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ATMOSPHERIC AIR POLLUTION BY THE GAS EMISSIONS OF COAL-FIRED THERMAL POWER PLANTS II. AMBIENT AIR POLLUTION OF THE STARA ZAGORA REGION FROM THE "MARITSA EAST" POWER COMPLEX

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ABSTRACT

Analysis has been made of the processes that take place in the atmosphere with the emissions of SO_2, NO_x and particulate matter from thermal power plants, and lead to the formation of secondary pollutants, photochemical and acidic smog. The monitoring of the atmospheric air in the Stara Zagora region in 2003 - 2005 has shown that the main source of pollution are the three thermal power plants of the "Maritsa East" power complex. It has been found that the ambient air pollution of the region is influenced by the following factors: · considerable primary oxidation of SO_2 to SO_3 in the fuel installations of the thermal power plant at high levels of the pollutants in flue gases; · absence of purification of SO_3 in the emitted flue gases; · joint action of the factors above with high humidity of the atmospheric air leads to the formation of acidic fog; · secondary oxidation processes with pollutants in the atmosphere; and · formation of photochemical smog under certain meteorological conditions. In order to control and forecast the danger of air pollution in the region,in addition to the conducted monitoring of the main pollutants in the air, the secondary pollutants formed in the atmosphere and the fuel installations of the thermal power plant have to be set under permanent control.

Keywords: *acidic and/or photochemical smog formation.*

INTRODUCTION

Main sources for pollution of the atmospheric air in the Stara Zagora region are the three thermal power plants (TPP's) of the "Maritsa East' power complex. Because of the enormous quantities of the emissions, the TPP's produce pollution levels with SO_2, NO_x and particulate matter that considerably exceed the permitted levels in the country [1 - 4]. The amount of the emitted flue gases to the atmosphere is 4.5×10^{10} Nm^3 per year with an average content of 15 000 mg SO_2 and 250 mg NO_x pro each normal cubic meter [1]. During the past few years frequent ambient air pollution cases in the region have been observed. Two of them, in the summer of 2005, were very serious and grew up into an ecological and social problem for the region. Until now, the reasons for these air pollution cases have not been correctly clarified.

Our analysis of the problem has shown that the air pollution of the region is the result of the joint ac-

tion of several factors. In a previous work of ours [1], analysis was made of the level of SO_3 emissions in flue gases, discharged to the atmosphere from the TPP's. In the present work the role of the processes in the atmosphere, leading to secondary pollutants will be examined.

Essential factors for the ecological effect of the pollutants are the climatic and meteorological conditions in the region. The three stations of the "Maritsa East" power complex are situated in the territorial scope of the Stara Zagora field which is part of the Upper Thracian Plain. The climate is transcontinental with sensible Mediterranean influence, average annual temperature around 13 °C and low average annual rainfall (around 550 mm). The main winds are from: east – north-east (45 %), north (20 %), and the other directions of the wind are equally included with 5 – 8 % [5]. The calm windless time is 32 % of the year. Recently the changes in the climate of the region, characterized by rise in the average temperature and sharp increase of the rainfall in spring and summer months, have essential influence on the behavior of pollutants and their effect on the environment.

THEORETICAL ASPECTS

Behavior of the main pollutants - SO_2, NO_x and dust in the atmosphere

As it has been shown [1], partial condensation with formation of fine acid mist takes place in the flue gases. The opacity of the plume visible at the stack exit is due to liquid acid droplets and fine fly ash particles. Under meteorological conditions, that are favorable for weak dispersion of the pollutants, the oxidation processes of SO_2 to SO_3 continue in the atmosphere and can lead to secondary formation of a fog from sulphuric acid. In sunshine and high levels of air pollution with sulphur dioxide, in the presence of nitrogen oxide and dust, the oxidation of SO_2 results from photochemical and chemical reactions. Analysis in such cases shows that the oxidation rate of SO_2 in polluted air can vary from 1 to 10 % per hour [6, 7].

It is well known, that the key role for the generation of sulphur dioxide oxidizers in the atmosphere have the nitrogen oxides – NO and NO_2. Once in the air, NO oxidizes to NO_2 by two possible mechanisms [6, 8, 9]:

· The first one follows complicated chemical reactions with the participation of atmospheric oxygen and volatile organic compounds (VOC):

$$2NO + O_2 \xrightarrow{VOC} 2NO_2 \quad (1)$$

·

The second is based on the photolysis of water

$$H_2O \xrightarrow{h\nu} H + OH^- \quad (2)$$

$$H + O_2 \rightarrow HO_2 \quad (2')$$

$$HO_2 + NO \rightarrow NO_2 + OH^- \quad (2'')$$

The content of VOC in the atmospheric air in the Stara Zagora region is relatively low – about 4 - 5 ppm [10]. This is the reason why, the second chemical scheme is of main importance for the oxidation of NO to NO_2 .

For the degree of the above processes taking place in the air of the Stara Zagora region can be judged by the data established so far - in the plume at the stack exit of Maritsa East power plants, the share of NO_2 in the total content of nitrogen oxides is comparatively low and does not exceed 4 - 5 % [11]. In the air of Stara Zagora its share grows up to 35 - 40 % [10].

The nitrogen dioxide in the air undergoes photochemical dissociation under the influence of UV radiation.

$$NO_2 \xrightarrow{h\nu} NO + O \quad (3)$$

The oxygen atom and UV-rays later are of great importance for the formation of active oxidizers of SO_2 in the atmosphere – organic radicals, $HO^{\cdot}$ and $HO_2^{\cdot}$, O_3 and H_2O_2. The oxidation of SO_2 runs mainly according to following reactions [6, 8]:

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \quad (4)$$

$$SO_2 + OH^- \rightarrow SO_3 + H \quad (5)$$

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \quad (6)$$

At low air humidity, the sulphur trioxide and nitrogen oxides are connected as vapors of sulphuric and nitric acids. At saturation above the critical point

and especially in the presence of submicron solid particles, condensation with forming of fine droplets from acid mist takes place. In the presence of basic pollutants and salts in the air (NH_3, CaO, NaCl, etc.) the sulphuric and nitric acids react with them and turn into secondary fine particles from sulphates and nitrates [6, 12, 13]. Aerosol liquid droplets, ultra-fine solid particles of primary and secondary origin (fly ash, ammonium sulphate, ammonium sulphite, nitrates and others) of size 0,1 to 1 μm, cause a local opacity of the air [14]. Thus, the described processes and phenomena are in fact formation of photochemical smog in the lower layers of the atmosphere.

At heavy rainfall and high humidity of the air, the photochemical reactions proceed with a lower rate. When such atmospheric conditions combine with calm weather, the stack plumes fall down to the earth surface and form an acidic fog. Because the flue gases cool at their mixing with ground air, additional condensation including intensive mist droplets formation in which parts of the sulphur dioxide and nitrogen oxides dissolve takes place. The oxidation of SO_2 from the dissolved in the liquid phase ozone, (with the highest concentration from the oxidizers in the system) proceeds at higher rate than in the air [8]. A catalytic mechanism of oxidation by condensation of the liquid phase on the surface of the dust particles is also possible.

With such a mechanism of the processes, acid smog with high level of opacity close to the earth surface is formed, or acid rain falls. An essential contribution for the opacity of the acid fog is due to the secondary formed sulphate and nitrate particles [15], which accumulate water and grow to dimensions that intensively scatter light.

Reasons for the ambient air pollution of the region in 2003 - 2005

Monitoring of the air pollutants.

The content of SO_2, NO, NO_2 and particulate matter (PM) in the atmospheric air in the Stara Zagora region in the period 2003 - 2005, was systematically controlled by the Regional Environmental Inspectorate according to the approved state standard methods [2 - 4] and the measured data were presented graphically on the web. The content of particulate matters - PM_{10}, was

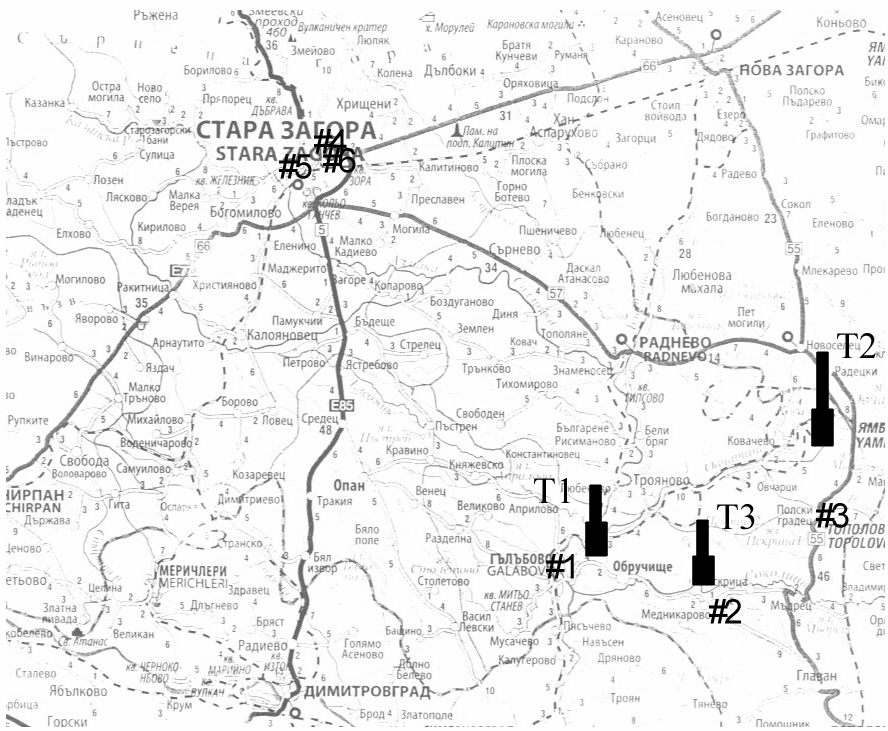

Fig. 1. Scheme of the location of TPP's (T1-T3) and measuring points (#1 - #6) for monitoring the quality of ambient air in Stara Zagora region

Table 1. Average annual PM_{total} concentration, SO_2 and NO_2 in the ambient air in the Stara Zagora Region, μg m^{-3}.

Measuring point	2003			2004		
	PM	SO_2	NO_2	PM	SO_2	NO_2
#1	129	37	3	118	56	2
#2	77	26	1	54	29	4
#3	121	32	4	106	41	6
#4	177	9	34	182	19	49
#5	148	2	9	167	3	14
#6	165	9	8	212	10	12

Table 2. Data for the soil composition of the Stara Zagora region and for the fly ash from ME power complex.

Sample type	Measured concentration, ppm																	
	As	Ba	Bi	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	P	Pb	S	Sb	Sr	Zn
Soil sample after the acid smog in 2005 [5]	8	26	-	0.7	2.2	4.6	16.4	4475	-	103.1	0.5	5	617.6	4.2	1452	-	-	135
Fly ash from TPP ME-1 [17]	298	1227	108	20	84	90	295	11700	0.4	790	106	111	68	67	72900	21	2081	602
Fly ash from ME-1 dissolved in 0,1 *n* HNO_3 [17]	9	72	-	7	5	27	41	32600	-	262	3	30	30	21	22860	-	145	44

determined only for a period of 6 months in 2003. Control was not imposed over the content of sulphuric acid, nitric acid, secondary formed sulphate and nitrate particles in the flue gases of the TPP's, or in the atmosphere.

Monitoring of the ambient air during the period mentioned above was made in three measuring points, within the 10th kilometer zone around the three TPP's – the populated areas of Gulubovo (#1), Mednikarovo (#2) and Polski Gradetz (#3). Three other measuring points were situated on the territory of the city of Stara Zagora, denoted respectively as "HEI" (#4), "Kazanski" district (#5) and "RIOSV" (#6). The location of the measuring points is seen on the map (Figure1).

The geographical position of the three TPP's and the main town in the region – Stara Zagora, define two atmospheric zones that are particularly important for the control of the atmospheric processes:

- The region between the three TPP's forms a triangle, where the composition of the ground air is supposed to be with higher level of pollution independently on the wind direction.

- The region where the polluted air moves from different points of this triangle towards the main town of the region - Stara Zagora.

The measuring points are situated out of the specified zones. For this reason the data about the highest pollution levels and the direction of air flow in the most important sense is limited and incomplete.

Summarized data about the average annual concentrations of pollutants from the six measuring points is given in Table 1 (the sum of NO_x is expressed as NO_2). Because of the graphical source of the experimental data, an error of about ±5% by deriving of their numerical values is possible.

The analysis of data, shown in Table 1, allows for the establishment of the following relations:

· The ratio of sulphur dioxide concentration to the concentration of nitrogen oxides in the flue gases and in the air for the specified period in the region around the power plants,

$$R = \frac{c_{SO_2}}{c_{NO_x}},$$

is:

• at the chimney exit $R \approx$ 50-55 [1];

• in the ground air at the measuring points #1, #2 and #3 (7 - 10 km away from TPP), R varies from 8 to 26.

It is seen that a part of the SO_2 emissions cannot be proved in the ground air in the 10-kilometer area around the three TPP's. Presumably, a considerable part of SO_2 is oxidized to SO_3 and due to its reaction ability turns into H_2SO_4 and sulphates.

In the city of Stara Zagora the situation is different. The content of SO_2 in the air is lower than the content in the region close to the TPP's. Obviously this is a result of dilution from the atmospheric air and continuing oxidation of a part of this component in the air flow during its moving towards the town. But the content of nitrogen oxides in the air is higher than that in the region around the three TPP's. The sources for this additional pollution have not been identified; probably the heavier traffic in the town is one of them.

The content of total particulate matter in the ground air of the region is high and the values for the town exceed those for the other parts of the region, and are often above the maximum permitted levels [2-4, 10]. The content of PM_{10} is also high. For the 6 months period in 2003 the average annual concentration is 63 μg m^{-3}.

Because of increased content of nitrogen oxides and total particulate matter in the air above the town, the oxidation potential of the atmosphere there is higher than the one in the region of the three power stations. Therefore, there are stronger preconditions for more intensive oxidation of SO_2 in the ambient air above the city and formation of smog, than in the other parts of the region.

The observed air pollutions in the region:

In calm weather. Increased concentrations of SO_2 in the region and above the town were determined within the period whereby the average daily and hourly concentrations periodically reach values from 200 to 700 μg m^{-3} [10]. In calm and cloudless weather, above the town of Stara Zagora, formation of photochemical smog has been repeatedly registered - the visibility is low; the air is grey-blue, with specific odor and irritates the respiratory and sense organs [5]. The color is sometimes yellow-brown, most probably from the increased concentration of micro-dispersed particles. There is systematic dependency between the increased pollution

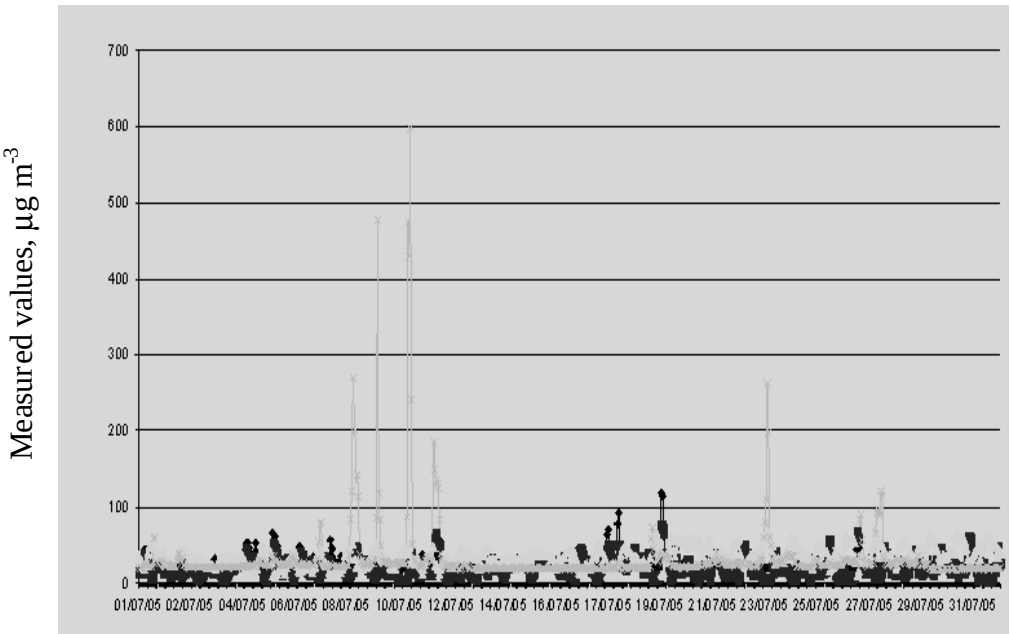

Fig. 2. Average hourly concentrations (in μg m^{-3}) in the ambient air of the city of Stara Zagora, July 7-12, 2005 (SO_2 - x; NO - ◆; NO_2 - ■; O_3 -●).

levels of the air and the symptoms of photochemical smog above the town.

From the monitoring data about the air pollutants and the characteristic of the observed phenomena, it can be concluded that the air pollution above the town of Stara Zagora during the period, is caused by accumulation of air pollutants from the power plants and secondary processes with their participation.

During continuous rainfall. The two heavy air pollution cases in the summer of 2005 that affected mainly the town of Stara Zagora happened during heavy and continuous rainfall. An opaque cloud covered the earth surface. Its influence on the population was expressed by the following symptoms: unpleasant odor, running eyes, hard breathing, headache, vertigo, slow reactions and low visibility.

Data for one of the air pollution cases in July 2005 is given in Figure 2. The pollution continued for about a week but for short (about 3 h) periods in the late afternoons. The acidic fog moved from the region of the three TPP's towards the town with a flow rate of 3 - 4 km h^{-1}. The short periods of air pollution per day were connected with changes of the air flows as a result of the unstable meteorological conditions at that time.

Fig. 2 shows that the concentration of SO_2 reaches its maximum levels of 600 μg m^{-3} by basic level 20-25 μg m^{-3}. The concentration of NO_2 and NO is in the order of 10 - 15 μg m^{-3}, that of O_3 is 40 - 50 μg m^{-3}. Deviations in particulate matter emissions PM_{10} have been found up to 1,7 times above the norm. The ratio of SO_2 to NO_x concentrations, *R*, at the top content of SO_2 in the acid cloud is about 20-25.

Data analysis of the two air pollution cases of Stata Zagora in the summer of 2005, has shown that by their characteristic and origin, they are **acid smog**, caused mainly by the combination of high concentrations of sulphur and nitrogen oxides in the flue gases of the three power stations and appropriate meteorological conditions. This smog resembles the Great London Smog of 1952 [16]. The differences between the two phenomena are also essential:

• the pollution level with sulphur dioxide of Stara Zagora in July 2005, was about three times lower than the registered one in London in December 1952;

• there is no data about other hazardous pollutants in the cloud that polluted Stara Zagora - the content of acids and micro dispersed salt particles. However, the data given in [1], suggest that this content is very high.

This leads to the conclusion that the air pollution of Stara Zagora in the studied period is comparable, by its harm and danger, with the Great London Smog in 1952. Obviously, the short periods of daily air pollution are the reason why the consequences for the population of Stara Zagora and the effect on the environment were lighter than those in London in 1952.

Monitoring data shows that special attention should be paid to PM air pollution. The content of PM_{total} in the ground air in the period is high. In the analysis of control authorities this dust is estimated as "non-toxic" [10]. However, from Table 2, compiled according to published data [5, 17, 18], it is seen that the content of heavy metals and trace elements in the fly ash is high, too. A correlation is observed between these elements in the air dust and in the soil. This is an indication for intensive long-term transfer of ash dust through the air and high general air pollution of the region.

Shumkova [17] has found that larger part of the toxic elements are concentrated in the surface layer of the dust particles from the "Maritsa East" power complex. This is a result of evaporation of toxic element compounds in combustion chambers and their deposition on the ash particle surface in the steam generators. The solubility data for these toxic elements, at room temperature in weak acid medium (last row of Table 2), logically shows that they are characterized by high mobility.

On the grounds of all this, it can be concluded that the PM pollution in the ground air of the region in this period has been incorrectly regarded as safe. It should be regarded as toxic, with the resulting conclusions for its influence on people's health and the environment.

CONCLUSIONS

Monitoring of the purity of the atmospheric air in the Stara Zagora region, in the period 2003 - 2005, shows that the main sources of air pollution are the three TPP's - ME-1, 2 and 3. The consistent air pollution during the recent years should be looked at as a result of the complex action of several factors:

• Primary oxidation of considerable part of the sulphur dioxide to sulphur trioxide in the combustion

installations of the power plants, at very high levels of the two pollutants compared to globally accepted norms. No measures for lowering SO_3 concentration in the flue gases have been taken, before their discharging in the atmosphere. This in combination with heavy rainfall in the summer of 2005, is the reason which has led sometimes to formation and continuous hold of an hazardous acid smog in the air near the ground surface;

• Secondary oxidation processes of the atmospheric pollutants constantly take place. But because of the increased oxidation potential of the atmospheric air above the town of Stara Zagora, these processes are more strongly manifested there. When there are appropriate meteorological conditions, the consequence for the town is periodical formation of photochemical smog.

Other sources in the region could have some contribution to the air pollution of Stara Zagora if they emit components that accelerate the secondary processes of the main atmospheric pollutants (PM, VOC, strong oxidizers). Due to the lack of experimental data, these possibilities have not been analyzed.

To throw light upon these factors, it is necessary to conduct specialized research and the on-going monitoring to be carried out according to a specific program, that includes control of the main primary and secondary atmospheric pollutants.

The construction of wet flow gas desulphurization (FGD) systems in the three power stations of Maritsa East power complex, is expected to be finished by the middle of 2008 [11]. Thus, the problem with the ambient air purity in the region will be solved in broad outlines. But the removal efficiency of the commercial FGD units is about 50 % with respect to the acid fog [12, 14]. Finer sulphuric acid droplets, formed in the combustion installation of the power plants, cannot be absorbed with the established technology, and will continue passing in the atmosphere. In order to cut down the amount of SO_3, discharged in the atmosphere after the FGD devices, technological measures for control have to be used before the desulphurization.

REFERENCES

1. A. Lenchev, J. Ninov, I. Grancharov, Atmospheric Air Pollution by the Gas Emissions of Coal-fired Thermal Power Plants. I. SO_3 formation by combustion of Maritsa East lignite coal, Bulg. Chem. and Ind., 77 (2006) 14.
2. Council Directive 1999/30/EC relating to Limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, 22 April 1999, (http://eur-lex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=en&numdoc=31999L0030&model=guichett)
3. Regulation No 9 on Limit values for sulphur dioxide, nitrogen dioxide, fine particulate matter and lead in ambient air, Ministry of Environment and Waters of Bulgaria, May 1999. (http://www.moew.government.bg/index.html)
4. Regulation No 14 on Limit concentrations for harmful substances in ambient air of populated areas, Ministry of Environment and Water of Bulgaria, Sept. 1997 (http://www.moew.government.bg/index.html)
5. G. Georgiev, Mining and Geology, 6, 2006, 8-15.
6. S.E. Manahan, Environmental Chemistry, 7th edn., CRC Press, N.Y., 2000.
7. A.E.J. Eggleton, R.A. Cox, Atmospheric Environment, 1978, as cited in Monitoring and Assessment Research Centre; Report #7 (1978) 11, (http://www.frankmckinnon.com/sulfur_dioxide.htm).
8. I.J. Tinsley, Chemical Concepts in Pollutant Behavior, Oregon State Univ., John Wiley&Sons, 2004.
9. A. Heintz, G. Reinhardt, Chemie und Umwelt, Friedr. Vieweg & Sohn Verlagsgesellschaft mbH, Braunschweig/Wiesbaden, 1991.
10. Regional Environmental Inspectorate, 6000 Stara Zagora, 2 Stara Planina str., PB 143, http://www.stz.riew.e-gov.bg/
11. Environmental Impact Assessment Report for Project for extension of Maritsa East 2 power plant and building of FGD Units, Ministry of Environment and Water of Bulgaria, March 2004.
12. W. Buckley, B. Altschuler, Power Engineering, Nov. 2002, p.3.
13. J.O'M. Bockris, Environmental Chemistry, Plenum Press, N.Y, 1977.
14. R.K. Srivastava, C.A. Miller, C. Erickson, R. Jambhekar, Emissions of sulfur trioxide from coal-fired power plants, POWER-GEN International, Orlando, Florida, Dec. 10-12, 2002. (http://www.babcockpower.com/pdf/t-178.pdf).

15. Understanding particle pollution: Visibility, United States Environmental Protection Agency, (http://www.epa.gov/air/airtrends/aqtrnd04/pmreport03/pmunderstand_2405.pdf#page=2)
16. The London Smog Disaster of 1952. (http://www.portfolio.mvm.ed.ac.uk/studentwebs/session4/27/greatsmog52.htm)
17. A.S. Schumkova, PhD Thesis, UCTM, Sofia, 2006.
18. V. Vassilev, Chr. Vassileva, Fuel Proc. Tech., 51 (1997) p. 19.