



EXPERIMENTAL MODEL FOR POLLUTANTS MONITORING INTO THE COKE-CHEMICAL PLANT

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ABSTRACT

The Coke-Chemical plants contribute heavily to producing and emitting in the atmosphere a big amount of polluting agents.

Polluting emissions diminution and situating them within the international specific standards, can be realized by introducing a monitoring model with automate prominence of atmospheric noxa concentrations and with the possibility of connecting it to an open communication system. In the paper is conceived an experimental model for noxa and pollutants monitoring and in a frame of a polluting field existing in the coke-chemical sector from an integrated iron and steel complex.

KEYWORDS: coke-chemical plant, atmospheric pollutants, air samples, coke coking, suspension powders

1. Introduction

Worldwide there is a constant preoccupation among the environment agencies towards diminishing noxious emissions from the plants. The already existing programs permit a rigorous control of the polluting emissions level through which can be avoided the maximum acceptable concentrations provided by the international standards.

These result from the processes needed in coking, from the raw materials variety, from the adjustment of installations functional parameters etc., resulting in big amounts of polluting agents to be liberated in atmosphere, with major impact on environment and on health of the workers.

By estimating the polluting level and by comparing the specific noxa concentrations with the maximum admissible values regulated through norms, there can be dignified their deviation and can be established which atmospheric pollutants can be selected to be monitored.

2. The technological flux from a coke chemical plant

The technological flux from a coke-chemical plant contains:

a) *The coke preparation sector* with important role in feeding the coking ovens. They have the role of obtaining a quality coke and a coke gas abundant in coal by-products. The main operations from the coke

packing flux are: reception, homogenization and coke storage, coke grinding, the coke packing burdening, coke packing moistening and mixing, preparation for loading the coking oven.

b) *Coking section*, in which is situated the coking oven, with an attribution in pyrogenated decomposition for coke obtaining. There are created two heating front-sides that are progressively advancing from the periphery to the center of the oven, the coal layers passing successively through drying, plastifying, mass hardening and degassing phases. The raw coke gas liberated from the oven due to the coal pyrogenetical decomposition is a complex mix of gas and steam, in which composition exists: tar vapor and water, ammonia, benzoic hydrocarbons, sulphuretted hydrogen, alborcarbon, hydrocyanic acid, basic pyridine, organic compounds with sulfur (alkyl hydrosulphide, tiophene, carbon sulphide etc.), phenols, hydrochloric acid and chlorides, nitrogen oxides.

c) *The chemical section*. After exiting the oven, the raw coke gas is passed in the purification-treatment sections, respectively that of chemical products collecting. The raw coke gas, at the oven exit passes through circulation raise pipe towards the gas collector. In the circulation rise pipes elduite is made a first aspersion with raw ammonium water, the coke gas being cooled from $\sim 700^{\circ}\text{C}$ to $\sim 90^{\circ}\text{C}$, hereby considering $50 \div 60\%$ from the contained tar. In the oven's loading-unloading periods, the cover of circulation rise pipe is opened, and the raw gas is evacuated in the atmosphere.



c₁) the cooling-condensing subsection. The cooled coke gas is sucked by the exhaust fans through un-tarring electrofilters. The tar content after the main coolers is about $\sim 3 \text{ g/Nm}^3$, and after the electrofilters about $\sim 0,02 \text{ g}_{\text{tar}}/\text{Nm}^3_{\text{coke gas}}$. The insolubles in the resulted tars from the two coking sections are of different qualities. From the superior side of the mechanized settlers, the raw ammonia water, that represents the main component of the introduced liquid debit, is draining continuously into the water reservoirs. From here it is aspirated and pumped in the conducts that feed the cooling installation by sprinkling the gas collector of the batteries. This way is opened the so called barilet's circuit. Pursuant to partial vaporization of the water in the barilet, it is growing the concentration of un-volatile ammonia salts dissolved in the water, conducting to the impossibility of tar separation from water.

c₂) ammonia subsection. The raw coke gas after cooling and un-tarring in electrofilters gets to the ammonia subsection with a content of about $\sim 5,0 \div 7,0 \text{ g}_{\text{ammonia}}/\text{Nm}^3_{\text{gas}}$. Regardless the ulterior use of the purified coke gas, the ammonia catching as completely as possible from the gas is obligatory, for environment pollution but also for avoiding the corrosion in the coke gas process installations and sub-products impurity. The ammonia is found fixed in two ways: 1) as free or volatile ammonia, dissolved in water or fixed in dissociable combinations that are decomposing simply by heating; 2) as tied ammonia (fixedly) in combinations from which no longer can be drawn out by the chemical action of NaOH. Besides the ammonia, the raw waters from the condensation area, contain CO_2 , H_2S , phenols, tars, pyridine bases etc. The coke gas from the cooling-condensation subsection, after the un-tarring in the electrofilters and compression in exhaust fans, having the temperature of about $45 \div 50^\circ\text{C}$ is conducted towards the saturation chambers. At the exit of the saturation chamber the gas is passing through drops captivator to retain the carried solution (lye) drops. The coke gas with a content of $\sim 0,03 \text{ g/Nm}^3_{\text{ammonia}}$ is conducted towards the final coolers and the benzene washers. The main phases in the process of obtaining the ammonia sulphate are:

- the ammonia catching by coke gas barbotage in a solution of about $4 \div 8\% \text{ H}_2\text{SO}_4$. By the reaction of the sulfuric acid with the ammonia from the gas, ammonia sulphate crystals are formed that are evacuated from the back side of the saturation chamber;
- the ammonia sulphate crystals separation from the acid solution by settling in the salt reservoir and by centrifuging in centrifuges with strainers;
- the ammonia sulphate drying by hot blow in a salt dryer;

- the ammonia sulphate transport and storage;
- the neutralization with concentrated ammonia water of acid tar separated from the separator.

To obtain the concentrated ammonia water, the raw ammonia water is taken over and passed through rubble filters to obtain the tar at a content of $30 \div 50 \text{ mg/l}$. After the filtration, the raw ammonia water is preheated with steam up to 80°C in pre-heaters, from which is conducted in the distillation columns. After the cooling in the dephlegmator of the water – ammonia vapors at $35 \div 40^\circ\text{C}$ mixing, concentrated ammonia water is obtained as finite product and waste water that is continuously sent to the stripping installation in order to reduce the contaminants (fixed ammonia). Due to cooling and water vapors condensation, the ammonia concentration from vapors is rising from $6 \div 8\%$ to $18 \div 20\%$. The stripping installation has in endowment two columns that can take over the resulted waste ammonia waters from the process. By NaOH proportioning (sol. $8 \div 10\%$) and maintaining the $\text{pH}=11$, the fixed ammonia salts (NH_4SCN , NH_4Cl and $(\text{NH}_4)_2\text{S}_2\text{O}_3$) are transformed in the volatile ammonia salts: $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{S}$, NH_4HCO_3 , NH_4CN .

c₃) the Benzene subsection. After the ammonia catching in the settling chambers, the coke gas is passed in the Benzene subsection for benzene hydrocarbons to be collected. Because the gas leaves the settling chambers with a temperature of $50 \div 55^\circ\text{C}$, its cooling is necessary before entering the benzene washers. The gas cooling takes place in the final cooler where by re-circulated water sprinkling the gas is cooled down to $20 \div 30^\circ\text{C}$. In the final cooler, by cold water contact, from the gas is also separated the naphthalene which, together with the water is drained in the inferior part of the final cooler. For the naphthalene absorption the heavy tar is introduced, pumped from the cooling-condensation subsection. The tar in which the naphthalene was absorbed is draining through the superabundance regulator in the tar reservoirs from where is re-circulated in the cooling-condensing subsection. The cooling water, naphthalene purified are settling in the vertical settler and then are re-circulated at the water Household where are cooled in the cooling towers with forced ventilation. The coke gas cooled at $\sim 25^\circ\text{C}$ containing $\sim 30 \div 34 \text{ g}_{\text{benzene}}/\text{Nm}_{\text{gas}}$, enters the washers mounted in range and provided with ceramic filling.

d) The tar processing section is formed of following installations: oils and tar storage, tar distillation, coal-tar thermal treatment, raw naphthalene obtaining, rectified naphthalene obtaining; biochemical purification. The tar is received from the chemical Section in the tar and oil storage where is heated, homogenized and dehydrated



for distillation purposes. For the tar heating at 80 ÷ 85°C there is introduced steam of 4,5÷6 atm in the reservoir's serpentines, where also is taking place its settling. By settling is separated the ammonia water that is sent in the Chemical Section. The main activities that are developed in the tar distillation installation are:

- the tar storage in reservoirs;
- the tar heating in the first heating step of the tubular oven;
- the tar heating in the evaporator – first step and its dehydration;
- the tar heating in the second step of the tubular oven;
- the tar heating in the evaporator – second step;
- vapors heating and separation in the tar distillation column;
- cooling of the obtained fractions.

The tar fractioned distillation consists in separation on the basis of inequalities between boiling temperatures of fractions: easy, phenolic, naphthalenic, absorption, anthracene I and II.

3. Experimentations

3.1. Settling the noxa testing areas

There were taken gas samples and powders from the next areas: The Coking Section, The Chemical Section and The Tar Preparation Section. During the experimentations period there were also registered the main meteorological parameters that counted for the analyses results interpretation. For choosing the points of sampling it was taken into consideration: knowing all the polluting sources and the main climate characteristics in the area. The three activity sectors specific polluting sources are determining the noxa accumulation that is emitted simultaneously. The diversity of emitted pollutants and of their concentrations, determines the liberation in the atmosphere of a mix noxa complex. The meteorological factors influence the auto-purifying processes through air temperature, humidity, precipitations, air currents and radiations. Regarding the air temperature, the density changes have neglecting influence, very important being the thermal gradient. Depending on the area where the pollutant is emitted and the temperature, there are situations where along with the temperature diminution a pollutants dilution takes place, because the ascendant currents that push them towards higher altitudes. The temperature inequalities are frequent in the periods with unstable weather (fall, the winter beginning, and the spring beginning). The air raised humidity blocks generally the noxa diffusion and so the dilution of pollutants in the air, and the suspensions constitutes condensing cores that favors the fog apparition.

The fog represents one of the meteorological conditions most aversive to the air purifying, by reducing the diffusion capacity and by favoring the dissolution of the pollutants soluble in the water that can confer it toxic properties. The precipitations, favors the atmospheric pollutants deposition on the soil and plays an important purifier role. In exchange the water from precipitations can modify its natural properties due to some pollutants dissolution; a phenomenon meets also at appreciable distances from their emission place.

3.2. Sampling

For air sampling the apparatus and the reagents provided in the working methodology specific for the determination of each type of pollutant have been used. When the sampling period was established, it was pursued the obtaining of information on pollutants high concentrations on a short period of time (30 minutes). At gases determination, parallel with the sampling device was prepared an identical device, without sampling air through it that represented the blank test. To ensure the total retention of the gas that will be gathered there were used two gathering devices linked in succession. The results referred to the entire absorption liquid quantity. The gathered air volume was established based on the supposed concentration of the pollutant from the air and on the sensibility of the method. After air sampling, the devices were transported to the laboratory in appropriate conditions, so as the samples would not undergo changes during the transportation.

The experimentations took place in two stages: in spring – S₁ (15 April - 15 May) and in summer – S₂ (15 July - 15 August). For the three sections the determined pollutants by standardized methods were:

- At the Coking Section (CS): ammonia, sulfur dioxide, carbon monoxide, nitrogen dioxide, sulfured hydrogen, aromatic hydrocarbons (AH), aromatic poly-cyclic hydrocarbons (APH), sedimentary and in suspension powders.
- At the Chemical Section (ChS): ammonia, sulfur dioxide, carbon monoxide, nitrogen dioxide, AH;
- At the Tar Preparation Section (TPS): carbon monoxide, AH, APH.

In the spring season (S₁), wind medium speed was included between 1 and 8 m/s, the daily maximum temperature was included between 11 and 25 °C, and the wind blew preponderant from the SSW and ESE. In the summer season (S₂), the wind speed was included between 0 and 9 m/s, the maximum daily temperature of the air was included between 27,5 and 36,2 °C, and at the soil level, was included between 47.8 and 60,8°C. The medium daily humidity was included between 39 and 50 %, and the wind blew with maximum speed from the N and NNW direction.



Table 1. The results centralizing of medium analyses made during the experiments

Sampling area	Period	Pollutant, [mg/m ³ _{air}]								
		NH ₃	SO ₂	CO	NO ₂	H ₂ S	AH	APH	Sedimentary powders	Suspended powders
CS	S ₁	0,327	0,18	17,72	0,017	0,014	0,416	0,198	12,53**	1,098
	S ₂	0,607	0,53	19,38	0,022	0,028	0,625	0,33 1,012*	15,16	1,167
ChS	S ₁	0,924	0,221	11,59	0,0043	-	1,52	-	-	-
	S ₂	1,664	0,274	14,47	0,0053	-	1,79	0,098	-	-
TPS	S ₁	-	-	6,57	-	-	0,131	0,201 0,616*	-	-
	S ₂	-	-	7,01	-	-	0,160	0,260 0,797*	-	-

The blank spaces indicate that those analyses were not made.

* 3,4 benzopyrene, in µg/m³_{air}; ** in g/m²_{month}

Because the air samplings were made in different temperature conditions, it was made the air volume correction for normal conditions with the next formula:

$$V_0 = V \cdot 273 \cdot p / (273 + t) \cdot 760$$

where: V₀ – the air volume in liters, at the air standard temperature and pressure;

V – the air volume in liters, at the temperature and pressure at the sampling moment;

p – the atmospheric pressure at the sampling moment;

t – the air temperature at the sampling moment.

The results centralizing of medium analyses made during the experiments are presented in table 1.

3.3. Results interpretation

The results of analyses made on the air samples taken in the industrial experimentations, proved that in a coke-chemical plant is emitted considerable quantities of pollutants that can exceed the maximum

- acceptable concentrations (MAC).

These exceeds are on the one hand due to different meteorological conditions (wind speed and direction, the temperature, the humidity etc), and on the other hand due to the technological factors involved in the coking process (the coking batteries loading regularity reflected by the coking time and also by the chemical characteristics of the charge).

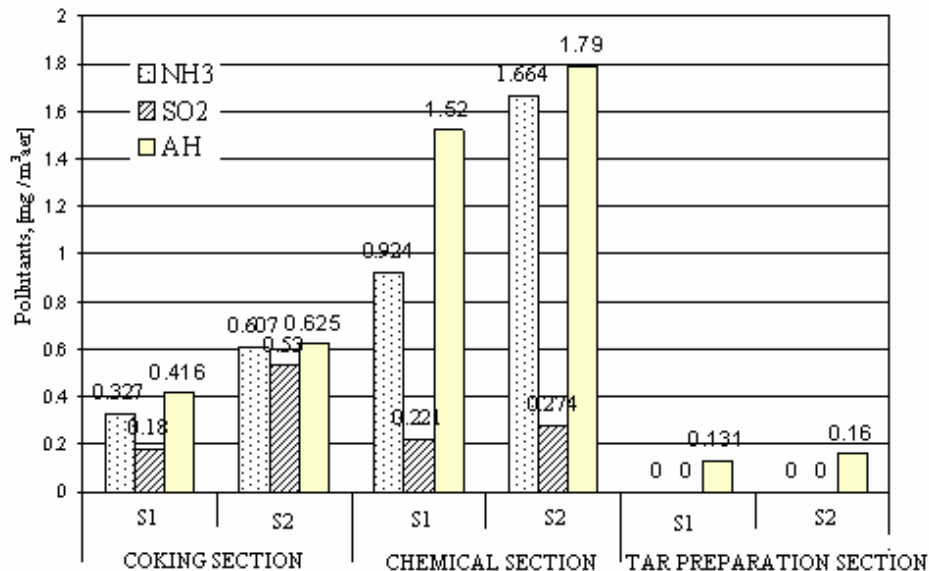


Fig. 1. The NH₃, SO₂ and AH noxa variation, in the spring and in the summer, respectively in the Coking Section, the Chemical Section and the Tar Preparation Section

Generally, in all the plant's sections, were registered low concentrations of the pollutants in the spring season in comparison with the summer season:

- In the Coking Section were surpassed the MAC values for: ammonia (in both seasons), carbon monoxide (in both seasons), sulfured hydrogen (in the

summer season), and also for the suspended powders (in both seasons), figures 2 - 4;

- In the Chemical Section, the performed analyses indicated values that exceeded the MAC values, except for the concentrations of SO₂ and NO₂, figures 1 - 4;

- In the TPS, were registered medium values of CO concentrations, close to the maximum admissible concentrations, for the two seasons' samplings, figure 3.

Because the coke-chemical industry is classically associated with the exposure to aromatic

poly-cyclic hydrocarbons (APH), starting from the coal coking and ending with tars and coal tars processing, the performed actions demonstrated their presence in the three sections.

There have been observed that the concentration level for APH from the Coking Section is higher than in the other sections due to high temperatures registered in the batteries zone, figure 2.

The settling and in suspension powders have visibly passed the maximum acceptable values in both sampling periods, figure 4.

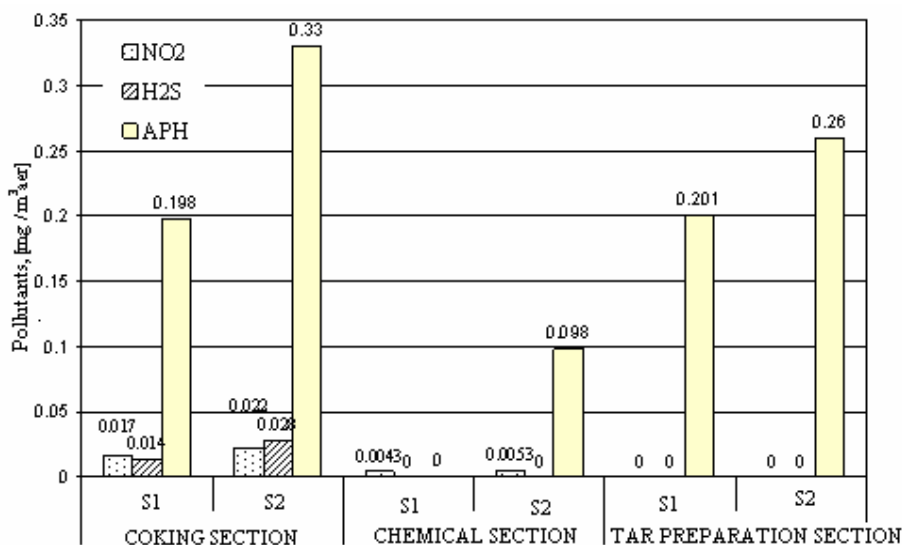


Fig. 2. The NO₂, H₂S and APH noxa variation, in spring and in summer respectively in Coking Section, Chemical Section and Tar Preparation Section

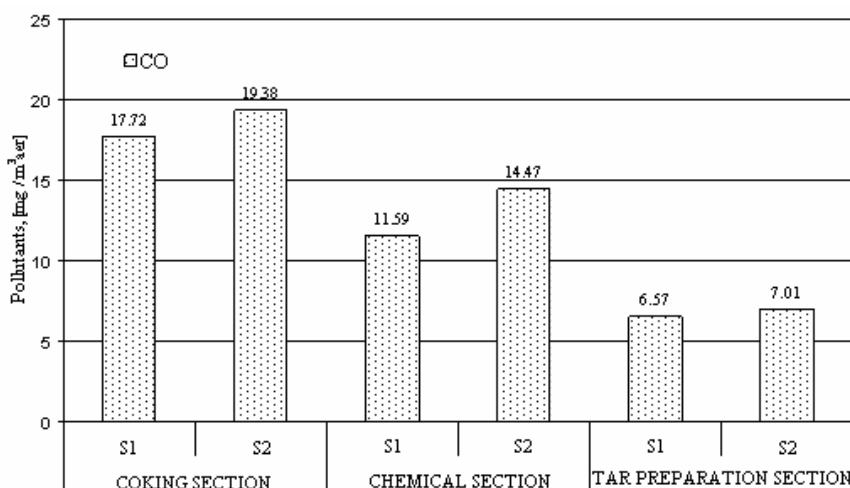


Fig. 3. The CO variation, in spring and in summer, respectively in Coking Section, Chemical Section and Tar Preparation Section

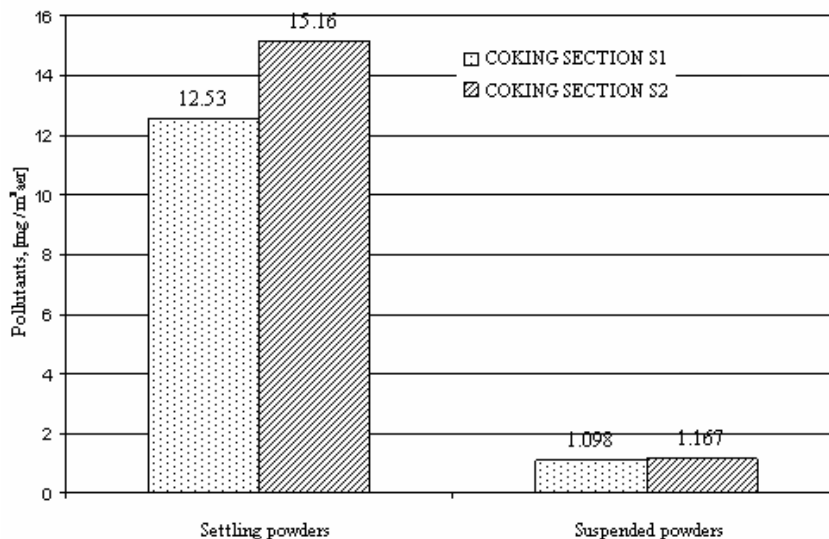


Fig. 4. Quantity variation of settling powders, in the spring and in the summer in the Coking Section

4. Conclusions

There have been established for each section, the specific pollutants taking into consideration the concentrations level and the representative noxa type.

According to the season, some particular pollutants were present in the air in different concentrations, contributing to this mostly the meteorological conditions but also the technological parameters of installations functioning.

Between the analyzed pollutants, the NH₃ determined in the Chemical Section atmosphere has averagely surpassed the maximum admitted value (0,3 mg/m³), of about 5 times, CO has been the pollutant whose concentration has surpassed the maximum admitted limit (6mg/m³) of about 3,5 times. The suspended powders determined in the no. 3 coking-battery area have surpassed the MAC (0,5 mg/m³) about 2 times. Beside these, there have been pollutants of whose concentrations have been with

in the maximum limits (NO₂, SO₂, H₂S, settling powders), but through their cumulative effect the professional illness risk is increased.

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