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Report

Degradation of the Natural Environment Resulting from the Presence of Sulphur Compounds in the Atmosphere

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Abstract

The influence of sulphur compounds in the atmosphere on the natural environment has been discussed. Today, production of sulphuric acid is not ecologically clean regardless of the employed technology. The year 1996 was decisive in the production of H_2SO_4 sulphuric acid as the modern method of non-reacted SO_x sulphur compound evacuation was applied in the POLCHEM - Toruń Inorganic Chemical Plant.

Keywords: sulphuric acid, air ecology, technology of sulphuric acid.

The natural environment is undergoing a systematic degradation due in part to, the emission of sulphuric compounds in to the atmosphere and the influence of their transformation products on the ecosystem.

Progressive degradation of the natural environment is a well known process, and atmospheric pollution should be treated as a global threat which crosses national boundaries. One of the main factors which threatens the environment is an increasing concentration of various chemical compounds, including sulphuric compounds, in the atmosphere. Degradation of the environment caused by sulphuric compounds results from:

* acidification of the ecosystem as a result of the emission of sulphuric compounds and the influence of acid rains
* increasing soil mobility of heavy metals and their assimilation by food chains
* formation of sulphate aerosols, which results in a change of thermal air currents in the troposphere

The emission of sulphur compounds may be of natural or anthropogenic origin. Natural sources of SO_2 are volcanoes and decay processes of organic matter. The process of chemical change of sulphur dimethyl to sulphur dioxide, which takes place in the ocean, has a considerable share in the emission of natural origin. Anthropogenic emission, which dominates in industrial areas, results mainly from burning coal as well as other industrial chemical processes. These include production of sulphuric acid from elemental sulphur and production of non-ferrous metals [1].

The Polish share in the balance of European anthropogenic emission of SO_2 amounts to 19%, while the share of the Polish population in Europe is only 5.36%.

The concentration of SO_2 in many cities in Europe exceeds acceptable standards and amounts to, e.g: in London [2] 44-77 $\mu g/m^3$, in Rome [3] 60-75 $\mu g/m^3$, while for the whole of Europe [4] the concentration is estimated at 2.7 to 7.0 $\mu g/m^3$ depending on the season.

The amount of mass emission of sulphur compounds from sulphuric is acid plants depends on the technology applied. The production of sulphuric acid can be either one-stage (SC/SA - single conversion/single absorption of the manufactured sulphur trioxide) or two-stage (DC/DA - double conversion/double absorption). Every sulphuric acid plant discharges some sulphuric compounds into the atmosphere. The year 1996 was decisive in the production of H_2SO_4 sulphuric acid because the modern technology of non-reacted SO_x sulphur compound evacuation was applied in POLCHEM - Toruń Inorganic Chemical Plant [5-10]. This method of the autothermal process was based on three-stage contact of SO_2 and three-stage absorption

of the synthesized trioxide (TC/TA). The application of this technology allowed decreasing SO_x in waste gas to 70 ppm. This technology has a clear advantage as it is an ecologically safe process.

It is estimated that $2.8*10^9$ tons of SO_2 falls on Poland annually [11]. The percentages of particular sectors of the industry in the global emission of SO_2 are: vocational power engineering 46.4%, industrial power engineering 14.9% and industrial technologies 8.9%. In the period 1991-1992 the emission of sulphur dioxide dropped by 15%, partly the result of an economic recession in the sulphuric acid industry. It is estimated that in 1985 merely 3.8% of emitted SO_2 was removed, and losses resulting from the emission amounted to hundreds of millions of zlotys.

Negative effects of the influence of sulphuric compounds on the environment are well known and this is why their emission is being limited both in burning processes by increasing the process efficiency and by removing sulphuric compounds from post-process gasses. In Poland, however, merely 1.3% of the gross national product is being allocated to pro-ecological initiatives ($ 6/person), while in the USA it is $ 380/person, and in Germany 268DM/person. Wayne [12] provides data which show that the emission of sulphur dioxide caused by human activity is about 20 times higher than the emission of SO_2 from natural sources. Table 1 illustrates the emission distribution of several gasses.

Sulphur dioxide is the main sulphur compound which occurs in the atmosphere, though there are also compounds such as: H_2S, CS_2, COS, SO_3, H_2SO_4, $(NH_4)_2SO_4$ as well as organic sulphides $(CH_3)_2S$ and $(CH_3)_2S_2$. These compounds can be divided into:

1. Compounds which contain sulphuric atoms in the negative oxidation state (S^{2-}).

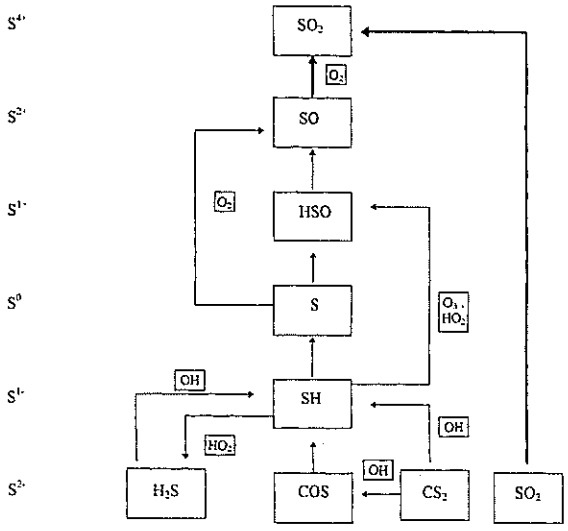
2. Compounds which contain sulphur in higher oxidation states

Possible mechanisms of tropospheric transformations of sulphuric compounds were given earlier, demonstrating that mechanisms of those transformations can be varying, depending on the oxidation state of sulphur [12]. The final product of those transformations, however, is always sulphur dioxide.

Table 1. Anthropogenic and natural emissions (estimates for 1976) [12]

Species	[10^9kg/y]	
	anthropogenic	natural
CO_2	$2*10^4$	106
hydrocarbons	188	1800
CO	600	2500
SO_2	**207**	**10**
H_2S	2	50
NOx	90	1200
NH_3	7	1200

In the troposphere sulphur dioxide can undergo hydrolysis and common, catalytic (in homogenous and heterogenous catalysic processes), and photochemical oxidation or oxidation by means of nitric oxides.



It is widely emphasized that transformation mechanisms of sulphuric compounds are very complex [13]. The process of oxidation of SO_2 during homogenous catalysis is mainly of radical character and the arising radicals are oxidated to SO_2 by means of oxygen, ozone or nitric oxides.

The oxidation of SO_2 during heterogenous catalysis takes place with cations or complexes of heavy metals contained in drops of water.

The photochemical process can be induced by light of a proper wavelength, and as a result of photochemical dissociation SO_3 is created.

The final product of all tropospheric transformations of sulphur dioxide is sulphuric acid(IV). The very process of transformation to H_2SO_4 is complex and it has not yet been revealed in detail.

Nitric oxides which are present in the atmosphere can react similarly producing sulphuric and nitric acids. The acids which are produced during the tropospheric transformations of sulphur and nitrogen are the source of acid rain. The lifetime of the arising sulphuric acid is restricted by its natural circulation (acid rain). The major place in which acid rains are created in the atmosphere are drops of water of various sizes (0.1-100 μm). Aerosols which contain sulphuric compounds can arise in the atmosphere as well as being emitted from the surface of the earth. It is estimated that the emission of aerosols from natural sources is $1100*10^{12}$ g,

while emissions due to human activity total $200*10^{12}$ g of sulphur [13]. Aerosols with big drops (1-100 μm) occur mainly in the low layers of the atmosphere (20% from 0 to 250 m, 50% in the layer up to 1000 m).

The lifetime of aerosols depends on the size of a micelle and reaches from 0.01 day in small and big micelles to 10 days in case of intermediate systems (0.1-1 μm). The distance to which aerosols can be carried reaches from 8 to 8000 km, depending on the size of a micelle. The phenomenon of condensation and falling of water to the surface of the earth in the form of precipitation (rain, snow) is a natural process of cleaning the atmosphere. The value of pH of the rain in natural conditions is 4.5-5.6 due to dissolving CO_2 in the water and due to the natural cycle of sulphur in the environment. However, for so called acid rains which result from the atmospheric transformations of sulphuric compounds, pH can even amount to 3. In acid rains sulphuric acid has the greatest influence on pH (up to 70%), then nitric acid (up to 40%), while other acids have little influence. Acid rain causes acidifying of the soil, which is a very harmful process because of the increase in mobility of heavy metals in the soil. The heavy metals content of the soil is climbing systematically due to human activity. Depending on pH of the soil, heavy metals form different chemical compounds - usually insoluble oxides or hydroxides (when the soil reaction is basic) or soluble sulphates (when the soil reaction is acid).

Employed agricultural treatment is aimed at neutralizing soil reaction, causing increasing immobility of heavy metals according to the general scheme:

$$Me^{2+}+(SO_4)^{2-}+Ca/Mg^{2+}+(CO_3)^{2-}+H^{+}+(OH)^{1-} \rightarrow \rightarrow Ca/MgSO_4+\mathbf{Me(OH)_2}+CO_2+H_2O \quad (1)$$

$$Me^{2+}+(SO_4)^{2-}+CaO(OH)+H^{+}+(OH)^{1-} \rightarrow \rightarrow CaSO_4+\mathbf{Me(OH)_2}+H_2O \quad (2)$$

An increase in acidity resulting from, among others thing, acid rain causes an increase in soil mobility according to the general scheme:

$$\mathbf{MeO}+2H^{1+}+(SO_4)^{2-} \rightarrow Me^{2+}+(SO_4)^{2-}+H_2O \quad (3)$$

$$\mathbf{Me(OH)_2}+2H^{1+}+(SO_4)^{2-} \rightarrow Me^{2+}+(SO_4)^{2-}+2H_2O \quad (4)$$

One can claim that, depending on pH, one can observe the following general soil mechanism:

$$\underset{pH<7}{Me^{2+}} + (SO_4)^{2-} \Longleftrightarrow \underset{pH>7}{MeSO_4} \Longleftrightarrow Me(OH)_2 \quad (5)$$

The increase of mobility of heavy metals is a very dangerous phenomenon because of the possibility of their entering food chains. The products of tropospheric transformations of sulphur compounds are aerosols. The appearance of sulphate aerosols suggests another view of the greenhouse effect. The presence in the atmosphere of sulphate aerosols measuring from 0.1 to 1 mm increases the ability of reflecting sun rays back to outer space. In a cloudless sky, sulphur dioxide and dimethyl sulphide accompanied by water vapour create gas sulphuric acid(VI), whose particles measure a fraction of a micron. This phenomenon is called gas/particle transformation. The arising sulphuric acid reacts further with a minimal amount of ammonia and creates hydrated forms of sulphate(VI) of ammonia. Moreover, dimethyl sulphide in an analogical reaction creates methylosulphuric acid(IV) (CH_3SO_3H), called MSA. The role of this acid in the process of protecting the earth against radiation is considerable, though not fully known. Aerosols also arise in clouds. This process starts by dissolving SO_2 in drops of water, creating sulphuric acid(IV), which is further oxidated to sulphuric acid (IV) or [ammonia/ammonium] salts of this acid. Thus, in drops of water which measure several micrometers, hydrated sulphates called sulphate aerosols arise. Creating sulphate aerosols in the atmosphere can cool down the climate in two ways: by reflecting sun rays or, indirectly, by increasing the ability of clouds to reflect sun rays during cloudy days. All sulphuric compounds (IV, VI) getting into the ecosystem as a process remainder, not only from sulphuric acid installations but as a product of tropospheric transformations of those compounds (sulphuric acid), harm live organisms [14].

Sulphur dioxide is an irritant to the respiratory system and mucous membranes [15]. It is toxic to fungi, bacteria, fish, and seaweeds and is harmful to plants.

Sulphur trioxide is absorbed into the organism through the respiratory system, the alimentary canal and the skin. It has a strong caustic attack, destroys the epidermis, penetrates the subcutaneous tissue and muscles, causing necrosis [16]. It also causes excessive acidity of soil and water, poisons fish and plankton, causes growth control in roots of sprouting seeds.

Sulphuric acid (IV, VI) influences all live organisms similarly to sulphur trioxide, but the effects of the activity of sulphuric acid are considerably worse [17].

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