REVIEW ON FORMATION, TREATMENT
AND UTILIZATION METHODS OF COKE
OVEN WASTEWATER

POWSTAWANIE, SPOSOBY Oczyszczania
I METODY UTYLIZACJI ŚCIEKÓW KOKSOWNICZYCH

Abstract: Coke making process results in generation of highly loaded and contaminated stream called coke oven wastewater. Its proper management, treatment and utilization is found to require sophisticated methods and technologies. This wastewater comprises of a mixture of technological aqueous waste streams, which are formed during coke oven gas cleaning and coal-derivatives production, and sanitary wastewater generated at coke oven plant. Due to the composition and specificity of contaminants present in coke oven wastewater (PAHs, phenols, cyanides, thiocyanates, ammonia, etc.), its proper treatment requires the involvement of physical, chemical and biological methods, which may also be proceeded with additional polishing. In dependence on its further use (deposition to environment or sewage system, coke wet quenching loop supply) different types of contaminants are regarded as priority ones and various technological cycles are applied.

In the article, a review on worldwide, European and domestic coke production, coke oven wastewater formation, its parameters, applied technologies of treatment and utilization methods is presented. The special focus on the applied treatment techniques, which were found to be the key factor in further stream utilization, was given. Additionally, issues related with nowadays used systems were pointed out.

Keywords: coke production, coke oven gas cleaning, coke oven wastewater, treatment of coke oven wastewater

Coke production

Coke is produced by the thermal destruction of coal. For this purpose, dedicated coal blend comprising of various types of bituminous coals of desired coking parameters is heated in an anaerobic atmosphere (coked) until most volatile components in the coal are removed [1–3]. Cokemaking takes place in batteries which house 10–100 coke ovens. Coal is charged into the ovens from their top and the heat needed for coal decomposition is provided by the combustion of recycled coke oven gas, natural gas or

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other gas fuel [4]. The coking process usually lasts 16–20 hours. The carbon mass remaining after the process is called coke, and it is used in various processes, among which pig iron production is the most significant one. Over 90% of worldwide coke production is used in blast furnace process, in which coke acts as [5]:

– energy source – it is a fuel that supplies energy needed for endothermic chemical reactions and melting of metal and slag,
– chemical reagent – it is a source of gases involved in reduction of iron oxides and a source of carbon to carbonize a pig iron,
– gas-permeable bed – it is a mechanical support for feedstock materials which enables downflow of metal and slag and up flow of hot gases within the furnace.

All the branches of coke application are shown in Fig. 1.

There are over 560 coke oven plants in the world (Fig. 2). Most of them (ca. 400, each with over 600,000 Mg/yr capacity) are located in China. The annual worldwide production of coke in 2015 reached 716 Tg \( (T = 10^{12}) \), while only for Asian coke oven plants it was 582 Tg [6–10].

Approximately 6% of total world coke production is generated in Europe at 59 coke oven plants. In 2015 the production capacity of EU coke producers reached 44 Tg (Fig. 3), among which above 19 Tg were generated in Germany (9.7 Tg) and Poland (9.6 Tg) [6–10].

Domestic market of coke production is based on 9 coke oven plants equipped with 24 coke oven batteries, among which Zdziezowice coke oven plant, of annual capacity 4.2 Tg is the biggest plant in Europe, while Przyjazn coke oven plant (in Dabrowa Gornicza) is the youngest European plant. The overall maximum capacity of all domestic coke oven plants equals to ca. 10.9 Tg of coke. Most of coke produced in Poland is exported outside the country (ca. 5.7 Tg of coke produced in 2015 was...
Fig. 2. Number of coke oven plants (top) and production capacity [in Tg/year] of particular regions (left) and countries (right) over the world [6–10]

Fig. 3. Number of coke oven plants (top) and production capacity [Tg/year] of particular countries (bottom) in Europe [6–10]
exported), what places Poland in top 10 of the world coke exporters. Most of the coke oven plants is localized in Upper Silesia (6), while the remaining 3 are in Opolskie (Zdzieszowice), Lower Silesia (Walbrzych) and Lesser Poland (Krakow) Voivodships (Fig. 4). 4 coke oven plants are owned by JSW KOKS (in Dabrowa Gornicza, Zabrze, Radlin and Debiensko), 2 by ArcelorMittal (in Zdzieszowice and Krakow) and the remaining 3 are individual (Walbrzych, Czestochowa and Bytom). Polish coke oven batteries are the youngest in Europe, as the average age of national batteries is estimated at 15.4 years, while for Europe it is 24.3 years and for the world it is 25 years [6–10].

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. At coal landfill the storage of coal assuring at least 30 days production continuity is run, while at coal preparation site special blend comprised of different types of coals of various coking properties assuring the production of coke of desired quality are prepared. At coking site the thermal destruction and coal-to-coke transformation occur. The produced coke is next quenched, grade and screened and finally shipped to the various destination point, while the generated gas is directed to cleaning cycle, during which the recovery of coal-derived products (tars, benzol, ammonium sulphate, sulphur, etc.) can be run. The scheme of a coke oven plant is presented in Fig. 5.

The coal-to-coke transformation starts from the heating of coal by the energy transfer from the heated brick walls into the oven interior. At 375°C to 475°C, the coal starts to
change the structure and forms plastic layers near heat source. At about 475°C to 600°C, tars and aromatic hydrocarbon compound are evolved and the plastic mass becomes solid again forming so called semi-coke. At 600°C to 1100°C, the coke stabilization comprising of contraction of coke mass, structural development of coke and final hydrogen evolution begins. When the mass is still plasticized, the plastic layers move from each wall towards the oven center and trap the liberated gas. It leads to the gas pressure build up, which is transferred to the heating wall. Once the plastic layers meet at the oven center, the entire mass is carbonized. The hot coke mass is pushed from the oven and is directed to quenching with the use of dry or wet system, while the raw coke oven gas is collected and directed to further processing [11–13]. 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 [14–16]. The share of particular product in the overall production cycle per 1 ton of coal can be established at:

- coke – 70–80% (700–800 kg);
- tar – 2.5–4.5% (25–45 kg);
- pyrogenetic water – 3–5% (3–5 kg);
- ammonia – up to 0.4% (4 kg);
- hydrogen sulphide – up to 0.25% (2.5 kg);
- BTX – up to 1.5% (15 kg);
- clean coke oven gas – 12–18% (285–345 m³).

**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 coke oven wastewater. The liquor is formed at coke oven gas cooling stage (gas cooling/condensation unit), at which tars, water vapor 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 is partially use to provide water for the gooseneck spray equipment, while the rest can be involved in further gas treatment for removal of ammonia and hydrogen sulphide by means of absorption. The most popular methods based on absorptive removal of ammonia and hydrogen sulphide from coke oven gas are [17]:
  – ASK or Diamex;
  – Vacuum Carbonate;
  – Sulfiban;
  – Desulf.

In Europe, the most commonly applied process is the absorptive process using an ammonia liquor to scrub the \( \text{H}_2\text{S} \) from the coke oven gas (Ammoniumsulphide Kreislaufwasche (ASK) process or Diamex). Absorptive processes do not usually exceed 95% desulphurization efficiency and residual \( \text{H}_2\text{S} \) concentrations in the coke oven gas are usually around 500 mg/Nm\(^3\)COG.

The surplus amount of ammoniacal liquid, before the deposition to coke oven wastewater treatment plant, is directed to ammonia stripping. Typical levels of total ammonia in stripped liquor range from < 50 mg/dm\(^3\) to 150 mg/dm\(^3\) [17–21]. The formation of coke oven wastewater at a plant is shown in Fig. 6.

![Diagram](image_url)  
**Fig. 6.** The formation of coke oven wastewater at a plant [21]
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, cyanides, polyaromatic hydrocarbons (PAHs), oil and tars, etc. Typical pollutants concentration may reach up to 1200 mg/dm³ of phenol and 20 mg/dm³ of cyanides, respectively [22, 23]. A typical composition of raw coke oven wastewaters together in permissible concentrations of selected contaminants at coke oven wastewater treatment plant effluent deposited to environment are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration in raw stream</th>
<th>Permissible concentration in effluent*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>—</td>
<td>7–9.5</td>
<td>—</td>
</tr>
<tr>
<td>Specific conductivity</td>
<td>µS/cm</td>
<td>5000–12500</td>
<td>—</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>mg/dm³</td>
<td>30–150</td>
<td>—</td>
</tr>
<tr>
<td>COD</td>
<td>mgO₂/dm³</td>
<td>2400–4200</td>
<td>&lt;220</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mgO₂/dm³</td>
<td>500–1500</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Tars</td>
<td>mg/dm³</td>
<td>5–150</td>
<td>—</td>
</tr>
<tr>
<td>Sulphides</td>
<td>mg/dm³</td>
<td>10–50</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cyanides</td>
<td>mg/dm³</td>
<td>5–20</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Thiocyanates</td>
<td>mg/dm³</td>
<td>50–420</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Phenols</td>
<td>mg/dm³</td>
<td>150–1200</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>PAHs (6 Borneff)**</td>
<td>mg/dm³</td>
<td>180–220</td>
<td>50</td>
</tr>
<tr>
<td>Oil and tars</td>
<td>mg/dm³</td>
<td>30–50</td>
<td>—</td>
</tr>
<tr>
<td>Ammonia</td>
<td>mg/dm³</td>
<td>120–790</td>
<td>&lt;15–50***</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg/dm³</td>
<td>2500–3500</td>
<td>—</td>
</tr>
<tr>
<td>Sulphates</td>
<td>mg/dm³</td>
<td>900–1200</td>
<td>—</td>
</tr>
</tbody>
</table>


Together with parts of the steam used in ammonia stripper and other technological effluents, it is assumed that per every 10⁶ g of coke 0.6 to 1.6 m³ of wastewater is generated. It means that ca. 7.5 · 10⁸ m³ of coke oven wastewater is annually generated at worldwide coke oven plants (in Europe it is ca. 9.2 · 10⁷ m³, in Poland ca. 1 · 10⁷ m³) and it will continue to increase [18–24].

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 traditional 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. 7). The purified wastewater, after the treatment process, can be managed by means of its use to wet coke quenching or deposition to the environment [24–27].

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/dm³ for free form of the compound and 5 mg/dm³ for its complexes [28–30].

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 SO₄²⁻). 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/dm³ [31–33].

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 favorable solution would be the reclamation of technological grade water from the wastewater stream [33–35].

In recent years, the increasing water scarcity, sharpening of regulations and public awareness have caused the industry to upgrade or install new wastewater treatment plants. The highest affection of water bodies have been established to the coke-ovens and coal-derivatives plants from which highly contaminated toxic wastewater. The proper treatment of coke oven wastewater is an important topic not only from a point of nitrogen discharge decrease, but also of destruction of other hazardous contaminants, which appear in the stream (ca. cyanides, thiocyanates, sulphides, phenols and PAHs). Hence, in order to assure proper treatment effect and achieve environmental targets, at nowadays operated coke oven wastewater treatment plants two main technological sites, comprised of chemical and biological loops can be found. At some plants, chemical site is preceded with physical separation, in order to remove larger particulates (e.g. large particles of tars), while biological site can be followed by polishing stage, which assures the removal of eventual refractory compounds, over amount of ammonia or phenols.

The treatment of coke oven wastewater, as one of the most complex and problematic industrial waste stream, is often discussed in the literature and widely investigated by many scientific and industrial R&D centres all over the world [22–35]. Different processes are used for purification of wastewater are investigated.

A range of studies have been carried out in order to improve the operation of coke oven wastewater treatment plants. They were devoted mainly to chemical [24, 29, 35] or biological treatment techniques [23, 25, 29, 34] modification or complete change. For example Maranon et al. [23] studied the treatment of coke wastewater in a pilot plant using ammonia stripping unit, a homogenization tank and a biological reactor. The authors obtained high efficiencies for HRT of 66 h, while the biological treatment (after stripping and subsequent neutralization with H₂SO₄) led to even higher removal efficiencies at lower HRT (56 h).
There is also a range of studies focused on the use of adsorption techniques for the elimination of various contaminants present in the coke oven wastewater [28, 32, 34]. After biological treatment, coke wastewater contains small amounts of refractory phenolic compounds. Vasquez et al. [34] studied the removal of phenols and COD from coke wastewater subjected to biological treatment using different adsorbents (granular activated carbon and various resins). They found that residual phenols from high load industrial wastewater biological treatment plants can be efficiently removed using activated carbon, while the resins were less adequate due to their lower adsorption capacities.

Moreover, several papers discussing the possibility of water reclamation by means of, e.g. membrane processes [24, 25] can be found. Hence, the problem of proper treatment and utilization of coke oven wastewater is very actual and requires many efforts.

**Summary and conclusions**

In the article, the coke production review, discussion on coke oven gas cleaning methods and coke oven wastewater formation and treatment techniques has been made. The presented data clearly stated that coke oven wastewater amount and composition generates a serious issue and is a topic of interest of many R&D and industrial center over the world. One may notice, that novel methods, techniques and processes are proposed for optimization and improvement of coke oven wastewater treatment, including possibility of water reclamation. In summary, a list of issues related with the proper treatment and utilization of coke oven wastewater can be made, 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.

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References


Abstrakt: Proces koksowania wiąże się z powstawaniem silnie zanieczyszczonych strumieni technologicznych, tzw. ścieków koksowniczych. Odpowiednie zagospodarowanie i oczyszczenie strumienia wymaga złożonych metod i technologii. Ścieki koksownicze można zdefiniować jako mieszaninę strumieni wodnych powstających w procesie produkcji koksu i produktów węglowych w trakcie oczyszczania gazu koksowniczego oraz ścieków sanitarnych generowanych na koksowni. Ze względu na skład i specyfikę zanieczyszczeń występujących w ściekach koksowniczych (WWA, fenole, cyjanki, rodanki, amoniak itp.) proces ich oczyszczania stanowi zwykle połączenie metod fizycznych, chemicznych i biologicznych, po których stosuje się dodatkowe doczyszczanie. W zależności od dalszego wykorzystania bądź utylizacji strumienia (odprowadzenie do środowiska lub kanalizacji, zasilanie obiegu mokrego gaszenia koksu) stosowane są zróżnicowane systemy oczyszczania.

POWSTAWANIE, SPOSOBY OCZYSZCZANIA I METODY UTYLIZACJI ŚCIEKÓW KOKSOWNICZYCH

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W niniejszym artykule przedstawiono przegląd informacji związanych ze światową, europejską i krajową produkcją koksu, powstawaniem ścieków koksowniczych, ich parametrami i sposobami oczyszczania i zagospodarowania. Szczególną uwagę poświęcono oczyszczaniu ścieków, jako że stanowi ono o możliwościach dalszego zagospodarowania strumienia. Dodatkowo przedyskutowano problemy występujące na obecnie pracujących oczyszczalniach ścieków koksowniczych.

Słowa kluczowe: produkcja koksu, oczyszczanie gazu koksowniczego, oczyszczanie ścieków koksowniczych, ścieki koksownicze