The chemical mechanism of SOx formation and elimination in coal combustion process

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Introduction
Coal is one of the key sources of energy in the modern world. Particularly in developing countries coal is the most favourable fuel for electric power generation due to low costs and high availability, which makes it less vulnerable to political restrictions than natural gas and crude oil.

Research is conducted worldwide to improve the understanding of the large-scale, multiphase phenomenon occurring during coal combustion. Coal combustion emits pollutants such as SOx, NOx, CO2 and CO, which affect the environment and human health. The volume of emitted sulphur is estimated at ca. 200 million Mg annually, which is comparable to the volume of sulphur released by natural decay and emitted by oceans and volcanoes. During combustion over 95% of sulphur contained in fuels is oxidised to SO2. In the atmosphere this compound oxidises with free OH and HO2 radicals. Sulphur trioxide (SO3) reacts with vapour or water drops in the clouds, thus forming sulphuric acid, and with dusts containing metal oxides, forming sulphites [4, 12, 11, 8].

1. Nature of solid fuels combustion process
Combustion is a process that can be described as rapid oxidation of fuels with heat release, resulting in the external effect of flame. Oxidation is possible if the furnace is fed with appropriate amount of oxygen and fuel, the flash point is exceeded and the reaction products are continually removed. Oxidation may be: theoretical (stoichiometric), i.e. neutral $\lambda = 1$; oxygen-enriched, i.e. oxidising $\lambda < 1$; or oxygen-deficient, i.e. reductive $\lambda > 1$.

During the combustion of solid fuels large amounts of pollutants are released (Fig. 1), significantly impacting the natural environment [7].

2. Sulphur changes during coal combustion
During combustion the organic and inorganic sulphur compounds undergo rapid decomposition and are changed into exhaust fumes. Organic sulphur is more susceptible to combustion. Iron oxidates, combining with slag in the form of hematite, while pyrite decomposes, as shown in reaction (1) [4, 7]:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$ (1)

H2S may be the product of decomposition, but only in oxygen deficit conditions. Next, sulphur compounds undergo oxidation to SO2 and, to a small extent, to SO3. Only a few percent of the sulphur remains in the ash (Fig. 2).

3. Methods of reducing SOx emission
The methods of reducing SOx emission from the process of solid fuels combustion can be divided into three groups. The first method is based on the removal of sulphur from the fuel, whereby sulphur is mostly removable from natural gas (hydrogen sulphide) and from crude oil products. This method ensures over 99% desulphurisation efficiency. Removing sulphur from coal is more difficult. There are three methods of coal desulphurisation: chemical, biological and mechanical. The mechanical method utilises high density differences between pyrite and organic carbon in coal. This method is employed in the enrichment technology, where mineral substances are separated from coal by gravity separation and 30–50% of pyritic sulphur is removed. The mechanical method does not enable the removal of organic sulphur from coal; this is possible only with the chemical and biological methods. There are also technical methods of sulphur removal from fuels; from crude oil products and natural gas sulphur can be removed to the S-values of several dozen ppm. In the coal enrichment process the sulphur content in mineral coal is reduced below 1% [4, 7].

The second method of reducing emissions is SO2 bonding during combustion (the dry method). The dry method of exhaust fumes desulphurisation (pulverized coal-fired boiler) is based (Fig. 3) on the chemical bonding of SO2 in the gas-solid system (sorbent) and the desulphurisation products (utility or waste) are obtained in dry form. The basic sorbents include calcium carbonate, dolomite or calcium hydroxide Ca(OH)2. Calcium carbonate (CaCO3) fed into...
the combustion chamber decomposes into calcium oxide and carbon dioxide. CaO reacts with sulphur dioxide, forming first a sulphite and then calcium sulphate (Fig. 4) [5].

![Fig. 4. SO₂ bonds with limestone (CaCO₃)](image)

In the furnace the calcium carbonate particles undergo calcination. The process comprises endothermic decomposition of CaCO₃ (2) at 750°C with simultaneous CO₂ release. Calcium hydroxide Ca(OH)₂ (3) in the exhaust fumes decomposes in the dehydration process at 400°C with water release. Exothermally formed CaO reacts in the furnace with SO₂, forming a thermodynamically stable product CaSO₄ anhydrite (mineral) (4).

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad - 183 \text{kJ/mol} \\
\text{Ca(OH)}_2 + \text{Q} & \rightarrow \text{CaO} + \text{H}_2\text{O} \\
\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 & \rightarrow \text{CaSO}_4 \quad - 486 \text{kJ/mol}
\end{align*}
\]

The mechanism of exothermic gas-solid reaction (4) is a complex one. SO₂ bonding in the reaction with limestone occurs in a broad range of temperatures (780–1200°C), therefore it requires appropriate amount of time for the process of calcination and CaO reaction with SO₂. CaO reaction occurs only in 30–40%. The smaller the CaO particles, the higher the desulphurisation efficiency. The efficacy of the desulphurisation process also depends on the mixing of sorbent with the exhaust fumes. Using the limestone meal as the SO₂ sorbent it will be difficult to achieve the efficiency of dry exhaust fumes desulphurisation of more than 30–50%. In order to improve the desulphurisation efficacy (50–60%), the limestone is replaced with the more expensive hydrated lime Ca(OH)₂ or calcinated lime CaO. The advantages of the dry method of exhaust fumes desulphurisation include lower investment cost, small installation area and simplicity of operation. The disadvantages, however, include low efficacy, too high sorbent demand, ash quality deterioration and higher dust content in the exhaust fumes.

One of the key reasons for using exhaust fumes desulphurisation in fluidised-bed boilers is the possibility of achieving appropriate SO₂ reduction with cheap limestone. The bed temperature range (800–900°C) and prolonged contact time have impact on the efficacy of SO₂ bonding on fluidised bed. The conditions in which a 90% desulphurisation efficacy may be achieved include bed temperature of approx. 850°C, oxidative atmosphere and the excess of sorbent Ca/S = 2.4 (utilisation rate does not exceed 30%) [2].

In the fluidised bed the SO₂ bonding occurs in accordance with formula (5). In order to improve desulphurisation efficacy, an oxidative bed atmosphere is required, since with oxygen deficit the calcium sulphide content rises, reacting with the anhydrite and releasing SO₂.

\[
\text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2
\]

The fluidised bed has an oxidative atmosphere that may have a reductive nature; in the presence of CO₂ instead of desulphurisation, a reverse process may occur (6):

\[
\text{CaSO}_3 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{O}_2
\]

The methods of desulphurisation of waste gases can be divided into [6, 7, 12, 14]:

- semi-dry – desulphurisation takes place in the absorber, in which the aqueous suspension of the sorbent (usually Ca(OH)₂) at 15–25%) is pulversed at the top of the absorber and the exhaust fumes flow concurrently. The water content in the water-sorbent suspension and the output temperature of exhaust fumes are adjusted so that the water evaporates completely and the exhaust fumes temperature at the absorber output is higher than the dew point by 10–20 degrees. The quality of pulversation and the time of sorbent’s contact with exhaust fumes (10–20 s) have impact on the efficacy of this method. The advantage of semi-dry methods is that they do not require pre-heating of exhaust fumes before the stack, while their disadvantage is higher dust content in the fumes and higher deduster load. The efficacy of desulphurisation using semi-dry method reaches 75%

- wet – the wet method is based on the water solubility of sulphur dioxide, acidic nature and capacity to bond with alkalis. In this method desulphurisation with calcium sorbent occurs in the reactions of absorbent with calcium carbonate, resulting in the formation of sulphates and sulphides. The sulphate and sulphide slime, obtained through absorption, is oxidised in the retention section of the absorber to calcium sulphate which (after drying, purification and partial dehydration) is then directed to further processing in the form of gypsum. The temperature of exhaust fumes leaving the absorber is lower than dew point; therefore, a number of methods are used to remove the desulphurised fumes. The key solutions include: increasing the temperature of desulphurised exhaust fumes above the dew point in the rotary fumes heater and release of desulphurised fumes into the atmosphere by cooling stack. The wet method of exhaust fumes desulphurisation produces virtually no waste, since the resulting gypsum can be used in the construction industry. The efficacy of this method reaches 95%

- adsorption – this method is based on the adsorptive properties of active carbon. In the Hitachi method the exhaust fumes flow through an active carbon deposit, which absorbs sulphur dioxide. Sulphur dioxide is then oxidised to sulphur trioxide and, in the regeneration process, washed out in the form of sulphuric acid. The adsorption methods are used for small emitters (boiler rooms, heating plants)

- catalytic – this method is based on oxidising SO₂ to SO₃ in a converter with vanadium catalyst at approx. 430°C and then cooling the exhaust fumes in the condenser below the dew point. The vapour in the exhaust fumes condenses and combines with SO₃, forming sulphuric acid, which then flows down to the bottom of the condenser. The exhaust fumes before the exhaust stack should be pre-heated to temperatures above the dew point. The efficacy of this method reaches 95%

**Examples of practical solutions for reducing SO₂ emissions**

**– experimental and model research**

A great number of methods and kinetic models of reducing the emissions of sulphur compounds have been developed, though only a few have found practical applications.

Czarkiewicz and Bis [3] presented the basic principles of the process of fuel combustion in fluidised bed in oxygen-enriched atmosphere, focusing particularly on the separation of fuel
into volatile components and coke residuals (with reference to sulphur and nitrogen content). Such separation enabled the authors to determine which part of sulphur and nitrogen in the process of combustion in oxygen-enriched atmosphere undergoes conversion. As the fuel conversion rate the coal conversion rate was used, determined on the basis of coal balance in the exhaust fumes. At 1133K, regardless of the type of mixture and oxygen concentration, the conversion of sulphur was always complete and proportional to fuel conversion. This indicates that the combustion of fuels without pyritic sulphur in the fluidised bed enables complete sulphur conversion. The process of combustion of charcoal in the circulatory fluidised bed in oxygen-enriched atmosphere yielded a higher conversion rate of the sulphur in the fuel.

Zajemśka et al. [13] discussed the issues related to the prediction of the chemical composition of coal using numerical methods. The authors performed the numerical simulations using CHEMKIN-PRO software. The subject of their analysis was a 0.1 MW pilot CFB boiler with 0.1 m in diameter and 5 m in height. The effect of the performed numerical calculations was the chemical composition of exhaust fumes for different process conditions. The authors showed that the composition of the gas atmosphere has significant impact on the composition of the combustion products. Furthermore, they confirmed that the retention time and the combustion temperature also have considerable influence on the concentration of the combustion products. According to the authors [3, 1], it is possible to determine the optimal retention time of the reagents in the temperature range in question using numerical methods.

Olszewska et al. [10] compared two types of mineral coal – “Julian” from the Upper Silesian Coal Basin and “Bogdanka” from the Lublin Coal Basin, and the SO\textsubscript{2} emissions formed during combustion of those coal types. The authors presented a method of reducing emissions using combustion catalysts. The method of desulphurisation using the DESONOX-type catalyst has technological and economic advantages over the traditional methods. However, it is necessary to adjust the catalyst composition to the type of combusted coal. The rate of removal of sulphur dioxide from the exhaust fumes with the DESONOX-type catalyst depends on the method of catalyst preparation, catalyst composition, the carriers used for catalyst active phases, calcium content in coal and coal combustion quality. The authors compared the reduction of SO\textsubscript{2} emissions by using montmorillonite supported cobalt catalyst in both coal types. The analysis indicated an SO\textsubscript{2} emission reduction of only 44% for the “Julian” coal and 82% for the “Bogdanka” coal. The comparison of those two types of Polish coal indicated that using the DESONOX method with montmorillonite catalysts significantly reduces the sulphur dioxide emissions.

Kudelko [9] developed a model of assessment of the functioning of the sulphur dioxide emissions reduction management instruments in the power industry. His model includes three groups of decision variables: coal supply level, SO\textsubscript{2} reduction rate and dust and NO\textsubscript{x} emission reduction rate. As the optimisation criterion the minimisation of discounted fuel cost of generating electric power was used, including: costs related to mineral coal supply, SO\textsubscript{2} reduction costs, dust and NO\textsubscript{x} emissions reduction cost, as well as costs of environmental fees and the cost of purchasing emission permits. The value of SO\textsubscript{2} emission reduction costs was the criterion of efficiency of economic instruments. The subjects analysed by the model included selected power plants and mineral coal suppliers, utilising specific production technologies. The two basic processes mapped in the model are the mineral coal supplies to the power plant and the reduction of SO\textsubscript{2} emission. The first process is related to the balance of mineral coal supply (domestic and imported) to the power plant. The second process characterises the SO\textsubscript{2} emission reduction capacity. The power plants, in order to meet the imposed requirements, employ the following strategies:

- building desulphurisation installations and continuing to burn coal with high sulphur content
- reduction of coal with high sulphur content, shift to burning coal with low sulphur content
- change of fuel type or purchasing electric power from other vendors,
- limiting the electric power generation.

The model analyses all of the above strategies. The results of proceeding pursuant to the model of assessment of functioning of the economic instruments of atmospheric protection in the power industry suggest that compliance with the emission level norms does not require building additional desulphurisation installations.

The advantages of numerical methods [1] include low costs; the capacity to run diagnostics in sites where real-time measurements are difficult or impossible; analysis of the chemical pathway of the formed pollutants for various process parameters; usability for both the design of new devices (burners, furnaces, boilers) and the optimisation of existing ones; the capacity of assessing the chemical composition of compounds during combustion, in particular those that cannot be measured using control and measuring equipment (low measurement range), as well as identification of compounds formed and reacting in specific temperature and flow conditions).

Conclusions

The combustion of power coal is accompanied by formation and emission of gases harmful to the environment, i.e. sulphur dioxides. The volume of sulphur in exhaust gases is strictly correlated to the sulphur content of the combusted coal. To reduce the SO\textsubscript{2} emission levels it has proven necessary to develop processes of efficient and environmentally friendly heat and electric power generation from coal combustion-based sources. This arises from the continuous implementation of restrictive norms on environmental protection, which enforces further research and development. An indispensable element of experimental research is the use of numerical methods which, together with laboratory testing, enable improvement of coal combustion processes, including the improvement of thermal efficiency and SO\textsubscript{2} removal efficacy.

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