

Reducing SO₂ Emissions in the Czech Republic in Accordance with Legislation Valid from 2021

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Abstract. This article discusses the impact of new emission limits for sulphur dioxide (SO₂) emissions which will be effective from 2021 for large combustion plants (LCP) in the Czech Republic and as well as possible ways and techniques to achieve these emission limits.

1. Introduction

Reduction of SO₂ emission is essentially a permanent trend of last decades and it is an ongoing task for all employees in operations, maintenance and development of energy equipment. Permanent emissions reductions targets are included in the legislations of all industrialized countries.

This article provides information about current SO₂ emissions of selected combustions plants, which are divided into several performance classes (predominantly large combustion plants). Article also provides an overview of the most common desulphurisation methods for these combustion plants. In article are listed new BAT emission limits (approved by the Parliament on July 31, 2017), which will come into force in 2021. Now, it is therefore possible to compare the status of current SO₂ emissions with new limits and to estimate if it will be necessary to invest in new desulphurisation units.

2. Emission limits of SO₂ for existing and new energy sources valid from 2021

Table 1 compares the daily and yearly average of SO₂ emission limits (mg/Nm³) for individual combustion plants with different heat input (MWt) according to valid and planned legislation since 2021.

Table 1. SO₂ emission limits values for LCP.

| IED 2010/75/ES since 2016 | | Direction BAT-AELs-FD BREF LCP | | | | |
|------------------------------|------------------------------------|--------------------------------|----------------------------------|-------------|----------------------------------|-------------|
| | | New plant | | | Existing plant | |
| Heat input [MW] | Monthly avg. [mg/Nm ³] | Heat input [MW] | Daily avg. [mg/Nm ³] | Yearly avg. | Daily avg. [mg/Nm ³] | Yearly avg. |
| 50-100 | 400 | <100 | 170-220 | 150-200 | 170-400 | 150-360 |
| 100-300 | 250 | 100-300 | 135-200 | 80-150 | 135-220 | 95-200 |
| | | >300 | 25-110 | 10-75 | 25-165 | 10-130 |
| >300 | 200 | PC coal >300 | 25-110 | 20-75 | 50-220 | 20-180 |
| | | FBC coal | | | | |



3. Actual situation of emission SO₂ in the Czech Republic

In the Czech Republic 3 desulphurisation methods are used. There are dry desulphurisation method (mostly used in fluidized bed boilers), wet desulphurisation method (mostly in large power plants) and semi-dry desulphurisation method (mostly smaller plants). Nowadays there is no problem in the fossil fuel combustion plants to meet the current emission limit. As it can be seen in the table 2, most desulphurisation devices will easily meet the new emissions limit according BAT. Existing desulphurisation units are not working at their maximum.

Value of emission is inversely proportional to the operating costs of the desulphurisation units. Desulphurisation units based on wet desulphurisation process is characterized among other things, almost linear relationship between consumption of sorbent and desulphurisation efficiency. For desulphurisation units based on a dry and semi-dry method, this dependence is not linear but exponential.

Table 2. SO₂ emission of real combustion plants in the Czech Republic.

| Output of Heat Station | Power/Fuel | Desulphurisation Method | Limit According [mg/Nm ³] | Current BATEmission SO ₂ [mg/Nm ³] |
|---------------------------|------------|-------------------------|---------------------------------------|---|
| >300 MW _t | Brown Coal | Wet method | 10 - 130 | 110 |
| 100 - 300 MW _t | Black Coal | Semi – dry method | 95 - 200 | 190 |
| <100 MW _t | Brown Coal | Wet method | 150 - 360 | 80 |
| <100 MW _t | Black Coal | Dry method | 150 - 360 | 366 |
| <100 MW _t | Black Coal | Dry method | 150 - 360 | 290 |

4. Flue gas desulphurisation

Flue gas desulphurisation is the most frequently used method of reducing SO₂ emissions. This method can be based on a variety of chemical or physico-chemical principles. The basic principle is the application of absorption substances to the flue gas stream. These substances react with SO₂ and then they are separated from the flue gas. Methods can be systematically divided into several groups according to different criteria. One of the basic criteria is phase of used substance. According this we can desulphurisation methods divide into: wet, semi-dry and dry methods.

4.1. Wet desulphurisation method

Wet method of desulphurisation is the most common method of flue gas desulphurisation on large energy sources in the Czech Republic. The functional principle is capturing acid components of the flue gas in an alkaline medium substance, in this case in calcium carbonate suspension (CaCO₃). The basic parts of the wet desulphurisation absorber can be seen in figure 1.

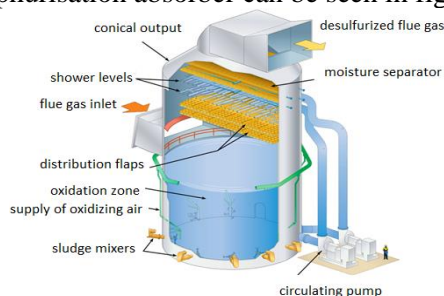
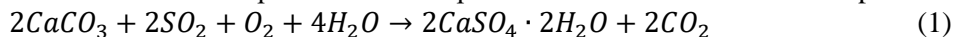
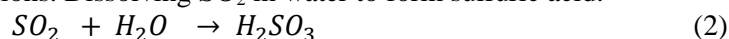


Figure 1. Description of basic parts of wet desulphurisation unit.

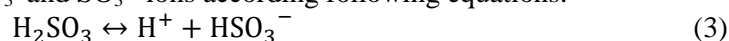
Optimal temperature for reaction is between 55 °C to 60 °C. It means that the flue gas must be cooled before entering the absorber. Regenerative or recuperative heat exchangers are most often used. Exiting flue gas is fed into the chimney through the heating part of the heat exchanger. Temperature increases by about 20 - 30 °C with respect to the dew point. Total reaction of the desulphurization process is:



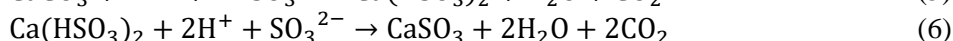
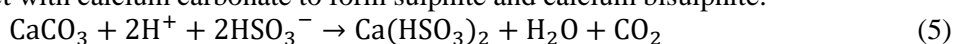
In current embodiment, desulphurisation unit primarily consists of absorber tower, where flue gas is contacted with liquid phase (slurry) and where the desulphurisation process is primarily carried out. Suspension is sputtered in the plane of the nozzles in the absorber tower. Wet limestone scrubbing can be described with the following equations. Dissolving SO_2 in water to form sulfuric acid:



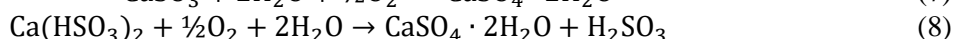
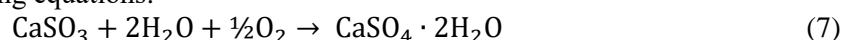
This acid dissociates into H^+ , HSO_3^- and SO_3^{2-} ions according following equations:



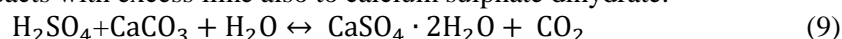
These ions react with calcium carbonate to form sulphite and calcium bisulphite:



The ultimate desulphurisation product is formed at the bottom of absorber, where droplets of the suspension fall and where sulphite and calcium bisulphite are oxidized to calcium sulphate dihydrate according following equations:



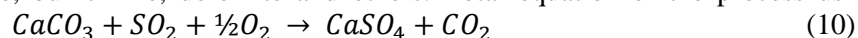
Resulting sulfuric acid reacts with excess lime also to calcium sulphate dihydrate:



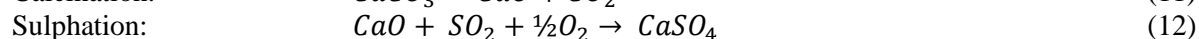
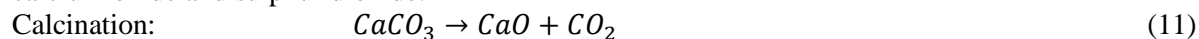
Suspension is continuously pumped into the spray nozzles from bottom of the tank. Spray nozzles are located at the top of the absorber tower. At the bottom of the absorber is suspension aerated with oxidizing air and mixed with circulating pumps and agitators. Fresh water suspension of finely ground limestone is also fed to the sump. Product of the desulphurisation (gypsum) forms crystals which must be separated from suspension. At first suspension is concentrated in hydro cyclones and then is concentrated mixture put to belt filter, where is process water removing.

4.2. Dry additive method of desulphurisation with limestone

Flue gas can be desulphurised also at high temperatures. Dry additive method is based on reaction between solid and gaseous phase. Product of reaction is a solid phase. So, it can be easy separated from flue gas. For example, in an electrostatic precipitator or a fabric filter. This method can be used for the desulphurisation of flue gas from conventional pulverized or fluidized boilers. The sorbent can be limestone, hydrated lime, burnt lime, dolomite and others. Total equation of the process using calcium carbonate is:



The whole *desulphurisation* process can be divided into two partial reactions, thermal decomposition of calcium carbonate “calcination” and “sulphation”, which is a reaction between calcium oxide and sulphur dioxide.



The individual reaction processes can be seen in Figure 2. During sulphation process is first formed a surface layer of calcium sulphite. In the next phase a barrier to next sulphation of core is formed, so sulphur dioxide must diffuse over the product of the desulphurisation reaction.

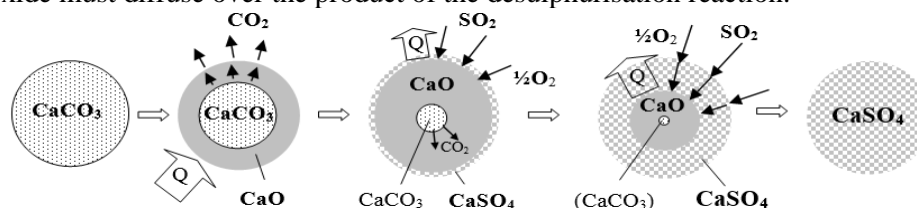


Figure 2. Schematic picture of reaction processes of dry additive desulphurisation.

The ideal reaction conditions are temperature - $t < 900^{\circ}\text{C}$, excess air - $n > 1$ and sufficient reaction time. At higher temperatures calcinate is deactivated because of change in porous structure and resulting calcium sulphate is decomposed to the original reactants. This desulphurisation method can be used for granulation and fluid boilers. These types of boilers are characterized by a different combustion process, so the ways of their desulphurisation are also differ.

4.2.1. Dry additive desulphurisation method for granulation boilers

The basic principle of additive desulfurization is absorption of SO_2 on CaO particles. There are several ways to dose CaO . It can be dosed with coal, pneumatically into the area of the burner zone or in the area above the burner zone. One of the main parameters of this process is temperature. Based on experience ideal temperature range is between $750 - 1200^{\circ}\text{C}$. Reaction takes place only on the surface of sorbent particles, because of limited residence time of both phases. Sulphur dioxide doesn't have enough time to diffuse into the core of sorbent particles. Sorbent is not sulphated more than 15%. The advantage of this method is low investment costs. The disadvantages include low efficiency which is between 20 to 40%.

4.2.2. Dry additive desulphurisation method for fluidized bed boiler

Calcium and calcium-magnesium salts are used for additive desulfurisation in fluidized bed boilers. Sorbent is fed to the fluidized bed. Residence time of both phases is several times longer than in granulating boilers and can take up to tens of minutes. SO_2 molecules have sufficient time to diffuse into sorbent particle cores. Sorbent is sulphated much higher than in the previous desulfurization process. To achieve 80-90% desulphurisation is necessary to supply limestone with an excess of 2 to 3 times corresponding amount of combustible sulphur in the fuel.

4.3. Semi-dry method of desulphurisation

This method is something between dry and wet desulphurisation. Substances, which capture sulphur oxides, enter the process in the liquid phase and stand out in the solid phase.

4.3.1. Absorption of sulphur dioxide in a water suspension of lime

The method is based on injecting lime milk into the flue gas stream at temperature $140-250^{\circ}\text{C}$. In this reaction sulphur dioxide is absorbed by slurry and then oxidized to calcium sulphate. During this process all water evaporated is, so product of reaction can be separated on fabric or electrostatic filters. Desulphurisation product, unreacted sorbent and ash are collected on the filters. Captured mixture is recirculated for better utilization CaO . The efficiency of this method may reach up to 92%. Description of basic parts of spray dryer can be seen in figure 3.

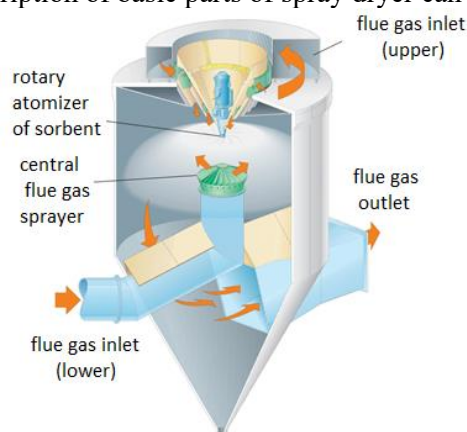


Figure 3. Description of the basic parts of the spray dryer of the semi-dry desulphurisation method.

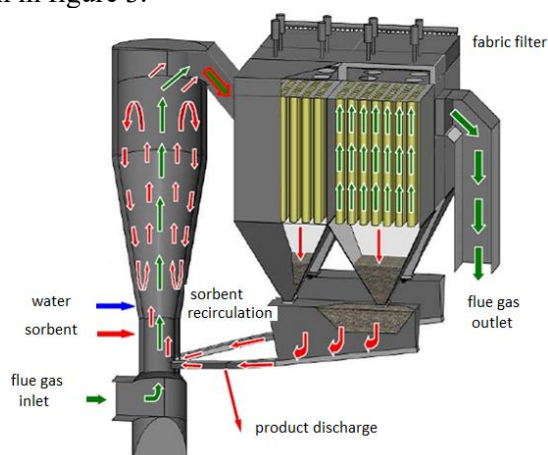
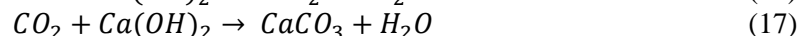
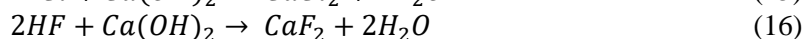
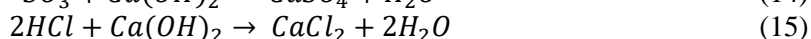
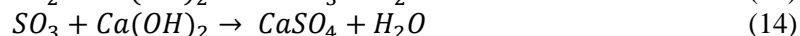
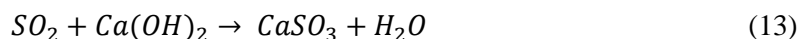


Figure 4. Description of basic parts of fluidized bed desulphurisation reactor.

4.3.2. Absorption of sulphur dioxide in fluidized bed reactor

This technology is based on adsorption of SO₂ in reactor. Description of basic parts of this technology can be seen in figure 4. Flue gas flows through reactor and at the same time is into it injected water and sorbent. As a sorbent is most commonly used CaO and Ca(OH)₂. Optimal temperature of desulphurisation process is ensured by adiabatic injection of water into reactor. Chemical reactions of desulphurisation process are:



Desulphurisation of flue gas takes place mainly in a fabric filter which is located just behind the fluidized bed reactor. A major part of separated product is returned to the reactor to better utilization of sorbent. The rest of separated product is taken from the process into product silo.

Advantages of this method include the high efficiency of SO₂ desulphurisation up to 90%. The efficiency of removing HF, HCl and SO₃ is high too. Another advantage is absence of waste water and low consumption of process water. There is also reduction of dust emissions. The technological part of desulphurisation unit is compact, and for flue gas flows up to 800,000 Nm³/h, it is more investment-friendly than wet desulphurisation method. Disadvantages of this method are high demands on compressed air and the low usability of desulphurisation product, which must be deposited in the landfill.

5. Conclusion

Most of installed desulphurisation units in the Czech Republic fulfil current emission limits without any problems. It can be assumed that new emission limits will be met for most of large energy sources. The necessary increase in efficiency of flue gas desulphurisation will be accompanied only by an increase in the operating costs of the individual desulphurisation units.

Acknowledgments

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