Utilization of innovative system for coke oven wastewater treatment as an element of stabilization technology for post-process waste from municipal incineration plants

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Abstract. The article discuss the possibility of using the system for coke oven wastewater treatment process that has been developed within the framework of the project: The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies — INNOWATREAT that has received funding from the Research Fund for Coal and Steel under Grant Agreement No. 710078 and from the Ministry of Science and Higher Education Poland from financial resources on science in 2016–2019, for the removing the hazardous elements and compounds from wastewater from leaching ashes from municipal waste incineration plants. The results achieved in the project are compared with analysis provided for two different sources of ash from Poland and one Lithuania. The article discuss predicted effectiveness of the method and possibility their use in wider method of post-process waste stabilization technology as well as potential risk connected with implementation this solution into practice.

1. Introduction

Contemporary, there are about 540 coke plants in the world [1, 2]. The largest number is in Asia, where the leader is China – about 400 plants, but also the significant amount is in Europe – almost 60 plants [2, 3]. Among the European countries Poland is one of the biggest coke maker – table 1.

The production of the coke is connected with large requirements for water. It, after the industrial process, is one of the most contaminated and toxic aqueous stream of wastes [4, 5]. The coke wastewater contains organic and also inorganic pollutants [2, 4]. Moreover, their amount is significant - between 0.3 to 4 m³ per ton of coke [1, 5].

Table 1. The top 10 of coke producers in 2014 - 2017 [3].

| No. | Country | Coke oven, coke production (thousand metric tons) |
|-----|---------|-------------------------------------------------|
|     |         | 2014  | 2015  | 2016  | 2017  |
| 1.  | China   | 479,809 | 448,225 | 449,115 | N/A   |
| 2.  | Russia  | 39,512   | 40,342   | 26,236   | 39,934   |
| 3.  | Japan   | 33,340   | 32,005   | 32,689   | 32,200   |
It is worth to notice that the problem of highly contaminated water is not only connected with coke making industry. The hazardous elements and compounds are also present in waste from others industry such as energy production, especially form coal. Producing and using coal affects the environment not only the air quality trough the gas emissions but also trough the combustion residues such as fly ash (FA) and bottom ash [6, 7]. The solid products of coal combustion such as coarse bottom ash and fine FA are usually between 5 and 20 wt.% of the feed coal [6, 8]. The similar situation is for the municipal waste incineration plants, where instead of coal the solid wastes are burned. In this case bottom ash is between 15 and 25% by mass of the feed material and about 80–90% of the total residues [9].

The most of the residues form burning process, form coal as well as from municipal waste, consists of oxides of Si, Al, Fe, Ca and Ti (95-99%) and about 0.5% to 3.5% consists of Na, P, K, Mg, Mn and S. The rest of the FA is composed of trace elements such as As, B, Ba, Br, Cd, Cl, Co, Cu, Cr, Fe, Ga, Hg, I, In, Mo, Ni, Pb, Po, Rb, Sb, Sc, Se, Sr, Ti, W, V and Zn [10, 11], among them also toxic elements such as: Cr, Pb, Hg, Ni, V, As, and Ba. The presence of hazardous elements is more likely when we use as a feed municipal waste than coal. The concentration of the toxic elements in the FA is from 4 to 10 times higher than in feed material [6, 10, 12]. Because of that the most of FAs form municipal waste incineration requires pre-treatment before the further application. One of the most popular is leaching. As a results of this process we received FA that could be used for further production process in many areas [13, 14] and contaminated wastewater [15].

The article compare the waste water form coke production and the results of leaching test for three FA - two different sources of FA from Poland and one Lithuania. The article discuss possibility of use the technology dedicated for treatment the wastewater form coke production to the treatment of post-process waste.

2. Technology

2.1. Technology - overall view

The new technology of the wastewater treatment has been developed in the framework of the project: *The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies - INNOWATREAT*. The project was implemented between 1 July 2016 and 30 June 2019. Project consortium include the partners with wide experience and knowledge on the field of coke making, coke oven wastewater characteristics and wastewater treatment and utilization methods, such as:

- Institute for Chemical Processing of Coal (Poland) - leader,
- Wroclaw University of Technology (Poland),
- Czech Technical University in Prague (Czech Republic),
- Cracow University of Technology (Poland),
- Akvola Technologies (Germany).

The main goal of the project was the development of the complex system for coke oven wastewater treatment and utilization of hazardous liquid waste. The performed activities included:
- Coke oven wastewater characteristics.
- Development of Akvofloat™ technology for tars removal.
- The replacement of conventional coagulation with electrocoagulation process.
- The feasibility studies preparation using computer modelling.
- Application of low pressure driven membrane processes in coke oven wastewater treatment.
- Technological grade water recovery from biologically purified coke oven wastewater.

This project allowed to develop the some conception of the complex systems for coke oven wastewater characteristics, treatment and utilization. The information about particular systems are available by the database: http://www.ichpw.pl/en/innowatreat-database/ [16].

2.2. Development of the technologies – exemplary solutions

The developed systems are presents as the schemes – figure 1 [16]. They could be a part of larger innovative system for coke oven wastewater treatment and water recovery.

![Diagram of water treatment schemes](image-url)

**Figure 1.** The schemes of the systems for water treatments [16].
The different systems are dedicated for different wastewater treatment technologies and have a little bit different efficiency.

2.3. Effectiveness of the technologies for water treatment
During the project INNOWATER the efficiency of different systems has been tested. The detailed description of the effects is presented in tables 2-6. The chemical analysis include the most characteristic elements and compounds was compared with permissible concentration in effluent for the best available technology (BAT). The numbers in table are connected with places marked on the schemes in the figure 1.

The table 2 presents the results for scheme 1. The final results (point 3) are worse than for BAT in case of amount of phenols and ammonia/ammonium nitrogen. The technology achieved better results in case of sulphides.

**Table 2.** Results of the wastewater treatment for the technology illustrated on scheme 1 [16].

| Substance                  | Tar (sum 6 WWA) [mg/dm³] | Cyanides (CN-) [mg/dm³] | Sulphides [mg/dm³] | Phenols [mg/dm³] | Ammonia/Ammonium nitrogen [mg/dm³] | Chemical oxygen demand [mgO₂/dm³] |
|----------------------------|--------------------------|-------------------------|--------------------|-----------------|-----------------------------------|----------------------------------|
| BAT permissible concentration in effluent | ∑6 WWA: <0,05 | <0,1 | <0,5 | total nitrogen: <50 | COD<220 |
| 1 - coke oven wastewater | 0,426 | 2-9-5,7 | 0,6-34,2 | 684-792 | 43-140 (92) | 4101-5450 |
| 2 - after oxidation | 0,081 | 0,05-0,24 | 0,15 | 7-13 (10) | 24-105 (65) | 344-375 |
| 3 - after nitrification | 0,035 | 0,05-0,16 | 0,11 | 4-6 (5) | 15-60 (38) | 288-363 |

The table 3 presents the results for scheme 2. The final results (point 4) are worse than for BAT in case of amount of phenols. The technology achieved better results in case of tar and sulphides.

**Table 3.** Results of the wastewater treatment for the technology illustrated on scheme 2 [16].

| Substance                  | Tar (sum 6 WWA) [mg/dm³] | Cyanides (CN-) [mg/dm³] | Sulphides [mg/dm³] | Phenols [mg/dm³] | Ammonia/Ammonium nitrogen [mg/dm³] | Chemical oxygen demand [mgO₂/dm³] |
|----------------------------|--------------------------|-------------------------|--------------------|-----------------|-----------------------------------|----------------------------------|
| BAT permissible concentration in effluent | ∑6 WWA: <0,05 | <0,1 | <0,5 | total nitrogen: <50 | COD<220 |
| 1 - coke oven wastewater | 0,17-3,38 | 0,4-25 (14) | <0,05 | 642-982 | 25-70 (37) | 2740-4746 |
| 2 - equalization tank | 0,09-0,07 | 0,5-11 (7) | <0,05 | 404-534 | 15-56 (32) | 1750-2436 |
| 3 - after biological loop | 0-0,022 | 0,05-1,5 | <0,05 | 3-82 (20) | 12-72 (58) | 233-513 |
| 4 - water to coke wet quenching loop supply | 0-0,022 | 0,05-1,5 | <0,05 | 3-82 (20) | 12-72 (58) | 233-513 |
The table 4 presents the results for scheme 3. The final results (point 4) are much worse than for BAT in case of amount of phenols and ammonia/ammonium nitrogen. The technology achieved much better results in case of tar and sulphides.

Table 4. Results of the wastewater treatment for the technology illustrated on scheme 3 [16].

| Substance | Tar (sum 6 WWA) [mg/dm³] | Cyanides [mg/dm³] | Sulphides [mg/dm³] | Phenols [mg/dm³] | Ammonia/Ammonium nitrogen [mg/dm³] | Chemical oxygen demand [mgO₂/dm³] |
|-----------|--------------------------|------------------|--------------------|-----------------|-----------------------------------|----------------------------------|
| BAT permissible concentration in effluent |∑₆ WWA: <0,05 | (CN-) <0,1 | <0,1 | <0,5 | total nitrogen: <50 | COD<220 |
| 1 - coke oven wastewater | 0,28 | 13 | 0,4-2,4 (1,4) | 632-1500 (1066) | 50-1900 (975) | 6185-7650 (6917) |
| 2 - equalization tank | 0,07 | 0,05-2,8 (1,4) | 0,05-1,2 (0,6) | 265 | 44-1300 (630) | 2134-2810 (2472) |
| 3 - after nitrification | 0,044-0,298 (0,171) | 0,05-0,65 (0,35) | <0,05 | 15 | 38-1220 (478) | 572-2029 (1290) |
| 4 - water to coke wet quenching loop supply | 0,046 (0,023) | 0,05-0,5 (0,28) | <0,05 | 11-12,5 (11,7) | 36-1140 (478) | 378-1621 (1117) |

The table 5 presents the results for scheme 4. The final results (point 5) are worse than for BAT in case of amount of phenols. The technology achieved much better results in case of tar, cyanides and ammonia/ammonium nitrogen sulphides.

Table 5. Results of the wastewater treatment for the technology illustrated on scheme 4 [16].

| Substance | Tar (sum 6 WWA) [mg/dm³] | Cyanides [mg/dm³] | Sulphides [mg/dm³] | Phenols [mg/dm³] | Ammonia/Ammonium nitrogen [mg/dm³] | Chemical oxygen demand [mgO₂/dm³] |
|-----------|--------------------------|------------------|--------------------|-----------------|-----------------------------------|----------------------------------|
| BAT permissible concentration in effluent |∑₆ WWA: <0,05 | (CN-) <0,1 | <0,1 | <0,5 | total nitrogen: <50 | COD<220 |
| 1 - coke oven wastewater | 0,021-0,051 (0,024) | 0,3-15,8 (7,6) | <0,05 | 674-700 (686) | 60-125 (87) | 3057-4384 (3858) |
| 2 - after mechanical-chemical loop | 0,023 (0,012) | 0,3-2,4 (1,6) | <0,05 | 610-632 (621) | 60-125 (87) | 3048-3622 (3335) |
| 3 - after equalization tank | <0,01 | 0,19-27 (1,47) | <0,05 | 179 | | |
| 4 - after biological loop | <0,01 | 0,05-0,5 (0,28) | <0,05 | 1,1-6 (3,6) | <0,5 | 220-428 (323) |
| 5 - after polishing loop | <0,01 | 0,05-0,6 (0,3) | <0,05 | 0,5-4 (2,2) | <0,5 | 201-335 (252) |

Table 6. Results of the wastewater treatment for the technology illustrated on scheme 5 [16].

| Substance | Tar (sum 6 WWA) [mg/dm³] | Cyanides [mg/dm³] | Sulphides [mg/dm³] | Phenols [mg/dm³] | Ammonia/Ammonium nitrogen [mg/dm³] |
|-----------|--------------------------|------------------|--------------------|-----------------|-----------------------------------|
| BAT permissible concentration in effluent |∑₆ WWA: <0,05 | (CN-) <0,1 | <0,1 | <0,5 | total nitrogen: <50 |
| 1 - coke oven wastewater | 0,2 | 16,7 | 6,6 | 884 | 106 |
The table 6 presents the results for scheme 5. The final results (point 4) are much worse than for BAT in case of amount of phenols. The technology achieved better results in case of tar, cyanides and sulphides. The information for and ammonia / ammonium nitrogen is not given.

Taking into consideration the amount of the contamination in the coke oven wastewater the achieved results are satisfactory.

3. Leaching results for fly ashes and discussion
The leaching test was carried out using 3 types of waste from municipal waste incineration plants: one FA proceeding from a waste incineration plant in the city of Klaipeda in Lithuania - FA1, and two FAs from a waste incineration plant in Konin (Poland) - FA2 (fly ash containing hazardous substances) and FA3 (boiler dust containing hazardous substances). In all cases the pre-treatment of waste was made by the same method - the washing process. The FA was rinsed with running water in the ratio of 1:5 in a slow-running laboratory mixer (time: 15 minutes), then the excess water was filtered and dried in a dryer to a constant mass.

The samples for the leaching test were prepared according to the PN-EN ISO 15587-2:2005 standard on the samples witch mass approximately 2.5 kg each. The tests were conducted according to the PN-EN 12457-4:2006 standard. The results are shown in table 7.

**Table 7.** The results of water leaching tests for FAs.

| Analysed substance | Criteria for admission of hazardous waste | FA1 | FA2 | FA3 |
|--------------------|-------------------------------------------|-----|-----|-----|
|                    | mg/kg                                     |     |     |     |
| Arsenic (As)       | 25                                        | <0.5| <1.0| <0.2|
| Barium (Ba)        | 300                                       | 76.5| 82  | 3   |
| Cadmium (Cd)       | 5                                         | 0.25| <0.05| <0.01|
| Chromium (total amount) (Cr) | 70                        | 0.26| 0.5 | 2.1 |
| Copper (Cu)        | 100                                       | 225 | <0.2| <0.05|
| Mercury (Hg)       | 2                                         | <0.01| <0.01| <0.01|
| Molybdenum (Mo)    | 30                                        | 1.5 | 1.6 | 1.8 |
| Nickel (Ni)        | 40                                        | <0.05| <0.05| <0.05|
| Lead (Pb)          | 50                                        | 365 | 125 | 2.1 |
| Antimony (Sb)      | 5                                         | <0.5| <0.5| <0.2|
| Selene (Se)        | 7                                         | <0.1| <0.5| <0.2|
| Zinc (Zn)          | 200                                       | 44.5| 58  | 18.5|
| Chlorides (Cl\(^-\)) | 25 000                                  | 162 000| 177 000| 15 000|
| Fluorides (F\(^-\)) | 500                                     | 44  | 51  | 34  |
| Sulphates (SO\(_4^{2-}\)) | 50 000                                 | 27 800| 8 880| 14 200|
| Dissolved organic carbon (DOC) | 1 000                                 | 24  | 60  | 26  |
| Total dissolved solids (TDS) | 100 000                               | 360 000| 448 000| 69 900|
| Chromium (VI)      | <1.0                                      |     |     |     |
The achieved results was compared with the criteria for admission of hazardous waste. The FA3 do not exceed the regulations. The some problems appears in case of FA1 and FA2. For the FA1 the amount of cooper, lead and TDS is over the limit. On case of FA2 the values for lead and TDS are too high. In this two cases the wastes required further treatment and limitation of TDS up to 100,000 mg / kg.

The technologies of the wastewater treatment developed in the framework of the project: The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies – INNOWATREAT do not taken into consideration the compounds of cooper and lead, so there is impossible to investigate their efficiency for this two elements. The main question in this area is connected with possibilities of TDS removing.

TDS is the combination content of dissolved all inorganic and organic substances present in a liquid – wastewater [17, 18]. The particular chemical composition of TDS is unknown. It limited the speculation about effectiveness of the technology, but taking into consideration the wide range the pollutions that has been removed from coke wastewater it could be also possible to use this system for the treatment the waste water after leaching the FA. The using this system will required further investigation and probably optimization some procedures, because the effectiveness of this procedure in case of FAs is strongly depended on time [18, 19]. That is mean in practice that the treatment procedures required the proper time and it effectiveness will be limited by amount of wastes. Other problem could be the risk associated with changeability of wastes. The usefulness of implemented technology will be depended on the amount of contamination is the base material. It could limited the application the proposed solution in practice.

4. Conclusions
The content of heavy metals and toxic elements content in FAs is important factor than give a possibility of their safe utilization. The presented FAs were pre-treated by leaching because they exceeded the limits for hazardous waste landfills. In the case of one of them the procedure was effective, but for two of them it was not sufficient. In this case the more advanced treatment technologies are required. The article discussed the possibility of using the system for coke oven wastewater treatment process for the removing the hazardous elements and compounds from wastewater from leaching ashes from municipal waste incineration plants. The comparison achieved results show that is impossible to use this system without any changes and it required further research works to be applicable in wider process of post-process waste stabilization technology for municipal waste incineration plants.

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