DOI: 10.2429/proc.2017.11(1)002 2017;11(1)

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COKE OVEN WASTEWATER - FORMATION, TREATMENT AND UTILIZATION METHODS - A REVIEW

ŚCIEKI KOKSOWNICZE - MIEJSCA POWSTAWANIA, SPOSOBY OCZYSZCZANIA I METODY UTYLIZACJI - PRZEGLĄD LITERATURY

Abstract: Coke making process is strictly connected with formation of coke oven wastewater, highly loaded and contaminated stream, proper treatment and utilization of which requires sophisticated methods and technologies. This wastewater is defined as a mixture of technological streams, which are formed during coke oven gas cleaning and coal-derivatives production, and sanitary wastewater formed at coke oven plant. Due to the composition and specificity of contaminants present in coke oven wastewater, its proper treatment requires the involvement of physical, chemical and biological methods, which are often proceeded with additional polishing. In dependence on its further use (deposition to environment or wet quenching of coke) different types of contaminants are found to be priority substances, removal of which during the stream treatment is especially important. In the article, a literature review on coke production, coke oven wastewater formation, its parameters, applied technologies of treatment and utilization methods is presented. The special attention was given to the applied treatment techniques, which were found to be the key factor in further stream utilization. Additionally, issues related with nowadays used systems were pointed out.

Keywords: coke oven wastewater formation, coke oven wastewater characteristics, coke oven wastewater treatment, coke oven wastewater utilization

Coke production

Coke is produced by the destructive distillation of coal in coke ovens. Specially prepared coal blend comprising of various types of coals of desired coking parameters is heated in an oxygen-free atmosphere (coked) until most volatile components in the coal are removed [1-3]. The remaining material is a carbon mass called coke, and it is used in various processes, among which pig iron production of the most significant one. The branches of coke application are shown in Figure 1.

There are over 560 coke oven plants in the world (Fig. 2). Most of them (ca. 400, each with over 600,000 Mg/y capacity) are located in China. The annual worldwide production of coke in 2015 reached 716 Gg, while only for Asian coke oven plants it was 582 Gg.

Ca. 6% of total world coke production is generated in European Union. In 2015 the production capacity of EU coke producers reached 44 Gg (Fig. 3), among which above 19 Gg were generated in Germany (9.7 Gg) and Poland (9.6 Gg). Domestic market of coke production is based on 9 coke oven plants, among which Zdzieszowice coke oven plant, of annual capacity 4.2 Gg is the biggest plant in Europe, while Przyjazn coke oven plant (in Dabrowa Gornicza) is the youngest European plant [4-7].

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Contribution was presented during ECOpole'16 Conference, Zakopane, 5-8.10.2016

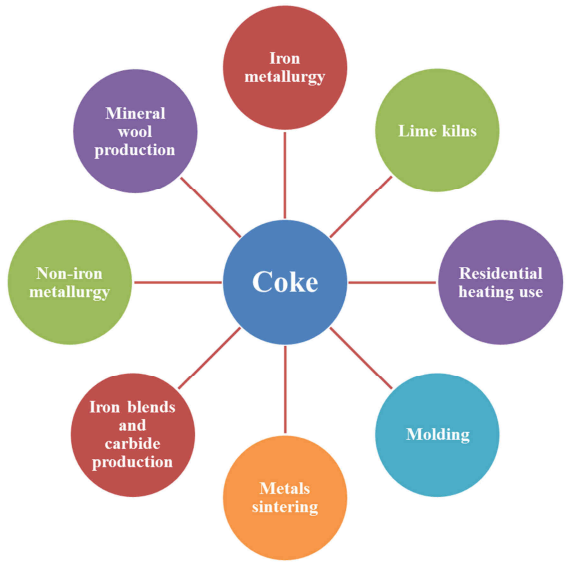

Fig. 1. Branches of coke application

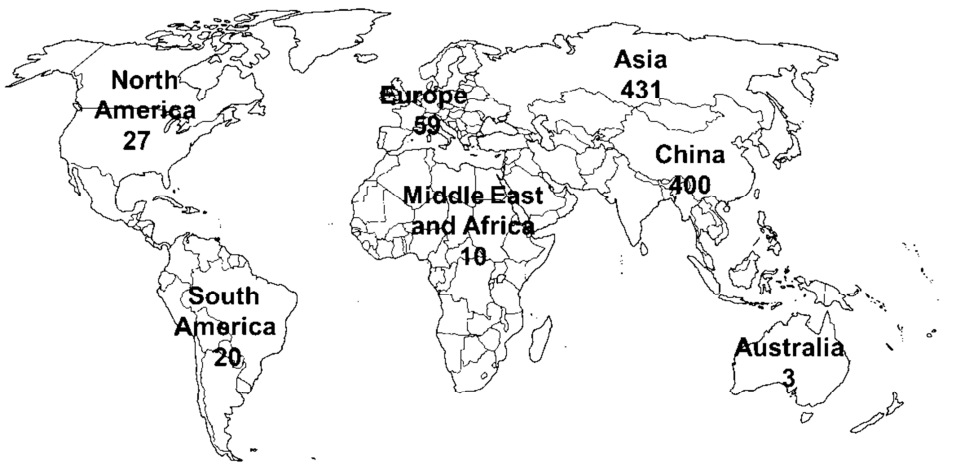

Fig. 2. Number of coke oven plants over the world

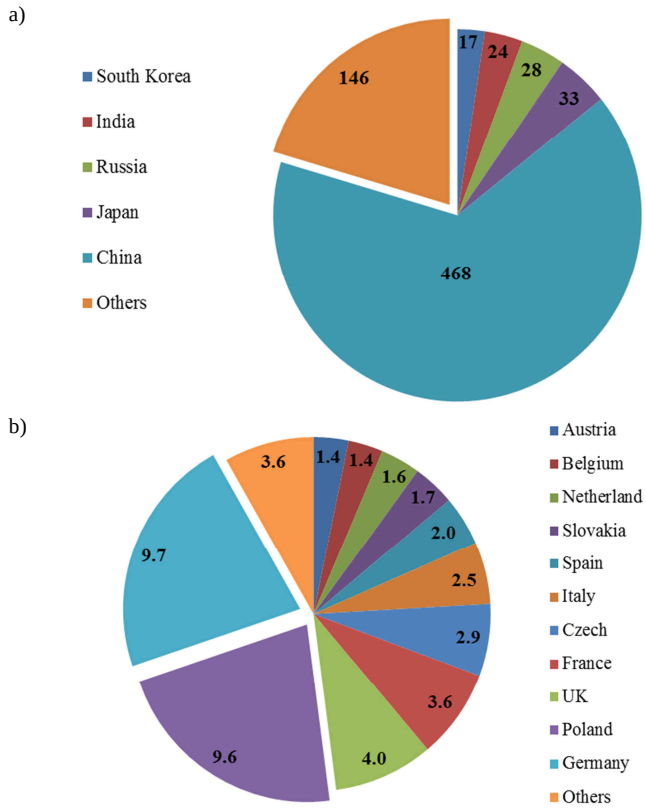

Fig. 3. World (a) and EU (b) production of coke [Gg] in selected countries in 2015

Coke oven plant operation

Coke oven plants are complex technological plants, which comprise of different technological sites, at which coal preparation, coking and coal derivatives recovery and upgrading occurs. The scheme of a coke oven plant is presented in Figure 4.

The coal-to-coke transformation starts from the transfer of heat from the heated brick walls into the coal charge. From about 375 to 475°C, the coal decomposes to form plastic layers near each wall. At about 475 to 600°C, there is a marked evolution of tars and aromatic hydrocarbon compounds, followed by re-solidification of the plastic mass into semi-coke. At 600 to 1100°C, the coke stabilization phase begins. This is characterized by contraction of coke mass, structural development of coke and final hydrogen evolution. During the plastic stage, the plastic layers move from each wall towards the centre of the oven trapping the liberated gas and creating gas pressure build up, which is transferred to the heating wall. Once the plastic layers have met at the centre of the oven, the entire mass has been carbonized. The incandescent coke mass is pushed from the oven and is wet or dry quenched, while the raw coke oven gas is collected and directed to further processing [8, 9]. During the coking process, except for coke, there is a range of other products

(coal-derivatives) also obtained, and they are mostly recovered during gas processing [10-12]. The share of particular product in the overall production cycle per 1 Mg of coal can be established at:

- coke - 70-80%
- tar - 2.5-4.5%
- pyrogenetic water - 3-5%
- ammonia - up to 0.4%
- BTX (benzene, toluene, xylene) - up to 1.3%
- clean coke oven gas - 12-18%

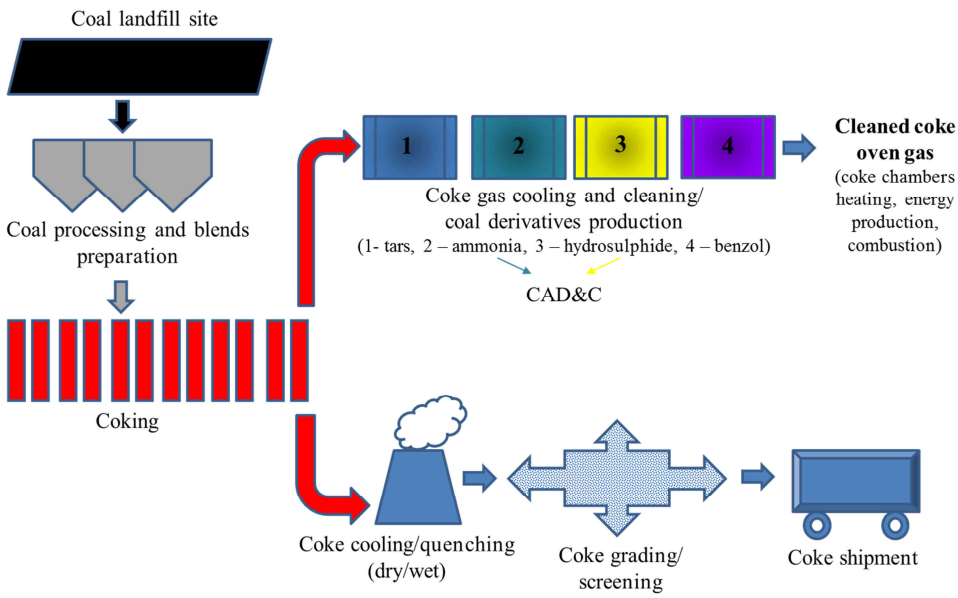

Fig. 4. The scheme of coke oven plant

Coke oven wastewater formation

The processing of coke oven gas and the recovery of coal derivatives results in the formation of highly contaminated liquor which, after separation of tars and ammonia, becomes so called coke oven wastewater. The liquor is formed at coke oven gas cooling stage (gas cooling/condensation unit), at which tars, water vapour and other substances present in the gas condensate or are partially washed out from the gas. The liquor is firstly directed to tars separation unit, at which two major streams are formed: organic stream (tars) and aqueous phase. The latter phase can be involved in further gas treatment for removal of ammonia and hydrogen sulphide by means of scrubbing. However, the amount of initially formed liquid always exceeds the requirement of scrubbing units. In such a case, over amount of liquid is directed to ammonia stripping and the remaining stream is deposited to coke oven plant [13-16]. The formation of coke oven wastewater at a plant is shown in Figure 5.

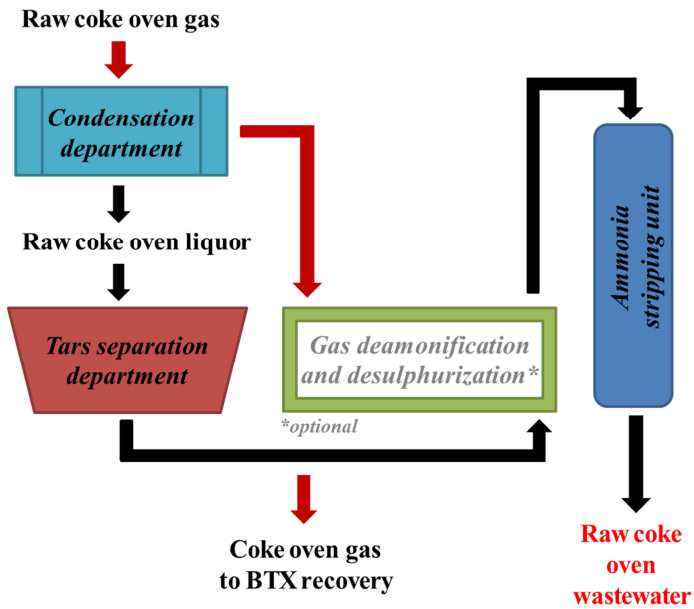

Fig. 5. The formation of coke oven wastewater at a plant

Coke oven wastewater characteristic and treatment

Wastewater produced at coke oven plants, contains toxic xenobiotics, phenols and their derivatives (pyrocatechol, quinone, pyrogallol), as well as ammonia, thiocyanates and cyanides. Typical pollutants concentration may reach up to 1200 mg/dm^3 of phenol and 20 mg/dm^3 of cyanides, respectively [17-19]. A typical composition of coke oven raw wastewaters is shown in Table 1.

Table 1

Typical composition of raw coke oven wastewater

Parameter	Unit	Concentration
pH	[-]	7-9.5
Specific conductivity	[µS/cm]	5000-12 500
COD	[mg O_2/dm^3]	2400-4200
BOD_5	[mg O_2/dm^3]	500-1500
Tars	[mg/dm^3]	5-150
Sulphides	[mg/dm^3]	10-50
Cyanides	[mg/dm^3]	5-20
Thiocyanates	[mg/dm^3]	50-420
Phenols	[mg/dm^3]	150-1200
Ammonia	[mg/dm^3]	120-790
Chlorides	[mg/dm^3]	2500-3500
Sulphates	[mg/dm^3]	900-1200

Per every Mg of coke 0.6 to 1.6 m^3 of wastewater is generated. It means that ca. $75 \cdot 10^7$ m^3 of coke oven wastewater is annually generated at worldwide coke oven plants (in Europe it is ca. $9.2 \cdot 10^7$ m^3, in Poland ca. $1 \cdot 10^7$ m^3) and it will continue to increase.

The removal of pollutants from coke oven wastewaters is a significant issue due to the environmental impact of these compounds. Especially cyanides and thiocyanates represent an important problem in wastewater treatment plants, due to their toxic properties, including reduction of enzymatic activity of unicellular organisms, such as the typical bacteria inhabiting in the activated sludge. The technological cycle of coke oven wastewater treatment is based on the conventional arrangement, i.e. physical separation of larger solids by means of grids and/or grates, chemical coagulation for removal of suspensions and precipitation of inorganic contaminants and biological nitrification/denitrification systems for ammonia and soluble (DOC) organics elimination (Fig. 6). The purified wastewater, after the treatment process, can be managed by means of its use to wet coke quenching or deposition to the environment [20-22].

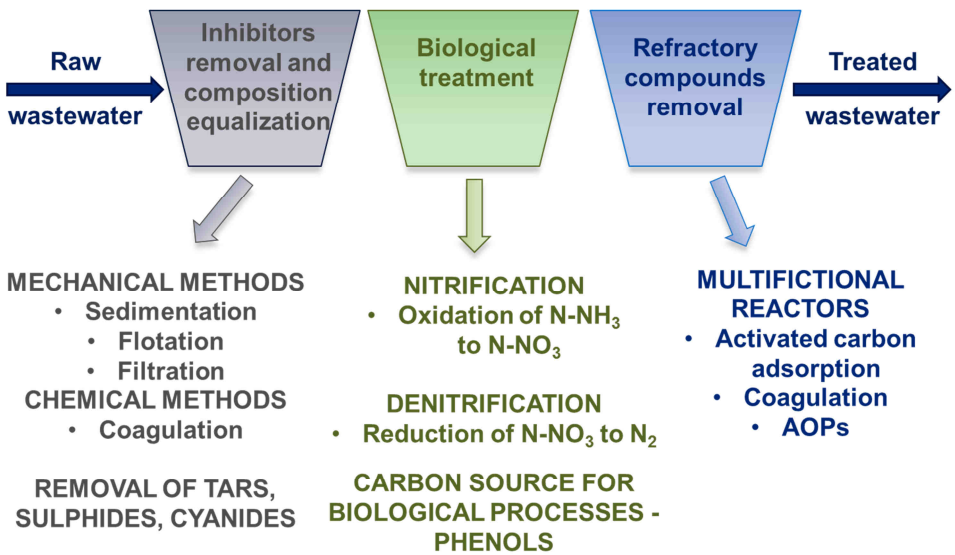

Fig. 6. The arrangement of typical coke oven wastewater treatment plant

Despite the fact, that the coke oven wastewater treatment process is the complex operation it is often not enough sufficient to remove all the contaminants present in the treated stream and to achieve the limits established in various regulations (regulations on quality of wastewater deposited to the environment, industrial wastewater standards, etc.). The most problematic treatment operation is connected with the efficient removal of cyanides. They appear in the raw wastewater as a simple CN^- ions and their removal should be obtained during chemical coagulation. However, the efficiency of traditional process is poor, especially in the case of high load of the stream with dispersed organic contaminants (tars), hence it requires the addition of high amounts of chemicals. The insufficient removal

of cyanides during chemical treatment stages is highly undesired, especially considering proceeding biological processes. Cyanides, as well as sulphides, are known to be toxic to activated sludge microorganisms, and their presence in the influent to biological treatment stage results in the inhibition of the process and its improper run. Additionally, standards on cyanides content in coke oven wastewater after treatment are very sharp and the permissible levels are usually established below 0.1 mg/dm^3 for free form of the compound and 5 mg/dm^3 for its complexes [23-25].

Chemical coagulants, which are used for dispersed tars, cyanides and sulphides removal, comprise of metal ion, which is responsible for the coagulation process performance, and inorganic ion support (usually chloride Cl^- or sulphate SO_4^{2-}). If the coke oven wastewater treatment influent contains high amount of tars, cyanides and sulphides, the efficient run of coagulation requires the addition of significant amounts of chemicals. Hence, the excess of inorganic ions, the amount of which is already quite high in the raw stream, is introduced to the wastewater. The high salinity of purified wastewater possesses many disadvantages considering further stream management methods. If the purified wastewater is dedicated to wet quenching of coke, the presence of inorganic ions, especially chlorides, may seriously affect the quality of the final product. On the other hand, the regulations on purified industrial wastewater quality, which is deposited to the environment, limit the maximum content of salts at the level of 1500 mg/dm^3 [26, 27].

The water/wastewater management of coke oven plant do not only face the efficient treatment and utilization of wastewater, but also need to assure huge amount of properly treated water dedicated to various technological purposes (heating/cooling systems, steam generators, wet gas cleaning, etc.). Hence, there exists a high demand for fresh water, which need to be in-taken either from the municipal water network or from natural sources (surface or ground water). Depending on the further destination, the water needs to be softened or completely demineralized, what requires the use of sophisticated treatment techniques and results in generation of additional waste streams (e.g. effluent from washing of ionites). The most favourable solution would be the reclamation of technological grade water from the wastewater stream [28-30].

Summary and conclusions

In the article, the worldwide coke production review, discussion on coke oven gas cleaning and coke oven wastewater formation and treatment techniques has been made. It clearly indicated a list of issues related with the proper treatment and utilization of coke oven wastewater, i.e.:

- to improve the removal of cyanides,
- to enhance the performance of biological treatment stage,
- to decrease the load of harmless substances (e.g. salts),
- to limit the need of introduction of additional unit operation,
- to enable the recovery of technological water from the purified stream,
- to apply relatively simple solutions,
- to propose modifications and supporting methods for existing techniques.

The above notes were used to formulate the main objectives of INNOWATREAT project (The innovative system for coke oven wastewater treatment and water recovery

with the use of clean technologies), the main goal of which is to develop the novel system for coke oven wastewater treatment based on clean technologies, including enhanced flotation, membrane filtration and electrocoagulation, suitable to be applied at both, future and currently operate coke oven wastewater treatment plant. The project should bring many benefits considering both, cokemaking operations and environmental protection areas.

Acknowledgements

The investigations in this paper were within INNOWATREAT project that has received funding from the Research Fund for Coal and Steel under grant agreement No 710078 and from Ministry of Science and Higher Education from financial resources on science in 2016-2019.

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Abstrakt: Proces koksowania jest nieodłącznie połączony z powstawaniem silnie zanieczyszczonych ścieków, które wymagają odpowiednich metod oczyszczania i utylizacji. Ścieki te definiuje się jako mieszaninę wód technologicznych powstających w procesie oczyszczania i produkcji produktów węglopochodnych z gazu koksowniczego oraz ścieków sanitarnych powstających na koksowni. Ze względu na skład i specyfikę zanieczyszczeń występujących w ściekach koksowniczych ich oczyszczanie wymaga zastosowania fizycznych,

chemicznych oraz biologicznych procesów, po których często stosuje się dodatkowe procesy doczyszczania. W zależności od dalszego wykorzystania (odprowadzenie do środowiska lub uzupełnianie obiegu mokrego gaszenia koksu) różne rodzaje zanieczyszczeń uznaje się jako priorytetowe dla zastosowanego systemu oczyszczania. W niniejszym artykule przedstawiono przegląd literatury dotyczącej formowania, właściwości, oczyszczania i zagospodarowania ścieków koksowniczych ze szczególnym uwzględnieniem stosowanych metod usuwania poszczególnych zanieczyszczeń oraz wskazaniem zagadnień problematycznych obserwowanych w obecnie pracujących oczyszczalniach.

Słowa kluczowe: powstawanie ścieków koksowniczych, oczyszczanie ścieków koksowniczych, charakterystyka ścieków koksowniczych, utylizacja ścieków koksowniczych