DETERMINATION OF SULFUR ISOTOPE RATIO IN COAL COMBUSTION PROCESS

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Abstract
On a global scale, combustion of fossil fuels accounts for 82% of the total sulfur dioxide emissions with 56% arising from coal. Major environmental impact of atmospheric sulfur compounds is related to rain acidity, human health, climate, visibility and materials. Very important is evaluation of economic responsibility for emitted pollution. Therefore scientists look for suitable marker which could be used as environmental tracer.
The isotope ratio can be used as a tracer for environmental samples (aerosol, air, plants, rain, and water) to track the products of the combustion of the particular coal.
This method was applied for determination of sulfur isotope ratio in lignite combustion process at the big power complex: lignite mine – power station in Bełchatów. The solid samples (lignite, ashes and slag) were collected from the systems of the power station and samples of the flue gas, and product (gypsum) from the desulphurization line were investigated .
Each form of sulfur has been prepared by extraction of solid samples taken from power plant and transformed into stable compounds, which can be subsequently converted to a gas phase (SO_2) for mass spectrometric analysis.
The result presented in the paper concerns differentiation of the isotope ratio in the different solid and gaseous samples, these data can be used for further investigation of the migration of the sulfur compounds in the groundwater and atmosphere.

Introduction
Europe, what means Poland too, are places, where a great increase of social awareness for problems of environmental protection took places for a period of last twenty years. Production activity is usually connected which consequence to a certain degree in wastes production and pollutants emission. It has visible influence on wholesomeness of the natural environment, what can be proved by such occurrences as acid rains, greenhouse effect, worsening condition of forests, or destruction of ozone layer. Very important is evaluation of economic responsibility for emitted pollution. Therefore scientists look for suitable marker which could be used as environmental tracer. SO_2 emission has a great impact on environment and human health conditions. Therefore different technologies have been applied for air pollution control.
There are no other methods beside sulfur isotope ratio measurements to investigate fate of anthropogenic sulfur (emission and desulphurization products) in the atmosphere and environment. Literature review shows that there are few data on sulfur isotope ratio in Polish coals and on fractionation of sulfur isotopes in coal combustion process. Results of available preliminary investigation concerning characteristics of the Polish coals were presented earlier[1]. The obtained results ($\delta^{34}S/^{32}S$ -6,62 to +15,88‰) suggest that the sulfur in coal originates from the sulfur being originally bounded by plant and depleted in the isotope S34. In some deposits isotopic composition is similar on different depths of the whole region, while in the other, this composition can even change on the deep of several meters [2]. There is a big differentiation in the results obtained not only in the concentration of the sulfur but also in composition of its isotope ratio.

$\delta^{34}S/^{32}S$ in coal combustion process.
The isotope ratio can be used as a tracer for environmental samples (aerosol, air, plants, rain, water) to track the products of the combustion of the particular coal.
The one of the stages of this work was to check possibility of application of sulfur isotope ratio to investigate pollution by sulfur which originates from coal combustion. The solid samples (coal, ashes,

slag) were taken from power station Kaweczyn to determine sulfur isotope ratio in coal combustion process. Coal used in this power station originate from Upper Silesian Basin.
Each form of sulfur has been prepared by extraction [3] of solid samples taken from power plant and transformed into a stable compounds, which can be subsequently converted to a gas phase (SO_2) for mass spectrometric analysis [4]. The obtained results are present in table 1.

Table 1: Sulfur isotope ratio $\delta^{34}S/^{32}S$ in particular form of sulfur in different stable samples [‰].

	coal	slag	ash
organic sulfur	7,45 ± 0,04	8,07 ± 0,07	29,35 ± 0,03
pyrite sulfur	9,78 ± 0,03	0,81 ± 0,05	-
sulfate sulfur	15,83 ± 0,07	0,94 ± 0,02	-4,09 ± 0,02

The obtained results ($\delta^{34}S/^{32}S$ values range from +7,45 to +15,83 ‰) suggest that the sulfur in coal originates from the sulfur bounded by plants and depleted in the isotope ^{34}S. The sulfur was probably produced in the process of sulfate bacterial reduction. $\delta^{34}S$ values in slag are enriched in light isotope ^{32}S in coal combustion process.
Similar results were observed for sulfate sulfur in ashes. $\delta^{34}S$ organic sulfur in ashes (29,35‰) is enriched in heavy isotope ^{34}S in the same process. We do not confirm presence of pyrite sulfur in analyzed ash samples.

$\delta^{34}S/^{32}S$ in desulphurization process
The desulphurization process was checked at the electron beam/ammonia experimental installation. Sulfur from outlet gas was absorbed in hydrogen peroxide solution:

$$SO_{2(gas)} + H_2O \longrightarrow H_2SO_3 \xrightarrow{H_2O} H_2SO_4$$

The sulfate ions produced in this way were quantatively recovered as BaSO4 by precipitation with BaCl2 solution [4].
Product is a mixture of sulfate and nitrogen of ammonium with fly ash. This mixture has been formed as a consequence of outlet gases irradiation. The product is removed as by-product in desulphurization process. The received results are presented in table 2.

Table 2. Sulfate sulfur in flue gas and product from desulphurization process [‰].

inlet gas	outlet gas	product
-1,33 ± 0,03	-4,88 ± 0,03	1,21 ± 0,03

We observed difference between inlet and outlet gases. α = 0,996 for this process means that sulfur in outlet gas is depleted in heavy isotope ^{34}S.

Conclusions
Power generation is based on the fossil fuel combustion all over the world. These fuels contain sulfur and are the main source of anthropogenic sulfur, mostly emitted to the atmosphere in the form of sulfur dioxide. Sulfuric acid which is the product of oxidation and reaction with atmospheric water in one of the components of acidic rain. Since SO_2 emission has a great impact on environment and human health conditions, different technologies have been applied for air pollution control.
This investigation may be use for:
- monitoring of water;
- investigation of gypsum dissolution;
- investigation of ashes leaching;
- investigation of deposition of sulfur from gases after desulphurization process;

References
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