ECOLOGY

Research on coke production wastes of PJSC "ArcelorMittal Kryvyi Rih"

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Abstract: Coking industry is one the main pollutants due to the variety of complex operations. Beside coke it produces significant quantities of waste material or by-products every day such as coke gas, coal tar, coke oven sludge, benzene, anthracene, that are used as raw materials for medicaments, dyes, binders, antiseptics etc. In this article the main type of wastes were investigated, their chemical and physical properties. This paper outlines the recycling system on the example of the coke plant PJSC "ArcelorMittal Kryvyi Rih" and notes that some of wastes are not put in use. Therefore further development of rational utilization schemes is necessary.

Keywords: *coke plant, coal tar, coke oven gas, coke sludge, emission, wastewater, utilization*

Introduction. The importance of coke industries in Ukraine is very high and growing at a rapid pace. They are producing gas and coke on a one hand and by-products on the other. Coke plants provide other industries with different supplies such as anthracene, toluene, benzene, coal tar, benzol, ammonium sulphate, sulphuric acid and/or sulphur. These products meet requirements of technical standards and legal provisions related to the trade of goods.[14]

Coke plant PJSC "ArcelorMittal Kryvyi Rih" is a modern coke enterprise, provides a set of complex processes characterized by large-tonnage consumed raw and supported materials, continuous production, a variety of devices, a wide range of products that is inevitably linked with the formation of pollutant emissions, by-products and waste.

A brief review of publications on the subject. A problem of coke waste utilization has been investigated by many authors. In USA, Germany, Japan heated coke oven gas is captured, cooled, cleaned and recycled back into the system as energy for heating and electricity generation, replacing the need to purchase natural gas.[11] Another waste material is coal tar, a by-product of coke oven gas cleaning. A. Furman and D. Smith investigated [2] a possibility to use coal tar as a binder for coal in a preparation stage of production. SE "UKHIN" suggested[10] using coal tar as an addition to coal charge in coking process. Also there were numbers of researches [15] devoted to coal tar-based pavement sealcoats. Janusz Zielirlski wrote [16] that pitch can be used as a binder or as a base substance in insulating-seal materials for the building, road construction and machinery industries.

The goal. By studying the environmental documentation and laboratory research, to identify the main waste at coke plant PJSC "ArcelorMittal Kryvyi Rih". Set the extent of involvement of these wastes in resource use in the production of marketable products or recycling (back to the coking processes). Determine the wastes that cannot find their application in the enterprise to be able to further develop their rational utilization schemes.

Materials and methods. The following characterization methods were used for: coke oven gas – TU U (UA Specifications) 322-00190443-101-99, coal tar – TU U 322-001900443-100-97, coal tar pitch - Toxicological-Hygienic passport "Coal tar pitch of sulphate section", polymers – TU U 322-00190443-093-2000 and GOST (Ukraine National Standards) 12.1.007, coke oven sludge – Toxicological-Hygienic passport "Coke oven sludge", TU U 10.1-00190443-032 "Coal charge for coking PJSC "ArcelorMittal Kryvyi Rih", M 319- KH-04 Selection technique of technological samples, SanPiN (sanitary rules and norms) 2.2.7.029 Hygienic requirements for industrial waste management and determination of their class of danger to human health, TR (Technical Regulation) TR 228-KH-01-2013, TR 228-KH-02-2014, TR 228-KH-03-2014, TR 228-KH-04-2014.

Results and discussion. Today, on the coke plant PJSC "ArcelorMittal Kryvyi Rih" coke is produced by one method - high-temperature pyrolysis of coal charge in a coke oven. Cleaning, processing and use of the resulting coke oven gas as an energy fuel is carried out in a single continuous process cycle of coke production, consisting of separate sequential processes, the distinguishing feature of which is the great value of the mass transfer rate and the flow of coke oven gas. This entire process is accompanied by formation of large amounts of polluting emissions and toxic wastes.

Air Emissions

According to the latest inventory of emissions, the plant has 171 stationary sources of emissions from the main and auxiliary facilities. According to its results, taking into account the design of coke production in 2013, the amount of pollutants emitted into the atmosphere was 6509.71 tons of primary and secondary production. The list of main pollutants and their contribution to the total emissions of PJSC "ArcelorMittal Kryvyi Rih" is shown in Table. 1.

Typical emission sources considering the the features of the coke oven can be seen on Fig. 1. There are two type of emission sources directed and fugitive. Fugitive emissions passing through leaks at the closed openings of the coke oven (charging hole lids, doors, and offtakes) and could be caused by non-captured emissions during coal charging and coke pushing. These emissions can not be avoided completely, also when considering closure facilities according state of the art in technology and being under best state of maintenance.[7]

Wastewater Cleaning

The wastewater produced during the carbonization and classification of fuel consists of three basic types:

– Water used for quenching the coke discharged from the ovens;
– Waste formed during cooling and washing the gas;
– Waste formed during the purification of by-products.

Design capacity for the wastewater that will be biochemical cleaned, including rain and drainage water will be – 470 m^3/h. The actual capacity is – 158.4 m^3/h also:

Table 1. Emissions of main pollutants of coke plant PJSC "ArcelorMittal Kryvyi Rih"

Pollutant	Emissions, t/year	Contribution to total emissions, %	Emission factor, gram/t	Emissions, t/year	Contribution to total emissions, %	Emission factor, gram/t
	2009			2014		
Carbon dioxide	1567,71	17,3	811,3	1789,41	28,7	891,7
Sulfur dioxide	4320,80	53	2302,1	2780,17	38,2	891,3
Nitrogen oxide	1601,14	21,6	871,2	1934,4	32.4	812.21
Hydrogen sulphide	34,12	0,45	19,4	25,12	0,28	8,45
Sulfuric acid	6,26	0,078	3,8	4,56	0,089	2,1
Carbon disulfide	4,81	0,07	2,5	1,91	0,035	0,83
substance in the form of suspended solids	561,8	7,9	294,2	582,67	9,89	254,2
Toluene	7,28	0,095	4,5	5,87	0,084	2,5
Naphthalene	68,91	0,94	39,12	34,91	0,41	16,5
Phenol	7,14	0,08	3,31	7,81	0,17	3,4
Cyanide hydrogen	69,12	0,87	39,6	8,89	0,15	4,1
Benzene	165,3	2,12	72.5	27,82	0,42	12,61
Ammiac	159,7	2,43	63,7	83,94	1,65	38.49
Saturated hydrocarbons	6,18	0,068	3,1	3,42	0,05	1,46

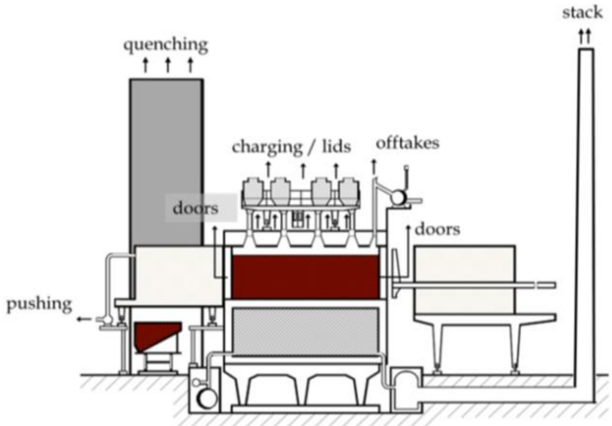

Fig. 1. Schematic drawing of emission sources at a coking plant

Table 2. Characteristics of wastewater before and after biological treatment

Pollutant	Concentration, mg/l	
	Before cleaning	After cleaning
Phenols	400	0,06
Thiocyanate	317	0,5
COD	1480	27
BOD5	700	0,15
Ammonia nitrogen	51	11
Ammonia	600	0,02
Cyanides	16,9	0,04
pH	7-9	7,6-8,0
Suspended solids	132	24,1
Pyridine compounds	110	0,12

Table 3. Comparative characteristics of waste for the main coke enterprises in Ukraine

Waste	Plant	Quantity, t/year
Coal tar	Ukrainian coke plants	435000
	PJSC "ArcelorMittal Kryvyi Rih"	28000
	Donetsk coke plant	26500
	Avdiivka Coke Plant	24000
Polymers	Ukrainian coke plants	22000
	PJSC "ArcelorMittal Kryvyi Rih"	3200
	Donetsk coke plant	2430
	Avdiivka Coke Plant	2150
Coke oven sludge	Ukrainian coke plants	100000
	PJSC "ArcelorMittal Kryvyi Rih"	14750
	Donetsk coke plant	12500
	Avdiivka Coke Plant	22000

– 66.5 m^3/h – phenolic wastewater plant desulfurization plant and carbon capture;
– 79.5 m^3/h – ammonia water;
– 3.0 m^3/h – drainage water;
– 15.6 m^3/h – protecting the rain water from of chemical plants.

After cleaning waste water is used for wet quenching of coke, refilling water return cycle. Table 2 shows the characteristics of water before and after cleaning.

Coke plant PJSC "ArcelorMittal Kryvyi Rih" has separate sewage system: phenol, household, sludge. Phenolic waste water is the most contaminated, they are formed primarily during the cooling of coke oven gas. Coke plant wastewater contains a large amount of suspended solids, high BOD, COD, phenols, ammonia and other toxic substances. They are causing serious surface water pollution problem in area. [6, 13]

Waste management

Coke production technology involves formation of following liquid toxic waste: coke oven sludge, coal tar, coal tar pitch, polymers, oils of wastewater biological treatment.[5, 12] Only in the last 4-5 years, coke plants in Ukraine have organized a partial recycling of generated waste in the chemical plants. Prior to this (for decades!) these wastes were not used. Plants collected them in designated areas - storages. The main wastes of coke plant Arcelor Mittal and comparison with other plants can be seen in table 3.

Coke oven sludge formats due to carryover of charge and semi-coke particles with coke oven gas from the coking chamber to gas collector during loading the coke oven. It is used for coking together with the coal charge, by a method that allow to utilize this waste as additive to the main raw material in amounts that are not lowering the quality of the coke. Composition of sludge:
– Charge and semi-coke particles – 50-55%;
– Coal tar – 40-45%;
– Water – 5-10%.

In 2014 year for the production of dry bulk coke *G*=2902501 tons, the charge in dry weight is needed in the amount of:

$$Q_{dc} = G \cdot Q_{cdc} = 2902501 \cdot 1{,}291 = 3747128\ t \qquad (1)$$

Q_{cdc} – dry charge consumption per 1 ton of dry coke.

When coking this amount of coal charge per year, the amount of coke oven sludge is formed:

$$Q_{csr} = Q_{dc} \cdot 0{,}02 \div 1000 = 3747128 \cdot 0{,}002 = 749\ t \quad (2)$$

Depending of carryover of coke dust and soot the amount of coke oven sludge is formed:

$$Q_{csd} = 2902501 \cdot 0{,}0025 = 7256\ t \quad (3)$$

Coke oven sludge is formed during cleaning of tanks for transportation of coal tar and crude benzene. According to the results of inspection the average data on the accumulation of sediment in tanks for the transportation of coal tar

Total amount of coke oven sludge in by-product recovery plant is formed:

$$Q_{cst} = 7494 + 7256 = 14750\ t \quad (4)$$

After that coke oven sludge is sent to the recycling by dosing it in small amount to the charge.

One important product of coal pyrolysis is coal tar. Coal tar can be utilized as raw materials for different industries such as medication, synthetic fiber, coating, dyestuff. It is also a type of raw materials from which phenols, anthracene and naphthalene can be extracted for the production of cement binders, washing oil, antiseptics, and catalytic hydrogenated to produce gasoline, diesel oil, etc.[1, 9] The weight percentage of tar fractions is shown in Table 4.

Table 4. Fraction of coal tar

Group	Percentage (%)
Aliphatics	19,81
Aromatics	29,41
Polar	6,82
Asphaltene	35,22
Ester	5,94

Amount of utilized coal tar in dry weight, tons:

$$G_{ct} = Q_p + Q_{ctc} \quad (5)$$

Q_p – amount of saturated hydrocarbons that are polymerized, t;

Q_{ctc} – amount of coal tar that is condensed in absorbers.

$$Q_p = 116466 \cdot 10^3 \cdot 0{,}000531 \cdot 0{,}410 = 25355\ t, \quad (6)$$

116466 – amount of coke oven gas (in 2014 year), km^3,

0,410 – density of coke oven gas, kg/m^3,

0,000531 – weight percentage of polymers (0,0177*0,03), that are formed in 1 m^3 of coke oven gas.

Coal tar is utilized in a plant for the production of binding construction material (TU U 322-00190443-131-98)

Coke breeze is the fine particles of coke that result from the screening of coke after being quenched. Typically, these particles will pass through a 0.5 inch or 0.25 inch screen opening. Breeze may be reused in the by-product ovens for fuel or it may be utilized by integrated iron and steel producers as a fuel source in blast furnaces for the agglomeration of iron ore. It was indicated that 100 to 200 pounds of coke breeze are recovered per ton of coal charged.[4, 8] The fraction analysis is shown in Table 5.

Table 5. Screen analysis of coke breeze

Size fraction, mm	Percentage,%
-0,25+0,125	97,54
-0,125+0,063	2,23

During the coke quenching, handling, and screening operation, coke breeze is produced. It is either reused on site (e.g., in the sinter plant) or sold off site as a by-product Solid Waste generated in Coke oven are mainly from[3]:

– Coal dust generated during coal crushing;

– Coal spillage from conveyer and chute areas.

Coke production facilities generate solid wastes as coke breeze (which averages 1 kg/t of product). Approximate amount of coke breeze on the coke plant PJSC "ArcelorMittal Kryvyi Rih" is about 18000-20000 tons per year. According to the Technical Regulation of the plant this type of wastes are storage in metal tanks.

Conclusions. There are many co-products and by-products of the coke production process. The first is coke breeze, the fine fractions that result from the crushing of coke and the second is "other coke", the coke that does not meet size requirements of steel producers. In addition, the by-product coke making process results in other waste materials such as coke-oven gas, polymers, tar and coke oven sludge. On the coke plant PJSC "ArcelorMittal Kryvyi Rih" liquid wastes and by-products (coal tar, polymers, waste production of phthalic anhydride, coke oven sludge) are fed to the charge on coking through chemical utilization plant. Solid wastes are fed into the charge through the car dumper and coal preparation plant. This scheme of waste utilization not only causes huge pollutant emissions in atmosphere but also not very profitable, considering presence of valuable materials. Also according to technical regulation TU U 322-00190443-011 coke breeze is stored in tanks and burnt in coke ovens that strongly reduce its profit for enterprise taking into account calorific value of this waste. Therefore it is important to develop new scheme of rational utilization for this type of waste considering its chemical and physical parameters.

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