Annals of the University of Petroșani, Mining Engineering, 14 (2013)

RISK OF ACID RAIN PRODUCTION, DUE TO THE EMISSIONS GENERATED BY THE THERMAL POWER PLANT PAROŞENI

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Abstract. *Production risk may occur due to the conduct of certain human activities, with a potential risk, and it includes thermal power plants that run on fossil fuel. Any risk is the result of hazard and exposure, the present paper being aimed at analyzing the hazards (gas emissions that generate acid rain) and the exposure (vulnerability) of the environmental factors (the consequences of that acid rain production on the environment).*

Key words: *acid rain; power plant; emissions; risk assessment; environment*

1. APPROACHING THE ENVIRONMENTAL RISKS

Risks depend on the magnitude of the impact generated by pollution and become significant with exceeding pollution limits beyond which the risk factor affects the value of ecosystems and the human factor /1/. Thus, we can highlight two aspects of risk:

- Risks that produce short-term effects are felt particularly in the ecosystem, requiring pollution mitigation measures to protect the ecosystems. This category includes the expected risks assumed by man.
- Risks that produce long-term effects generated by major changes over a long period of time very large, effects that are difficult to predict. Due to the complexity of estimating these risks, they perceived are insufficient or distorted, the behavior of decision makers often depends on their power to think ahead. These risks involve strategies, policies, instruments and funding, in other words, a joint effort of all individuals in the human ecosystem.

Any risk can be defined as the probability of an adverse effect to a certain period of time, which allows for its expression in the form of:

$$\text{Risk} = \text{Hazard x Exposure} \quad (1)$$

Risk assessment has the purpose of controlling possible risks due to the conduct of human activities by identifying the following:

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- the most important pollutants or hazards;
- the resources and receptors exposed to the risk;
- mechanisms through which the risks take place;
- important risks that are likely to take place;
- general measures necessary to reduce the risk to an acceptable level.

2. FORMATION AND EFFECTS OF ACID RAIN ON THE ENVIRONMENT

2.1. The mechanism of acid rain formation

Sulphur dioxide and nitrogen oxides present a significant risk, because once released into the atmosphere have the ability to produce a number of negative effects over the environment of which the most important may be their ability to produce acid rain that has a negative effect not only on flora and fauna present in the affected area, but also to the structures present in the area where they form. /2, 3/.

The acidity of the precipitation depends not only on the level of emissions, but also mixtures of chemicals which interact with the SO2 and NOx in the atmosphere. Formation of sulfuric acid and nitric acid is a complex process consisting of several chemical reactions. It is important to consider both phases, solution and gas, in the conversion process.

One possibility is photooxidation of sulfur dioxide by ultraviolet light. Light from this region of the electromagnetic spectrum has the potential to excite molecules and lead to subsequent excitation of O_2. This reaction has a negligible contribution to the formation of sulfuric acid. A second possibility is the reaction of sulfur dioxide with oxygen in the atmosphere, through the following reactions:

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (3)$$

The second reaction occurs rapidly, and therefore the formation of sulfur trioxide in a humidified atmosphere leads to the formation of sulfuric acid. Anyway first reaction is very slow in the absence of a catalyst, although it does not have a significant contribution. There are also several other potential reactions but for different reasons prove to be insignificant. Although each of these effects may contribute to the oxidation of sulfur dioxide, there is only one significant reaction. The reaction occurs thus:

$$HO + SO_2(+M) \rightarrow HOSO_2(+M) \qquad (4)$$

In the solution phase sulfur dioxide exist in three forms:

$$[S(IV)] = [SO_2(sol)] + [HSO_3] + [SO_3] \quad (5)$$

This dissociation occurs through two processes:

$$SO_2(sol) = H + HSO_3 \quad (6)$$

$$HSO_3(sol) = H + SO_3 \quad (7)$$

The establishment of balance depends on factors such as pH, droplet size, etc.

Solution of sulfur dioxide oxidation with molecular oxygen is based on a metal catalyst such as Fe or Mn, or a combination of these. Oxidation through ozone is a more considerable because it does not require a catalyst and is more abundant in the atmosphere than molecular oxygen.

The oxidation process is dominated by hydrogen peroxide (formed in the gas phase with free-radicals). The reaction involves the formation of an intermediate (A), possibly an acid peroximonosulfuros ion and occurs as follows:

$$HSO_3 + H_2O_2 \rightarrow A + H_2O \quad (8)$$

$$A + H \rightarrow H_2SO_4 \quad (9)$$

Like with the Sulphur dioxide, the most important contribution in forming nitric acid, is the reaction with hydroxyl radicals. These radicals are highly reactive and abundant in the atmosphere. The reaction takes place in the following manner:

$$HO + NO_2(+M) \rightarrow HONO_2(+M) \quad (10)$$

There are several other possibilities, such as oxidation with atmospheric oxygen, however none are produced at a substantial rate in the atmosphere to contribute significantly to the formation of nitric acid.

There are 3 equations to be considered in the oxidation of the NOx solution:

$$2NO_2(g) + H_2O(l) \rightarrow 2H + NO_3 + NO_2 \quad (11)$$

$$NO(g) + NO(g) + H_20(l) \rightarrow 2H + 2NO_2 \quad (12)$$

$$3NO_2(g) + H_20(l) \rightarrow 2H + 2NO_3 + NO(g) \quad (13)$$

These reactions are limited by their dependence on the partial pressure of NO_x present in the atmosphere and NO_x solubility law.

2.2. Sulfur dioxide and nitrogen oxides imissions generated by thermal Paroşeni

Data regarding emissions generated by the power plant Paroşeni during the years 2011 - 2013 were taken from website of the National Environmental Protection

Agency and are presented in table 1. It is noted that continuity exists only in the sulfur dioxide concentration measurements, because for the most part of the analysis period, nitrogen oxides analyzer was defective.

Although the nitrogen oxides analyzer was defective the data can still be used estimate the risk of acid rain nitrogen oxides are within the limits imposed by the by legislation in effect, and they remain in the atmosphere for a longer period of time, being transported by currents air distance from the source of emission.

Table 1 Measurement made at the station HD-5

Month	Pollutant (UM)	Minimum hourly	Average hourly	Maximum hourly	Exceeding
2011					
January	SO_2 (µg/mc)	-	-	-	-
	NO_2 (µg/mc)	1,68	14,88	47,03	-
February	SO_2 (µg/mc)	-	-	-	-
	NO_2 (µg/mc)	3,29	14,15	39,69	-
March	SO_2 (µg/mc)	-	-	-	-
	NO_2 (µg/mc)	1,45	15,39	33,86	-
April	SO_2 (µg/mc)	-	-	-	-
	NO_2 (µg/mc)	3,88	13,98	27,71	-
May	SO_2 (µg/mc)	3,50	*	309,19	-
	NO_2 (µg/mc)	4,72	13,04	26,67	-
June	SO_2 (µg/mc)	3,91	15,58	330,49	-
	NO_2 (µg/mc)	1,1	*	18,66	-
July	SO_2 (µg/mc)	4,73	6,81	27,21	-
	NO_2 (µg/mc)	0,5	6,40	14,09	-
August	SO_2 (µg/mc)	6,04	20,61	567,47	-
	NO_2 (µg/mc)	-	-	-	-
September	SO_2 (µg/mc)	-	-	-	-
	NO_2 (µg/mc)	-	-	-	-
October	SO_2 (µg/mc)	9,32	26,31	368,27	1
	NO_2 (µg/mc)	-	-	-	-
November	SO_2 (µg/mc)	14,76	43,66	380,26	1
	NO_2 (µg/mc)	-	-	-	-
December	SO_2 (µg/mc)	15,38	43,78	271,32	-
	NO_2 (µg/mc)	-	-	-	-
2012					
January	SO_2 (µg/mc)	16,22	37,45	249,02	-
	NO_2 (µg/mc)	-	-	-	-
February	SO_2 (µg/mc)	17,38	47,57	364,06	1
	NO_2 (µg/mc)	-	-	-	-
March	SO_2 (µg/mc)	16,28	35,72	526,73	3
	NO_2 (µg/mc)	-	-	-	-

(continues table 1)

April	SO_2 (µg/mc)	17,79	30,26	345,12	-
	NO_2 (µg/mc)	-	-	-	-
Month	Pollutant (UM)	Minimum hourly	Average hourly	Maximum hourly	Exceeding
May	SO_2 (µg/mc)	17,78	29,43	463,23	2
	NO_2 (µg/mc)	-	-	-	-
June	SO_2 (µg/mc)	17,14	28,36	274,16	-
	NO_2 (µg/mc)	-	-	-	-
July	SO_2 (µg/mc)	18,46	38,23	350,17	1
	NO_2 (µg/mc)	-	-	-	-
August	SO_2 (µg/mc)	14,65	25,82	357,93	1
	NO_2 (µg/mc)	-	-	-	-
September	SO_2 (µg/mc)	18,88	26,19	371,89	1
	NO_2 (µg/mc)	-	-	-	-
October	SO_2 (µg/mc)	21,08	39,29	681,55	4
	NO_2 (µg/mc)	-	-	-	-
November	SO_2 (µg/mc)	4,92	29,57	667,36	8
	NO_2 (µg/mc)	-	-	-	-
December	SO_2 (µg/mc)	4,03	29,89	163,58	-
	NO_2 (µg/mc)	-	-	-	-
2013					
January	SO_2 (µg/mc)	4,61	28,42	184,33	-
	NO_2 (µg/mc)	-	-	-	-
February	SO_2 (µg/mc)	4,32	22,93	272,75	-
	NO_2 (µg/mc)	-	-	-	-
March	SO_2 (µg/mc)	4,06	19,74	345,32	-
	NO_2 (µg/mc)	-	-	-	-
April	SO_2 (µg/mc)	4,32	19,52	397,91	2
	NO_2 (µg/mc)	-	-	-	-
May	SO_2 (µg/mc)	2,75	15,48	336,29	-
	NO_2 (µg/mc)	-	-	-	-

The excess emissions are analyzed in relation to the standards provided by the regulations in effect (Law. 104/2011).

2.3 Acid rain effects of on the environment

Effects on the atmosphere

Besides their ability to produce acid rain these pollutants, can exist as particles in the air and contribute to the formation of fog affecting visibility. This makes travel difficult, especially for pilots.

Effects on architecture

Acid particles are also deposited on buildings and statues, causing corrosion. For example, the building of the capitol building of Ottawa was disintegrated due to excess sulfur dioxide in the atmosphere.

Limestone and marble turns into a powdery substance called gypsum upon contact with the acid, which explains the corrosion of buildings and statues. Bridges corrode faster, and road and airline industry must invest more money in repairing the damage caused by acid rain.

Effects on materials

Acid rain also affects materials such as fabrics. For example, flags are "eaten" by chemicals in acidic precipitation. Books and art objects dating back hundreds of years are also affected.

Ventilation systems of libraries and museums, where they are kept, do not prevent acid particles from entering the buildings therefore the pollutants can reach the objects in question and cause considerable damage.

Effects on trees and soils

One of the most serious impacts of acid precipitation is the one on forests and soils. Major damage occurs when sulfuric acid falls to earth as rain and the nutrients found in soils are removed. Therefore the trees are doomed to die, being deprived of vital nutrients such as calcium and magnesium which are replaced by hydrogen atoms useless that slow photosynthesis. Aluminum also present in the soil is released and this element is toxic to tree roots /2, 3/.

Severe frosts may worsen this situation. With sulfur dioxide, ammonia and ozone present in the air reduces the tree's resistance to low temperatures. Ammonia oxidizes with sulfur dioxide to form ammonium sulfide.

When the ammonium sulphide reaches the ground, it reacts to form sulfuric acid and nitric acid. Such conditions, also stimulates the appearance of fungi and pests. Nitrogen monoxide and nitrogen dioxide are also components of acid rain can force trees to grow, even if they have do not have the necessary nutrients. Therefore trees are often forced to grow in late autumn when they should to prepare for winter.

Effect on lakes and aquatic ecosystems

There are several ways in which acidic chemicals can enter the lakes. Some chemicals exist as dry particles in the air, while others end up in lakes as wet particles such as rain, snow, sleet and fog.

Furthermore lakes can be considered as the 'sinks' of the earth, because of the water that flows in them during rains. Acid rain that falls on the ground also washes nutrients from the soil and carries toxic metals released from the ground into the lakes.

Another way the acids can reach the lakes is in springtime, when the snow melts and the chemicals seep into the earth being carried to rivers and lakes. This causes a drastic change in lake's pH level.

In addition the spring is a vulnerable season of many species being the breeding period for amphibians, fish and insects. Many of these species lay their eggs in water, and the sudden change in pH is dangerous because these acids can cause malformation to the young or could even annihilate an entire species, since they spend most of their life in water.

3. RISK ANALYSIS AND ASSESSMENT OF THE RISK OF ACID RAIN

Environmental risk analysis requires a broader approach, including quantitative and qualitative descriptions of an environmental hazard, potential negative effects, and the risk involved in these effects, and uncertainties related to each aspect.

The analysis and qualitative assessment of environmental risk undergoes three main stages /1/:

- Hazard identification that determines specific causes or particular effect on the environment;
- Exposure - effect assessment, this step determines the relationship between the magnitude of exposure and the probability of an effect on the environment;
- Risk characterization, which describes the nature and magnitude of risk, including the degree of uncertainty, determined by the first three stages.

One of the risks with long term effects is the risk of acid rain due to sulfur dioxide emissions and nitrogen oxides generated by the functioning of power plants, which are found in high concentration in the atmosphere.

Acid rains are related to a number of negative effects, including:

- destruction of vegetation, especially coniferous forests through direct destruction of chlorophyll;
- soil over fertilization, plants growing very quickly, prematurely;
- acidification of lakes, which leads to the loss of fish fauna;
- dissolved calcium and magnesium salts in the soil, thus causing deficiencies in these elements, acidification of soil and plant nutrition deficiencies.

Risk assessment involves identifying the danger and consequences that may occur as a result of the events considered risk sources.

Depending on the importance of the consequences, it will be decided whether or not remedial action is needed.

Risk quantification is based on a simple system of classification, where the probability and severity of an event is considered descending and given a random value.

$$R = H \times E \qquad (14)$$

The matrix proposed for qualitative estimation of risk is shown in Fig. 1 and takes into consideration, on the one hand, the probability of exceeding limit values for emission and immission of sulfur dioxide, on the other hand, the severity of the effects of acid rain on the environment affected.

Data obtained through monitoring emissions were statistically processed and determined a probability of exceeding the limits provided by legislation by 31.42%, corresponding to a medium exposure, which is assigned the value 3.

Acid rains can cause a significant impact on soil, water and biota in the area of influence and, therefore, the hazard was assessed as high, which is assigned a value 4.

Hazard / Exposure	Very low 1	Low 2	Medium 3	High 4	Very high 5
Very high (90-100%) 5	**5**	**10**	**15**	**20**	**25**
High (70-90%) 4	**4**	**8**	**12**	**16**	**20**
Medium (30-70%) 3	**3**	**6**	**9**	**12**	**15**
Low (10-30%) 2	**2**	**4**	**6**	**8**	**10**
Very low (0-10%) 1	**1**	**2**	**3**	**4**	**5**

1 – 5	**5 – 12**	**15 – 25**
Low risk	**Medium risk**	**High risk**

Fig. 1 Risk assessment matrix

$$R = E \times H = 3 \times 4 = 12 \qquad (15)$$

According matrix designed for qualitative assessment, the risk of acid rain in the influence area has an average level, which means that it is very likely that such precipitation could occur and affect the environment.

4. CONCLUSIONS

Due to the location and mode of operation of the power plant Paroşeni, there is a risk of sulfur dioxide and nitrogen oxides being released into the atmosphere as a result of the combustion of fossil fuels that may lead to the formation of acids by chemical reactions described in the paper.

Either through dry deposition or acid rain, all environmental factors in the emissions dispersion area can be affected more or less serious depending on their vulnerability.

The qualitative risk assessment matrix was built starting from emissions and from vulnerability of the environmental factors found in Jiu Valley basin, which shows that the occurrence of acid rain and their effects in the studied area is possible and very likely.

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