Journal of Energy Technology

JET Volume 11 (2018) p.p. 37-46
Issue 3, November 2018
Type of article 1.01
www.fe.um.si/en/jet.html

A MAGNESIUM-ENHANCED LIME CLEANING PROCESS OF FLUE GASES

PROCES ČIŠČENJA DIMNIH PLINOV Z UPORABO MAGNEZIJSKO OBOGATENE APNENČEVE MOKE

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Keywords: magnesium-enhanced lime, cleaning of flue gases, thermal power plant, sulphur dioxide.

Abstract

The cleaning of flue gases in thermal power plants has been mandatory since the 1990s in the EU. The most commonly applied process for flue gas cleaning is a wet calcite process that enables the high efficiency of cleaning flue gases with the usage of a reagent that is readily available in nature. This paper presents the process of cleaning the flue gases on a wet basis, but using slaked lime with the content of the magnesium as the reagent. This sort of cleaning process works very well, but the reagent is usually very difficult to find in nature itself.

Povzetek

Čiščenje dimnih plinov v termoenergetskih objektih je prisotno in obvezno v EU že vrsto let. Najbolj razširjen postopek za čiščenje žveplovega dioksida iz dimnih plinov je tako imenovan mokri kalcitni postopek, ki omogoča visoko učinkovitost čiščenja dimnih plinov, z uporabo reagenta, ki je v naravi lahko dostopen – apnenec. Članek predstavlja alternativni postopek čiščenja dimnik plinov, je prav tako moker, a kot reagent uporablja gašeno apno z vsebnostjo magnezija. Uporaba takšnega reagenta v postopku čiščenja dimnih plinov se je izkazala za zelo uspešno, a reagent kot takšen težko najdemo v naravi.

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1 INTRODUCTION

With the combustion of fossil fuels, such as coal and oil, large amounts of sulphur dioxide are emitted into the atmosphere. Sulphur dioxide emissions are well known as having a severe impact on human health and the environment. The major health risks of exposure to high concentrations of sulphur dioxide are breathing difficulties, respiratory illness, and the aggravation of the existing cardiovascular disease. Sulphur dioxide leads to depositions of this harmful substance in the environment, causing serious problems, including the acidification of lakes and streams, and damage to plants, trees and crops. Sulphur dioxide depositions are also responsible for decay and damage on the monuments, buildings, and infrastructure. When particles of sulphur dioxide are in the air (airborne), they might also cause difficulties with visibility.

2 MAGNESIUM-ENHANCED LIME

Magnesium-enhanced lime can be used as the reagent in the desulphurization process of raw flue gases in thermal power plants, where high amounts of the sulphur dioxide are present. Magnesium-enhanced lime is produced as a mixture of slaked lime, which contains calcium hydroxide $Ca(OH)_2$ and magnesium hydroxide $Mg(OH)_2$, *[1]*.

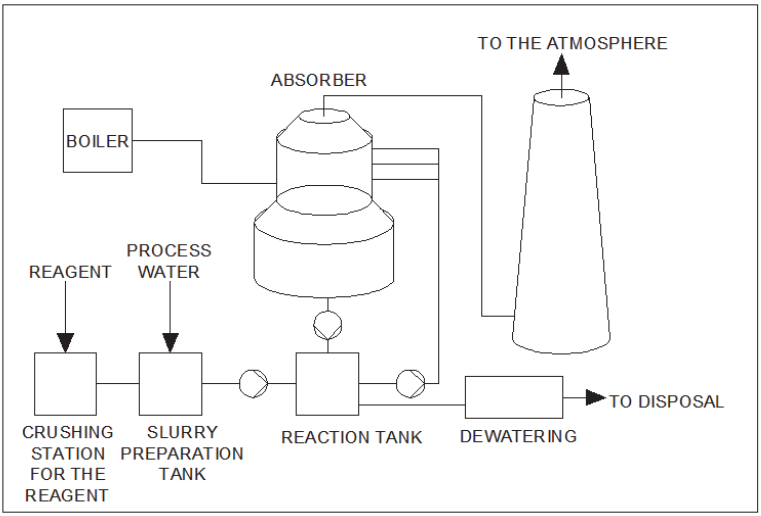


Figure 1: *Desulphurization process with the usage of magnesium-enhanced lime as the primary reagent. The system contains the following main equipment: a crushing station for the reagent, slurry preparation plant, reaction plant, absorber, dewatering station and the wet stack through which the clean flue gases enter the atmosphere.*

The reagent with the proper formation of the two-component mixture is delivered to the absorber into the bottom of it, where pH control is used to replenish the consumed reagent. The fresh slurry is transported from the bottom of the absorber with the assistance of the recirculation pumps to the spraying levels, where the full impact between the flue gases from the boiler unit and the fresh slurry occurs. During the spraying of the slurry on the flue gases that rise from the inlet towards the outlet of the absorber, the chemical reactions between acid components in flue gases and the neutral components in the fresh slurry happen.

3 MAGNESIUM-ENHANCED LIME & DESULPHURIZATION

Calcium hydroxide in the slurry reacts with most of the acid components, primarily with the sulphur dioxide in the raw flue gases, and the calcium sulphates are formed ($CaSO_3 \bullet 1/2H_2O$). Magnesium hydroxide reacts with the remaining acid components in the flue gases. During this reaction, the soluble magnesium salts (magnesium sulphide $MgSO_3$ and magnesium disulphide $Mg(HSO_3)_2$) are formed.

The presence of the magnesium components in the slurry significantly increases the SO_2 capture and enables the further reduction in the consumed power for the process, the reagent, and the equipment costs. Its presence in the slurry also prevents the pH from sharply decreasing during the operation of the flue gas desulphurization process, which means that this mechanism allows higher and better performance of the flue gas desulphurization process, since there is increased solubility of the sulphur dioxide in the slurry and this consequently means a lower liquid/gas ratio in the absorber.

The presence of the salts that are formed with the help of the magnesium in the slurry prevent the formation of the build-ups on the internal surfaces of the absorber and other essential equipment of the absorber, such as pipes for the recirculation of the slurry or spraying nozzles on the spraying levels.

The primary chemical reactions that occur during the flue gas desulphurization process with magnesium-enhanced lime are shown hereinafter.

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 \bullet \tfrac{1}{2} H_2O + \tfrac{1}{2} H_2O \quad (3.1)$$

$$4SO_2 + 3Mg(OH)_2 \rightarrow 2MgSO_3 + Mg(HSO_3) + 2H_2O \quad (3.2)$$

$$CaSO_3 \bullet \tfrac{1}{2} H_2O + \tfrac{1}{2} O_2 + 3/2\, H_2O \rightarrow CaSO_4 \bullet 2H_2O \quad (3.3)$$

$$MgSO_3 + \tfrac{1}{2} O_2 \rightarrow MgSO_4 \quad (3.4)$$

$$Mg(HSO_3) + O_2 \rightarrow MgSO_4 + H_2SO_4 \quad (3.5)$$

The portion of the slurry that is already present in the absorber has reacted with the acid components of the flue gases. The slurry falls from the spraying levels (it is pumped to there from the bottom of the absorber with the assistance of the recirculation pumps) back to the bottom of the absorber. When the pH in the bottom of the absorber reaches the level of 5.5, some of the existing slurry must be extracted from the sump of the absorber. The slurry with mentioned pH level is further pumped to the external forced oxidation tank, where it contacts the air. Calcium sulphite is converted to the gypsum (in crystalline form), magnesium salts are oxidized to the $MgSO_4$ (in solution) as shown in chemical reactions (3) to (5). The slurry is from the external tank transported to the dewatering station, where the by-product of the process is formed (i.e. gypsum in the shape of the cake). The remaining liquid from the dewatering process, still containing the $MgSO_4$, is transported back to the absorber to help enhance the quality of the slurry and to save the amount of the reagent that is needed for the efficient cleaning of the flue gases.

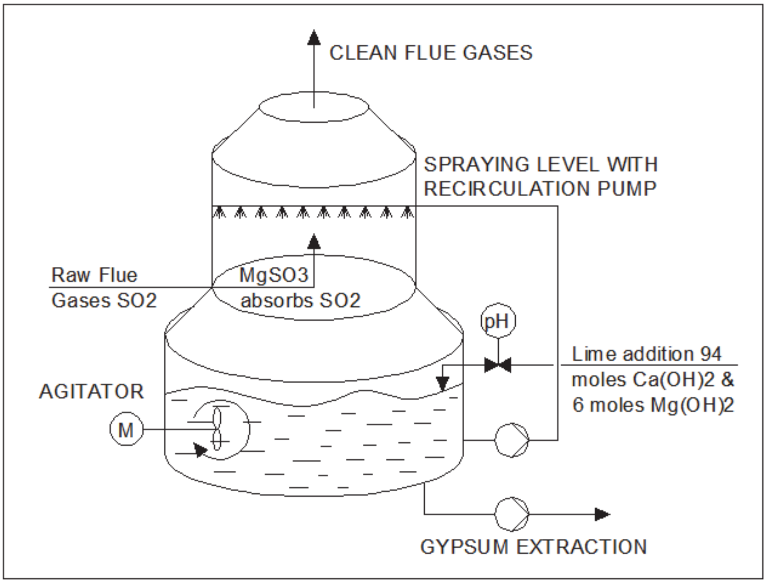


Figure 2: *Magnesium enhanced lime process of cleaning the raw flue gases in the thermal power plant. Raw flue gases and the addition of the fresh lime enter the process, gypsum suspension and clean flue gases exit the process.*

4 NEEDED REAGENT AND BY-PRODUCT OF THE MEL PROCESS

For the preparation of the reagent, calcium oxide and magnesium oxide are needed. The amount of the calcium oxide can be up to 91% by weight, and the amount of the magnesium oxide can be up to 8% by weight. The total amount of the oxides is equivalent to the sulphur dioxide neutralizing value to about 94% CaO.

There are two possibilities for producing the magnesium-enhanced lime: to produce it from limestone with suitable magnesium content, or to blend high-calcium and dolomitic limes (containing approximately 40% MgO).

To properly prepare the reagent for the MEL process, the water must be mixed with the lime in the tank, where the calcium hydroxide and the magnesium hydroxide are formed. The resulting slurry is further added to the lower part of the absorber (i.e. theabsorber recycle tank). The slurry pH 6 is kept in the recycle tank of the absorber to ensure that all of the lime reacts with the sulphur dioxide.

5 SULPHUR DIOXIDE REMOVAL PROCESS RESULTS

In general, we can conclude that the magnesium-enhanced limestone process achieves higher sulphur dioxide removal results than, for example, the traditional wet flue gas desulphurization process that uses lime as the reagent.

The level of efficiency that the MEL process can achieve is between 98% and 99% in thermal power plants that utilize a variety of high- and low-sulphur coals. In the absorber, the liquid-gas ratio is estimated between 40 and 30 to achieve 98% sulphur dioxide removal efficiency.

The MEL desulphurization process can be added to the existing or new thermal power plant blocks, ranging from less than 100MW and up to 1000MW. The sulphur content in coal can be between 2% and 5%, *[2]*, to still achieve the sufficient effect of the desulphurization of the raw flue gases from the boiler.

6 SYSTEM COMPONENTS

6.1 Reagent Handling and Preparation System

Lime is delivered to the site with the transportation truck, after which it is stored in a lime silo. From there, the lime is pneumatically transported to the day silo. With the assistance of the gravimetric feeder, the lime is supplied to the slaking system. When the slurry is ready and mixed, the pumps transport the prepared slurry to the slurry tank. From the fresh slurry tank, the slurry is transported to the absorber recycle tank.

6.2 Sulphur Dioxide Removal System

The primary sulphur dioxide removal process occurs inside the absorber tower. The absorber is a vertical open spray tower in which the counter-current between the upward raw flue gases from the boiler side, and the downward fresh slurry suspension from the spraying levels is achieved, *[3].* Inside the absorber, the primary chemical reactions of absorption of the acid components to the freshly prepared slurry from the spraying levels is happening. When the acid components are removed from the up-stream flue gases, they fall to the bottom of the absorber where they are involved in the process of crystallization and further disposed from the system process to the by-product and handling treatment plant. There, they are properly processed and forwarded to the disposal area or further transported to the consumers of such by-products.

6.3 Flue Gas System with The Stack

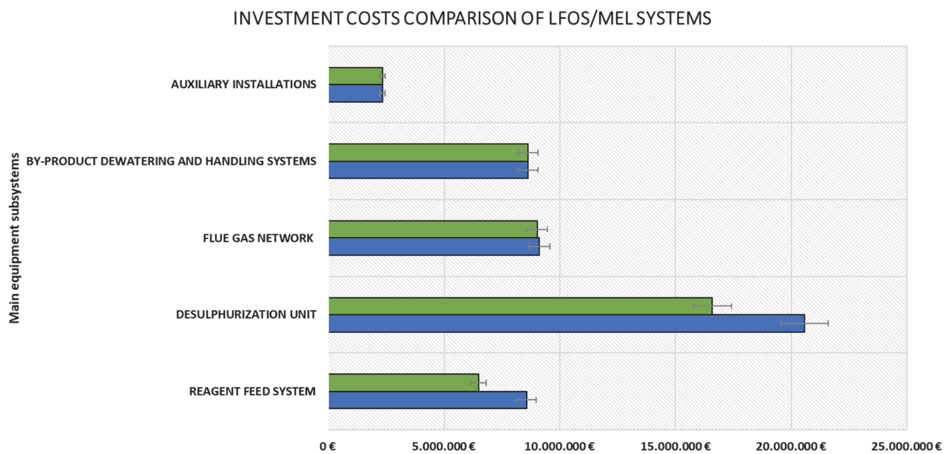
The flue gas ducts are intended to lead the raw, untreated flue gases from the boiler exit side to the absorber inlet. Acid protection of the flue gas duct system is not necessarily needed if the flue gases do not condensate and the liquid acid condensate is not in the direct contact with the flue gas ducts. To lead the treated flue gases from the absorber to the atmosphere, we can use the existing chimney of the installation, or we can plan to build the new wet stack. Because of the absorber and the stack newly attached to the existing installation, the needed draft must be overcome. The additional fan in front of the absorber should usually deliver 170 –2000 Pa, *[4].*

6.4 By-Product Handling and Treatment System

The by-product of the MEL process is gypsum. The used slurry from the absorber is transported from the absorber recycle tank to the dewatering system. With the usage of the vacuum belt filters, we can achieve the dewatered product in the shape of a cake, *[5]*, that can be transported to the covered storage area. From there, it can (if the by-product is of sellable quality) be sold to the offsite user.

7 COST AND PERFORMANCE ANALYSIS OF THE MEL PROCESS

7.1 Cost Comparison Between LFOS and MEL Process



	REAGENT FEED SYSTEM	DESULPHURIZATION UNIT	FLUE GAS NETWORK	BY-PRODUCT DEWATERING AND HANDLING SYSTEMS	AUXILIARY INSTALLATIONS
Magnesium Enhanced Lime Process	6.503.310 €	16.595.053 €	9.022.181 €	8.615.724 €	2.335.385 €
Limestone Forced Oxidation Process	8.562.304 €	20.569.040 €	9.124.376 €	8.615.724 €	2.335.385 €

Figure 3: *The costs comparison of the magnesium-enhanced the lime process, and the limestone forced oxidation process for cleaning of the flue gases in thermal power plants. The magnesium-enhanced lime process requires lower investment costs, but its operational costs can be higher than with the Limestone forced oxidation process.*

The main difference in costs between the two mentioned systems are mainly in initial investment costs and later the variable operational costs. When comparing the investment costs of both systems, it can bee is seen in Figure 3 that the investment costs in flue gas network with ducts, by-product dewatering and handling system and auxiliary installations, are almost at the same level in both systems. The higher investment costs require the limestone forced oxidation system, since the reagent preparation system cost €2 million and the desulphurization unit is €4 million higher, corresponding to the proposed systems for the magnesium-enhanced lime process.

To analyse the operational costs of the magnesium-enhanced lime-cleaning process, the fixed and variable operational and maintenance costs must be analysed. Hereinafter are described the operational and maintenance costs of such a cleaning unit, expressed as the percentage of the total amount of the operational and the maintenance costs.

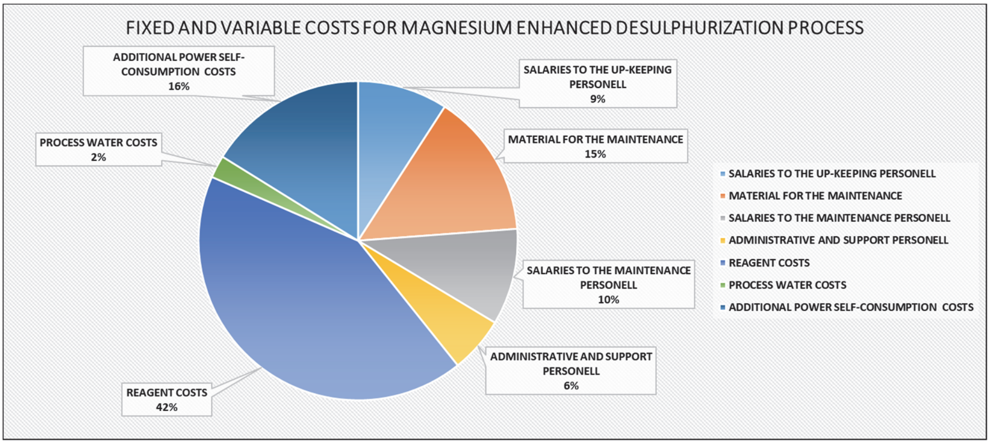


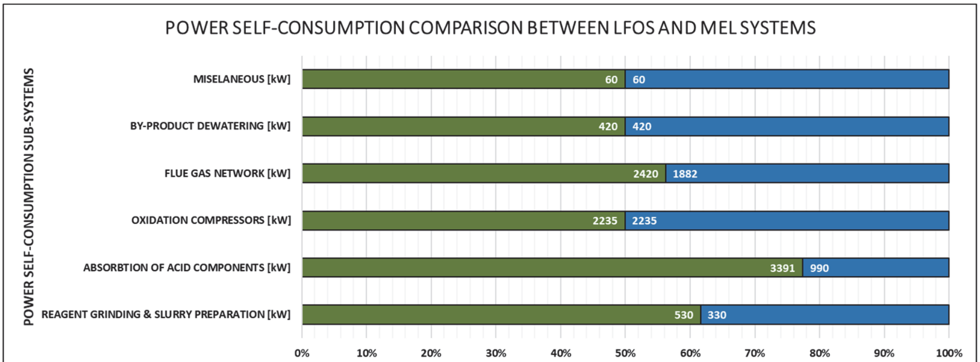
Figure 4: *The pie diagram shows the fixed and variable costs for the magnesium-enhanced desulfurization process, in percentages of the total sum of costs.*

The fixed operational costs of the magnesium-enhanced lime process are mainly the salaries for the maintenance personnel (9%), costs of the material for the maintenance of the flue gas cleaning plant (15%), salaries to the maintenance personnel (10%), and the costs of the administrative and the support personnel (10%).

The variable operational costs are the costs that are dependent on the current price situation on the market, the movement of which dictates the demand and possible supply. Among these costs, we number reagent costs for the chemical reaction to successfully absorb acid components of the untreated flue gases (42%), costs of the process water consumption (2%), and the costs connected with the power self-consumption (16%).

From Figure 4, it is clearly seen that the main cost in operation of the magnesium-enhanced lime desulphurization process is the consumption of the freshly prepared reagent. For that reason, it is sensible to find the location of the lime quarry near the existing thermal power plant; this can reduce the cost of the purchase, delivery and preparation of the reagent.

The power self-consumption of the magnesium-enhanced lime desulphurization process is better than that of the limestone forced oxidation desulphurization process. The reason for that is mainly in the size of the absorption unit, where the primary cleaning of the flue gases is achieved. Because the MEL process uses an enhanced reagent, the reactivity of it is better, and the impact time of the fresh reagent from the spraying level and raw flue gases from the inlet can be shorter, resulting in savings on the expensive anti-corrosion construction materials. Lower construction of the absorber unit results in fewer spraying levels, which consequently means fewer recirculation pumps and other equipment, which results in the savings of the consumed power or electricity. In Figure 5, the consumption of the electricity for operation of the desulphurization unit of the limestone forced oxidation process (green) and magnesium-enhanced lime process (blue) is presented. Note that for the absorption of the acid components from the raw flue gases, the LFOS process consume almost three times more electricity than the MEL process does.



	REAGENT GRINDING & SLURRY PREPARATION [kW]	ABSORBTION OF ACID COMPONENTS [kW]	OXIDATION COMPRESSORS [kW]	FLUE GAS NETWORK [kW]	BY-PRODUCT DEWATERING [kW]	MISELANEOUS [kW]
Limestone Forced Oxidation System	530	3391	2235	2420	420	60
Magnesium Enhanced Lime System	330	990	2235	1882	420	60

Figure 5: *Power (electricity) self-consumption between limestone forced oxidation process and the magnesium-enhanced the lime process. The most significant savings at MEL process are available in the scope of the absorption of the acid components and the reagent grinding and slurry preparation.*

8 TECHNOLOGY APPLICATION CONSTRAINTS

There are some technical constraints of usage of the magnesium-enhanced lime desulphurization process applications. The absorber size of the magnesium-enhanced lime desulphurization process is limited due to engineering constraints and statical stability of the construction. In praxis, the individual units for the MEL desulphurization can range up to 1000 MW per boiler unit, for bituminous coals. The sulphur content in coal can range from 2% to 5% to still achieve the sufficient cleaning efficiency of the MEL process, which can up to 98% removal guarantees of SO_2 removal. The by-product of the MEL process can be disposed to the covered disposal area, although it can also be further used in the cement and construction industry. The main constraint of the usage of magnesium-enhanced lime desulphurization process is the availability of the reagent. Although there are some concerns that limestone contains a sufficiently high percentage of the magnesium in lime, it is very difficult to find a quarry of it in nature. As described previously, we can enhance the usual lime by adding magnesium to it, but this is not cost effective for the operation costs of the desulphurization process.

9 CONCLUSION

This paper has presented the alternative process of the wet calcite flue gas cleaning. The process presented uses magnesium-enhanced limestone as the reagent in the wet desulphurization process of flue gas cleaning. The disadvantages and advantages of such a process have been presented. The most favourable advantage of that process is its very reactive magnesium-enhanced limestone slurry, which eliminates the acid components in the flue gases. Because of the enhanced reactivity, the contact between the slurry and the flue gases can be shorter regarding the time needed for chemical reaction to fully recover acid components from the raw flue gases. That means smaller absorber unit, less spraying levels for the slurry, fewer recirculation pumps and a smaller amount of needed expensive construction materials to build the application. This directly results in smaller investment costs for such a desulphurization unit. The biggest disadvantage is the difficulty to find the needed reagent (limestone with the addition of the magnesium) in nature, i.e. at a quarry. If the reagent is not widely available in nature, such as limestone, this composition must be prepared and mixed with the proper mixture in a dedicated plant. That raises the operational costs of the magnesium-enhanced lime desulphurization process and makes it economically less-favourable for the installation in the existing thermal power plants. Nevertheless, the process is worth considering for the raw flue gases desulphurization process if the quarry of the proper reagent mixture is available in the surroundings of the existing thermo-electrical installation.

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Nomenclature

(Symbols)	(Symbol meaning)
MEL	Magnesium Enhanced Lime
LFOS	Limestone Forced Oxidation System
pH	Level of acidity or alkalinity
Pa	Pascal
$Ca(OH)_2$	Calcium hydroxide
$Mg(OH)_2$	Magnesium hydroxide
$CaSO_3 \cdot ½H_2O$	Calcium sulphates
$MgSO_3$	Magnesium sulphide
$Mg(HSO_3)_2$	Magnesium disulphide
SO_2	Sulphur dioxide
$MgSO_4$	Magnesium sulfate
CaO	Calcium oxide