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IDENTIFICATION OF POLLUTION SOURCES AND TYPES OF POLLUTANTS IN AN ECONOMIC AGENT PRODUCING REFRACTORY MATERIALS

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Abstract: The effects of industrial activity in the refractory products sector on the environment can be estimated depending on the pollutant emissions, pollutants that affect in various ways the quality of the environmental factors. The recoverable products resulting from the activity of these companies are accompanied by emissions that are presented in solid, liquid and gaseous form. In this paper the authors present the sources of pollution and the type of pollutants emitted by an economic agent producing refractory materials. In order to maintain the confidentiality of the data, the name of the commercial company to which this study was made is used generically by S.C. Refractare S.A. Romania. The work was drawn up on the basis of the documentation made on the spot, with the agreement of the management of the respective company, of the observations made in the field, based on the technological data made available by the management of the company and based on the determinations of pollutants discharged into the environment.
Keywords: refractory materials, industrial waste, air pollution, water pollution, ground pollution, noise pollution

1. INTRODUCTION

The effects of industrial activity in the refractory products sector on the environment can be estimated according to the pollutant emissions, pollutants that affect in various ways the quality of the environmental factors [1]. The recoverable products resulting from the activity of these companies are accompanied by emissions that are presented in solid, liquid and gaseous form. The reduction and / or elimination of these emissions is imposed by the continuation of the productive processes, the solution practiced at present being the evacuation in the environment of large quantities of pollutants and large quantities of raw materials [2].

Within the analysed company the entire range of sorts–type–dimensions of construction bricks provided in the Romanian standards is manufactured:

The methods of manufacture of building bricks are the manufacture of construction bricks by the semi–dry pressing method and the manufacture of bricks and ceramic blocks by the wet method. The semi–dry pressing method is performed on one of the refractory bricks manufacturing lines. The raw material, the red argil, is prepared on the same flow as the refractory argil.

Forming of construction bricks is carried out on mechanical presses of type SM, using their associated manufacturing line. The combustion is also carried out on the tunnel furnace no. 1 at temperatures between 1130–1190^{0}C.

The manufacture of bricks and ceramic blocks by the wet method is carried out on an independent flow. It consists of springs of raw materials where they are brought with the help of auto means argil, sawdust, prepared waste (red chamotte). From the bunker the raw materials are extracted, volumetric dosed and transported with the help of a conveyor belt to a crushing, where the crushing, wetting and homogenization of the mixture takes place. The products are shaped using the snail press.

ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665

The combustion is done in the tunnel furnace no. 1 at the temperature of the semi–dry pressing method 900–1100°C, depending on the network, format and the thrust rate.
The unloading, sorting, storage and shipping of the products is done in the covered warehouse, located in the continuation of the sorting dump. The activity in this company is carried out on one exchange (8 h/day), or two shifts/day depending on the production requirement, five days/week, 280 days/year.
The raw materials used were Butan gray argil, Groza sort I argil, Groza sort II argil, red argil, refractory waste, red waste, sand, varnish, hardener, micronized argil, feldspar, sawdust, calcined diatomite and sodium silicate. The annual consumption of raw materials was about 58000 tons.
The range of products made using the presented raw materials and the current technologies included refractory bricks, silico – alumina, red brick, antacid tiles, ceramic blocks, laminated sand, thermal insulation plates and ingots for the classic steel casting. The annual production was about 38,500 tons. The annual consumption of utilities for this production were 5,406,682 kWh electricity, 4,378.1 t gas, 484,220 m3 drinking water, 156,780 m3 industrial water, 110,423 l diesel and 680.2 l gasoline.

2. EXPERIMENTS

— Air pollution analysis

On the preparation flow, considering that, generally, the moisture with which the argil is supplied is quite high, the pollution with argil powders starts from the drying operation. After drying, the transport equipment, elevators and belts, as well as the granulation machines (the 4 disintegrators) are the sources of dust pollution. The argil and chamotte milling sector, through the equipment it contains (mills, impact mills, granulators, vibrating sieves, transport equipment, etc.) and which are connected to the dusting installations in operation, is an important source of pollution. Emissions emitted into the atmosphere are CO_2, CO, NO_x, SO_2 powders.
Within the waste recovery stream, the material being dry, starting from the unloading ramp and until the silage of all the obtained fractions, noxious powders are produced in the form of silico–alumina wastes, especially when grinding and sifting.
In the tower of the trimming sector, the sources of dust pollution represent the dosing, transport (equipment), mixers, disk dossers and homogenizers. After making the trimming mixture with 14–18% humidity for trimming by plastic process and 6–8% humidity for trimming by semi–dry process, the powders released in the atmosphere are reduced.
In the dressing room, next to powders, the possible noxious ones are also those resulting from the manoeuvres of the forklifts, respectively the exhaust gases.
Drying and burning are carried out in eight tunnel dryers and two tunnel kilns with included dryers that run on clean fuel. The emissions are CO_2, CO, NO_2, SO_2 and powders that are taken up by the ventilation system and discharged into the atmosphere.
On the manufacturing flow of construction bricks from storage of raw materials to drying the noxious are:

» Powders of raw materials in small quantity, considering that the argil enters the wet state;
» The gases resulted in the drying process – CO_2, CO, NO_2, SO_2.

The evaluation of the emission potential at sources was made in accordance with the provisions of MAPPM Order no. 462/1993 comprising "Technical conditions regarding the protection of the atmosphere", "Methodological norm regarding the determination of pollutant emissions into the atmosphere, produced from stationary sources" and Order MMGA 592/2002 regarding the establishment of limit values, threshold values and criteria and methods evaluation [3, 4,5].
According to Order 462/1993, annex 2, for the pollutants from the atmosphere resulting in the burning process of the used fuel (fuel) and for the substances in the form of gases and vapours, the following limit values are issued. Pollutants resulting from the combustion process in outbreaks fuelled with liquid fuel are presented in table 1.

Table 1. Pollutants resulting in the combustion process of liquid fuels

No. crt	Type of emission	Maximum emission limit values in mg/m³	
1	Combustion gas powders	50 *	
2	CO	170 *	
3	NO_2	450 *	
4	SO_2	* 1700	P termic < 100 and 100–300 kV/t
		* 400	P termic > 500 and 100–500 kV/t

* The limit values refer to an oxygen content of the gas effluents of 3% volume

As regards total powders, if the mass flow rate is greater than 0.5 kg/h, the emissions in the form of powders for all categories of pollutants should not exceed 50 mg/m3.
The maximum permissible quantity of sedimentary powders (STAS 12574/87) is 17 g/m2/month.
In table 2 are given the limit values according to Order 592/2002, with which the values obtained by dispersion calculations and by measurements at fixed points (immission) will be compared, in order to establish the impact produced on the environment, by the noxiousness within the analysed company.

Table 2. Limit values of pollutants according to Order 592/2002, in mg / m³

Emission	Alert threshold	Hourly Value limit	Alert threshold		Val. limitt daily	Margin of tolerance	Alert threshold		Val. limitt annual	Alert threshold	
			Sup.	Inf.			Sup.	Inf.		Sup.	Inf .
NO_X	0.40	0.20	0.1	0.1	–	–	–	–	0.04	0.03	0.026
SO_2	0.50	0.35	–	–	0.125	–	0.07	0.05	0.02	–	–
Suspended powders	–	–	–	–	0.05	0.025	0.03	0.02	0.04	0.01	0.01

— Emission measurement

Considering the technological process and investigating the directed and undirected emission sources, it turns out that the most important noxious are those that affect the air, namely the flue gases and powders.
In order to estimate the level of air pollution generated by the production activity in the sections and production workshops of the company, measurements were made at the emission and emission sources in the potentially affected areas.
The following steps were taken when taking the air samples:

» Coding of sampling points,
» Identification of sampling points in the field,
» Sampling, according to order 462/93 and 592/2002.

The measurements for the powders in suspension were made with a four–channel sampler, P491 – manufactured by CAST SA Bucharest, vacuum cleaner provided with a pump with flow rate of 20 l / min and with the probe with a collection filter.
For the determination of the powders in suspension (see STAS 10813/76 and Ord.462/93), the method involves the initial gravimetric measurement of the paper filter used for the sampling of an air volume with an established flow rate, the final gravimetric measurement of the filter and the calculation of the suspension concentration in the air.
For the sampling of gases, an absorber vessel fitted with the absorbent substance corresponding to the observed polluting substance is attached to the pump. The determination is then made using a gas chromatographic spectrophotometer. The measurements for the combustion gases were made with a portable flue gas analyzer type: COMBILYZER RGT – 03 manufactured by the company AFRISO, with digital display and built–in printer.
In the case of emission sources, the pollutants were harvested under isokinetic conditions, and the harvesting periods were chosen so as to correspond to the periods when the emissions are high.

Table 3. The emission sources of the powders and the related concentrations in mg / m³

Source	Source name	Emission	Conc. measured Cm	Conc. Calculation Cc=1,10XCm
P1	Basket installation dust dedusting grinding argil	Argil powder	251,7	276,8
P2	Basket installation dust dedusting facility – old section	Argil powder and chamotte	162,5	178,7
P3	Basket installation dust dedusting facility – new section	Argil powder and chamotte	142,5	156,7
S1	Argil dryer basket	Argil powder	74	81,4
S2	Rotary oven basket	Burnt argil powder	204,5	224,9

The directed emission sources of the powders consist of the ponds of the dusting installations.
It should be mentioned that the efficiency of these installations is low due to the lack of tightness of the piping and the lack of carcasses of the machines connected to the installation or they are in a malfunctioning state. For this reason, the machines, although they are connected to dusting, are

also sources of pollution not directed. Table 3 shows the emission sources of the powders and the corresponding dust concentrations according to the measurements.

—Measurement of emissions from combustion gases

The sources controlled by the combustion gases within the company are the chimneys of the thermal units in operation. The fuel used in the company is fuel with maximum 1% sulphur (according to the specifications). The main pollutants resulting from the combustion of this type of fuel are sulphur dioxide, carbon oxide, nitrogen oxides, carbon dioxide, powders. In table 4 are presented the physical characteristics of the sources of flue gas emission and in table 5 are presented the values of the measurements made for the noises released after the combustion process, and in. The values of the immissions determined by various points are presented in table 6.

Table 4. Physical characteristics of the flue gas emission sources

Source name	Height, m	Diameter m	Volume flow, m^3/h	Fuel consumption, kg / h
Tunnel furnace	50	1,5	12,4	800
Argil dryer basket	10	0,5	2,77	50
The central heating system	30	0,5	6,01	450

Table 5. New results from burning the fuel

Source name	Emission	Measured value		Allowed value according to Ord.462/93 mg/m^3
		%	ppm	
Tunnel furnace	SO_2	1,6	4	400 – 1700
	CO		225	170
	CO_2			
	NO		21	450
	NO_X		22	450
Argil dryer basket	SO_2	0,9	3	400 – 1700
	CO		40	170
	CO_2			
	NO		16	450
	NO_X		17	450
Thermal power station	SO_2	7,8	0	400 – 1700
	CO		10	170
	CO_2			
	NO		213	
	NO_X		220	450

Table 6. Analysis of measured immissions

Sampling place	The determined parameter	Concentration mg/m^3	Permissible concentration mg/m^3	Index of exceedance
Hall mill with impact	powder	8,8–12,0	50	–
Vibrating site	powder	12,6–18,2	50	–
From exhaust basket 1	powder	198,0–198,8	50	3,96–3,97
From exhaust basket 2	powder	220–252	50	4,4–5,04

—Water pollution analysis

The residual waters resulting from the analysed company are the pluvial–industrial waters and the domestic waters.

The pluvial waters consisting of drains collected at different points of the company as well as the used industrial waters from the garage–workshop, mixing–press workshop, locomotive draw, are evacuated by the pluvial sewerage in the drainage channel of the hydroelectric power station that serves the company.

There are two types of waters that are poured into the pluvial sewage industrial wastewater and drainage. The domestic waters are the waters resulting from the respective sanitary groups: mechanical workshop, laboratory, AMC workshop, administrative offices, canteen, and club.

The main sources of water pollution can be mentioned:

- The station for unloading and storing the fuel tank, where the fuel tank extends from the tank cars, the unloading system and the fuel tanks;
- The delivery of locomotives, where they can reach by washing and maintaining the diesel locomotive, oil products in the water;
- Car wash ramp where oil products can also reach the water;
- The waters from the sanitary groups.

Table 7. Average values of water pollution indicators

Parameter	mg/l	Kg/day
ph	7,15	–
Total suspensions	25,723	3,287
Fixed residue	248,855	32,532
CCOMn	14,210	1,866
CBO5	6,845	0,896
NH4 +	1,767	0,22
Extractive substance	1,67	0,217

From the activities carried out at the analysed economic agent it results a pollution of the evacuated waters not very important. The average results of the analyses performed are presented in table 7. In this paper, the results of the analyses of the water samples taken at the exit of the treatment station and at the rainfall discharge were considered. The water analyses were performed both within the company's own laboratory and at the Environmental Hygiene Laboratory within the Sanitary Police Inspectorate. The activity of the company does not essentially influence the environmental–water factor [6, 7].

The quality of the discharged waters is monitored daily by the company and periodically by the Sanitary Police Inspectorate, taking immediate measures whenever the observed parameters are exceeded. The confirmatory minutes indicate the registration of the quality of the evacuated water within the limits imposed by the Water Management Authorization no. 74 / 22.11.2018.

From the findings, it turns out that the waters evacuated by the economic agent do not have a negative influence on the surface waters, almost all the indicators measured falling within the limits imposed by the Water Management Authorization and within the limits imposed according to STAS 4706 / 88– for category III– of water.

— Ground pollution analysis

Ground is the third environmental factor that must be protected with the same attention as air and water.

The importance of ground preparation is obvious if we think that it is the main factor in providing food for humans, animals and plants. Careful monitoring of it can result in a good development of life on earth. A centimetre of ground, in thickness, is realized in tens even hundreds of years. Ground and humus can be lost, even forever, in a single year by training during strong winds, after heavy rainfall, clearing the forest, irrational use of chemicals for agriculture, etc.

The sources of risk regarding ground pollution in the area of S.C. Refractare S.A. due to the production processes carried out by them, they do not lead to significant pollution of the ground outside the scope of activity, and inside the pollutions are reduced. The storage of brick waste on unorganized spaces is the main source of ground pollution and implicitly groundwater.

Physical pollution of grounds is also determined by the accidental storage of various solid materials such as scrap iron, non–ferrous waste, rubber waste [8, 9]. Another source of ground pollution is sulphur dioxide (SO_2) present in the flue gases as a result of burning the fuel. It reaches the ground again with raindrops. Fuel leaks are found in the fuel area and at the pump house and in the fuel tank containers.

Garbage sludge is also a source of ground pollution it occupies an area of 36,270 square meters. Outside the company premises, land that is thus permanently removed from the agricultural circuit. The materials deposited on the dump are a source of pollution also for the neighbouring lands; they can be driven with ease by the wind. Of the pollutants emitted in the atmosphere and which could influence the modifications of ground indicators in the situation where the emissions would be well above the permissible limit are CO_2, SO_2 and powders. Carbon dioxide eliminated in the atmosphere is the result of burning fuels. It is not a pollutant for ground. The level of CO_2 in the ground is determined more by the microbial activity which, in turn, is determined by the quantitative presence of organic nature, temperature, humidity, nitrogen content and not lastly the presence of some pollutants.

Sulphur is another important element found in the company's industrial emissions. It is generally present in the form of SO_2 result as a result of burning the fuel. From the flue gases it can reach the ground again through the rains. The rains thus become acidic and can affect the extended vegetation, causing numerous burns on the tongue. Also, acid rain can change over time the reaction of grounds, their reaction becoming ultimately equal to that of acid rain. The sulphur content of the grounds in the studied territory is a normal one and so we can appreciate that the pollutant emissions from this company do not contribute to the quantitative increase of sulphur in the ground. Also, the ground reaction is not modified and there are no traces of burns of the leaves of plants, it can be said that the SO_2 content of the exhaust gases is not so great as to cause the formation of strong acid rain.

Powder pollution is another important element of ground pollution. The dust particles in the atmosphere are deposited on the foliage tongue of the plants, on the bark of the trees and lastly on the ground. The particles that reach the ground are maintained at the level of the litter not decomposed and will be with it the subject of subsequent mineralization by ground microorganisms.

In order to reduce pollution, in 1983 a black pine seedling (20,000 pieces) was planted around the company. No difference was found between the vegetation in the surrounding forests and the pine forest around the factory. Also, inside the company there are green spaces of various species of poplar, black pine, chestnut, lime, etc. whose vegetation status was not affected by the emissions resulting from the activity of the company.

Table 8. Types of solid wastes stored in waste dumps

The type of waste	The amount	U.M.
Ferrous waste	168,040	t
Non–ferrous waste	2,09	t
Used tires	74	pcs.
Used batteries	24	pcs.
Waste of refractory materials	496,03	t
Waste red building materials	3.772,24	t
Used oil	0,639	t
Sludge from watter treatment	10,0	t
Industrial waste from in form of debris	550,0	t

From the industrial activity carried out in the company resulted in significant quantities of waste, presented in table 8, part of them being delivered to other companies for recovery, another part being deposited on the waste dump.
After analysing the grounds and the measurements made on the grounds from the vaccination of the company, it turns out that they have not undergone any essential changes from the structural or chemical point of view.
The pollution with powders being the most important factor of the society does not affect the ground or the vegetation, affecting in time the health of people producing occupational diseases such as fibrosis and silicosis. Also, even if one does not reach occupational diseases, it affects the health by reducing the general immunity of human organisms.

— Sound pollution analysis

The main sources of noise in the society are compressors, ball mills, crushers, argil dryers, vibrating screens and presses. The level of pollution of these machines increases when not properly maintained. Noise–producing machines are mostly located inside the halls [10]. The measurements were made at the main sources of noise. The resulting data are presented in table 9.

Table 9. Results of noise pollution measurements

No. crt.	Place of measurement	UM	Equivalent acoustic level	The allowable limit cf. STAS 10.009/88
1.	Brick shaped hall	dB	96,96	90
2.	Thermal power station	dB	91,05	90
3.	Samotization section	dB	91,92	90
4.	Dryer argil	dB	91,99	90
5.	Oven source prod. insulation	dB	95,85	90
6.	Thermal insulation section – diatomite milling	dB	88,06	90
7.	Mill tower	dB	86,06	90
8.	At gate no.1	dB	65,03	65
9.	dispensary	dB	62,88	65
10.	Water station	dB	64,27	65

The determinations were made with a digital sound level meter type CDA 830, made in France, with built–in calibrator and analogy display, with the measuring range between 35–130 dB. The assessment of the classification within the permissible limits was carried out in accordance with STAS 10009/88. Ensuring optimal working conditions inside the halls, requires the revision, replacement of the carcasses of machines that produce noises that exceed the maximum limit allowed for the noise sources discussed.

3. RESULTS AND DISCUSSION

From the ones presented so far, it turns out that the water discharged from the companies producing refractory materials does not have a negative influence on the surface waters.
In order to improve the pollutant loading of the natural emissions and in accordance with the premises of the Sustainable Development, it is advisable that in this company be provided with water recycling facilities, either at the level of the whole company or locally; these being also the

recommendations provided by BATs (the Best Available Techniques) within the legislation on Industrial Pollution Control (GEO 34/2002).

The main components of the emissions that can reach the grounds in the area of influence are the sedimentable powders from the atmosphere and the storable wastes. Ground is the environmental factor that records all the consequences of pollution, presenting the smallest variable in time. The sedimentable powders reached the ground results from the economic activities of these companies, come from materials that are found in nature (argil, alumina, limestone, diatomite, etc.) and do not present a danger for the environmental ground factor.

Acid gases (SO_2, NO_2) discharged into the atmosphere as a result of the combustion processes of fuels, are deposited on the ground, by dry or wet deposition can lead to its acidity, causing disturbances of its regeneration processes, modification of the composition, release of metal ions, with negative effects on vegetation and on groundwater.

Uncontrolled storage of waste in unmanaged places can influence the quality of the environmental factor ground. Also, the deposit of waste on the ground leads to the impoverishment of the grounds and obviously to their removal from the agricultural circuit.

Industrial waste dumped on important areas is an important pollution factor, which is why, under the environmental legislation in force (GD 268/2018), all non–compliant waste deposits will have to be closed, ecological reconstruction works carried out and new ones compliant. The emitted powders are mostly (70%) large powders, with diameters of 0.1–1 mm and they are deposited in the immediate approximation of the emission places. The powders in suspension have small diameters of up to 20 microns, so we can consider that a relatively small fraction of powders with diameters between 0–0.5 mm is the powders in suspension.

4. CONCLUSIONS

The reduction and / or elimination of these emissions is required by the continuation of the productive processes, the solution practiced at present being the evacuation in the environment of large quantities of pollutants and large quantities of raw materials. The main environmental factors affected by the interaction with these emissions are air, water, ground, vegetation and of course, as well as humans, both as a result of direct pollution in the area and due to air, water and ground pollution.

The specific of the industrial activities in the branch producing refractory materials generates as the main pollutant emitted in the atmosphere powders. These powders are collected by various technological installations and only a small part is emitted in a controlled manner in the atmosphere, by means of evacuation baskets.

As a result of the determinations made, it was found that the largest amount of powders is released into the atmosphere in the sectors of milling, granulation, dosing and pressing mixture. It is found that the dusting machines did not work at the parameters designed due to the physical and moral wear.

There are also important quantities of powders that are emitted due to leaks, lack of doors, windows, due to the natural ventilation of the production halls but also due to the failure of the dusting machines.

As a result, it is necessary to execute some technical projects for the modernization of the dusting installations, of the technological flows, in order to follow the connection of all the equipment generating noxious to the capture installations.

Acknowledgment:

The work has been funded by the Operational Programme Human Capital of the Ministry of European Funds, Work–based learning systems through entrepreneur scholarships for doctoral and post–doctoral students through the financial agreement 51668/09.07.2019, SMIS code 124705.

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ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665