

MALGORZATA DERDA\*, ANDRZEJ G. CHMIELEWSKI\*,  
JANUSZ LICKI\*\*

## STABLE ISOTOPES OF SULPHUR IN INVESTIGATING POLLUTION SOURCES

Determination of sulphur isotope ratio ( $^{34}\text{S}/^{32}\text{S}$ ) by mass spectrometry is the only method to distinguish anthropogenic sulphur sources from natural ones. Identification of sulphur sources and the compounds of its transformations are essential in investigating migration of pollutants in the environment. Sulphur isotope ratio can be treated as an environmental tracer, and may be applied to study the distribution of sulphur from coal mining and combustion processes.

This study consists in determining sulphur isotope ratio of products from coal and lignite combustion as a method for sulphate migration monitoring. The possibility of applying this method to the monitoring of pollutant migration from landfill deposits of ash from coal combustion and gypsum generated in flue gas treatment installation is presented in this paper.

### 1. INTRODUCTION

Because of the evolution of industry, which contributes to the environmental pollution, new monitoring methods are indispensable. One of these methods is based on determination of sulphur isotopic composition by mass spectrometry, which allows distinguishing natural sulphur sources from anthropogenic ones.

The power industry is a main emitter of environmental pollutants. Coal and heavy oil combustion leads to the emission of the vast quantities of  $\text{SO}_2$  and other pollutants. Due to the hazardous effects of  $\text{SO}_2$  emissions on environment and human health, the emission control technologies have been introduced. Sulphur content in coal can be reduced before its combustion by physical, chemical, or biological purification [1], [2]. However, this technology reduces mostly the sulfur in pyrite forms. Therefore most often the technologies of flue gas desulphurization are applied. The most popular is a wet flue gas desulphurization (FGD), using lime or limestone water suspension for  $\text{SO}_2$  absorption [3]. Other technologies in which simultaneously  $\text{SO}_2$  and  $\text{NO}_x$  are re-

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\* Institute of Nuclear Chemistry and Technology (INCT), Dorodna 16, 03-195 Warszawa, Poland.

\*\* Institute of Atomic Energy, 05-400 Otwock – Świerk, Poland.

moved and the by-product obtained is used as fertilizer component are being implemented as well [4]. Due to the chemistry of the process [5] the change in sulphur isotope ratio in SO<sub>2</sub> emitted to the atmosphere can be expected.

Literature review shows that there are a few data available on sulphur isotope ratio in Polish coals and on fractionation of sulphur isotopes in the process of coal combustion. Many studies have been carried out in Europe [6], Australia [7] and U.S.A. [8], [9], [10] in order to use the sulphur isotope as a marker of anthropogenic sulphur in the environment.

In the first step of the investigation, the coals from Polish coal mines were characterized. This study seems to be the preliminary and can be the basis for further geological and hydrological investigations [5]. In the second step, we deal with the possibility of applying the sulphur isotope ratio to investigate the sulphur pollution due to coal combustion. In order to compare two different kinds of coals, two power plants were chosen.

In the Kawęczyn Power Station, a hard coal from Upper Silesian Basin of Upper Carboniferous age has been used. Electron-beam flue gas treatment method for coal desulphurization has been applied in the Kawęczyn Power Station.

Bełchatów Power Station is situated on the south edge of the Szczerców valley, in the area of the Great Polish Lowlands. Lignite deposit, exploited in a neighbouring open pit, is placed not very deep and for this a reason a strip mine was built there. In the Bełchatów Power Station, “wet” lime technology has been applied to desulphurize the outlet gases.

## 2. SULPHUR ISOTOPE COMPOSITION IN COAL AND PRODUCTS OF COAL COMBUSTION

Sulphur isotopic composition in coal and coal combustion products was determined in the solid samples of hard coal, lignite, ash and slug. Extraction method for determining different forms of sulphur was used. Then sulphur was precipitated in the form of barium sulphate (BaSO<sub>4</sub>) or silver sulphide (Ag<sub>2</sub>S) [11] and these compounds were reduced in vacuum line to sulphur dioxide (SO<sub>2</sub>) [12]. Gaseous samples were introduced to a mass spectrometer for isotopic analysis. Isotopic composition was defined in (‰) as follows:

$$\delta = \left( \frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}} - {}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}}{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}}} \right) \times 1000. \quad (1)$$

The standard is the troilite from the Canyon Diablo (CDT) [12].

If  $\delta_A > \delta_B$ , it is assumed that *A* is being enriched with a rare isotope or the isotope “heavier” than *B* isotope.

The sulphur isotopic composition of coal and coal combustion products from the Kawęczyn Power Station is presented in table 1. The same data for sulphur isotopic composition of lignite combustion products from Bełchatów Power Station are given in table 2. The results obtained ( $^{34}\text{S}/^{32}\text{S}$  values for coal samples) suggest that sulphur is released from the tissues of plants and depleted in the isotope  $\text{S}^{34}$ . The sulphur was probably produced by sulphur-reducing bacteria.

Table 1  
Sulphur isotopic composition of coal and coal combustion products  
(Kawęczyn Power Station)

Type of sulphur	$^{34}\text{S}/^{32}\text{S}$ [‰] <sub>CDT</sub>		
	Coal	Slug	Ash
Organic sulphur	7.45 ± 0.04	8.07 ± 0.07	29.35 ± 0.03
Pyrite	9.78 ± 0.03	0.81 ± 0.05	–
Sulphates	15.83 ± 0.07	0.94 ± 0.02	–4.09 ± 0.02

Table 2  
Sulphur isotopic composition of lignite and lignite combustion products  
(Bełchatów Power Station)

Type of sulphur	$^{34}\text{S}/^{32}\text{S}$ [‰] <sub>CDT</sub>		
	Coal	Slug	Ash
Organic sulphur	7.81 ± 0.03	–	–
Pyrite	–4.6 ± 0.03	1.01 ± 0.04	–
Sulphate	–6.14 ± 0.03	0.82 ± 0.04	0.59 ± 0.03

### 3. FRACTIONATION OF SULPHUR ISOTOPES IN DESULPHURIZATION PROCESS

For determining the sulphur isotopic composition in outlet gases, sulphur dioxide was absorbed in hydrogen peroxide solution [13]. The sulphate ions produced this way were quantitatively recovered in the form of  $\text{BaSO}_4$  as a result of their precipitation with  $\text{BaCl}_2$  solution [12].

#### 3.1. "WET" LIME TECHNOLOGY

The product of the flue gas desulphurization is gypsum, which is the a product of a "wet" limestone technology. This flue gas is purified in an absorber by suspended limestone slurry flowing countercurrently. Sulphur dioxide, contained in the flue gas, reacts with calcium bicarbonate, the main component of the limestone introduced to the absorber in the form of a water slurry, to form calcium sulphide. After oxidation and crystallization, gypsum is obtained as a by-product.  $^{34}\text{S}/^{32}\text{S}$  val-

ue of sulphur dioxide before and after desulphurization (Bełchatów Power Station) is presented in table 3.

Table 3

$^{34}\text{S}/^{32}\text{S}$  value of sulphur dioxide before and after desulphurization process  
(Bełchatów Power Station)

$^{34}\text{S}/^{32}\text{S}_{\text{CDT}}$ [‰]			$\alpha$
Inlet to the desulphurization reactor	Product	Outlet from the desulphurization reactor	
$1.56 \pm 0.03$	$2.29 \pm 0.03$	$-4.03 \pm 0.03$	0.994

### 3.2. ELECTRON BEAM FLUE GAS TREATMENT

A desulphurization unit is installed at a bypass of the main flue gas stream from boiler WP-120 [14]. The flue gases are cooled down in a spray cooler working under “dry-bottom” conditions and then irradiated in two steps in a reaction vessel. Gaseous ammonia is injected by nozzles upstream flue gas irradiation. The by-product is collected in a bag filter. The mixture of  $(\text{NH}_4)_2\text{SO}_4$  (95%) and  $\text{NH}_4\text{NO}_3$  (5%) is the product of desulphurization. The value of  $^{34}\text{S}/^{32}\text{S}$  of sulphur dioxide before and after desulphurization (Kawęczyn Power Station) is presented in table 4.

Table 4

$^{34}\text{S}/^{32}\text{S}$  value of sulphur dioxide before and after desulphurization process  
(Kawęczyn Power Station)

$^{34}\text{S}/^{32}\text{S}_{\text{CDT}}$ [‰]			$\alpha$
Inlet	Product	Outlet	
$2.59 \pm 0.02$	$3.05 \pm 0.04$	$-5.88 \pm 0.02$	0.992

## 4. DISCUSSION

The study of the changes in sulphur isotopic ratio for hard coal and lignite and the products of their combustion shows that during coal combustion the fractionation of sulphur isotopes takes place. Two phenomena we observed:

1. The values of  $^{34}\text{S}/^{32}\text{S}$  in slag ( $^{34}\text{S}/^{32}\text{S}$ , 0.82‰) and ash ( $^{34}\text{S}/^{32}\text{S}$ , 0.59‰) from Bełchatów Power Station prove that the slag is enriched with a heavier isotope  $^{34}\text{S}$  during the coal combustion process.

2. The values of  $^{34}\text{S}/^{32}\text{S}$  obtained for Kawęczyn Power Station are different. Sulphur in ash ( $^{34}\text{S}/^{32}\text{S}$ , 4.09‰) and slag ( $^{34}\text{S}/^{32}\text{S}$ , 0.94‰) is depleted of heavy isotope  $^{34}\text{S}$  in the coal combustion process.

This is not a very clear why this difference arises, but probably it is due to different combustion conditions.

Contrary to the coal burnt in power plants, sulphates obtained from SO<sub>2</sub> present in outlet gases are enriched with a light isotope <sup>32</sup>S. Fractionation of sulphur isotopes in SO<sub>2</sub> present in inlet and outlet gases has been observed. However, for the products obtained due to desulphurization, the results are different (gypsum and ammonium sulphate), <sup>34</sup>S/<sup>32</sup>S is enriched with the solid by-product obtained in both desulphurization processes.

## 5. CONCLUSIONS

The method reported in the paper can be applied to investigate the reaction mechanism for different air pollution-control technologies. This method can be used to study further fate of the components of waste by-products, e.g., gypsum eluted from landfilled waste, to monitor water composition and to investigate the ashes leaching by precipitation. Moreover, desulphurization units can change isotopic ratio of sulphur in the outlet gas streams. Generally, SO<sub>2</sub> remaining in the outlet flue gas is depleted of the heavy isotope 34. These phenomena should be taken into account during the preparation of the sulphur balance for the country and the region.

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#### STABILNE IZOTOPY SIARKI W CHARAKTERYSTYCE ŹRÓDEŁ EMISJI ZANIECZYSZCZEŃ

Oznaczenie stosunków izotopowych siarki ( $^{34}\text{S}/^{32}\text{S}$ ) metodą spektrometrii masowej jest jedyną metodą umożliwiającą rozróżnienie siarki pochodzącej ze źródeł antropogenicznych i naturalnych. Siarka znajdująca się w węglu, który stanowi materiał energetyczny, przechodzi w różnym stopniu do wszystkich produktów jego spalania. Aby wykorzystać pomiar wielkości  $^{34}\text{S}/^{32}\text{S}$  jako znacznika, należy zbadać wszystkie procesy, które mają wpływ na zmianę tej wielkości. Określono zmiany składu izotopowego siarki podczas spalania węgla oraz wpływ procesu odsiarczania spalin na skład izotopowy siarki w gazach wylotowych.