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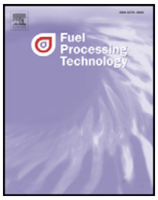

Application of modified montmorillonite for desulfurization during the combustion of hard coal

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ABSTRACT

Series of modified with vanadium, cobalt, nickel, manganese and copper montmorillonite were compared as additives for desulfurization during combustion of hard coal. Samples of coal with added montmorillonite were subject to a 2 h a flow reactor in the air atmosphere, at 1173 K. The weight ratio of montmorillonite: coal was 1:500. Changes in sulfur dioxide contents in flue gasses caused by the additive were investigated by means of an exhaust gas analyzer. During the co-combustion of coal with montmorillonite modified with vanadium was removed 58–84% of SO_2 from flue gasses. Application of Co and Ni led to a reduction in SO_2 emissions by 35–53% and 83–90%, respectively. For additions of Ni, Cu and Mn was observed to reduce emissions of SO_2 by 60–73%. As a result of using diversified preparatory procedures on montmorillonite additives DESOX obtained were materials with different physicochemical properties. Sulfate forms obtained after the combustion process with addition of montmorillonite additives are amorphous and very well dispersed.

1. Introduction

1.1. Sources and volume of SO_2 emissions

The term of SO_x means mainly sulfur dioxide SO_2 — which is generated in the process of sulfur oxidation, and sulfur trioxide SO_3. Natural sources of those gasses are volcano eruptions, decomposition processes occurring in organic matter, fires of woodlands and steppes or soil erosion. As far as anthropogenic sources are concerned, the biggest share in the emission of sulfur oxides in the air has fossil fuels; when burnt, they will release as oxides the sulfur contained in them, and this sulfur is emitted into the air, and this constitutes approximately 85% of total SO_2 emission. Another poisoner is metallurgical industry with a 10% share of air poisoning with the gas said. In Poland the main source of sulfur dioxide air pollution is mainly power industry; however, we must not forget about the role of chemical and metal industry (mainly copper branch) [1]. High SO_2 emissions in the air result from the predominant share of coal as energy winning raw material and relatively high sulfur contents in home coal deposits (on an average, the sulfur level is approximately 1.3% S). Be stressed that due to the application of new technologies and sulfur removal installations, the volume of emitted sulfur dioxides has been diminishing. In 2000, the volume was around 1511 thousand ton, whereas in 2008 it fell down to 999 thousand ton, which means that Poland complied with the assumptions of the II Sulphur Protocol of Geneva Convention in which Poland had promised to bring the SO_2 emission down to 1400 thousand ton [1]. The volume of sulfur oxide emitted in the air in Poland has been decreasing in the latest years. More than 99% of emission is attributed to stationary sources [1].

1.2. Effect of sulfur oxides upon the natural environment

Sulfur oxides are a serious danger to the natural environment [2,3]. This negative effect means acidification of lakes and rivers where sulfur dioxide reacts in the air with $^{\cdot}OH$ in the presence of oxygen according to the reaction:

$$^{\cdot}OH + SO_2 + (O_2, H_2O) \rightarrow H_2SO_4 + ^{\cdot}OOH$$

The resulting product – sulfuric acid (VI) with precipitations – causes the acidification of surface waters, which is a very dangerous phenomenon because acid rains may occur thousands miles away from the sources of SO_2 emissions. In addition, sulfur dioxide destroys tree foliage, which is best seen nearby large industrial plants, like power plants or metallurgical works. As far as living organisms are concerned, a deleterious effect of SO_2 can be observed at concentrations as low as 1–2 ppm, whereas the man can detect a level of 3–5 ppm. This gas attacks mainly the respiratory tracts and vocal cords. Inhalation of SO_2 causes the bronchia to contract. Sulfur dioxide pervades first into the walls of the respiratory tracts, then into blood and the entire body; it is accumulated in the walls of trachea, bronchia, liver, spleen,

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brain and lymphatic nodes. A high SO_2 in the air may lead to corneal lesions. Most endangered to direct action of SO_2 are buildings with limestone or marble finish, which are destroyed in the reaction:

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$$

It was also found that sulfur dioxide has a bad effect upon sandstones [3]. Moreover, such pollutions affect buildings because of acid rains [3]. Direct effect of SO_2 causes corrosion of such structural parts, like steel, zinc, copper or aluminum [3].

1.3. Methods aimed at limiting SO_2 emissions

Long time research done into this item has been crowned with various technologies which allow one to reduce emission of sulfur compounds on all three stages of coal combustion. Methods limiting SO_x emissions from combustion of fossil fuels can be divided into three groups [4–9]:

- fuel desulfurization
- limitation of SO_2 emission in the combustion processes; sulfur is bound by appropriate substances,
- desulfurization of exhaust gasses after coal burning.

1.3.1. Fuel desulfurization

The removal of coal sulfur (occurring as pyrite) is complex from the viewpoint of physics and chemistry [10–13]. In physical methods utilized are differences in densities (the density of pyrite is approximately 5 g/cm^3, of other materials around 2 g/cm^3), size and shape of particles as well as in surface, electric and magnetic properties [14]. Chemical methods are based upon oxidation (oxidant — air, oxygen, chlorine) [10,11,15–18] and caustification (solutions or molten NaOH, KOH, $Ca(OH)_2$) [19–24]. A disadvantage of the method said is a modification to coal properties in the purification process. A factor that impedes the development of chemical methods of desulfurization is expenditure which depends on the required degree of purification, waste volume, need of washing, coal properties etc.

A new promising method is microbiological coal desulfurization [9] which consists mainly in oxidizing pyrite sulfur to sulfate sulfur which is easy to be removed. The said process is run by sulfur bacteria, is very complicated and includes a series of reactions redox, hydrolysis and complexing. Practically, the coal pyrite is subject to the action of air and humidity, which will lead to sulfuric acid [VI] and iron [III] sulfate [VI] which participates in the chemical oxidation of pyrite to another portion of sulfate, and elementary sulfur.

Elementary sulfur is oxidized by bacteria to sulfuric acid [VI]. Pyrite sulfur is preferably removed by the strain *Thiobacillus ferrooxidans* which can bring the pyrite contents by around 90%. For the removal of organic sulfur, other microorganism strains must be used — *Sulfolobus* can eliminate only 20%, and *Pseudomonas* (which decompose tiophenes) — approximately 50% of organic sulfur contained in coal. An advantage of the method said is a high desulfurization selectivity which does not alter the carbon skeleton; hence, there are no losses and no changes in calorific value. In addition, coal can be purified of heavy metals and ashes contents can drop as well. A flaw is instead a slow rate, which means using high volume reactors. The use of desulfurized coal considerably simplifies its preparation for combustion, and the costs of desulfurization of exhaust gasses are also cut.

1.3.2. Desulfurization of exhaust gasses

The main rule of desulfurization of exhaust gasses is transforming SO_2 in a substance which is easily removed from the gas and cleaning system. Most typical methods are sorption processes in conjunction with SO_2 oxidation; for the recovery of sulfur as commercial goods or production of sulfur wastes, mentioned can be regeneration and waste [not regeneration] processes which can be run as wet or dry. Such terms can be referred to the final product, use or no use of liquids and moisturizing and cooling of cleaned gasses. Most common are the following methods of exhaust gas desulfurization [25–29]: wet methods (calcium and limestone, magnesium waste-free method, double alkaline method, Wellman–Lord's or ammonia methods); then, there are dry and semi-dry methods (SO_2 sorption on solid sorbents SO_2s injection into a gas stream, atomization drying desulfurization or desulfurization in the fluidized bed).

Currently, several methods are used and implemented on a large scale; anyway, each selection should be preceded by a detailed feasibility study to regard the given conditions. One should also take into consideration the issue of NO_x emission, since in some cases a part of those pollutions can be eliminated.

In the wet process, exhaust gasses contact directly the water solution of ligand. An advantage of that process is high yield. A flaw is, instead, a reduction of temperature of gasses which need reheating, and means extra investment costs.

As far as the dry process is concerned, the temperature of gasses does not fall below the condensation point of vapor. A relatively high temperature is an advantage, since there is no need of reheating exhaust gasses before they are emitted in the air. A flaw of this method is a lower efficiency, the necessity of extra devices (e.g. electrofilters) and of solid wastes utilization.

Investigations into the catalytic reduction of sulfur dioxide in the presence of ammonia aimed at desulfurization of exhaust gasses of stationary sources have been led since the 1960s.

1.3.3. Limitation of SO_2 emissions in the combustion process

Methods aimed at limiting SO_2 emissions in the combustion process consist in mixing solid, dry sorbent with fuel or in blowing sorbent in the furnace chamber over dust burners [30–34]. Most used sorbents are calcium carbonate and calcium hydroxide. When mixed up with exhaust gasses at high temperatures, those compounds are transformed into oxides. This method has an efficiency of 60–80%. The application of calcium sorbents allows using cheap, generally available deposits of limestone.

Generally applied are two solutions to limit SO_2 emissions during the combustion process. The first consists in injecting dry sorbent in dust-bearing exhaust gasses before an efficient deduster. This is a very economical option. The other method, considerably more expensive, needs another deduster (cloth filter). However, finally the efficiency of exhaust gas desulfurizing is higher and less sorbent is consumed.

Also, a combined option is applied. Additionally, practiced is the activation of sorbent carried in the exhaust gasses, viz. CaO or $Ca(OH)_2$; applicable are sorption solutions or water. Due to water, the humidity of exhaust gasses is increased, dust resistivity falls and the volume of SO_2 is also reduced thanks to higher reactivity of sorbent.

1.4. DESOX method

An alternative solution to the methods said is DESOX, elaborated by Nazimek [35,36]. In this method, the emission of sulfur oxides is reduced as early as in the coal combustion process. This method can be considered an improved option of SO_2 emission reduction, referred to in the preceding chapter. Anyway, the latter method completely changes the approach to the reduction of SO_x volumes, since the desulfurization of exhaust gasses occurs on the coal grain subject to combustion. DESOX materials used in this method are dry additives added to coal under burning. They bind sulfur compounds in furnace residuum. Due to such additives, the desulfurization process is shifted from the gaseous phase to the solid phase. There are no gaseous pollutions because desulfurization occurs in the combustion process, which eliminates the use of a series of technological lines to remove new pollutions (sulfur oxides, NO_x). DESOX allows one to separate desulfurization processes from the boiler type and efficiency. The