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## ON THE MECHANISM GOVERNING THE FORMATION OF SULPHATE ION COMPOUNDS IN THE VICINITY OF A COAL-FIRED POWER PLANT

A novel approach has been postulated to explain the mechanism by which sulphur dioxide in a power station plume is converted to sulphate-ion compounds. Compounds containing sulphate ions are formed in the immediate environment of the outlet from the flue. This oxidation reaction is admitted to yield sulphuric acid vapour as the main product. Sulphuric acid vapours are adsorbed on the available surface area of dust particulates to produce sulphates.

### 1. INTRODUCTION

The conversion of sulphur dioxide to sulphate-ion-containing compounds in the ambient air of coal-fired power plants has been investigated and reported many times in the past decades [1]–[3]. All of these investigations have aimed at determining the rate of conversion. No attempts have been made so far to explain the nature of the transformations involved or to define the mechanism governing them. In a number of publications devoted to the conversion of sulphur dioxide the assumption has been made that the oxidation of sulphur dioxide in power station plumes gives predominantly sulphates as the end product [4], [5]. However, such an assumption is not justified, and the conclusions drawn on the environmental impact of a coal-fired power plant remain uncertain.

The objective of the study reported in this paper was to contribute to a better understanding of the environmental hazards created by power stations. The authors made use of the results obtained by the Atmosphere Pollution Control Team, Technical University of Wrocław, in 1983 and 1984.

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## 2. SCOPE OF INVESTIGATIONS AND RESULTS

The area of interest is situated in the immediate vicinity of a large coal-fired power plant. In 1983, the annual emission included the following major pollutants:

fly ash — 14,100 kg/h,  
SO<sub>2</sub> — 28,170 kg/h,  
NO<sub>x</sub> — 580 kg/h.

The objective of the study was to determine the concentrations of the emitted pollutants and those of conversion products. The measuring sites were located at various distance from the emission source (300 m, 3000 m, and 11,000 m) along the prevailing direction of stack plume drift. The analyses involved aerosol samples for the determination of airborne sulphur dioxide, particulate matter and sulphuric acid vapours. The determinations also included sulphate ion compounds adsorbed on the surface area of airborne dust particulates. Concurrent measurements were carried out for dust depositions collected at the same points of immission.

Dust deposition samples were also investigated for the content of sulphate ions. The results are presented in more detail in the reports of the Institute of Environment Protection Engineering, Technical University of Wrocław [6], [7]. In this paper, fig. 1 shows the means of average daily concentrations for sulphur dioxide particulate matter and sulphuric acid vapour. It also gives the percentage of substances containing sulphate ions adsorbed on the surface of dust particles.

As shown by the data of fig. 1, the concentrations of sulphuric acid vapour reached very high values throughout the measuring period (they usually were eight times as high as the admissible value). They increased with distance up to 3000 m, and from there remained constant (at a level of approximately 0.9 mg/m<sup>3</sup>). A further increase in distance from the emission source was found to be without any effect. Sulphur dioxide concentration never exceeded 0.08 mg/m<sup>2</sup> (this means that it usually was as low as one seventh of the admissible value), and showed a slight tendency to increase with distance. Airborne particulate concentrations followed a different behavioral pattern: they decreased considerably as the distance of the immission points from the source increased. Although the measured concentration of particulates ranged between 0.42 mg/m<sup>3</sup> and 0.16 mg/m<sup>3</sup>, it did not drop below the admissible value (0.15 mg/m<sup>3</sup>). The percentage of sulphates in airborne dust particles increased continually with the increasing distance from the emission source.

## 3. INTERPRETATION OF RESULTS

As shown in fig. 1, sulphuric acid vapour, sulphur dioxide and dust particulate concentrations exhibit different distribution with the increasing distance of the immission points from the pollution source. These differences should be attributed to the specific gravity (which

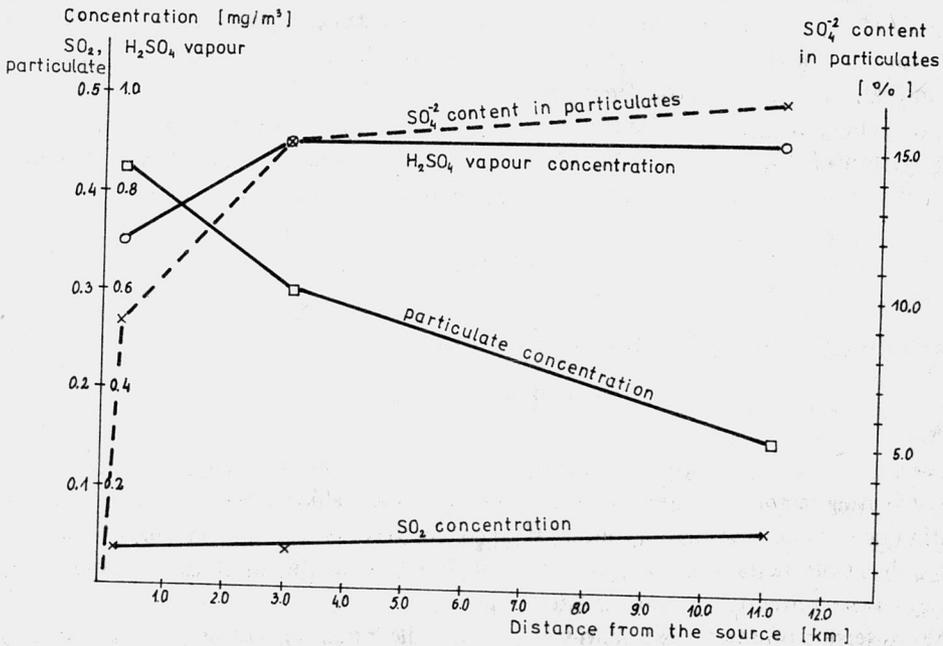


Fig. 1. Means of daily averages for SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> vapour, particulate and sulphate concentrations

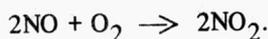
Rys. 1. Średnie wartości średniodobowych stężeń SO<sub>2</sub>, par H<sub>2</sub>SO<sub>4</sub>, pyłu i zawartości siarczanów w pyłe zawieszonym.

varies from one pollutant to the other) and, consequently, to the dynamics of migration typical of each of the three polluting substances. According to the dispersion model, the points of immission were situated in a zone where concentration increased with distance. While this relation holds for sulphur dioxide and sulphuric acid vapour, it is no longer so for dust particulates. Their weight density makes them more susceptible to gravitation, and that is why particulate matter concentration behaves differently with distance. The increased sulphate ion content measured at a farther distance from the emitter owes its origin primarily to the adsorption of sulphuric acid vapour on the available particulate surface. Adsorption occurs during transport in the power plant plume. It is also the adsorption process that accounts for the initiation of a chemical reaction between sulphuric acid vapour and metal ions present in the dust particles. And that is why sulphate ion compounds occurring in airborne particulates have the form of sulphates.

The (sulphate ion)/(sulphur dioxide + sulphate ion) ratio was found to be practically the same (0.9) in all of the immission points irrespective of the distance from the source. This is a clear indication which seems to demonstrate that 1) the conversion of sulphur dioxide to

compounds containing sulphate ions in the plume occurs in the vicinity of the source, 2) the reaction goes rapidly, and 3) the transport over farther distances has no effect on the process. Favourable conditions for the conversion of sulphur dioxide are primarily those occurring in the immediate vicinity of the coal-fired power plant.

It should be noted that it is also the immediate environment of the flue outlet where the largest quantities of nitrogen peroxide ( $\text{NO}_2$ ) are produced from a rapid oxidation of nitric oxide ( $\text{NO}$ ). The following equation illustrates the oxidation reaction:



The equation for the oxidation rate takes the form:

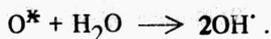
$$R = k \text{NO}^2 \cdot \text{O}_2.$$

The reaction rate is primarily influenced by nitric oxide concentration and temperature as the contributing factors. Needless to say that the most favourable conditions for increasing this oxidation rate are those at the flue outlet. High concentrations of nitrogen peroxide measured in the ambient of the stack account for the initiation of photochemical reactions, thus contributing to the formation of sulphuric acid vapour.

The conversion of interest is a multi-step process. The initial step consists of the following reaction:



Having a substantial energy, atomic oxygen  $\text{O}^*$  may add itself to oxygen to form ozone. But it can also react with a water vapour particle to produce hydroxyl radicals  $\text{OH}^\cdot$  according to the reaction



Hydroxyl radicals  $\text{OH}^\cdot$  were found to have a great ease of reacting with the particles of sulphur dioxide to yield end-product sulphuric-acid particles. The reaction goes very fast and can be elucidated by the following equation:



The over-all reaction consists of a number of intermediate reactions involving hydrocarbons and radicals other than  $\text{HO}_2^*$ . Although the mechanism which governs the oxidation of sulphur dioxide in the presence of radicals is still far from being well understood, it is certain that neither these radicals nor sulphuric acid vapour would form, if large quantities of water vapour

were absent. Water vapour enters the atmosphere together with the flue gases, but the portion that comes from the stack is insufficient to be the main contributing factor, as it forms only one third of the total emission from the adjacent cooling towers. We may, therefore, assume that the portion of water vapour emitted from the stack is insufficient to yield a 90% conversion of sulphur dioxide to the form of sulphuric acid vapour. The "missing portion" must be "delivered" by the cooling towers.

As it has already been mentioned, the sulphuric acid vapours produced via the above route are carried in the power station plume together with particulate matter leaving the stack. During their travel the vapour particles undergo adsorption on the available surface of the dust particles. The process depends on the contact time. Thus, as the time of contact increases, so does the degree of adsorption. And that is why the measured concentrations of compounds containing sulphate ion at the immission points tend to increase with distance from the emission source (fig. 1).

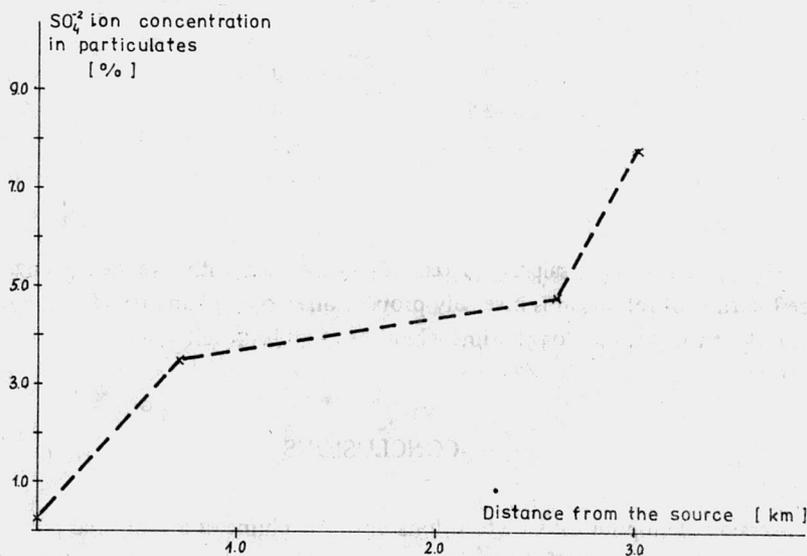


Fig. 2. Average concentrations of sulphates in dust deposition

Rys. 2. Średnie stężenia siarczanów w pyłe opadowym

Figure 2 gives sulphate ion concentrations measured in dust deposition samples, which substantiate what has been shown in fig. 1. But it is interesting to note that sulphate ion concentrations found in airborne particulates are always higher than those in the dust deposits collected at the same sites. This is an additional support for our finding that the adsorption of sulphuric acid vapour on the dust particle surface should be regarded as the main contributor

to the concentration of sulphate ions in particulate samples. In the case of dust deposition the time of contact is always shorter than in the case of airborne dust particulates. Table shows sulphate concentration values for various dust fraction samples collected at the distance of 3000 m from the emission source.

T a b l e  
Sulphate concentrations for various particle size  
( samples were collected 3000 m from the coal-fired  
power plant)  
Stężenia siarczanów dla różnych frakcji pyłów  
(próbki były pobrane w odległości 3000 m od elektrowni  
węglowej)

Fraction $\mu\text{m}$	Concentration of sulphates °/o
9.4	7.6
3.8-9.4	15.8
2.5-3.8	17.9
1.8-2.5	20.8
1.8	35.6

As shown by the data of table, sulphate concentration increases with the decreasing particle size. Since the time of retention is inversely proportional to the diameter of the particles, their retention in the air will take a longer time when they exhibit smaller sizes.

#### 4. CONCLUSIONS

The conversion of sulphur dioxide to sulphates in the plume of a coal-fired power plant occurs in the immediate vicinity of the emission source. The oxidation product is sulphuric acid vapour. Transported over far distances in a dispersing plume along with particulate matter, sulphuric acid vapour undergoes both adsorption and a chemical reaction on the available surface of the dust particles to form sulphates. The concentration of sulphates in airborne particulates and dust deposition increases with distance from the emitter. Atmospheric concentration of sulphuric acid vapour measured in the vicinity of the coal-fired power plant is approximately ten times as high as that of the sulphates. All these support the finding that sulphuric acid vapour should be regarded as the main contributor to the concentration of sulphur compounds in the proximity of a coal-fired power plant.



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MECHANIZM TWORZENIA SIĘ ZWIĄZKÓW ZAWIERAJĄCYCH JONY SIARCZANOWE  
W OTOCZENIU ELEKTROWNI WĘGLOWEJ

Przedstawiono nowy sposób wyjaśnienia mechanizmu tworzenia się związków zawierających jony siarczanowe jako wyniku konwersji dwutlenku siarki. Głównym produktem konwersji dwutlenku siarki są pary kwasu siarkowego, tworzące się w sąsiedztwie wylotów kominów elektrowni. Pary kwasu siarkowego adsorbują się na powierzchni pyłu w czasie transportu zanieczyszczeń tworząc siarczany stałe.

EIN BEITRAG ZU DEM MECHANISMUS DER SULFATIONENBILDUNG  
IN DER UMGEBUNG VON KOHLENKRAFTWERKEN

Es wird eine neue Erläuterung des für den Ablauf der Schwefeldioxidumwandlung zu Sulfationen enthaltenden Verbindungen verantwortlichen Mechanismus vorgeschlagen. Sulfationen enthaltende Verbindungen werden in der Nähe der Schornsteinmündung erzeugt. Es wird angenommen, dass die Umwandlungsreaktion zu der Erzeugung von Schwefelsäuredunst als Hauptprodukt führt. Der erzeugte Schwefelsäuredunst wird auf der Oberfläche der Staubpartikel adsorbiert und trägt zu der Bildung von Sulfaten bei.

МЕХАНИЗМ ОБРАЗОВАНИЯ СОЕДИНЕНИЙ, СОДЕРЖАЩИХ СУЛЬФАТНЫЕ ИОНЫ,  
В СОСЕДСТВЕ УГОЛЬНОЙ ЭЛЕКТРОСТАНЦИИ

Представлен новый способ объяснения механизма образования соединений, содержащих сульфатные ионы, как результата конверсии двуокиси серы. Основным продуктом конверсии двуокиси серы являются пары серной кислоты, которые образуются в соседстве выходящих отверстий дымоотводов электростанций. Пары серной кислоты, адсорбируются на поверхности пыли при транспортировании загрязнений, образуя твердые сульфаты.

