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mgr inż. Dariusz Łuszkiewicz

Title of dissertation

CONTAMINATION REMOVAL FROM EXHAUST GAS BY OZONATION METHOD – CHARACTERIZATION OF THE PRODUCTS

Promotor: **prof dr hab. inż.** ***Maria Jędrusik, prof.*** **nadzw. PWr**

Abstract:

Due to environmental hazards, NO_x, SO_2 and particulate matter emissions from boiler combustion are limited. In Poland, since 2016, the emission standards of these pollutants comply with the IED [1] and the Regulation of the Minister of the Environment [2]. Current limits have been tightened in the BAT conclusions. The conclusions include the tightening of NO_x and SO_2 standards and the introduction of limits for mercury, ammonia, HCL and HF. From 17.08.2017 starts the 4-year adjustment period for Polish power industry to comply with the emission requirements set out in the BAT conclusions [3].

The most common sulfur dioxide removal technology is the wet limestone method, whose efficiency is <95%. It is recommended for NO_x removal to use primary methods in combination with secondary method, eg SCR (Selective Catalytic Reduction) [3]. Selective catalytic reduction allows the NOx removal efficiency of up to 95% [5]. The disadvantage of using separate denitrification and desulfurization systems is high operating and investment costs, especially for smaller units [6, 7].

An alternative method for coal blocks may be to remove several impurities in one exhaust purification plant by ozonation of exhaust gas, which allows the reduction of emissions of nitrogen oxides, mercury and sulfur dioxide. Ozonation method is a member of group of methods consisting in oxidation of sparingly soluble (NO, Hg^0) pollutants into oxidized forms and absorbing them together with SO_2 in the FGD absorber (flue gas desulfurization) [5, 8]. The limitation of NO_x emission by ozonation is based on the oxidation of water insoluble nitric oxide (NO) into more soluble forms (NO_2, NO_3, N_2O_5) by ozone (O_3) and then absorbtion together with SO_2 in an alkaline absorbent (eg NaOH, KOH, $Ca(OH)_2$ or $Mg(OH)_2$). This method can be used in existing coal blocks equipped with a wet flue gas desulfurization system.

However, the removal of pollutants from exhaust gases is only a partial solution to the problem. The final product of the purification must have a form with is safety for the environment. The reaction products of the higher nitrogen oxides (produced by the reaction of NO with ozone) with alkali are nitrites and nitrites. In the case of sulfur dioxide they are sulfates and sulfites. If the flue-gas purification products from the absorber are to be discharged into the water, eg in the effluent form, it is important to distinguish concentrations of nitrites, nitrates, sulfites and sulfates due to the industrial effluent standards [9].

Taking into account the possibility of using the compounds obtained in the absorber, it is more advantageous to obtain nitrates and sulfates. Nitrates can be used on a large scale, as agricultural fertilizers, and sulfates, depending on the sorbent used, can be used in agriculture (as a fertilizer additive) or in construction (gypsum).

With this in mind, the main goal of the PhD thesis was to investigate the effect of the intensity and conditions of ozonation on the properties and composition of the products retained in the FGD absorber. The indirect effects were to investigate the effect of the composition of the exhaust gas on the chemical composition of the products obtained in the absorber and optimize the process to maximize nitrate and sulfate concentrations.

The dissertation presents the thesis: application of the ozonation method for exhaust gases from coal combustion promotes the conversion of nitrogen oxides to nitrates and sulfur dioxide to sulfates in alkaline solutions, which allows the use of reaction products and can make this method waste-free.

In order to prove this thesis, studies have been carried out to determine the effect of the ozonation of flue gases on the desulfurization products composition (sulfates and sulfites) and denitrification products (nitrates and nitrites) retained in the FGD absorber. The tests were carried out on a laboratory scale and pilot

scale on flue gas from the OP-430 pulverized coal boiler located at ZEC "Kogeneracja" Wrocław. On the laboratory scale, a Dreschel washers was used to simulate the conditions in the FGD absorber and a vertical spray column was used on the pilot scale. A 0.1 molar sodium hydroxide solution (NaOH) was used as absorbent in laboratory and pilot scale tests. In order to determine the composition of the reaction products in the absorber, samples of the sorption solution were collected and analyzed for ion content. The method of UV absorption spectrophotometry was used to determine the concentrations of nitrate (NO_3^-) and nitrite (NO_2^-) ions. The concentration of sulfate (SO_4^{2-}) was determined by the method ICP-OES and concentration of sulfite (SO_3^{2-}) ions was determined by jodometric method. In addition to the aforementioned ions, the concentrations of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions were also investigated by conductometric titration method.

Based on laboratory tests, it was determined that the use of the ozonation method favors the conversion of sulfite to sulfate and nitrite to nitrate in comparison to the ozone free system. In this paper, the mechanism of ion formation in NaOH solution was proposed, with separate removal from NO and SO_2 from carrier gas and simultaneous removal of them, and explained the effect of CO_2 and H_2O presence in the carrier gas prior to ozonation. In order to maximize the proportion of sulfates and nitrates in the sorption liquid, the use of an "oxidation reactor" which prolongs the contact time of ozone with flue gases, thus reducing the amount of ozone directed to the plant and positively influencing the conversion of nitrite to nitrate and sulfate to sulfate. The positive effect of ozonation on the oxidation of sulfites and nitrites in the absorber makes it possible to use ozonation products such as building materials or fertilizers, which makes the presented waste-free technology. Laboratory-scale studies were the basis for pilot scale studies.

On the basis of the results of the pilot scale measurements, it was confirmed that the ozonation method is extremely efficient and allows to meet the emission standards from the BAT conclusions. The positive effect of the ozonation on the formation of sulfates in the absorber liquid has been confirmed, which means that in the actual exhaust gas purification installation, the amount of air directed to the oxygenation of the solution in the wet flue gas desulfurization system can be reduced. The positive effect of the "oxidation reactor" on the denitrification efficiency and the reaction products in the absorber have also been confirmed.

Literature:

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