LIMESTONE PURITY AS THE DECISIVE FACTOR FOR ITS CONSUMPTION IN THE FLUE GAS DESULPHURISATION PROCESS

ČISTOST APNENCA KOT ODLOČILNI FAKTOR NJEGOVE PORABE V PROCESU RAZŽVEPLJEVANJA DIMNIH PLINOV

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Abstract

The wet flue gas cleaning process in thermal power plants uses limestone reagent, which is ground and mixed with process water, before coming in contact with flue gases, in order to form a homogeneous suspension, which then absorbs the gaseous acid components in the flue gas cleaning process in thermal power plants (mainly sulphur dioxide) from the flue gas stream. The purity of the limestone has a significant effect on its consumption, as cleaner limestone enables the absorption of a larger amount of acidic components from the flue gas stream, with lower total consumption of the reagent - i.e. limestone.

Povzetek

Proces mokrega čiščenja dimnih plinov v termoenergetskih postrojenjih uporablja za reagent apnenec, ki se pred stikom z dimnimi plini zmelje in ustrezno zmeša z procesno vodo, z namenom tvorjenja homogene suspenzije, ki nato v proces čiščenja dimnih plinov v termoenergetskih objektih, absorbira plinaste kisle komponente (predvsem žveplov dioksid) iz toka dimnih plinov. Čistoča apnenca pomembno vpliva na porabo le tega, saj bolj čist apnenec omogoča absorbcijo večje količine kislih komponent iz toka dimnih plinov, pri manjši skupni porabi reagenta – torej apnenca.

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1   LIMESTONE AS A REAGENT IN THE WET FLUE GAS DESULPHURISATION PROCESS

The wet flue gas desulphurisation process is an industrial process through which the acid components in the flue gas flow are removed (mainly in big coal-fired thermal power plants). The main equipment of the flue gas desulphurisation process is an absorber, in which the raw hot flue gases are washed and sprayed with the limestone suspension. The reagent for the absorption of acid components from flue gases is limestone, which is crushed and mixed with the process water in order to form a homogeneous suspension, with which the raw flue gases are sprayed. When the acid components are absorbed by the alkaline parts of the limestone suspension, oxidation air is injected into the absorber, helping to form a crystallisation process in the sump of the absorber, which forms gypsum as the by-product of the wet flue gas desulphurisation process. The limestone as the reagent for the process is usually supplied from a nearby quarry [1]. Since the chemical composition of the limestone can vary because of different geological compositions at various geographical locations, the laboratory analysis of the foreseen limestone is necessary before entering the basic and detailed design of the project. The reaction part of the reagent is determined based on the performed chemical analysis of the reagent. Those data are crucial since they dictate the overall consumption of the reagent within the flue gas desulphurisation process.

1.1   Reagent preparation for entering the process

Limestone, as the reagent for the desulphurisation process, needs to go through the delivery and preparation process before entering the cleaning process. Hereinafter are described the steps during which the limestone is handled, from delivery to storage, and supplying the chemical reaction in an absorber with freshly prepared limestone slurry. Figure 1 shows a limestone system overview.
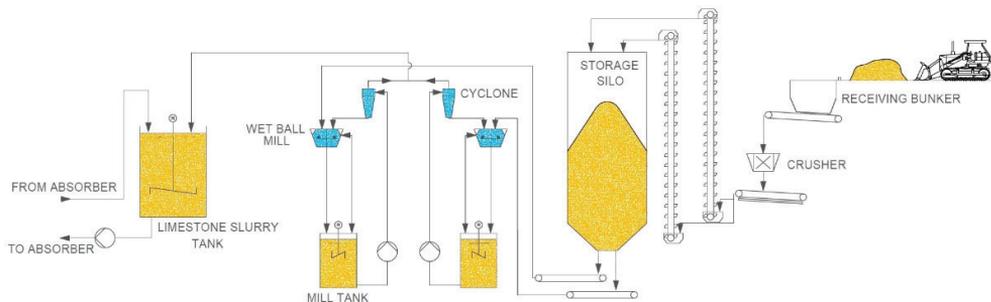
Figure 1: *Limestone receiving & storage system overview*

Handling of the limestone can be very challenging from the point of view of crushing and transporting it, since clogging of key equipment can occur [2]. Therefore, the redundancy in reagent preparation lines is meaningful. That enables the operator to operate and supply the flue gas desulphurisation process with the needed reagent through one operating reagent preparation line, while the other one is in standby just in case of clogging of the current

operational line. With that model, a thermal power plant can avoid big losses in the case of an unexpected shutdown at an inconvenient operational time period.

1.1.1 Limestone delivery and unloading

As aforementioned, limestone is delivered to the site of the thermal power plant from a quarry, using trucks or trains. The standard size of the delivered limestone is usually 250 mm in diameter. This limestone is then dumped on a paved area. Where available, a covered shed is supplied for the delivered limestone, since protection from rain can prevent limestone from becoming too sticky for further manipulation with it. Dumpers are used for manipulation of the limestone from the covered shed to the receiver hopper of the crusher.

1.1.2 Limestone crushing

When the limestone is delivered to the hopper of the crusher using a dumper, the limestone pieces of 250 mm in diameter are crushed using a hammer crusher. The main task of the hammer crusher is to crush the limestone parts from 250 mm in diameter to 50 mm in diameter [3, 4]. This size enables that the limestone pieces are then transported further through the process more easily. Before the hammer crusher, a magnetic separator is installed to remove potential ferrite pieces from the handled limestone. Belt conveyors and bucket elevators are used for transporting the crushed limestone from the crusher to the storage silo facility. From the crusher, the belt conveyor is used to transport the limestone from the crusher to the bucket elevator. When the limestone enters the bucket elevator, it is elevated to the top of the silo. Additional belt conveyors can be used for further manipulation on the top of the limestone storage silo.

1.1.3 Local silo storage of crushed limestone

Crushed limestone is stored in a storage silo, which can be made out of steel or reinforced concrete. It is meaningful to design a storage silo at least for consumption of reagent of one week, or 7 working days. The limestone is stored in the limestone storage silo and, when needed, is further transported to the wet ball mill area, where it is ground finely.

1.1.4 Wet ball mill grinding and limestone slurry preparation

The limestone is transported from the storage silo to the wet ball mill area, where it enters the wet ball mill. A wet ball mill is a cylindrical mill with steel balls in it [5]. With the presence of water and rotation, the steel balls and limestone parts encounter each other, and, consequently, the limestone parts are crushed into fine particles, generally corresponding to a 325 mesh (meaning that 90% of the limestone particles are smaller than 60μm in diameter). At the outlet of the wet ball mill the limestone slurry is delivered to the hydro cyclone group, from where the underflow is delivered back to the wet ball mill, and the overflow is delivered to the freshly prepared limestone slurry storage tanks.

1.1.5 Dosing of the fresh limestone slurry to the process

Fresh limestone slurry is delivered to the absorber with the help of the limestone slurry delivery pumps, one working and one on stand-by. Freshly prepared limestone slurry is taken from the limestone slurry storage tanks and is delivered through a pipeline to the absorber. The required

amount of fresh limestone slurry is then pumped into the absorber, in order to maintain a stable chemical reaction between the acid and alkali components inside the absorber. Unneeded freshly prepared limestone is returned to the limestone slurry storage tank.

2   CHEMICAL COMPOSITION OF LIMESTONE

An example of the chemical composition of the limestone [6] used as the reagent in the flue gas desulphurisation process, is presented in Table 1.

Table 1: *Example of the chemical composition of limestone*

Chemical composition of Limestone		
No.	Constituents	% by mass
1	CaO	51
2	MgO	3,8
3	Fe_2O_3	1
4	Al_2O_3	2,1
5	SiO_2	4,5
6	MnO_2	0,12
7	P_2O_5	0,01
8	Cl_2	0,015
9	Na_2O	0,16
10	K_2O	0,01
11	TiO_2	0,02
12	S	0,1
13	Bond work index	13
14	Size	250 mm

As presented in Table 1, twelve chemical elements and compounds are present in the limestone. The chemical compounds CaO and MgO represent the major part, in percentage by mass, [7]. Those two compounds are also the most important for the flue gas desulphurisation process, since they are delivering alkaline components back to the process. All the other elements do not have a significant impact on the process of flue gas cleaning itself. The initial delivered size of limestone is 250 mm in diameter before it enters the process of crushing, storing and fine wet grinding. The Bond work index [8, 9, 10] of the observed limestone sample is determined as follows.

$$W_i = 1,1 \cdot \frac{44,5}{P_c^{0,23} \cdot G^{0,82} \cdot \left(\frac{10}{\sqrt{P_{80}}} \cdot \frac{10}{\sqrt{F_{80}}} \right)} \tag{2.1}$$

$W_i -$ *Bond work index* $\left[\frac{kWh}{t} \right]$

$P_c -$ *Test sieve mesh size* $[\mu m]$

$G -$ *Weight of the test sieve undersize per mill revolution* $[g/rev]$

$P_{80} -$ *Opening of sieve passing* 80% *of the last cycle sieve undersize product* $[\mu m]$

$F_{80} -$ *Sieve mesh size passing* 80% *of the feed before grinding* $[\mu m]$

3 PURITY AND REACTIVE PART OF LIMESTONE VERSUS REAGENT CONSUMPTION

The purity of limestone and its reactive part are the most important factors that have an impact on the overall consumption of limestone in the process of flue gas desulphurisation. As seen in Table 1, the calcium and magnesium content is expressed as CaO and MgO [11]. The aforementioned compounds need to be recalculated with the help of the compound molecular mass to the $CaCO_3$ and $MgCO_3$ content in % by mass. This is achieved by the following equations.

$$CaCO_3 \text{ (\% by mass)} = CaO \text{ (\% by mass)} \cdot \frac{M\left(CaCO_3 \frac{g}{mol}\right)}{M\left(CaO \frac{g}{mol}\right)} = CaO \text{ (\% by mass)} \cdot \frac{100}{56} \tag{3.1}$$

$$MgCO_3 \text{ (\% by mass)} = MgO \text{ (\% by mass)} \cdot \frac{M\left(MgCO_3 \frac{g}{mol}\right)}{M\left(MgO \frac{g}{mol}\right)} = MgO \text{ (\% by mass)} \cdot \frac{84,3}{40,3} \tag{3.2}$$

3.1 CaCO₃ Reactivity

The reactivity of $CaCO_3$ is determined based on the different requests regarding dimensioning the process equipment, as well as issuing requested guarantees. For the purpose of designing and sizing the process equipment, the reactive content of $CaCO_3$ shall be 89%, and the remaining part shall be considered unreactive, since it contains particles of impurities. For determining the guaranties, the $CaCO_3$ reactive part [12, 13, 14] in limestone shall be considered 79%, while the remaining part is unreactive with impurities. The aforementioned reactive parts are presented in Table 2 below.

Table 2: CaCO₃ reactivity part for the design and guarantee scenario

Scenario	Compound	Reactive part (% by mass)	Non-reactive part (% by mass)
Design scenario	CaCO₃	89	11
Guarantee scenario	CaCO₃	79	21

3.2   MgCO₃ Reactivity

The reactivity of $MgCO_3$ is determined by chemical analysis. Based on the aforementioned, the presence of $MgCO_3$ is confirmed in the limestone compound. From the limestone analysis, we can see the quantitative presence of $MgCO_3$ in limestone. In the case that the limestone`s quality is lower and it is contaminated with many impurities, the reactivity part of the $MgCO_3$ compound can be negligible. Nevertheless, if the limestone has good quality, the $MgCO_3$ presence in limestone can be also around 3 % by weight, and its reactivity up to 30%. Hence, it is important to perform several different iterations, taking into consideration different presence (by weight) and different reactivity shares.

3.3   Reagent Consumption

For the evaluation of limestone consumption, we will take into consideration a thermal power plant unit with $600MW_{th}$ rated capacity. The considered limestone is used for the cleaning of the flue gases within the flue gas desulphurisation process. Limestone is used as the reagent in the process. The different limestone samples shall be taken into consideration in the phase of designing. Five limestone samples with different compositions are presented in Table 2. Those five samples will be used further in the process of determining the overall limestone consumption in the flue gas desulphurisation process for the $600MW_{th}$ thermal power plant unit. Limestone sample number 1 has the lowest $CaCO_3$ presence and the highest amount of inert compounds and remaining impurities. Limestone sample number five has the highest $CaCO_3$ presence, with a minimal amount of inert compound and remaining impurities. The limestone samples two, three, and four have different chemical structures, where the $CaCO_3$ presence is rising from sample number two to sample number four, and impurities are decreasing. The amount of $MgCO_3$ is distributed randomly between five limestone samples, in order to see its impact on the overall reagent consumption. The reactivity level of the $CaCO_3$ compound in the limestone sample is distributed randomly between five samples, ranging from 75% - 89%. The reactivity of the $MgCO_3$ is distributed evenly between the five samples, increasing from sample number one with 10% reactivity to sample number five with 30% of reactivity. The limestone samples are presented in Table 3.

Table 3: *Example of limestone samples` chemical composition*

Limestone Sample	CaCO3 presence*	Reactivity CaCO3	MgCO3 presence*	Reactivity MgCO3	Inert compounds*	Remaining compounds*
No. 1	75	75 - 85%	2	10%	5	18
No. 2	79	75 - 85%	1	15%	4	16
No. 3	85	75 - 85%	3	20%	3	9
No. 4	89	75 - 85%	1	25%	2	8
No. 5	95	75 - 85%	1	30%	2	2
* % by the limestone sample weight						

The corresponding limestone samples are further presented graphically with the following Figure 2. Limestone sample number 1 possesses the lowest $CaCO_3$ content with the highest amount of impurities in the sample, while limestone sample number five possesses the highest amount of $CaCO_3$ in the sample and the lowest amount of impurities in the sample. Based on the proposed

chemical composition of the limestone samples, we expect that sample number 1 will result in the highest reagent consumption in the flue gas desulphurisation process, while limestone sample number 5 will reflect the most optimal reagent consumption in the aforementioned process. It is important to highlight the fact that impurities that are entering the process with the reagent are blocking the chemical reactions of removing the acid components from the flow of the untreated flue gases. Therefore, it is important to supply limestone to the site as pure as possible.
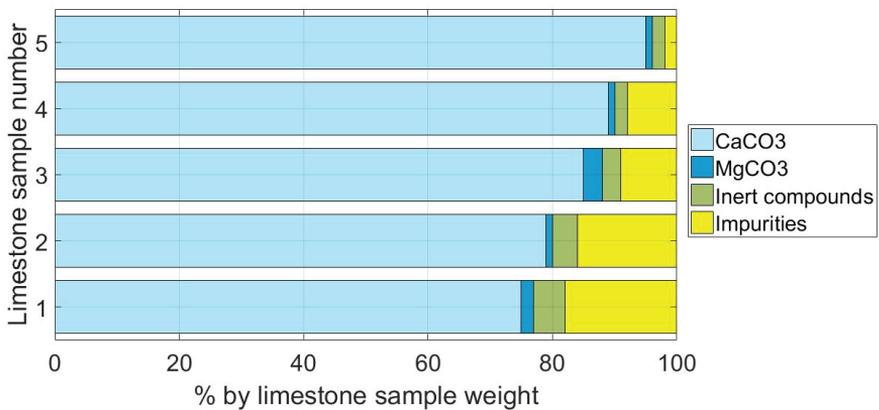
Figure 2: Limestone samples` chemical composition

Based on the chemical composition of five limestone samples, we calculated the expected overall limestone consumption of the flue gas desulphurisation process. As predicted previously, limestone sample 1 reflects the highest limestone consumption with only 75% $CaCO_3$ presence in the sample, and with the overall consumption of 10855 kg/h, taking into consideration that the sample has a 75% $CaCO_3$ reactivity part.
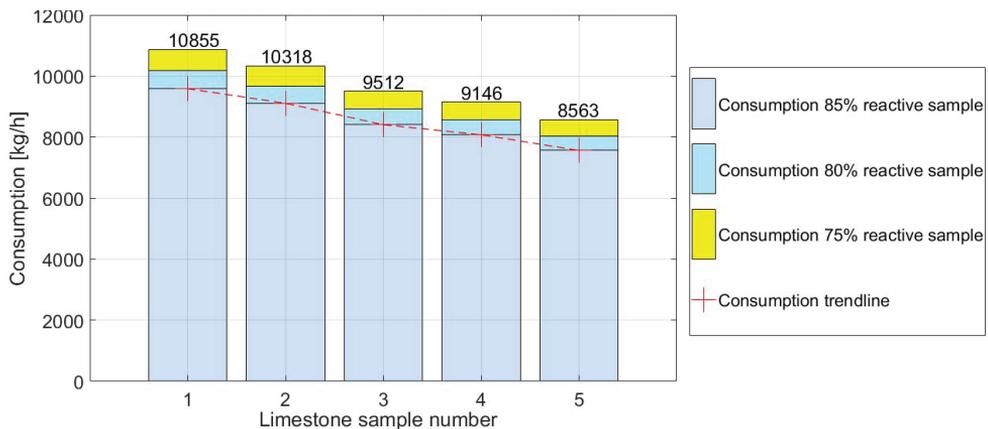
Figure 3: Limestone samples one to five and their overall consumption in kg/h in the flue gas desulphurisation process

Contrary to limestone sample one, limestone sample five possesses 95% $CaCO_3$ presence, and with the reaction part 75% of it, we can expect 8563 kg/h limestone consumption. The correlation

between the purity of the reagent limestone and its consumption we are presenting in the following Table 4. The difference between the consumption of different reagent reactivity samples is presented in the last two columns of Table 4. Based on the calculated and presented data, we can conclude that the correlation between the purity of the limestone sample and its consumption is inversely proportional. It is to be expected that the purest limestone will result in lower consumption, and vice versa. In Table 4, column number 5, the difference in overall limestone consumption is presented, between samples with a 75% reactivity part and 80% reactivity part samples. It is shown in column number 5 that this difference is approximately half of the tonne of the limestone reagent consumption per hour (12 tons of reagent limestone savings per operating day of the flue gas desulphurisation system). Furthermore, in Table 4, column number 6, the difference is presented in overall consumption between samples with 75% reactivity part and an 85% reactivity part. From the data in Table 4, column number 6, we can see that the limestone consumption savings are around 1 ton of the limestone reagent per operating hour of the flue gas desulphurisation system (24 tons of reagent limestone savings per operating day of the flue gas desulphurisation system). From the consumption analysis presented in Table 4, it is clear that it is in the highest interest of the thermal power plant owner or operator that the purest limestone is delivered to the site, with the highest reactivity part possible. This kind of limestone will allow smooth flue gas desulphurisation plant operation, without any unnecessary clogging, as well as lowering the operating and maintenance costs of the flue gas desulphurisation system.

Table 4: Limestone reagent samples 1 to 5 overall consumption in the FGD process

Limestone Sample No.	① 75% Reaction Sample Consumption [kg/h]	② 80% Reaction Sample Consumption [kg/h]	③ 85% Reaction Sample Consumption [kg/h]	Δ ① - ② [kg]	Δ ① - ③ [kg]
Sample 1	10855	10180	9583	675	1272
Sample 2	10318	9675	9107	643	1211
Sample 3	9512	8924	8404	588	1108
Sample 4	9146	8576	8074	570	1072
Sample 5	8563	8031	7560	532	1003

Savings of the limestone reagent **6,2%** (Δ ① - ②)

Savings of the limestone reagent **11,7%** (Δ ① - ③)

4   CONCLUSION

This paper presents the main effect of limestone purity (and its reactivity) on the overall consumption of the limestone as a reagent in the flue gas desulphurisation process. Five limestone samples with different purity rates, as well as different reactivity rates, are presented in the paper. A 600MW$_{th}$ thermal power plant FGD unit is considered for the purpose of the reagent consumption simulation. It is concluded that the limestone sample with the highest purity and reactivity is resulting in the lowest regent consumption. Therefore, it is highlighted in the concluding phase of this paper, that FGD unit operators (owners) should strive to supply as good a reagent as possible to their operating or planned FGD units, in order to establish a continuous and reliable chemical reaction that will remove a sufficient grade of the acid components in the raw flue gas flow from the thermal power plant boiler. Consequently, operating FGD costs will also be lower.

References

[1]   **J.A.H. Oates**: *Lime and Limestone Chemistry and Technology Production and Uses*, Wiley VCH Verlag GmbH, p.p. 169, 1998

[2]   **M. Kepniak, P. Woyciechowski, W. Franus**: *Chemical and physical properties of limestone powder as a potential microfiller of polymer composites*, Archives of Civil Engineering, Vol. LXIII, Issue 2, p.p. 67 – 78, 2017

[3]   **Ö. Kilic**: *Impact of physical properties and chemical composition of limestone on decomposition activation energy*, Asian Journal of Chemistry, Vol. 25, p.p. 8116 – 8120, 2013

[4]   **M.I. Smorodinov, E.A. Motovilov, V.A. Volkov**: *Determination of Correlation Relationship Between Strength and Some Physical Characteristics of Rocks*, Proceedings of the of the Second Congress of the International Society of Rock Mechanics, Vol. 2, p.p. 35, 1970

[5]   **L.M. Tavares, R.D.C. Kallemback**: *Grindability of Binary Ore Blends in Ball Mills*, Minerals Engineering, Vol. 41, p.p. 115 – 120, 2013

[6]   **P. Šiler, I. Kolarova, J. Bednarek, M. Janča, P. Musli, T. Opravil**: *The possibilities of analysis of limestone chemical composition*, International conference building materials, product and technologies, Vol. 379, p.p. 1 – 6, 2018

[7]   **F. Munawaroh, L. Khamsatul Muharrami, T. dan Zaenal Arifin**: *Calcium oxide characteristics prepared from Ambuten's calcined limestone*, Jurnal Pena Sains, Vol. 5, No. 1, p.p. 65 – 71, 2018

[8]   **D. Todorović, Z. Bartulović, V. Jovanović, B. Ivošević**: *The bond work index of limestone and andesite mixtures*, Mining and metallurgy BOR, No. 3 – 4, p.p. 21 – 28, 2017

[9]   **H. Ipek, Y. Ucbas, C. Hosten**: *The Bond Work Index of Mixtures of Ceramic Raw Materials*, Minerals Engineering, Vol. 18, p.p. 981 – 983, 2005

[10]   **P.C. Kapur, D.W. Fuerstenau**: *Simulation of Locked-Cycle Grinding Test Using Multicomponent Feeds*, Powder technology, Vol. 58, p.p. 39 – 48, 1989

[11]   **Y. Zhu, S. Wu, X. Wang**: *Nano CaO grain characteristics and growth model under calcination*, Chemical Engineering Journal, Vol. 175, p.p. 512 – 551, 2011

[12]   **Z. Arifin, N. F. Apriliani, M. Zainuri, M. Darminto**: *Characterization of Precipitated CaCO₃ Synthesized from Dolomite*, IOP Conference Series Material Science and Engineering, Vol. 196, p.p. 1 – 4, 2017

[13]   **M.V. Kök, W. Smykatz-Kloss**: *Characterization, Correlation and Kinetics of Dolomite sample as outlined by Thermal Methods*, Journal of Thermal Analysis and Calorimetry, Vol. 91, No. 2, p.p. 565 – 568, 2008

[14]   **N.L. Ross, R.J. Reeder**: *High pressure structural study of dolomite and ankerite*, American Mineralogist, Vol. 77, p.p. 412 – 421, 1992

Nomenclature

(Symbols)	(Symbol meaning)
mm	millimetres
µm	micrometres
FGD	Flue gas desulphurisation
CaO	Calcium oxide
MgO	Magnesium oxide
Fe₂O₃	Iron (III) oxide (ferric oxide)
Al₂O₃	Aluminium (II) oxide
SiO₂	Silicon dioxide
MnO₂	Manganese dioxide
P₂O₅	Phosphorus pentoxide
Cl₂	chlorine
Na₂O	Sodium oxide
K₂O	Potassium oxide
TiO₂	Titanium dioxide
S	sulphur
CaCO₃	Calcium carbonate
MgCO₃	Magnesium carbonate
MW	megawatt
th	thermal
kg	Kilogram
kg/h	Kilograms per hour