dependence of the reactor tank working volume on the parameters under investigation has been presented.

1. INTRODUCTION

Overly low tank volumes may result in excessive circulation of the absorption suspension in the SO₂ absorption unit (increased L/G ratio), and therefore in increased demand for electrical power consumed by the circulation pump engines, and in reduced degree of exploitation of the ground limestone in the absorption suspension. On the other hand, overly high tank volumes lead to increased investment costs and spatial demands with regard to the location of the tank in the flue gas desulfurization (FGD) systems. The retention time of the suspension in the tank and the volume of the tank working together with the absorber must be appropriately integrated.

From the analysis of unit processes occurring in the tank (dissolution of the ground limestone, oxidation of sulfites in the suspension, crystallization of calcium sulfate – synthetic gypsum) and the conclusions from the practice in the field of flue gas desulfurization, it may be inferred that the desulfurization degree depends on: the size of the sprayed droplets of the absorption suspension, the droplet residence time in the absorption zone, the amount of the suspension flowing down the absorber walls, the distribution of flue gas velocities within the absorber, chemical composition of the

*Research and Didactic Unit of Atmosphere Protection, Institute of Environmental Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. Corresponding author M. Głomba, e-mail: michal.glomba@pwr.wroc.pl

flue gas and the suspension sprayed in the absorber, SO₂ and oxygen concentrations in the flue gas and sodium and magnesium ions concentration in the liquid. Also important are the parameters affecting the pH value of the absorption suspension: limestone grinding degree, grindstone dissolution rate and its reactivity towards SO₂, as well as CaCO₃ content, retention time of limestone in the reactor tank and the temperature of the process.

2. LIMESTONE DISINTEGRATION

In most cases, the goal of limestone disintegration is to increase the specific surface area of the solid phase in order to accelerate e.g., dry or wet boiler gas desulfurization. Mechanical disintegration may be achieved in two ways. In the case of limestone (Mohs scale hardness of 3.0 [1]), the disintegration process is started in jaw, cone and roll crushers (preliminary and medium disintegration). Proper disintegration consists of fine and very fine grinding, usually in ball mills.

Disintegration of solids is characterized by an index known as the disintegration degree [1]:

$$n = \frac{d_{p1}}{d_{p2}}, \quad (1)$$

where: d_{p1} – largest raw material particle size, d_{p2} – largest product particle size.

The relationship between the type of disintegration and the degree of disintegration is presented in Table 1.

Table 1

Disintegration degrees achieved in various disintegration operations [1]

Operation	Disintegration degree, n	Largest product particle size, d_{p2} [mm]
Crushing		
preliminary	3–6	>50
medium	4–10	5–50
Coarse grinding	5–10	0.5–5
Grinding		
fine	10–50	0.05–0.5
very fine	>50	0.005–0.05
colloidal	>50	<0.005

Disintegration in crushers is usually performed in dry conditions, while grinding can be performed in both dry and wet conditions. Wet grinding is characterized by lower energy demand and elimination of dust formation and convection. Dry grinding

is accompanied by less abrasive wear of the steel grinding elements, and thus lower oxide contamination of the ground product.

Grindability of the same material collected from different beds may vary. To allow differentiation in grindability, enabling the comparison of various materials and solid grinding devices were introduced such as: material grindability, specific material flow capacity and unit grinding workload.

Grindability is defined by the following equation:

$$M = \frac{\dot{m}}{\dot{m}_{st.c}}, \quad (2)$$

where: \dot{m} – flow capacity of the material in the mill, kg/s, $\dot{m}_{st.c}$ – flow capacity of standard coal in the same mill, kg/s [2, 3].

3. REACTIVITY OF GROUND LIMESTONE

Limestone reactivity was determined by static titration of limestone suspension with 1 M sulfuric acid at constant pH corresponding to the project specific value (e.g. pH = 5.2) and at predefined temperature, corresponding to the project specific temperature of the absorption suspension in the reactor tank, e.g. 55 °C for flue gas emitted from an anthracite boiler and 65 °C for flue gas emitted from a lignite boiler [3]. Consumption of sulfuric acid until a constant pH value is achieved (e.g., pH = 5.2) is recalculated as a degree of ground limestone conversion, which is then compared to reference limestone meal giving acceptable FGD results. Overall test time is 60 min. The lower and upper limits of the reference limestone meal reactivity [4] are presented in Fig. 1.

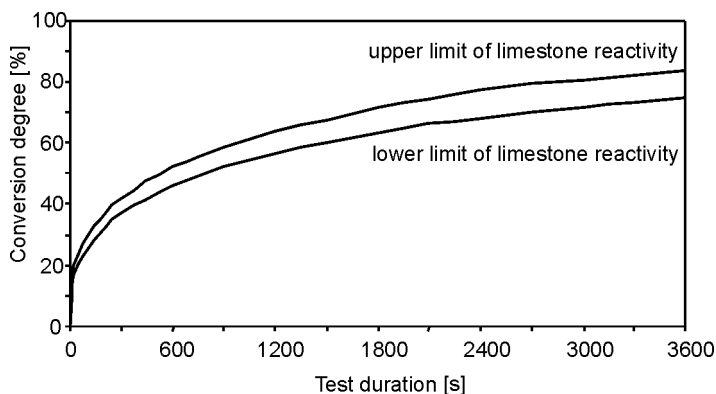


Fig. 1. Lower and upper limits of the reference limestone meal reactivity

Mokrosz [5] conducted reactivity tests for eight selected European carbonate based sorbents and chalk [5]. The results of this research are presented in Table 2.

Table 2

Results of reactivity tests for selected carbonate-based sorbents [5]

No.	Sorbent	CaCO ₃ content [%]	D ₄₃ [*] [μm]	Conversion rate after 60 min [%]
1	chalk	96.50	1.92	72
2	sorbent 6	97.24	3.28	60
3	sorbent 2	97.04	3.96	50
4	sorbent 7	95.40	6.27	40
5	sorbent 3	96.57	7.99	39
6	sorbent 4	95.36	7.62	35
7	sorbent 8	95.10	9.73	30
8	sorbent 5	96.36	9.72	30
9	sorbent 1	93.70	2.57	22

D₄₃^{*} – mean mass diameter (de Brouckere mean diameter).

The reactivity of the sorbents depends on the grinding degree and CaCO₃ content. Comparison of sorbents 7, 3, 4, 8 and 5, where CaCO₃ was found at concentrations of over 95%, shows large differences in reactivity. The reactivity is clearly reduced with the increase of the particle mean diameter. At the same time, sorbent 1, despite a relatively high grinding degree, is poorly reactive as it contains a small amount of CaCO₃. The results obtained for different sorbents [5], varying in terms of reactivity, allowed to identify one that was best for use in FGD systems.

4. GROUND LIMESTONE DISSOLUTION RATE

Kuciel [6] studied the rate of dissolution of ground limestone in the tank and its impact on selected parameters of SO₂ absorption in FGD systems. He collected three samples of ground limestone used in three flue gas desulfurization systems. The grain size distribution of the collected samples is presented in Fig. 2. The grain size is characterized by the volume/surface mean diameter (Sauter mean diameter) of the particles. The goal of the study was to determine the coefficient characterizing the kinetics of dissolution of limestone samples in the absorption suspension defined by:

$$\frac{dR}{dt} = -k, \quad (3)$$

where: R – radius of a spherical limestone particle, μm, t – time, s.

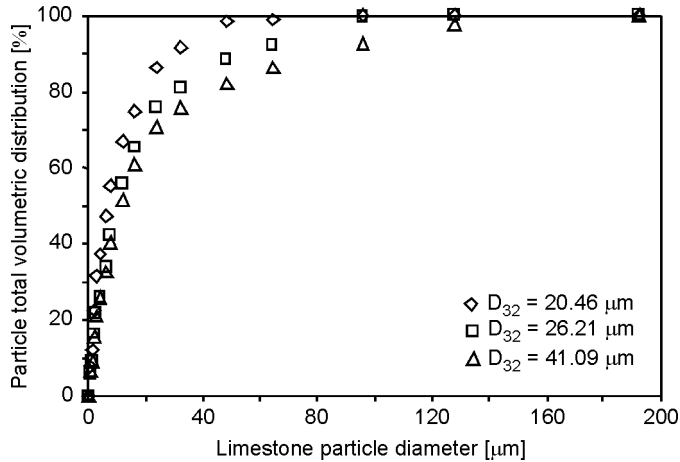


Fig. 2. Grain size distribution of the ground limestone test samples

Test limestone sample of mass m_0 was added to the suspension of the composition corresponding to that in the selected FGD system, then stirred and titrated with sulfuric acid so that the predefined pH value remained constant.

In this way, volumes of acid used per known time intervals (e.g. every minute) could be determined. From these results, time dependence of m/m_0 was calculated, where: m_0 – starting limestone sample mass, m – limestone sample mass after titration time t . This relationship was used to determine the coefficient k (Eq. (3)).

The calculated values of the coefficient k for three limestone samples and several pH values of the suspension are presented in Fig. 3.

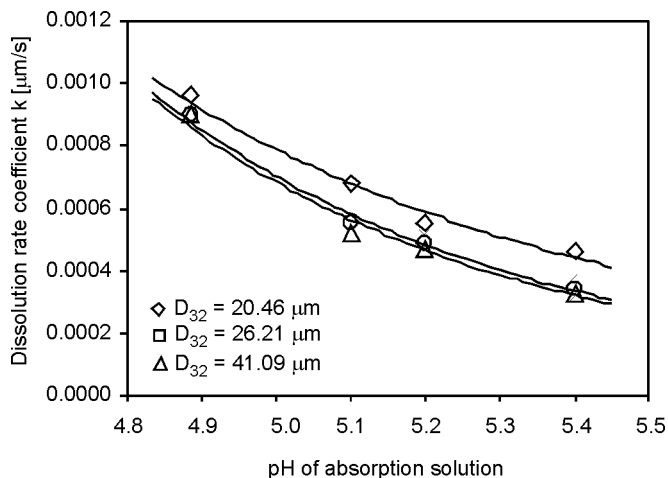


Fig. 3. Dissolution rate coefficient k for selected limestone samples in the absorption suspension in function of pH [6]

The limestone dissolution rate coefficient is higher for lower pH values and higher sorbent grinding degrees (lower D_{32} diameters). The impact of the latter parameter is slightly reduced upon reduction of the pH value of the suspension. Using the model described in [7], Kuciel calculated the tank volumes for the working conditions in selected systems and compared them with the values designed for the system [6]. The values calculated using the proposed formula did not differ from the actual volumes of the tanks by more than 10%.

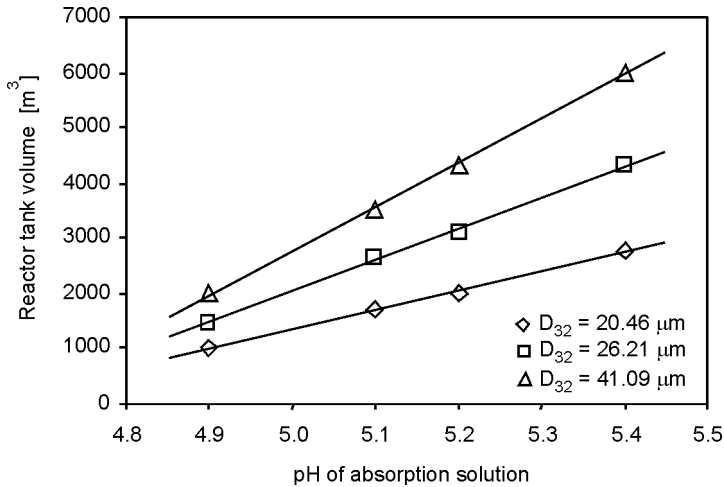


Fig. 4. The effect of pH and the mean limestone grain size on the reaction tank volume [6]

The dependences of the calculated values of the tank volume based on Kuciel results [6] on pH of the absorption suspension and the limestone disintegration degree are presented in Fig. 4. One may have serious objections to the dependence of the tank volume on pH, since an opposite effect is obvious – the higher pH of the suspension, the shorter its required retention time in the tank and the lower the tank volume itself is [8]. Kuciel [6] does not analyse the relationship presented in Fig. 3, suggesting that the dissolution rate of limestone particles increases along with increasing pH value.

5. SIMPLIFIED PROCEDURE OF CALCULATION OF THE TANK VOLUME

The design of systems for flue gas desulfurization in ground limestone suspensions starts with predefining the pH value of the suspension in the reactor tank based on literature data and, in the case of renowned design and installation companies, on the experience gained from installations designed and exploited in the past. The residence time of suspension in the reactor is also predefined based on the experience from pre-

vious installations. This operation is routine-based and does not result from a thorough knowledge of physicochemical properties of the sorbent (reagent), as it remains undefined at this stage; the material mining site or the supplier are not defined; nor are the exact chemical composition, reactivity and grain size distribution of the material.

Before designing of the process is started, one should initiate a simple and relatively inexpensive procedure consisting of samples collection from selected known limestone suppliers so as to avoid design mistakes and the resulting expensive adjustments of the working parameters of the FGD system. The samples should be tested for chemical composition and disintegration degree.

The samples prepared in this way should be tested with the purpose to determine the coefficient k of the limestone particle dissolution rate. To this end, a laboratory vessel (e.g., a flask) should be charged with a suspension prepared beforehand to correspond the intended composition in the FGD tank at nominal working conditions. The suspension in the vessel (flask) should be stirred and charged with a pre-weighed limestone sample of known chemical composition and grain size distribution and stirred again.

Thus prepared suspension is titrated with a sulfuric acid solution to maintain a constant, predefined pH value, e.g. pH = 5.2 (sulfuric acid is dosed so that the pH value of the solution remains constant). The volume of the sulfuric acid introduced to the suspension during titration in a given interval should be carefully monitored for subsequent calculation of the mass of converted limestone over time and the m/m_0 ratio. These data allow for determination of both coefficient k and the m/m_0 ratio in function of time t with the following equation:

$$m = m_0 \left(1 - \frac{kt}{R_0} \right)^3, \quad (4)$$

where: k – coefficient of the dissolution rate of a ground limestone particle, $\mu\text{m}/\text{min}$, m_0 – mass of spherical particles at the beginning of titration, g, m – mass of spherical particles after time t , g, R_0 – radius of a spherical particle of ground limestone, μm , t – time interval between two consecutive doses of sulfuric acid introduced into the flask, min.

The procedure allows determination of the volume of sulfuric acid consumed in known time intervals, e.g. every minute (if pH value of the suspension after that time is at the predefined level). Calculations of k may be carried out for mean diameters of each fraction of particles, and thus Eq. (4) should be applied to m_{0i} , m_i and R_{0i} , where i is the considered fraction of particles, or to the Sauter mean diameter (which simplifies and speeds up the procedure of determining the coefficient k). After determining the value of k and predefining pH of the absorption suspension and the mean particle size ($D_S = D_{32}$) as assumed in the installation design, one may use the simplified method to calculate the absorption suspension reactor tank volume.

Multiple regression analysis of data presented in this paper was performed to model the impact of the most important parameters characterizing the reagent ground limestone (mean diameter of ground limestone particles D_{32} and the coefficient k of limestone dissolution rate) and the absorption suspension (pH). At the confidence level of 95%, the following correlation equation was obtained:

$$V_{zb} = pH^{-3.4455} k^{-1.5416} D_{32}^{0.587}. \quad (5)$$

Statistical regression parameters of the correlation are: multiplicity $R = 0.9999$, $R^2 = 0.9999$; adjusted $R^2 = 0.88882$; standard error $S_e = 0.0691$; observations: 12. Maximum deviations of the designed suspension tank volumes from the calculated values were 9.6 and -11.83% , while mean deviations were 5.14 and -5.44% . The comparison between the designed and the calculated reactor tank volumes is presented in Fig. 5.

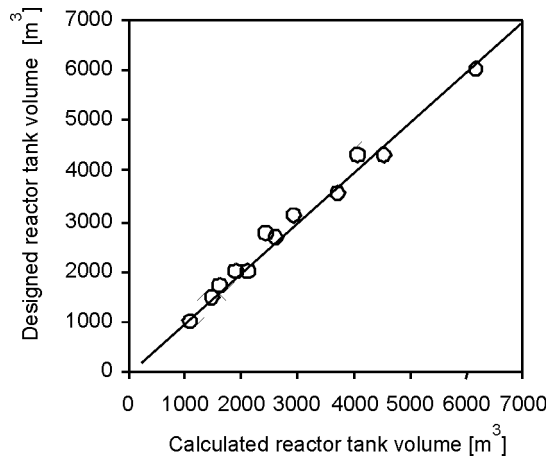


Fig. 5. Designed and calculated FGD system reactor tank volumes

According to Eq. (5), the volume of the reactor tank decreases upon increasing pH of the absorption suspension and sorbent dissolution rate, and increases upon increasing the ground limestone particle diameter. pH of the suspension has the greatest impact on the tank volume.

6. SUMMARY

Experimentally determined dissolution rate coefficients of limestone in the reactor tank, the reagent grinding degrees and pH values of the absorption suspension in three exploited FGD systems [6] were used to establish the correlation equation (5) which can be used to calculate the working tank volume. The equation is characterized by

relatively low deviation of actual reactor tank volumes from the calculated values; the mean deviation is about 5%.

In the case of known values of pH of suspension (either predefined or defined for particular FGD system exploitation conditions), rate of the limestone dissolution in the absorption suspension (characterized by limestone dissolution rate coefficient) and the limestone grinding degree (D_{32}), they may be used to calculate the volume of the reactor tank.

In order Eq. (5) be used in calculations of the suspension tank volumes of an FGD system being designed or already in operation, the limestone grinding degree (characterized by the mean particle diameter D_{32}), the coefficient k of the limestone dissolution rate and pH value of the absorption suspension should be experimentally determined by established chemical analyses as described in appropriate standards.

REFERENCES

- [1] KOCH R., NOWORYTA A., *Mechanical processes in chemical engineering*, WNT, Warszawa, 1992 (in Polish).
- [2] RUMPF H., *Chem. Ing. Techn.*, 1974, 46, 1.
- [3] RUMPF H., *Mechanische Verfahrenstechnik*, Carl Hanser Verlag, München, 1975.
- [4] BURZALA B., WOJNAR K., *The issue of chemical analysis of limestone powder and products from FGD*, [In:] Proc. IV Forums: *Operational Experience FGD*, Tatrzańska Łomnica, 22–24 April 2000, 219.
- [5] MOKROSZ W., *Chemik. Nauka – Technika – Rynek*, 2005, 58 (6), 301.
- [6] KUCIEL E., *Inż. Chem. Proc.*, 1995, 16, 232.
- [7] LEVENSPIEL O., *The chemical reactor omnibook*, Oregon, 1989, 54.1–54.12.
- [8] GŁOMBA M., *J. Air Waste Managem. Assoc.* 2010, 60 (8), 1009.