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MINISTRY OF EDUCATION, YOUTH AND SPORTS

Environmental friendly technologies

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Questions and answers III.

Reducing emissions from burning fossil fuels

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1. **What are the basic reasons and principles for decreasing emissions from burning processes?**

2. **What are the main ways to decrease emissions of sulphur oxides?**

3. **What are the general problems of decreasing emissions of sulphur oxides during burning?**

4. **What is the most simple proces of reduction sulphur oxide emissions?**

5. **Describe and explain Myersův principle of decreasin sulphur oxides.**

6. **Describe and explain Gravimelt principle of decreasin sulphur oxides.**

7. **How does the biological decreasing of sulphur oxides work?**

8. **Describe the chemism of biological sulphur oxide removal.**

9. **What are the features of bilogical sulphur oxide generation decreasing?**

10. **How does technology of flue gas desulphurisation work?**

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1.

The rapid development of industry after World War II necessitated a considerable need for energy, which was covered by the burning of fossil fuels, especially coal. Coal deposits are accompanied to a greater or lesser extent by sulfur, which during the combustion of coal changes mostly to sulfur dioxide, partly to sulfur trioxide and to a lesser extent binds solid combustion residues, which are fly ash and cinder blocks. The proportion of sulphur bound to fly ash and cinder block depends primarily on the character of the ash in the coal, but also on the combustion technology. Coal with a high content of alkalis and especially calcium binds a greater proportion of sulfur dioxide to fly ash and cinder blocks, while coal containing mainly SiO_2 and low alkali content only negligible amounts. Combustion processes taking place at lower temperatures (e.g. fluidized bed boilers) usually bind more sulphur oxides to solid residues than boilers burning coal at higher temperatures (e.g. melting or granulation boilers).

Measurements carried out on granulation boilers burning Czech brown coals, which have ash mostly acidic (SiO2 content of about 50 % w/w), showed that 95% of the sulphur contained in the coal escapes into the flue gases and only a small amount of sulphur (about 5%) binds to solid residues.

2.

There are a number of options to limit sulphur oxide emissions from combustion processes. They are:

- **absolute reduction of fuel consumption.** This can be achieved either directly by burning them in installations with higher energy efficiency, or indirectly by appliances with lower energy intensity, or by reducing heat consumption, e.g. by improving the thermal insulation properties of buildings;
- **replacing sulphur-containing fuels with low-sulphur or non-sulphur fuels.** It is a substitute for burnt coal with a high sulphur content for low-sulphur coal, for low-sulphur liquid fuels or natural gas;
- **coal desulphurization.** The effective reduction of sulphur in coal by coal desulphurisation processes has not yet been satisfactorily managed industrially. Sulfur is usually contained in coal in several forms that behave differently to individual separation processes;
- **by flue gas desulphurisation.** Flue gas desulphurization by some processes can be considered industrially mastered and is applied to a wide range of power plants and heating plants.

Decisive for each application are the level of emission reduction and the costs by which energy production becomes more expensive.

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3.

The development of an efficient coal desulphurization process for the purpose of reducing SO_2 emissions is based on the different behavior of individual forms of sulfur contained in coal. Sulfur in coal can occur as pyritic, organic, sulfate, sulfide and elemental. Each of these forms behaves differently in terms of the possibility of applying the chemical and physical processes of its separation from the coal mass. The decisive factor is whether the desulphurization of coal will achieve the emission limits for sulphur oxides set by the legislation after its subsequent combustion.

4.

The easiest way to separate pyritic sulfur from coal is to separate pyrite from coal if pyrite is embedded in coal mass in the form of large grains. In this case, the different melithability of coal and pyrite is used, which is more durable and preserves the original grain size. This is followed by one of the separation processes to separate pyrite from the coal mass.

Most Czech coals contain pyrite embedded in the coal mass in the form of small particles that are difficult to separate from the coal mass.

Partially or completely sulfur can be separated from the coal mass by the following processes.

5.

It consists in leaching pyritic sulfur with a solution of iron sulfate at a temperature of 90 - 130 oC and at increased pressure. The extraction mechanism is complex and can be affected by the following schematic reaction:

$$FeS_2 + Fe_2(SO_4)_3 + H_2O \rightarrow FeSO_4 + H_2SO_4 + S$$

Regeneration of the formed ferrous sulfate is carried out by air oxygen:

$$FeSO_4 + H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

6.

It consists in the extraction of ashes from coal mass by melted NaOH at temperatures of 320 - 415 °C. Ashes contained in coal are transformed in an alkaline medium into silicates, ferrites and sodium aluminates, which are separated from the insoluble coal mass.

The coal is first ground and then added together with the molten NaOH to the rotary furnace. The melt is transferred to an aqueous solution, the coal mass is separated and then washed with water. The alkalinity of the coal mass is neutralized in an appropriate way with acids. This almost completely separates the ashes from the coal mass. Desulphurised coal is obtained in the form of a coal suspension with an ash content of about 1 %.

The extract containing the dissolved ashes is neutralized, iron hydroxides are excreted, which are separated and which can be processed in the metallurgical industry into individual metals.

This process was developed in the USA in the late 80s for the separation of sulfur from black coal. It is not known to have been industrially implemented.

7.

Biological removal of sulphur from coal is based on these bacterias

- Thiobacilus ferrooxidans
- Thiobacilus thiooxidans

8.

The basic chemism can be described using these equations:

$2\ FeS_2 + H_2O + 7{,}5\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2SO_4$

$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3\ FeSO_4 + 2\ S$

$2\ S + 6\ Fe_2(SO_4)_3 + 8\ H_2O \rightarrow 12\ FeSO_4 + 8\ H_2SO_4$

9.

The application of coal desulphurization processes in power or heating practice encounters low coal desulphurization efficiency and thus the possibility of reaching the set values of emission limits. Research and development to date has shown that they are economically unable to compete with flue gas desulphurisation processes. Nevertheless, many power engineers expect that in the future they will be able to develop such a process of coal desulphurization that will make it possible to replace the current generation of flue gas desulphurization equipment and thus get rid of the operation of these complex end-of-pipe plants and energy-distant chemical plants.

10.

Flue gas desulphurization technology can be characterized by:

- significant volumes of flue gases to be purified;
- low concentrations of pollutants in the flue gas; which are SO_2, SO_3, Cl^- and F^-;
- huge mass flows of these substances.

The production of flue gases also depends on the type of fuel burned and on the excess of combustion air. The normal values for electricity generation at 200 MW calculated on standard terms are for:

- brown coal approx. 1.0 – 1.2 million m 3.h-1;
- black coal approx. 0.7 million m 3.h-1;
- liquid fuels approx. 0.5 – 0.6 million m 3.h-1.

Larger volumes of purified flue gases are disadvantageous in terms of costs because they require larger apparatuses. The higher the sulphur content of coal, the higher the sulphur oxide emissions that need to be separated from the flue gases. Large quantities of desulphurization products are difficult to recover.

The measure of emission of oxides during the combustion of fuels is considered to be the specific sulphurity of the fuel. This is defined as the mass sulphur content of coal per unit of fuel calorific value:

$$S_m = S^r_h * (Q^r)^{-1},$$

where S_m is the specific sulphurity of the fuel, S^r_h is the sulphur content in 1 kg of fuel in its original state

$$S_m = 20 * 15^{-1} = 1{,}33 \text{ g } S*MJ^{-1},$$