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TRACE ELEMENTS IN SOLUTIONS FROM ZEOLITE SYNTHESIS

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The paper presents the content of selected elements in solutions formed after the synthesis of zeolitic material based on fly ash. Fly ash samples were taken from two pulverized fuel-fired boilers at the Rybnik Power Plant: one boiler fired solely with coal and one co-fired with coal and biomass. The tests conducted have shown that solutions remaining after zeolite synthesis from fly ash generated in boilers co-fired with coal and biomass had higher content of elements than those derived from fly ash generated from burning only coal. It was also found that increasing NaOH concentration of the solution used in zeolite synthesis caused increased content of the individual elements.

Keywords: zeolite, trace elements, synthesis, solutions

1. INTRODUCTION

Zeolite synthesis from fly ash can be achieved by several methods:

- classical alkaline hydrothermal conversion of fly ash,
- alkaline fusion followed by classical alkaline conversion of fly ash,
- dry or molten salt conversion,
- two-stage synthesis.

The hydrothermal synthesis of zeolites from fly ash is the most widely used method. Hydrothermal synthesis is a physicochemical process conducted in an alkaline solution under atmospheric or increased pressure (in that case the process is carried out in an autoclave). Hydrothermal synthesis consists in processing a mixture of fly ash and hydroxide (usually sodium or potassium hydroxide) under defined conditions of temperature and pressure. Additives, such as sodium chloride or potassium chloride are also used. The process involves also filtration, washing and drying of the resultant material. The

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process duration, according to the literature, ranges in the various methods from a few hours to a few days, or even more than ten days. The process temperature range is also wide: from ambient temperature up to several hundred degrees Celsius. The higher reaction temperature, the shorter reaction duration may be [1-4].

In some of the zeolite synthesis methods a solution is generated after the reaction and after washing of the material obtained. No studies have been carried out before to determine the chemical/elemental composition of the generated solutions. These solutions may contain elements that are not present in the synthesized material. Depending on the concentration thereof, they may pose an environmental hazard.

The purpose of this study was to establish the content of selected elements in solutions formed after the synthesis of zeolitic material based on fly ash.

2. SAMPLING AND TESTING METHODS

Fly ash samples were taken from two pulverized fuel-fired boilers at the Rybnik Power Plant: one boiler fired solely with coal (W) and one co-fired with coal and biomass (plant and wood biomass – 8-9%) (Table 1).

Two synthesis trial runs were executed using the hydrothermal method with alkaline activation under the following conditions: synthesis duration – 6 h, synthesis temperature - 170°, fly ash quantity – 100 g, water quantity – 600 mL, NaOH concentration – 2M and 3M. A "blind" synthesis run was carried out for comparison. The conditions of the process were identical as in the two previous trial runs, but alkaline activation was not applied (NaOH concentration 0M). Sample designations are given in Table 1.

Table 1. List of samples of solutions after zeolite synthesis (numbering according to the research plan).

NaOH concentration	Sample no.	
	Boiler fired with coal	Boiler fired with coal and biomass
0.00M	1	15
2.00M	4	18
3.00M	5	19

After each synthesis the material obtained was washed with the same amount of water, enabling thereby comparison of the elemental contents of the solutions. Distilled water was used both in the synthesis process itself as well as for washing.

The following elements were determined in the solutions: Fe, Cr, Ni, Cu, Zn, Pb, Ti, V, Mn, Cd, Mo, Ba, Ca, Si, Al, Na, K, Mg, Sb, As. Determination was carried out by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a JY 2000 spectrometer.

3. RESULTS

K, Na, Ca, Mn, Mg and Fe were the most numerous elements found in all solutions. The elements concentrations were respectively: K (average concentration 571 ppm), Na (av. conc. 179 ppm), Ca (av. conc. 53 ppm), Mn (av. conc. 39 ppm), Mg (av. conc. 52 ppm) and Fe (av. conc. 19 ppm).

The concentrations of other determined elements found in the solutions were below 10 ppm and included: Cr, Ni, Cu, Zn, Pb, Ti, V, Cd, Ba, Si and Al (rys. 1-4).

The lowest content of elements was determined in the solutions from "blind" synthesis run (with no NaOH activation). There is certain relationship between the content of individual elements in the solutions and the type of fuel used (coal, coal and biomass co-firing), irrespective of NaOH concentration (Figs. 1-10:

- in the case of coal and biomass co-firing - higher content of Fe, Mn, Ca, Mg, V, Mn, Ca, Mg, Na, K, Pb, Ba, Ti and Al, as compared to firing with coal only,
- in the case of coal firing - higher content of Zn, Cr, Cd and Si, as compared to coal and biomass co-firing.

For such elements as Ni and Cu there is no clear relationship between their concentration in solutions and the type of fuel used (coal, coal and biomass co-firing).

There is a certain relationship between the occurrence of Mo, Sb and As only in solutions formed in the course of the synthesis from fly ash generated during coal and biomass co-firing:

- Mo is present only in samples nos. 18 and 19, that is in solutions formed in the course of synthesis in 2M and 3M NaOH solution,
- Sb and As are present only in the solution formed in the course of synthesis in 3M NaOH solution.

The results of element content determination in solutions formed in the synthesis of zeolitic material also indicate that the content thereof depends on the NaOH concentration in the activating solution, irrespective of the type of fuel burned (Figs. 1-4):

– 3M NaOH solutions have higher concentrations of Mn, Mg, Cr, Cd, Na, K, Ba and Ti than the 2M NaOH solutions,
– 2M NaOH solutions have higher concentrations of Ca, Ni, Al and Si than the 3M solutions.

For elements such as V, Cu and Pb there is no clear relationship between their concentration in solutions and the concentration of NaOH in solutions used in the synthesis process.

The decrease of Si and Al content with increasing NaOH concentration (in solutions used in the synthesis) found in solutions after the synthesis may be an indicator of increasing efficiency of zeolite crystallization in the synthesis process. At the same time increasing Na content is observed when NaOH concentration is increased, which suggests that some sodium does not participate in the synthesis reaction.

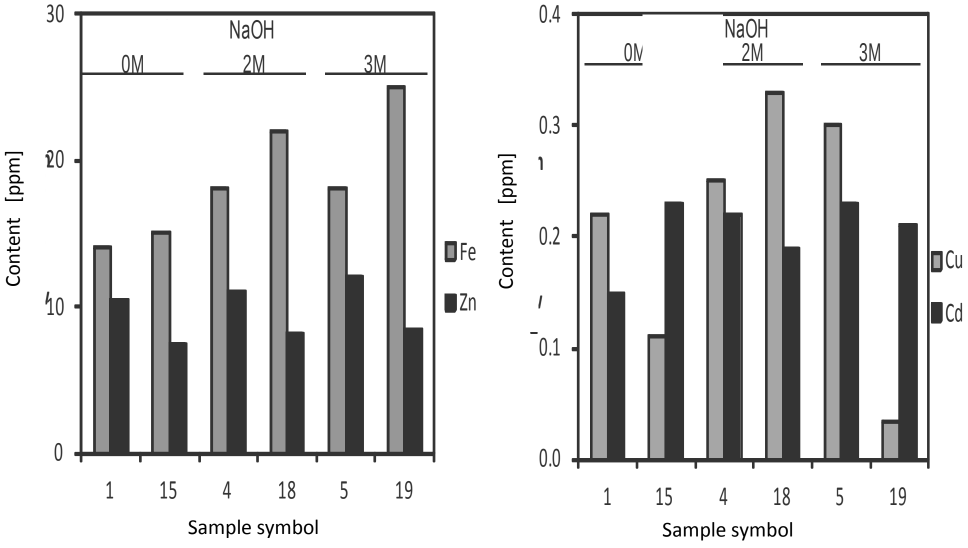

Fig. 1. Content of Fe, Zn, Cu and Cd in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

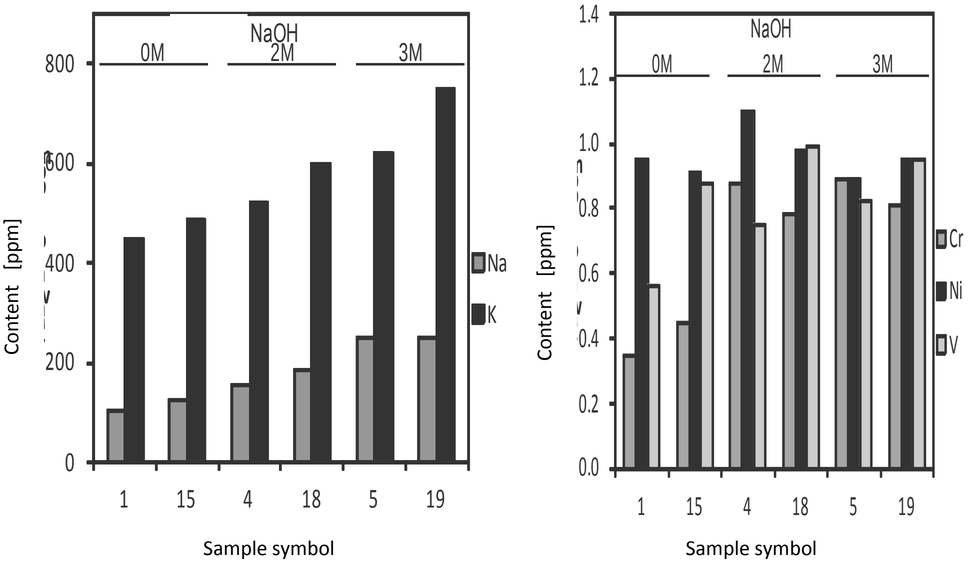

Fig. 2. Content of Na, K, Ni, Cr and V in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

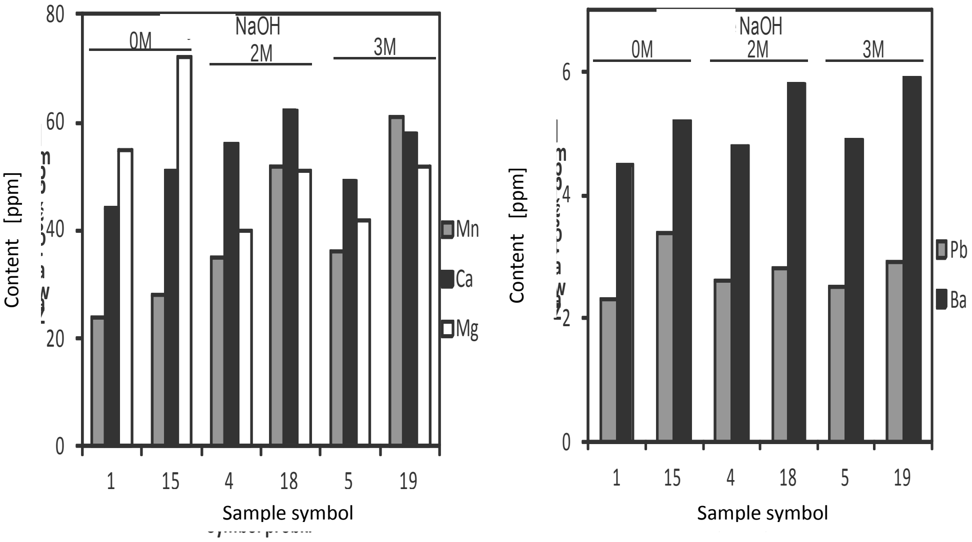

Fig. 3. Content of Mg, Ca, Mn, Pb and Ba in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

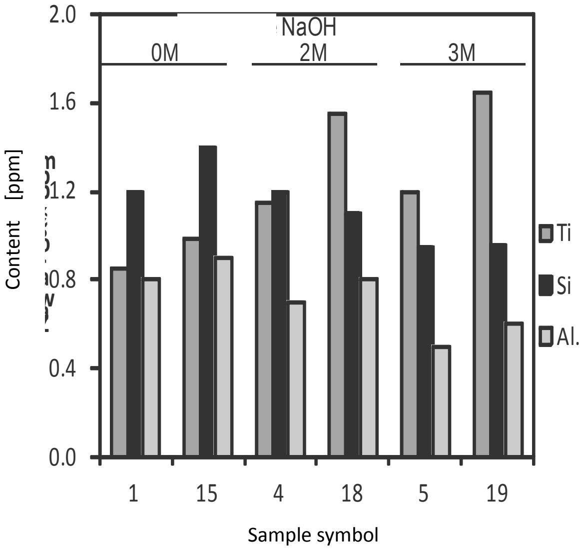

Fig. 4. Content of Ti, Si and Al in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

4. CONCLUSIONS

The following conclusions can be drawn from the study of results of elemental analyses of solutions formed in the course of zeolitic material synthesis from fly ash generated by burning coal or by co-burning coal and biomass at the Rybnik Power Plant:

- solutions formed after zeolite synthesis from fly ash generated by co-burning of coal and biomass have higher content of elements than those derived from fly ash generated by burning coal only,
- increasing NaOH concentration of the solution used in zeolite synthesis causes increased content of the individual elements,
- decrease of Si and Al content with increasing NaOH concentration (in solutions used in the synthesis) in solutions after the synthesis may be an indicator of increasing efficiency of zeolite crystallization in the process.

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PIERWIASTKI ŚLADOWE W ROZTWORACH PO SYNTEZIE ZEOLITÓW

Streszczenie

W artykule przedstawiono zawartości wybranych pierwiastków w powstałych roztworach po syntezie materiału zeolitowego na bazie popiołu lotnego. Próbki popiołu lotnego pochodziły z Elektrowni Rybnik z dwóch kotłów pyłowych: opalanego czystym węglem i ze współspalania węgla z biomasą. Przeprowadzone badania wykazały, że wyższe zawartości pierwiastków występują w roztworach poreakcyjnych, powstałych po syntezie popiołów pochodzących ze współspalania węgla z biomasą, niż w roztworach po syntezie popiołów będących produktem spalania czystego węgla. Stwierdzono ponadto, że wraz ze wzrostem stężenia NaOH roztworu zastosowanego do syntezy zeolitów wzrasta ilość poszczególnych pierwiastków.

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PHASE COMPOSITION OF METALLURGICAL ZINC AND LEAD SLAGS

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Slags formed in the “Miasteczko Śląskie” Zinc Smelting Plant process contain substantial amounts of heavy metals such as Pb, Zn, Cd, Cu. In hypergenic environment this elements may occur in stable or unstable phase. Environmental conditions and the forms of occurrence of elements decide about metals stability and mobility. On the basis of laboratory, microscopic and modeling studies it was found that the main phase present in slags from the current production of the shaft furnace is fayalite, which is unstable in Eh-pH wide range in water and soil environment of the surroundings of HC “Miasteczko Śląskie”.

Keywords: lags, Zinc Smelting Plant, metals, hypergenic environment, Eh-pH diagrams

1. INTRODUCTION

The “Miasteczko Śląskie” Zinc Smelting Plant (HC Miasteczko Śląskie) is the only zinc and lead manufacturer in Europe that uses the ISP (Imperial Smelting Process) pyrometallurgical process. The process is carried out in a shaft furnace in a manner enabling simultaneous production of Zn and Pb. The charge for this process comprises raw materials, i.e. sphalerite and galena concentrates from zinc and lead ore flotation, raw zinc oxide and recycled material, i.e. undersize particles of Zn-Pb sinter, dust, slurries, dross, steel-making dust [4, 5, 11].

Slags formed in the ISP process in an amount of 60,000 $t \cdot y^{-1}$ are the only waste at Zinc Smelting Plant Miasteczko Śląskie that is disposed at the Hazardous Waste Landfill. All other waste (dust, slurries, dross) is recycled within the process.

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Tests performed in the past [2] have shown that slags deposited in the landfill contain substantial amounts of heavy metals (such as Zn, Pb, Cu, Cd) and can therefore have a strong impact on the environment.

Identification of the forms of occurrence of selected metals in the slags will help determine the mobility thereof based on Eh and pH diagrams, and will thereby enable the prediction of environmental impact of the deposited slags.

2. SAMPLING AND TESTING METHODS

Slag samples from the Shaft Furnace Unit were taken in 1-2-monthly intervals (7 series in all), each sample weighing ca. 0.5 kg [7]. Average chemical composition was determined for the adequately prepared slag samples, while the content of Zn, Pb, Fe, Cu, Cd in each sample was determined by means of a JY 2000 inductively coupled plasma atomic emission (ICP-AES) spectrometer. Phase identification was based on microscope observations and X-ray diffraction method. Microscopic observations were conducted in transmitted light using a ZEISS microscope, whereas an HZG-4 diffractometer was used for the X-ray method (analysis conditions: Cu_{ka} lamp, 2 theta angle range – 4-64°, measuring increment – 0.05°, voltage – 35 kV, current – 16 mA). The Eh-pH diagrams were drawn on the basis of "Development and Interpretation of Computer-Generated Potential –pH Diagrams" by Tayer L. [8].

3. RESULTS

3.1. Chemical composition of slags from the Shaft Furnace Unit

The major constituents (> 10 wt.%) in the average chemical composition of the slags include iron (determined as FeO), silica (SiO_2) and calcium (CaO) (Table 1). These three constituents jointly comprise more than 76 wt.%, with FeO content (ca. 34 wt.%) much higher than that of SiO_2 (ca. 25 wt.%) and CaO (ca. 17 wt.%).

Table 1. Chemical composition of the from the Shaft Furnace Unit

Chemical component	Average conent [wt. %]
SiO_2	24,82
Al_2O_3	8,29
FeO	33,95
MgO	2,68
CaO	17,43

PbO	2,13
ZnO	7,86
SO_3	2,84
Sum	100,00

Apart from these chemical constituents, the other significant constituents include aluminium (Al_2O_3) and zinc (ZnO), the content of which amounts to ca. 8 wt.%. The content of MgO, PbO and SO_3 ranges from ca. 2 to ca. 3 wt.%. Therefore the chemical composition indicates that mineral constituents of the slag comprise mainly iron and calcium silicates and aluminosilicates.

Metal content was determined in a number of samples of slags of various deposition duration times (Table 2). Slags from the Shaft Furnace Unit are characterized by varying concentrations of the studied metals: 5.5%-9.5% Zn; 1.1%-3.9% Pb; 15.3%-27.8% Fe; 2.1%-3.8% Cu and 0.001%-0.019% Cd.

Differences in the content of these metals in the slags result from the varying chemical compositions of the charge material and from the changing conditions of the smelting process. The highest mean concentration (20.9 %) among the metals determined is that of Fe, which is the consequence of the fact that this element, along with SiO_2, the average content of which is ca. 25 %, is the main slag-forming constituent.

3.2. Phase composition of slags from the Shaft Furnace Unit

The only components identifiable under the microscope were glaze and crystals, most probably olivine crystals. The other constituents formed opaque grains.

The glaze showed characteristic optical isotropy and often contained opaque inclusions. Olivine crystals are idiomorphic, have a high relief, show dark yellowish pleochroism and high interference colours, which suggests that the olivines are rich in fayalite (Fig. 1 and 2).

By means of X-ray diffraction phase identification it was found that the main phase of slags from the Shaft Furnace Unit was fayalite. This is indicated in the diffraction pattern by the presence of reflections, which are characteristic of this phase (Table 2). In addition to fayalite, the slags contain oxides of iron, calcium, magnesium doped with Cu, Cd, Sb [5], wherein the content of these constituents is probably much lower than that of fayalite. The diffraction pattern also shows a stronger background within the 2-theta angle range, which indicates the presence of an amorphous substance (e.g. glaze observed under the microscope).

Fig. 1. Idiomorphic olivine crystals with characteristic high relief, one nicol, magnification 400x.

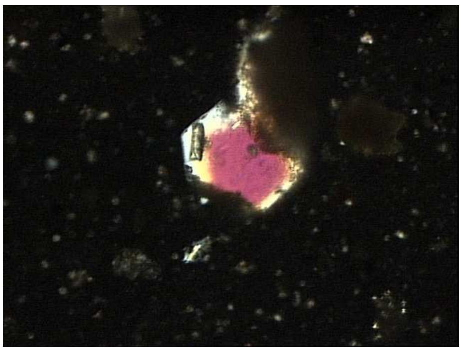

Fig. 2. Idiomorphic olivine crystals with characteristic interference colours, crossed nicoles, magnification 200x.

Table 2. Interpretation of averaged slag sample diffraction pattern

DiffractionReflex No.	d_{hkl}	θ [°]	I	Mineral
1	3,56	10,15	7,0	fayalite
2	3,06	11,16	6,5	fayalite
3	3,05	11,72	5,0	fayalite
4	2,82	12,50	10,0	fayalite
5	2,63	14,58	4,0	fayalite
6	2,55	14,63	7,0	fayalite
7	2,49	15,85	9,0	fayalite
8	2,45	15,93	1,0	fayalite
9	1,78	16,13	5,0	fayalite

4. DISCUSSION OF RESULTS

Interpretation of the results of phase examination of landfilled slags in the context of the environmental impact thereof should mainly apply to the basic phase, that is to fayalite. Based on the chemical composition of the slag (Table 1), considering the stoichiometric ratios of fayalite (chemical formula Fe_2SiO_4), the content of this phase was estimated at ca. 50 wt.%. Fayalite may contain admixtures of MgO and CaO.

In the surface region fayalite is decomposed by dissociated H_2O molecules in the following reaction:

$$Fe_2SiO_4 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- + SiO_2 + H_2O \qquad (4.1)$$

Products of this reaction comprise: stable phase of SiO_2 and unstable Fe ions or hydroxides thereof [3, 9].

The slag, and fayalite particularly, will be subject to hypergenic processes occurring under the influence of such factors as: seasonal temperature variability, atmospheric precipitation, insolation and Eh and pH conditions of soil-water environment. The Eh and pH conditions, in turn, depend on many other factors, principally on chemical interactions with precipitation water and soil. For this reason the following values were adopted when evaluating the environmental impact of slag: mean precipitation: 700 mm/year, mean temperature in winter season: -3°C, mean temperature in summer season: +18°C (maximum +25°C), mean annual temperature: 8°C. Studies were performed within the water stability field (Eh range: -1.0 + 1.4V and pH range of 0÷14 were adopted) [3]. Within these value ranges Eh-pH diagrams were plotted to show the stability fields of the main chemical constituents of fayalite (silicon and iron) under adopted temperatures (Fig. 3a-3d).

As shown in Eh-pH diagram for the temperature of -3°C (Fig. 3a), the fayalite stability field at pH=6.8 spans from Eh equal to -0.33 up to -0.30 V, and at pH=14 it spans from Eh = -0.75 up to -0.70V. With increasing temperature the stability field of fayalite is shifted towards lower pH values, to 6 at the temperature of 25°C, with insignificant changes of Eh values. On the other hand, a distinct decline of Eh value down to -0.85V is observed with temperature increase to 25°C at the extreme pH value of stability field.

Changes of Eh and pH that determine the stability field of fayalite in aqueous environment cause its decomposition. One of the products of this decomposition is always SiO_2, whereas iron, depending on the conditions, adopts the following forms: Fe_3O_4, FeO·OH, Fe^{2+} or Fe^{3+}. It may therefore be presumed that stable forms among these products will include SiO_2 and Fe_3O_4, while Fe^{2+} and Fe^{3+}, being ions, will be present in aqueous solution.

In an aqueous environment, within pH range of 14.0 - 7.8 and at the temperature of -3°C (Fig. 3a), where fayalite is stable at Eh values indicated by lines 1 and 7, this constituent decomposes to:

- Fe_3O_4 and silica (SiO_2), in the area defined by lines 2, 6 and 7,
- FeO·OH and silica (SiO_2), in the area bounded by line 6.

If pH change of the aqueous environment in the range of 7.0 - 7.9 and at the temperature of -3°C is considered (Fig. 3a), fayalite decomposition will be observed, depending on Eh value, in areas bounded by:

- lines 1 and 2, into Fe^{2+} ion and silica (SiO_2),
- lines 2 and 6, into Fe_3O_4 and silica (SiO_2),
- lines 3 and 6, into FeO·OH and silica (SiO_2).

If pH change of the aqueous environment in the range of 1.3 - 7.0 is considered, fayalite decomposition products, depending on Eh value in areas bounded by the lines specified, will include:

- lines 3 and 4 - Fe^{2+} ion and silica (SiO_2);
- lines 3 and 5 - FeO·OH and silica (SiO_2).

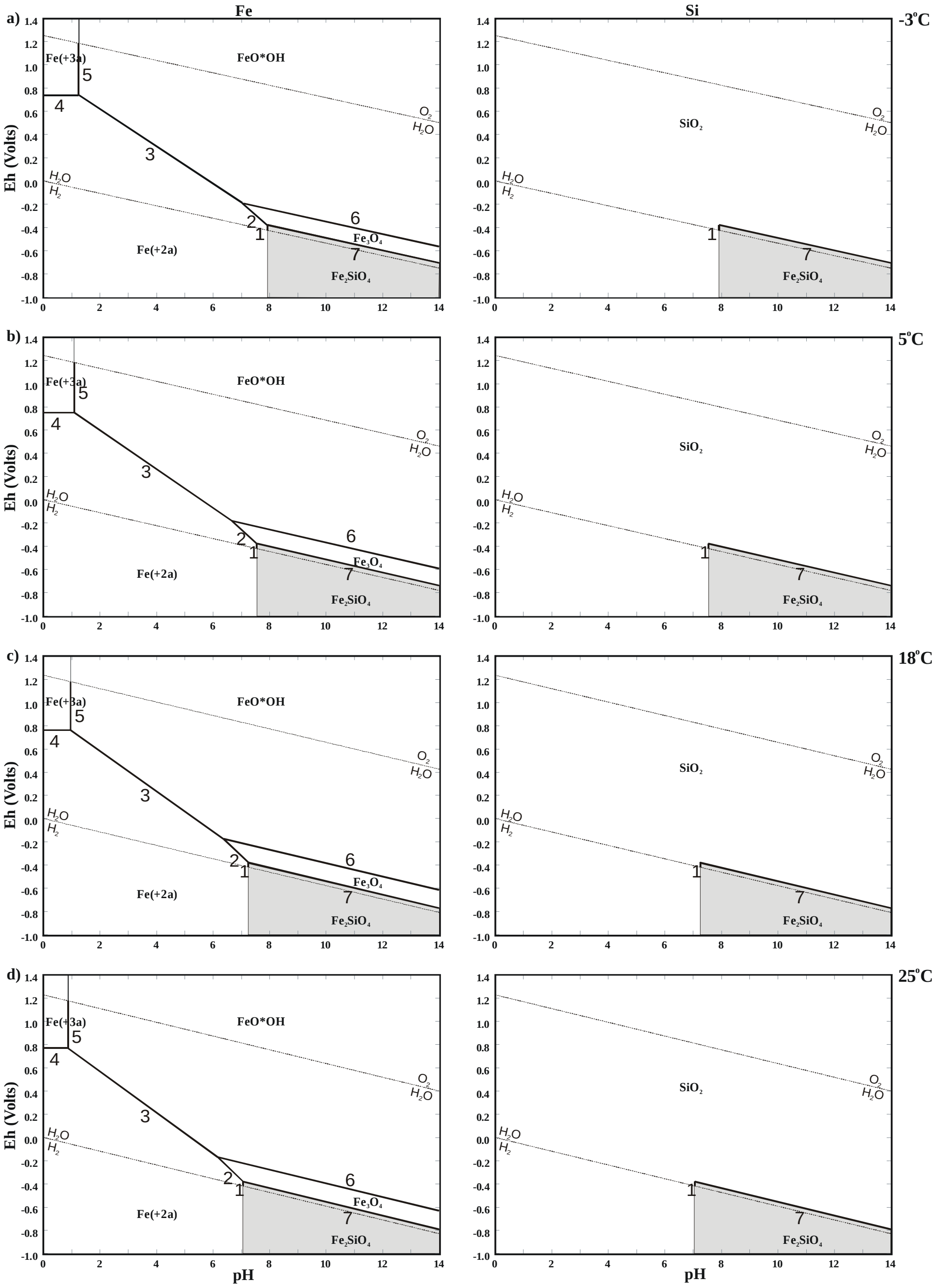

Fig. 3. Eh-pH diagrams of fayalite stability in temperatures:
-3°C (a), 8°C (b), 18°C (c) and 25°C (d).

The last case considered is pH range of 1.3 – 0.0, wherein fayalite decomposes, depending on Eh value in areas bounded by the lines specified, into:

- lines 3 and 4, Fe^{3+} ion and silica (SiO_2);
- lines 4 and 5, Fe^{3+} ion and silica (SiO_2).

The water and soil environment under investigation (Miasteczko Śląskie) has a pH range of 4.5 to 7.5 [10]. This range falls generally outside of the stability field of fayalite, with a partial overlap only at the temperature of -3°C. Fayalite will therefore undergo decomposition. It may be presumed that, depending on Eh of this environment, the products of fayalite decomposition at -3°C will always include silica, and additionally Fe^{2+} ion or FeO·OH compound.

At temperatures of +8, +18 and +28°C the stability field of fayalite is gradually shifted towards pH=7, with insignificant changes of Eh value. In the extreme case, at the temperature of 25°C, there is also a slight shift of the stability field of the Fe^{3+} ion towards lower pH values.

It should be noted that temperature increase within the pH range of the water and soil environment under consideration (4.5 – 7.5) results in fayalite being stable only in the pH range of 7.0 – 7.5 (Fig. 3).

Account should also be taken of the possibility of the presence of various metals in olivines, e.g. Mn, Ni, Zn, Co [1, 6] which will be released into the water and soil environment during fayalite decomposition.

5. CONCLUSIONS

In the course of investigations it was found that fayalite is the main phase present in slags from the current production of the shaft furnace at Zinc Smelting Plant Miasteczko Śląskie. The mineral composition of the slag is complemented with glaze and opaque constituents, which have not been identified.

Interpretation of pH-Eh diagrams has shown that fayalite will undergo decomposition at the temperatures of -3°C and +8°C in the hypergenic environment of the surroundings of Zinc Smelting Plant Miasteczko Śląskie. At higher temperatures of +18°C and +25°C the stability field of Fe_2SiO_4 is shifted towards lower pH values, the effect being that fayalite remains stable only within a narrow pH range of 7.0 to 7.5. Therefore, slags deposited in the landfill may constitute a potential source of contamination of the water and soil environment of Zinc Smelting Plant Miasteczko Śląskie. Potential contaminants include not only iron compounds, but also other metals geochemically bound in olivines.

In order to maintain fayalite stability in the water and soil environment, the pH value in the latter should be kept above 7.

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SKŁAD FAZOWY ŻUZLI POCHODZĄCYCH Z HUTNICTWA CYNKU I OŁOWIU

Streszczenie

Huta Cynku „Miasteczko Śląskie” jest jedynym w Europie producentem cynku i ołowiu wytapianych metodą ogniową w procesie Imperial Smelting Process (ISP). Proces prowadzony jest w piecu szybowym w sposób umożliwiający jednoczesne uzyskiwanie Zn i Pb. Wsad do procesu technologicznego stanowią surowce, tj. koncentraty blendowo-

galenowe z flotacji rud cynkowo- ołowiowych, surowy tlenek cynku oraz materiały zwrotne, tj. podziarno spieku Zn- Pb, pyły, szlamy, zgary, pyły stalownicze. Żużle powstające w procesie technologicznym Huty, zawierają w swym składzie ilości metali ciężkich (m.in. Zn, Pb, Cu, Cd). Identyfikacja form występowania wybranych metali w żużlach pozwoliła na określenie ich mobilności w środowisku hipergenicznym, w oparciu o diagramy Eh i pH. Na podstawie przeprowadzonych badań mikroskopowych i modelowych stwierdzono, że główną fazą występującą w żużlach z bieżącej produkcji pieca szybowego Huty jest fajalit, który w środowisku gruntowo-wodnym rejonu Zinc Smelting Plant „Miasteczko Śląskie”, jest niestabilny w szerokim zakresie Eh-pH.

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ANALYTICAL CONTROL OF DICLOFENAC REMOVAL IN THE PHOTOCATALYTIC OXIDATION PROCESS

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Continuously increasing pharmaceuticals consumption contributes to the increase of their concentration in the aqueous environment, which is at a level of a few ng/dm^3 to several µg/dm^3. A numerous group of pharmaceuticals occurring in surface waters are non-steroidal painkillers and anti-inflammatory drugs, which include diclofenac. The paper presents the possibility of the analytical control of diclofenac photocatalytic oxidation process in the aquatic environment. To examine the effectiveness of the process various instrumental methods including HPLC analysis preceded with solid phase extraction SPE, measurements of UV absorbance and total organic carbon were used.

Keywords: diclofenac, photocatalysis, SPE, HPLC, absorbance in UV, total organic carbon

1. INTRODUCTION

Micropollutants of pharmaceutical activity (drugs and their metabolites), apart from hormones and other endocrine substances i.e. perfluorinated acids both carboxylic and sulphonate, substances acting only as UV filters, naphthenic acids, dioxines, benzotriazoles, additives for liquid fuels, bromated derivatives of aromatic compounds and by-products of disinfection are included to the group of the antropogenic organic micropollutants [8,11].

Particular attention should be paid to the group of medicines which are available without prescription and the most commonly appear in water environment. This group includes non-steroidal painkillers and anti-inflammatory drugs which can be represented by diclophenac [1,13].

The concentration of pharmaceuticals and their metabolites in water environment is of a few ng/dm^3 to several µg/dm^3 and depends on the load of

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pharmaceutical contaminants in the treated wastewater, which is deposited to natural water reservoirs. The vast majority of research on the concentration of pharmaceuticals in water environment [2,5] shows that their low concentration have insignificant influence on water organisms subjected to short-term exposure of each pharmaceutical. However, it is not known what are the effects of the long-term exposure to seemingly low concentration of substances recognized as highly biologically reactive. Since there is no particular data concerning the toxic effect of pharmaceuticals present in water environment on living organisms including humans, it is necessary to eliminate them completly from water intended for human consumption.

The total removal of pharmaceuticals from wastewater or surface water (a potential source of drinking water) is a difficult procedure considering their polar structure as well as slight susceptibility to biochemical decomposition [6,10,12]. Photocatalytic oxidation is an alternative to the commonly used sorption and coagulation processes for surface water treatment or activated sludge microorganisms for wastewater treatment [3,4,7,9]. The evaluation of the effectiveness of photocatalysis and the selection of process parameters, which include, the choice of photocatalyst, pH, duration of the process and the wavelength is possible basing on the knowledge of the test compounds concentration in aquatic environment. The study on oxidation processes enables the determination of the possibility and the rate of the removed compound decomposition. Nevertheless, the resulting oxidation byproducts can reduce the final treatment effect. Thus, only a reduction of the initial compound concentration is observed, oppositely its degradation pathway.

The paper presents the possibility of analytical control of diclofenac removal from aquatic environment in the photocatalytic oxidation process. Various instrumental methods including HPLC analysis preceded with solid phase extraction SPE, UV absorbance and total organic carbon measurements were used to examine the effectiveness of the process.

2. EXPERIMENTAL

2.1. Apparatus, materials, reagents

Diclofenac in the form of diclofenac sodium salt supplied by Sigma-Aldrich (Poland) was used as a pattern of non-steroidal painkiller and anti-inflammatory drug.

Titanium dioxide (TiO_2) by Evonik Degussa (Germany) marked with the symbol P25 was used as catalyst.

Methanol, acetonitrile and water for HPLC were supplied by POCH S.A.

SPE Supelclean™ ENVI-8 tubes of a volume of 6 cm^3 (1.0 g) by Supelco and a SPE chamber also by Supelco were used during the solid phase extraction.

Heraeus laboratory reactor equipped with an immersed medium pressure lamp of 150 W.

Aeration pump with a capacity of 0.25 cm^3 air for 1 h.

Filtration set connected to a vacuum pump from AGA Labor equipped with glass fiber filters (0.45 µm) by Millipore.

2.2. Test samples

In the study, the simulated solutions were prepared on deionized water matrix, to which diclofenac in a constant concentration of 1 mg/dm^3 was introduced. The high concentration of the drug i.e. much higher than the environmental one, was used in order to increase the precision of the performed analytical measurements.

The solution pH was adjusted to 7 using 0.1 mol/dm^3 HCl and 0.1 mol/dm^3 NaOH.

The water solutions after addition of the catalyst (TiO_2) were undergone the photocatalytic oxidation process at different times i.e. 5, 15, 30, and 60 min.

2.3. Diclofenac determination procedure

The determination of diclofenac in the solutions before and after the photocatalytic oxidation process was preceded by the catalyst particles separation with the use of a glass fibers filter. Next,

- quantitative analysis of the tested drug with high performance liquid chromatography HPLC preceded by solid phase extraction SPE,
- measurement of UV absorbance,
- measurement of total organic carbon (TOC),
- measurement of conductivity

were performed.

The determination of diclofenac concentration was made using solid phase extraction SPE and HPLC analysis. The octylosilan tube phase (C8) was firstly conditioned with 5cm^3 of methanol and next washed with 5 cm^3 of distilled water of pH 7. Water sample of a volume 20 cm^3 (pH = 7) was used in the procedure. After the extraction the colum bed was dried for 5 min at vacuum. The separated compound was washed out with 1 cm^3 of methanol and dried in a nitrogen stream. After dissolution of the sample in 100 cm^3 of methanol it was subjected to HPLC analysis. A high performance liquid chromatograph Varian HPLC (UV detector, wavelength λ = 220 nm) was used. It was equipped with Hypersil GOLD column by Thermo Scientific of length 25 cm, diameter 4.6 mm and granulation – 5µm. The mobile phase consisted of a mixed water and acetonitrile in the ratio of 85:15 (v/v).

In the preliminary work the diclofenac maximum absorbance (λ_{max} = 276 nm) was identified from a designated UV-VIS spectra registered using of the

UV-VIS spectrophotometer Cecil 1000 by Jena AG for the wavelength range from 200 to 400 nm (Fig. 1).

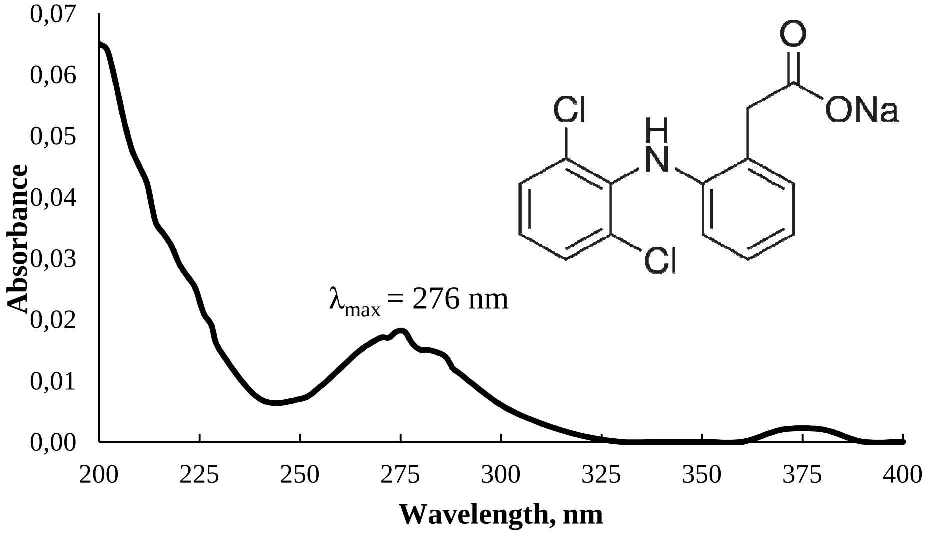

Fig. 1. UV-VIS spectrum of diclofenac sodium salt and its chemical structure

The measurement of total organic carbon was performed using multi C/N analyzer to liquid and solid samples IDC Analytik Jena by Jena AG.

3. RESULTS AND DISCUSSION

The decrease of diclofenac concentration during the photocatalysis process was determined by the use of HPLC analysis, which was preceded by solid phase extraction SPE (Fig. 2). The analyte separation efficiency and its precision (expressed by the average standard deviation,%) were determined basing on results obtained for four extractions. It was found that the extraction yield of diclofenac was 60% and the precision of determination between individual samples did not exceed 0.65%.

The chromatographic determination conducted for water sampled during the photocatalytic oxidation showed the decrease of the diclofenac concentration. It revealed that the removal efficiency increased with the elongation of the oxidation process (Fig. 2). The oxidation of the investigated compound carried out without the addition of catalyst (photolysis) was made as a comparative treatment. The obtained results confirmed that the presence of catalyst favored the pharmaceutical oxidation and after a 30 minute exposure 90% reduction of the pharmaceutical concentration was observed.

The elongation of the exposure time did not result in the increase of the value of the parameter. Additional peaks at the chromatogram were not observed, thus it was supposed that the formation of by-products during the oxidation of diclofenac did not occur. However, in order to confirm this observation GC-MS analysis, which is a more accurate method, should be performed.

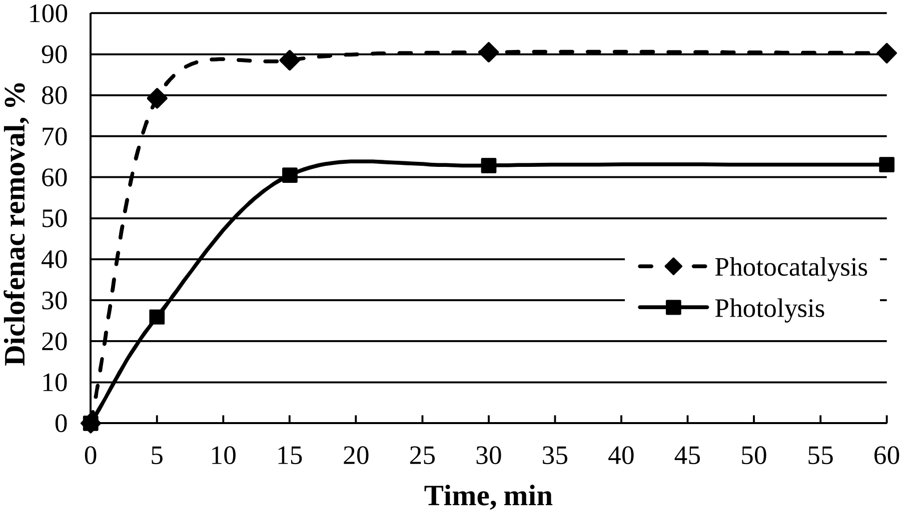

Fig. 2. The decrease of diclofenac concentration during the photolysis and photocatalysis

UV absorbance measurements of the treated water confirmed the photocatalytic decomposition of the investigated pharmaceutical (Fig. 3). The decomposition rates determined on the basis of this analytical method were lower than ones obtained during the chromatographic analysis. 74% reduction of diclofenac concentration was observed at the exposure time of 30 min. The differences in the removal rates of the invetigated pharmaceutical obtained during chromatographic analysis and the absorbance measurements resulted of a higher sensitivity of chromatography. The chromatographic method enabled also an unambiguously determination of the investigated drug concentration.

The concentration of total organic carbon was also determined in the treated water after photocatalysis. The values of the parameter decreased by 5 to 35%, depending on the photocatalysis reaction time (Fig. 4). The obtained results indicated on a significant contamination of the water with organic substances. As the decrease of the diclofenac concentration was confirmed with the use of chromatographic analysis, it was assumed that the contamination of the sample was related to the presence of oxidation by-products. Therefore, the measurement of total organic carbon did not only show the decrease of the diclofenac concentration, but also it revealed the presence of by-products formed during the photocatalysis of the investigated compound.

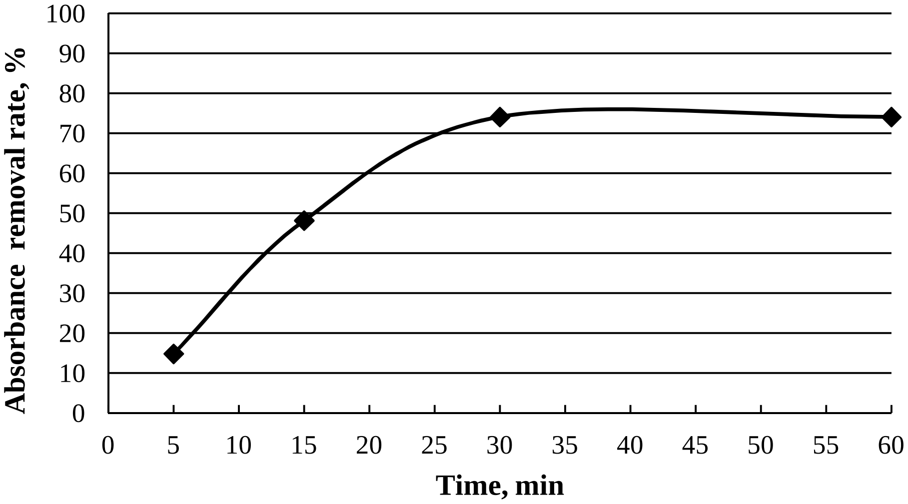

Fig. 3. The decrease of diclofenac during the photocatalysis process based on the UV absorbance removal rate

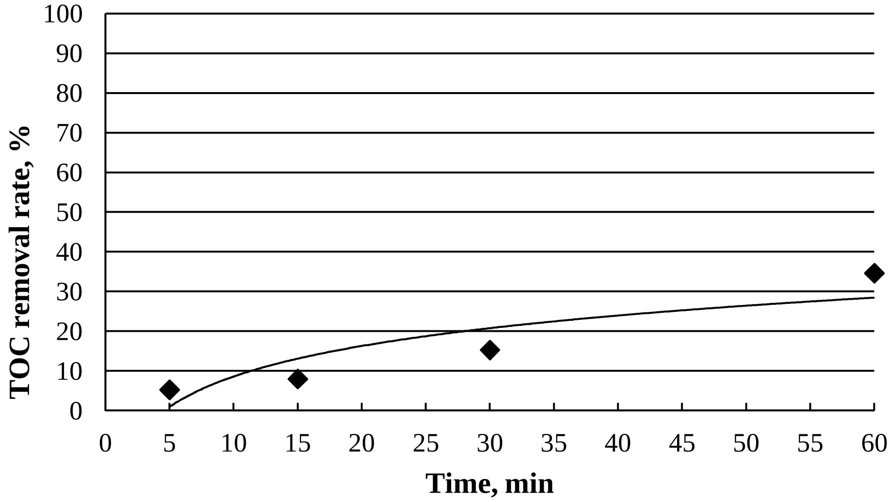

Fig. 4. The dependence of total organic carbon concentration on photocatalysis time

4. CONCLUSIONS

In the paper it was shown that for the complete analytical control of diclofenac concentration during the photocatalytic oxidation number of instrumental methods had to be used. Chromatographic analysis was found to be useful in order to determine the change of the pharmaceutical concentration. The results of the chromatographic analysis were comparable with ones of the UV absorbance measurements (λ = 276 nm). Although, the chromatographic measurements revealed the higher sensitivity than the absorbance ones. On the other hand, the total organic carbon analysis showed that the degradation of the removed compound was incomplete and by-products were formed during the process. However, for their identification it is necessary to continue the study with the use of more accurate analytical methods e.g. the GC-MS analysis.

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KONTORLA ANALITYCZNA USUWANIA DIKLOFENAKU W PROCESIE FOTOKATALITYCZNEGO UTLENIANIA

Streszczenie

Stale rosnąca konsumpcja farmaceutyków przyczynia się do zwiększenia ich stężenia w środowisku wodnym, które kształtuje się na poziomie od kilku ng/dm^3 do kilku µg/dm^3. Liczną grupę wśród farmaceutyków występujących w wodach powierzchniowych stanowią niesteroidowe leki przeciwbólowe i przeciwzapalne, do których należy m.in. diklofenak. W pracy przedstawiono możliwości kontroli analitycznej procesu fotokatalitycznego utleniania diklofenaku w środowisku wodnym. Do badania skuteczności procesu zastosowano różne metody instrumentalne, w tym analizę HPLC poprzedzoną ekstrakcją do fazy stałej oraz pomiar przewodności właściwej, absorbancji w UV (λ=276 nm) i ogólnego węgla organicznego. W celu określenia obniżenia stężenia usuwanego związku przydatna okazała się analiza chromatograficzna, z którą w dobrym stopniu korespondowały wyniki pomiarów absorbancji w UV. Dowiedziono, że pomiar chromatograficzny charakteryzuje się większą czułością niż pomiar absorbancji wody. Na podstawie pomiarów ogólnego węgla organicznego określono, że degradacja usuwanego związku nie jest kompletna i powstają produkty uboczne tego procesu.

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THE INFLUENCE OF pH ON SOLUBILITY OF COPPER IN SOILS CONTAMINATED BY COPPER INDUSTRY IN LEGNICA

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The aim of the study was to determine the influence of changes in pH on the solubility of copper in soils contaminated by copper industry. Soil samples were collected from the surface soil horizon (0-30 cm) at two sites situated in the vicinity of Legnica Copper Smelter. Soil material contained various concentrations of total Cu. Soil samples were treated with various doses of HCl and NaOH, in the presence of $CaCl_2$ as a background electrolyte. Copper concentrations and pH values were determined in the extracts obtained from the experiment. Buffering capacity curves were prepared on the basis of those results. The changes in pH affected the solubility of copper in contaminated soils. Addition of HCl resulted in increased copper solubility, particularly strong at the doses higher than 0,2 M HCl kg^{-1}.

Keywords: soil, copper, pH, mobility, copper mobility, soil pollution Legnica Copper Smelter

1. INTRODUCTION

Strategies of reclamation in Poland are based on the immobilization of contaminants, in particular heavy metals, and not on their removal from the environment. The choice of such solution results from economical and technical factors. Although the problem of soil pollution with heavy metals remains in Poland of local importance, in the surroundings of metal smelters, there are many multi-hectare polluted areas where soil decontamination would be very expensive and unprofitable [4, 11].

Toxicity and mobility of heavy metals in soil environment depends on soil properties and changes together with changing soil conditions.The most important factors that determine the mobility of heavy metals in soils include:

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the original geochemical form of the element, soil pH, sorption capacity, redox conditions, and the presence of competing ions or chelating compounds [4, 11].

Landscaping may cause the changes in soil conditions, for example it may affect soil pH, cation exchange capacity. A possible result of such changes may be mobilization of heavy metals and their migration to the groundwater or their uptake by soil organisms and plants [1, 5, 8, 10].

Legnica Copper Smelter was established in 1951 under the name of Legnica Metallurgical Plant. After the discovery of huge deposits of copper ore in Lubin by Jan Wyżykowski in 1957, the plant was modernized. The basic product of Legnica Smelter is electrolytic copper. For many years the plant remained on the black list of the biggest polluters in Poland. Nowadays the smelter produces 100 tousand tonnes of copper yearly [2, 3, 6, 7].

2. MATERIAL AND METHODS

Soil samples were collected at two afforested sites located in immediate vicinity of the Legnica Smelter at a distance of 50 m and 650 m from the smelter border – Fig. 1., fig. 2). These terrain are the most contaminated afforested areas in proximity of smelter. Dominant tree species are willow, birc-tree and juvenile pine. Samples of soil material were collected in 5 replicates. Dried soil material was sieved through a mesh with thickness of 1mm.

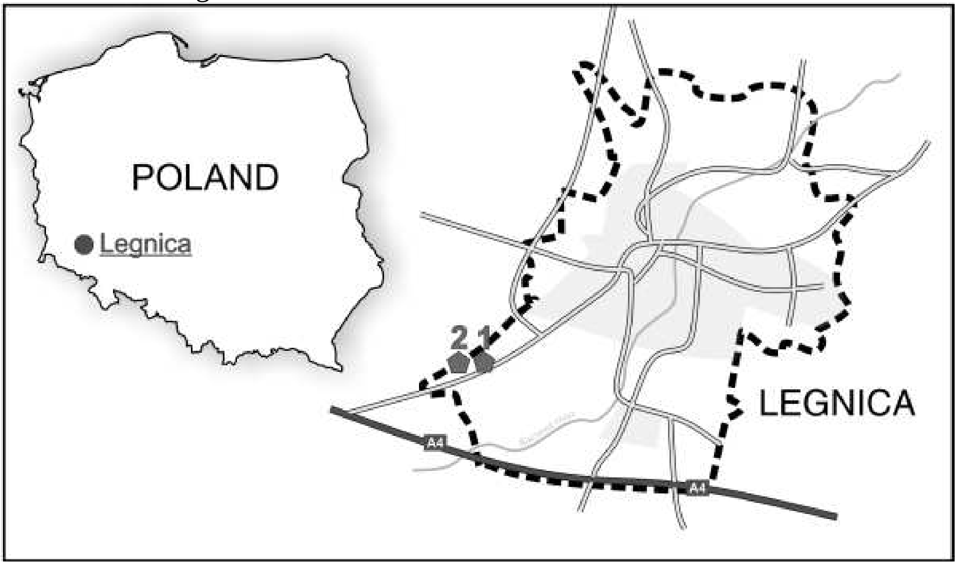

Fig. 1. Sampling locations (own elaboration)

Following parameters were determined: grain size distribution by areometric-sieve method modified by Prószyński, pH in H_2O and 1 M KCl by potentiometrical method, cation exhange capacity CEC by Kappen method, organic carbon content by CS-Mat 5500 machine and the total content of copper by AAS - after soil digestion in perchloric acid [12].

Prepared samples were extracted with 0.01 M calcium chloride ($CaCl_2$) in three replicates. Two sets of samples were independently treated by solutions of 1 M NaOH and 1 M HCl. The suspension (5 g of soil and 25 cm^3 of $CaCl_2$) was supplemented with 0.1 cm^3, 0.2 cm^3, 0.5 cm^3, 1 cm^3, 2 cm^3 and 5 cm^3 of 1 M HCl or 1 M NaOH and was made up to 50 cm^3 of appropriate amount of distilled water. The suspension was shaken on an overhead shaker. The extraction time was 1 hour. The solution was than filtered through paper filter. In the obtained extract, the concentration of the copper was measured by atomic absorption spectrophotometry AAS. The concentration of Cu in extract is a measure of the mobility of copper in soil, related to a specific pH value. In addition, the pH of the suspension was measured for each of the additives and water (control solution) [12].

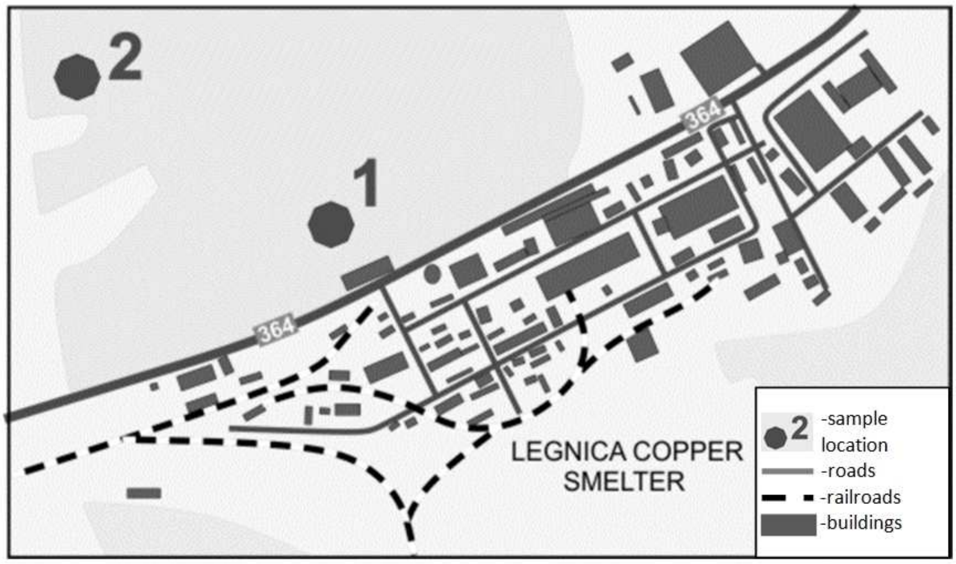

Fig. 2. Sampling locations (own elaboration)

3. RESULTS AND DISCUSSION

Both examined soils had a texture of silt loam. The reaction of both soils was acidic and their pH values, measured in KCl, were 5.3 and 4.5, in soils No.1 and No.2, respectively. Cation exchange capacity of soils was within the range of 6,36-6,56 cmol (+) · kg^{-1}. Total copper content was 927 mg Cu · kg^{-1} in soil No. 1 and 566 mg Cu · kg^{-1} in soil No. 2.

Total concentrations of copper in soils was assessed as typical, and representative of the contaminated soil occurring in the surroundings of Legnica

Copper Smelter. Physical and chemical properties of both soils, shown in Tab. 1, are also typical for this area [6, 7].

3.1. The effects of HCl and NaOH addition on pH of soils

Analysis showed that there were significant differences in pH values between the analyzed soils and control solution (in H_2O – fig. 3).

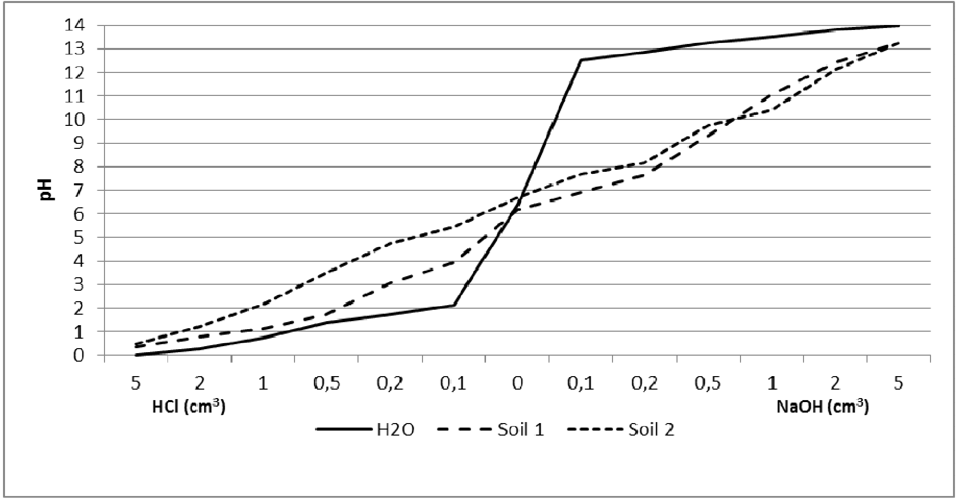

Fig. 3 The changes in pH after additon of various volumes of 1M HCl and 1M NaOH to analyzed soils.

The differences between pH values of contaminated soils and control sample proved relatively high buffering capacities against NaOH of soil No. 1 and soil No. 2. These capacities of both soils were similar.

On the other hand, addition of various doses of 1 M HCl showed higher buffering capacity of soil No. 2 against HCl if compared with soil No.1. These differences may be explained slightly higher content of organic carbon and a bit higher cation exchange capacity of soil No. 2 (Tab. 1).

Table 1. Basic properties of analyzed soils

Soil No.	Textural group	pH		CEC cmol(+)·kg^{-1}	C_{org} %	Fraction <0,002 mm content	Total Cu, mg·kg^{-}
		KCl	H_2O				
1	SiL	5,3	5,9	6,36	1,2	7	927
2	SiL	4,5	5,3	6,56	1,8	10	566

3.2. The influence of pH on copper solubility

The application of different doses of 1 M HCl and 1 M NaOH caused changes in copper solubility in soils. Increasing doses of hydrochloric acid caused an increase in solubility of copper in both soils. The highest solubility of copper in soil No. 1 was observed after application of the largests doses of acid, i.e. 1 and 5 cm^3 HCl. These doses are equivalent of 0.2 and 1.0 M HCl per kg soil. This effect of Cu solubilization was associated with an extreme decline in the pH value of the suspenions, to the values below 1.0, when iron and manganese oxides dissolve. As a result of this process, chemically bound and occluded copper was released into solution. Extremely low pH values may also cause breakdown of the primary and secondary clay minerals, which normally effectively bind heavy metal cations. In the extracts with the addition of 1M NaOH, copper concentrations were significantly lower than those found in extracts without additives. Fig. 4 presents the effects of pH on copper solubility in soil No. 1. It is worth mentioning that a slight increase of Cu solubility was observed after addition of the largest amount (5 cm^3) of NaOH. It could be a result of forming a negatively charged complex ions ($Me[OH]^{n-}$), complex bonding of copper with ammonium ions or with low molecular weight organic compounds.

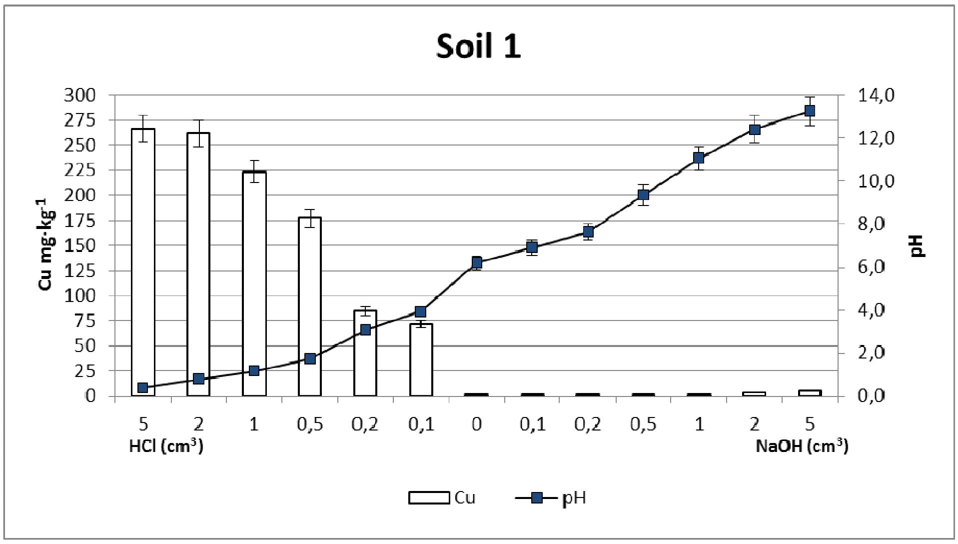

Fig. 4. The influence of pH on solubility of copper in soil No. 1.

The results obtained in the case of soil No. 2 were similar to those described above. Fig. 5 presents the effects of pH on solubility of copper in soil No. 2. Application of hydrochloric acid caused substantial increase in copper solubility in soil. There was a sharp increase in the amounts copper released to solution with the addition of 0,5 cm^3 HCl. Absolute amounts of Cu released from soil No. 2 were lower that those solubilized from soil No 1, that contained higher total copper concentration.

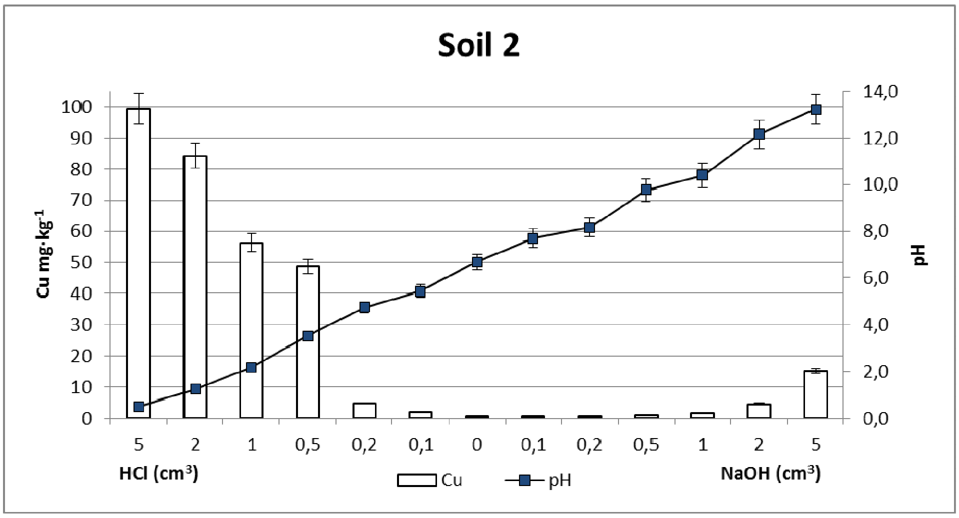

Fig. 5. The influence of pH changes on solubility of copper in soil No. 2.

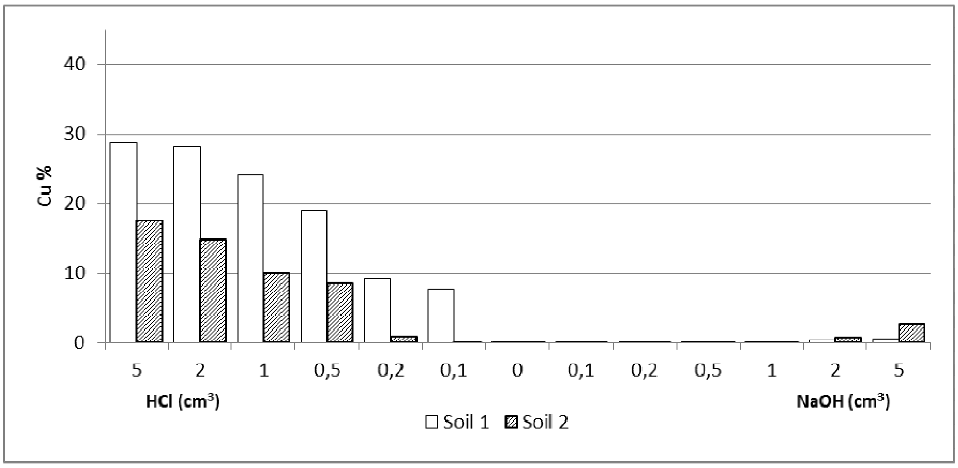

Fig. 6. Percentage of released Cu from contaminated soils, related to total Cu concentrations in soils No.1 and soil No. 2, as dependent on the rates of applied NaOH or HCl.

The maximum amount of copper released from soil No. 1 reached about 30% of total Cu, while in the case of soil No. 2 this quantity was about 18% (Fig. 6). This hypothesis is confirmed by the fact that higher contents of copper were leached by sodium hydroxide from soil No. 2. This indicates that the organic matter in soil No. 2 bonds higher quantities of copper. Further evidence of this is sharp increase of copper solubility in soil No. 1 with the 0,1 cm^3 HCl dose.

3.3. Assessment of copper solubility in relation to soil reclamation

Total content of copper in soil No. 2 exceeds the permissible value established in Regulation by the Minister of Environment (DzU. 165, poz. 1359). At the same time, the content of soluble forms of copper is negligible. Therefore, copper remains in fact unavailable to plants and does not pose a real environmental risk. In addition, as a result of an effective flue gas desulphurization, there is no risk of severe soil acidification from that source. Flue gases discharged from Legnica Copper Smelter contain, apart from large amounts of copper and lead, also such compounds as: $Ca[Mg_{0.67}Fe_{0.33}][CO_3]$ – dolomite, $Ca[FeMg][CO_3]_2$ – ankerite, $Ca[MgFe]Si_2O_6$ – augite, which effectively neutralize the pH of dust [9].

There is, however, another source of potential risk, i.e. the presence of forest litter and its decomposition in afforested ecosystems. Low molecular weight organic acids can bind copper into a form of mobile complexes. This may result in leaching of contaminant into the soil profile. Another factor that should be considered as a potential source of soil acidification, is “physiologically acidic” fertilizers used in forestry. Therefore, various kinds of soil treatment that may lead to copper mobilization, should be banned. It is also important to keep monitoring of soil pH value in this area [5, 7, 8].

4. CONCLUSIONS

1. Soil No. 2 has better buffering properties against acidification compared with soil No. 1. This difference results most likely from higher content of organic matter.
2. Increasing HCl doses caused a significant increase in the solubility of copper in soils, particularly dramatic at the doses of 0.2 M HCl per kg soil and higher.
3. At extremely high pH of extracts, a slight increase of copper solubility was observed in the soil No. 2.
4. Despite very high total concentrations of copper in soils in the vicinity of Legnica Smelter, copper solubility in neutral or slightly acidic conditions remains very low, and thanks to high buffering capacity of soils it does not pose a real environmental risk.

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WPŁYW PH NA MOBILNOSC MIEDZI W GLEBACH ZANIECZYSZCZONYCH PRZEZ PRZEMYSŁ MIEDZIOWY W LEGNICY

Streszczenie

Celem niniejszych badań było określenie wpływu odczynu na mobilność miedzi w glebach zanieczyszczonych przez przemysł miedziowy.W doświadczeniu pobrano dwie próbki glebowe z poziomów powierzchniowych (0-30cm) z otoczenia Huty Miedzi

Legnica. Materiał glebowy różnił się całkowitą zawartością miedzi w glebie. Próbki gleby traktowane były różnymi dawkami HCl i NaOH w obecności $CaCl_2$ stanowiącego elektrolit podstawowy. W ekstraktach oznaczano stężenie miedzi i pH. Na tej podstawie wykreślono krzywe buforowe dla obu gleb. Zmiany wartości pH wpłynęły na rozpuszczalność miedzi w glebach zanieczyszczonych. Dodatek HCl w ilości przekraczającej 0,2 M kg^{-1} spowodował radykalny wzrost rozpuszczalności miedzi.

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SHAPING THE WATER CONDITIONS IN THE POST-MINING AREAS (A CASE-STUDY OF BROWN COAL MINE „ADAMÓW”)

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The article presents the issues of shaping the water conditions in the mining areas given the example of Brown Coal Mine "Adamów". At the stage of the exploitation of deposit by opencast mining, the water conditions in the mining areas are transformed, which is associated with the need to adapt their functions to the needs of the mining and energy sectors. These changes relate to the deep dehydration of aquifer horizons, transformation of hydrographic network (removal of watercourses, reconstruction of the riverbeds, construction of drainage canals) and, consequently, changes in the water cycle. After the exploitation, the reconstruction of water resources becomes an essential condition to achieving the equilibrium of these areas. The concept of formation of water conditions in the post-mining areas of KWB (Brown Coal Mine) "Adamów" presented in the study, takes into account the environmental aspect of the functioning of the water management (shaping of landscape water retention through the construction of water reservoirs, limitation of water discharges from the drainage to the network of surface water and retention within the catchment area) as well as its social dimension (development of recreational-holiday functions).

Keywords: post- mining areas, water conditions, water reclamation

1. INTRODUCTION

The over forty years of the intensive exploitation process of lignite deposits in the Polish Lowland, constituting a priority against other environmental and social conditions, has forced the changes in the functioning of the natural environment. In particular, they concerned the deep dehydration of aquifer horizons, transformation of the terrain and vegetation, which are the key

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components that determine the formation of water conditions of the landscape. As a result, the surface water in mining areas form a complicated, multi-functional system that requires an integrated way of management, which takes into account the aspects of quantity and quality of water as a raw material for the power industry, but above all, as the most important factor necessary for the proper and sustainable functioning of the natural environment. The issue of water management endearing the issues outlined above will be discussed in this paper on the example of the mining areas of KWB "Adamów”.

2. TRANSFORMATION OF WATER CONDITIONS IN MINING AREAS

The area remaining within the range of influence of KWB “Adamów”, along with the currently exploited deposits Adamów and Koźmin, is located below the line of maximum glaciation of the Vistula River (Baltic) that separates the lake districts from the lowlands. It includes the mesoregion of Turku Plateau and Kolska Valley, which is a fragment formed during the Middle Poland glaciation of the South Greater Poland Lowland [5]. The total lack of natural surface water bodies is a characteristic feature of the old-glacier landscape formed during the older glaciation period. The deposits of Adamów and Koźmin are located in the catchment of the Kiełbaska river, Struga Janiszewska and Teleszyna, associated with the left-bank of the Warta river basin.

In the period preceding the exploitation of deposits and the functioning of "Adamów" power station, the Kiełbaska river’s catchment covered the area of 287 km². Due to the water needs of the power station, Teleszyna River, after the creation of Canal Warta-Kiełbaska, was partially used as an artery for water transfer. Having connected the Warta-Kiełbaska system to Kiełbaska river, which is the basin of the upper Teleszyna, the area of Kiełbaska’s catchment increased to 476 km², which is close to 66% [1]. During the exploitation of the opencast pit Adamów and Koźmin, the waterbed of the Kiełbaska will not be changed; only the eastern part of the catchment is under the influence of the cone of depression, causing depletion of its water resources. The planned Adamów reservoir, along with the supply canal (running from the water intake on the Central Kiełbaska), shall create its own catchment, contributing to a reduction in the catchment area of the Kiełbaska. Currently, the Kiełbaska’s hydrological regime is the result of interactions performed by the economic functions as well as environmental conditions of the anthropogenically modified river basin. The main components, which regulate the flow rate of the Kiełbaska are as follows:

- water from the natural catchment of the Kiełbaska

- water from the catchment of the Upper Teleszyna (covering the area of 206.26 km^2)
- water pumped by a pumping station Miłkowice (in Ostrów Warcki) with Jeziorsko Reservoir (on the Warta)
- mine water from the Adamów and Koźmin open pit drainages
- abstractions of non-returnable water for the cooling system of "Adamów" Power Station
- discharges of the excess water not used in the technological system of “Adamów” Power Station.

The size of the individual components are variable and shape the average annual flow of 1.45 m^3 s-1, and the average annual runoff per unit is 3.56 dm^3 s-1 km^2 [11]. The reduction of the unit outflow (3.56 dm^3 s-1 km^2) in relation to its characteristic value for the period preceding the development of mining (4.3 dm^3 s-1 km^2), despite an increase in the annual flow rate, is related to the influence of the cone of depression, within which, after the beginning of exploitation, there are fragments of the catchment.

The Teleszyna as well as its catchment have been permanently transformed due to mining activities. Part of the Teleszyna’s riverbed in the Przykona-Zimotki region was liquidated by the excavations of the open pit Adamów. Currently, water reservoir with a maximum flood area of 123.2 ha was built.

Struga Janiszewska and its catchment, within the exploitation period, along the whole section, are in the impact zone of the open pits. On the stretch of 2.99 km, the riverbed was destroyed by external dumping ground, and its function was overtaken by, so-called, Passive Channel, which was built along the eastern edge of the pit. Struga Janiszewska in its upper course carries periodic water - after a heavy rainfall, which is related to the impact of the cone of depression of the open pits Adamów and Koźmin. Having finished the exploitation and the creation of reservoirs Adamów, Janiszew, Koźmin, Głowy, the initial catchment area of Struga Janiszewska (49.08 km^2) will be reduced by 23.08 km^2, and the catchments created around the reservoirs Janiszew and Koźmin will divide it into two parts.

The Length of the Kiełbaska II (right tributary of the Kiełbaska), during the exploitation of the northern part of open pit Koźmin (years 2014-2020) will be reduced (from 15.49 to 11.25 km) due to the elimination of the source section of the river. After the construction of the reservoir Koźmin Końcowy, the catchment of the Kiełbaska II with the current area of 12.69 km^2, will be reduced by 2.75 km^2 and will cover the area of 9.94 km^2 [9].

The change of the course and order of watersheds, their uncertain nature within the mining areas, changes of the catchment area and the consequent difficulties of balancing them, are all the results of these transformations within the hydrographic network.

The changes in structure of groundwater are associated with dewatering of the deposit and its overburden. Within the area of the exploited deposits Adamów and Koźmin there are two main aquifer levels associated with the overburden (quaternary superficial) and subcarbonic-cretaceous complex. The dehydration of the open pit "Koźmin" located in the vicinity of the open pit "Adamów" results in joint cones of depression in both analyzed aquifer complexes of those pits. Their sizes are constantly changing due to the displacing exploitation of the open pits, as well as hydro-meteorological conditions. Hence, the ranges of the cones of depression are given and analyzed within specified period of time and state.

The above characterized transformations within the surface water and groundwater are marked also in the structure of the water balance of the catchment with the increase of the revenue side, where apart from rainfall, one must take into account the amount of the mine water discharged into the hydrographic network and the volume of water transferred from the Warta. The side of outgoing water gets reduced, because the catchments, or parts of them, which are within the coverage of the cone of depression, with the transformed surface layers of soil and changed moisture relations are characterized by reduced evaporation.

The above given examples of transformations of surface and groundwater within the influence of KWB "Adamów", help to identify that the most important feature which characterizes water conditions in the areas of the opencast lignite mines is deepening of the deficit of water resources by:

- water transfers between the catchments
- discharges of mine water directly to the surface water network (without trying to bring it into cultivation) outside the mining area, which perpetuates the dehydration process and prolongs the stagnation of the cone of depression
- change (usually decrease) of the unit outflow
- changes in physical parameters of the water associated with the exploitation and open-circuit cooling
- reduction of retention as a result of the liquidation of small water courses, streams, ditches, wetlands, small mid-field reservoirs that store large amounts of water [3].

Limiting the quantity and quality of disposable water resources by mining activities, which adds up to a shortage of water, due to natural conditions (typical of Polish Lowlands) is the main problem of water management in mining areas.

3. THE RATIONAL DEVELOPMENT OF WATER CONDITIONS IN MINING AREAS

The rational shaping of water relations means the implementation of the basic principles of proper water management: maintaining, as long as possible and as much water as possible in the landscape, thus, minimizing an idle outflow from the catchment. The opportunities to develop appropriate landscape structure in the process of multi-direction reclamation of post-mining areas accelerate the return of a degraded environment to a new state of equilibrium. In areas of the opencast lignite mining, prerequisite for the pursuit of balance is the reconstruction of water resources. The fulfillment of this condition is possible through an alignment of the outflow, and this process is associated with the need for retention of significant amounts of water. The largest volume of retained water is achieved through the construction of large reservoirs and proper shaping of the landscape structure, which will support the retention capacity of water resources and contribute to the increase in effectiveness and efficiency of the regulatory system of evaporation from the soil for transpiration [6].

Within the mining area subjected to analysis KWB "Adamów" in the 90's, after the period of transformation of water conditions as a result and the effect of the priority mining activities, began the stage of rational development of water resources through the development of water retention of landscape.

Shaping the landscape water retention is associated with undertakings that lead to the construction of water reservoirs. Currently, the four water reservoirs Bogdałów, Przykona and Janiszew, and Koźmin are the new elements of the post-mining landscape. Until the end of exploitation in this area (by the year 2023) there are plans to build three other ones. Realization of the project to build water reservoirs will mean that, in the landscape, where previously there were no natural water reservoirs, the share of surface water bodies will increase to 1062.17 ha, and the amount of retained water in the reservoirs will exceeds 231 million m^3. The list of the created and planned reservoirs and their parameters is presented on Table 1.

We shall pay special attention to the fact that the newly created and designed water reservoirs are located in areas completely transformed by mining activities, where the original ecosystems characteristic for the area of bio- and geo-diversity, have been permanently degraded. Construction of the reservoir bowl is carried out only with the use of land heaps from the overburden opening subsequent mining fields and hollow ends, and is a form of reclamation of post-mining areas.

Table 1. Present and planned reservoirs in the Adamów brown-coal mining area.

Reservoirs created in the post-mining areas of KWB „Adamów"								
Reservoir (name)	Completion date	Area of reservoir min-max	Capacity min-max	Usable capacity	Permanent flood reserve	Losses to evaporation	Function	Location
	year	ha	mln m^3	mln m^3	mln m^3	mln m^3		
Bogdałów	1994	9,5	0,6	unknown	unknown	unknown	initially fire-fighting, later recreational, natural	external dump open pit Bogdałów
Przykona	2004	242	5,9-7,2	bd	bd	bd	recreational, natural, firefighting	internal dump open pit Adamów
Janiszew	2008	56,39-59,57	3,5-4,05	0,55	0,119	0,161	recreational	internal dump open pit Koźmin
Koźmin	2012	106,0-108,5	5,50-6,1	0,54	0,217	0,293	natural	post-exploitation excavation.open pit Koźmin
Planned reservoirs								
Głowy	ca.2014	63,5-64,5	17,3-17,7	0,42	0,129	0,174	recreational	post-exploitation excavation open pit Koźmin
Koźmin-końcowy	ca.2020	115,2-116,1	33,4-34,1	0,66	0,232	0,313	natural	final excavation open pit Koźmin
Adamów	ca.2023	462,0-462,0	161,7	0,00	0,924	1,247	unknown	final excavation open pit Adamów

Source: Own study based on [9].

Therefore, the controversy on the building of water reservoirs, associated with their negative impact on the environment, is not, in this case, subject to discussion. Occupying the land under the reservoir, degradation of existing aquatic habitats, destruction of the soil profile, the movement of large quantities of land masses and transformations of the terrain are all the already made changes. Reservoirs, with the exception of the reservoirs Przykona and Koźmin Końcowy, are located outside riverbeds (so called side reservoirs) and are supplied by surface water through the tributary canals which enables the fulfillment of another essential condition, from the ecological point of view: continuity and integrity of watercourses.

Another element of rational development of new water relations in mining areas is an attempt to reduce discharges of water from the drainage to a network of surface water and its retention within the catchment. It can be achieved thanks to a developed and adopted system of filling newly created reservoirs. Reservoir Przykona, which has been functioning since 2004, was filled with groundwater from dehydration of open pit Adamów. Reservoirs Koźmin and Głowy will be filled with groundwater from deep drainage by wells from the deposit Koźmin. Reservoirs Koźmin Końcowy and Adamów Końcowy shall be created in post-exploitation excavation of deposits Koźmin and Adamów, at the end of exploitation. Reservoirs' bowl will be formed by slope excavation and their sills. Reservoirs will be filled with groundwater from drainage wells located on the edge of the pit (bowl). Along with filling up the cavities, the amount of infiltrating water from the reservoirs will increase and, concurrently, the amount of water pumped by wells will decrease. Both of these processes will extend the time of filling up the reservoirs, but, at the same time, they will affect the regression of the cone of depression and the reclamation of aquifers. During this period, reservoirs will go for surface water supply, the amount of which should compensate for the loss of infiltrating water into the cone of depression and evaporation [9].

After the completion of the filling up of the reservoirs, within their impacts new regime of the waters will be shaped. Water reservoirs shall combine quaternary aquifers with the subcarbon – cretaceous level. In the hydrographic network system, we can clearly observe the changes in the course of watersheds connected with the separation of the sub-catchments of existing and planned reservoirs (Fig.1).

Technical casing of watercourses and reservoirs, which involve distribution structures (weirs, sluices' shafts), intake structures (culverts, pipelines) and damming structures (monks, transfers), allow to conduct water management of the catchment and regulate water conditions within it (e.g. supplying the reservoirs, water abstraction from rivers, water transfers between reservoirs, emergency management of water during floods, irrigation, fish farming). Reservoirs are the local drainage base, which determines the relations

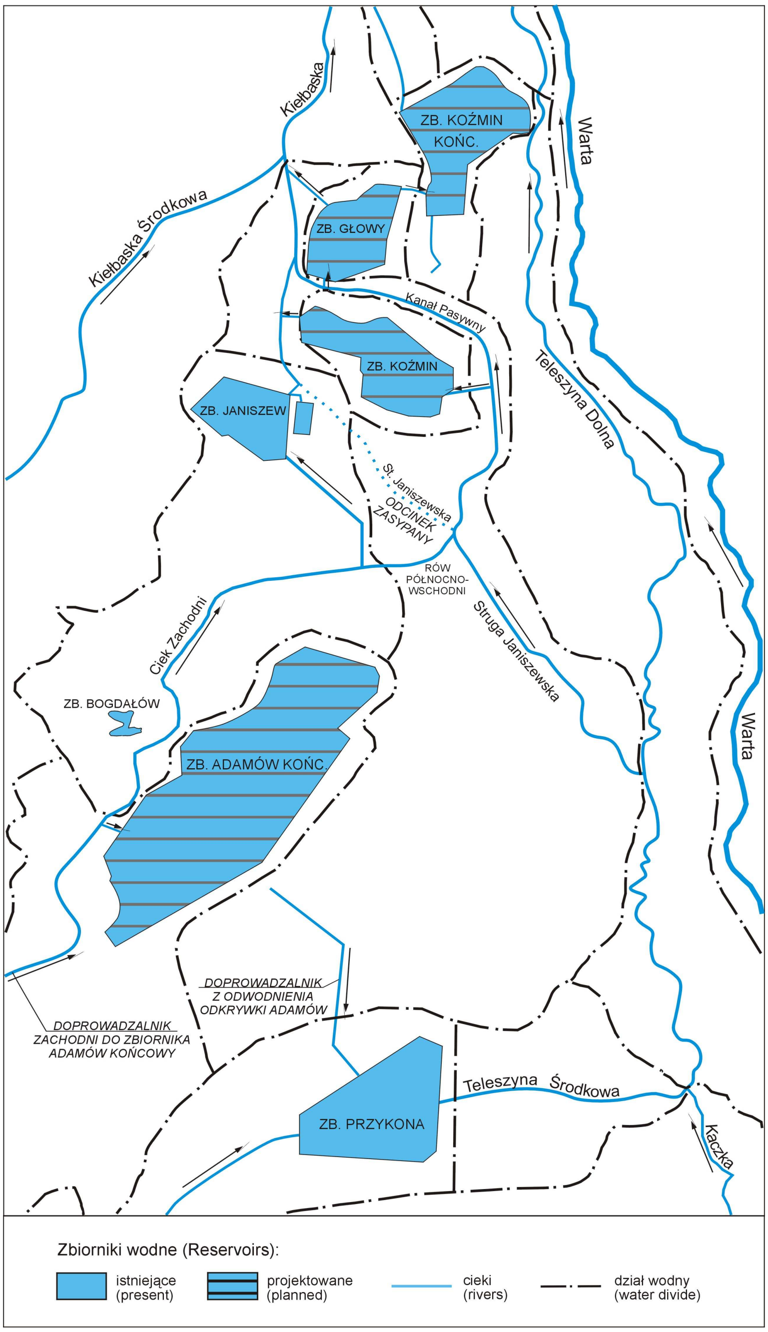

Fig. 1. Water conditions in the area of the Adamów Brown-Coal Mine on completion of exploitation (a conception). Source: [3] own study based on [9].

of the regime of surface and groundwater with the exploitation regime of reservoirs [12].

Reservoirs covering the extensive excavation, due to the water infiltration in the surrounding areas, will support the process of reconstruction of aquifers, and later, will contribute to the stabilization of the depth of the groundwater table and to the increase of the land retention resources. Thanks to the possibility to control the outflow from the catchment, by regulating the amount of the height of damming streams, there is a favorable hydraulic system between the groundwater table and the water flowing in the watercourse, which inhibits undesirable outflow to the groundwater, which underwent retention during the winter half-year, most often abundant in water [8]. Moreover, carrying out the irrigation with adjustable outflow increases retention of soil and promotes more efficient use of rainfall by vegetation, reducing the outflow. The creation of multiple possibilities, within a year, of renewal of capillary and groundwater retention allows the elimination of water shortage of 150 - 200 mm per year [7]. Usable capacity of reservoirs will come to between 420 – 660.000 m³ which gives a total of 2.17 million m³ Taking into account the possibility of 20 cm over-damming during flood releases, one can get flood reserve of 1.62 million m³ (Table 1).

4. THE IMPORTANCE OF WATER RESERVOIRS IN THE SHAPING OF POST-MINING LANDSCAPE

The most spectacular result of the implementation of the above concept of water reclamation is to change the landscape structure in the vicinity of Turku. Lake-density at the level of 6.97%. will be a new feature, which distinguishes this area (within the mining area of Adamów-Koźmin covering the area of 152.2 km²). For comparison, the lake-density index for Poland is 0.9% and for the areas with the highest concentration of lakes (according to Choiński, 2005): Mazury Lake District 3.05%, Pomeranian Lake District 2.03%, Greater Poland - Kujawy Lake District 1.23%.

Enriching the landscape structure with water reservoirs with a total area of 1,062.17 ha has an impact on different aspects of the functioning of the landscape. The first one is the increase in volume of evaporation, and consequently the increase of amount of water brought to the troposphere. According to the research of Rzętała [12] in the case of anthropogenic Rybnik Reservoir, one estimates 100 % increase in evaporation compared to the original terrain evaporation (before the formation of the reservoir), which provides, based on the total surface of the reservoir (450 ha), about 6 hm³ of water yearly. On this basis, it can be estimated that as a result of evaporation from the surface of all of the reservoirs formed in the area of KWB Adamów, the amount of water in the troposphere within one year will increase by 10 - 15 hm^3 and this estimation will be very significant in the water balance of the area and the reconstruction of water conditions. The presence of water reservoirs is also associated with the change of the topo-climatic conditions. The changes relate mainly to the increase in average daily air temperature, alleviating extreme low air temperatures in winter and hot in summer, with a lengthening of the growing season, limiting the occurrence of thermal inversions, increase in humidity and rainfall, more frequent fog and mist formation as well as a slight increase in wind speeds [4]. According to Lewińska (after [4]), the climate effects of large water reservoirs with the surfaces of 300 - 400 ha, might be noticeable at a distance of 2-3 km from the coastal zone.

Anthropogenic water reservoirs, either as a result of reclamation activities or as a result of spontaneous processes, take up ecological functions. Reservoir Bogdałów is such an example. Around it, in the process of natural succession, the sequence of aquatic, rushes and scrub vegetation, typical for limnetic reservoirs, has developed. New landscape elements, created in the process of reclamation, become biotopes for species-rich biocenosis. Artificial island on the "Przykona" reservoir, is currently a nesting colony of 6 species of gulls (including the only one in Greater Poland blackface gulls) and 2 species of terns, which makes it one of a few in Poland and Europe, mixed, multiple-species refuge of gulls and terns [13]. Within the settlers of dirty water in Piorunowe (open pit Władysławów) and Pęcherzewo (open pit Adamów) filled mainly by mineral - organic matter, rich habitat for many species of flora and fauna were shaped, especially waterfowls and wetland birds. In terms of natural valorization they form valuable communities. In order to preserve biodiversity of formed habitats, it is proposed to take the legal form of protection of settlers in the form of ecological grounds. These examples allow us to conclude that formation of habitats, which, previously, did not exist in this area and those related to it increase in biodiversity, thus becoming the most spectacular landscapes effect associated with the construction of water reservoirs.

Water reservoirs, formed in old-glacial area devoid of lakes, which are filled with clear waters of the deep drainage**,** around which the area with high natural values is created, are of significant importance for the development of tourism and recreation. The development of tourist-leisure facilities favors the use of reservoirs for leisure purposes. In the vicinity of the "Przykona" reservoir, there is a scouts’ base, three bridges, car parks, guarded bathing zone with a sandy beach, water equipment hire, a snack bar functioning during summer and a football pitch. About 30 hectares of land around the reservoir were allocated for building holiday resorts (400 recreational plots) and services related to tourism and recreation. The whole complex of recreational areas is equipped with the power grid, water supply, access road, parking lots and sewage system. During the next stage, volleyball, basketball and tennis courts, changing rooms, showers and the lighting system are to be built. Water reservoir and its comprehensive development contributed to the development of new, previously non-existent (due to the lack of natural conditions of the area) forms of tourism, mainly associated with water: canoeing, surfing and sailing. Development of the area around the reservoir offers excellent conditions for active recreation (swimming, fishing, team games, walking, jogging) and recreation (sunbathing, camping). Created as a result of the water reclamation reservoirs, it performs a variety of functions, but because of its location in the immediate vicinity of the city of Turku and at the back of the Łódź agglomeration, in a range of daily and weekend penetration, their recreational functions have had the most significant importance. Water reservoirs are currently one of the biggest tourist- recreational attractions of Turek district.

5. SUMMARY

There are two significant stages in the process of shaping of water conditions in the mining areas. The first is to convert water relations and adaptation of water management to the needs of the mining and energy sectors. Another one, which started in the last decade, is characterized by a rational and comprehensive development of water conditions. The complex approach takes into account the environmental aspect of functioning of water management (reclamation of water resources), but also its social dimension (development of the functions of tourist-recreational as well as leisure functions associated with water). The above outlined concept of shaping water conditions in the process of exploitation and after its completion, allows for modern water management in closed systems - river catchments and constructed reservoirs. These actions should then lead to an increase in the amount of water in the landscape, increase in the intensity of its circuit and thereby to produce a new balance in anthropogenic water systems.

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KSZTAŁTOWANIE STOSUNKÓW WODNYCH NA OBSZARACH GÓRNICZYCH (NA PRZYKŁADZIE KOPALNI WĘGLA BRUNATNEGO „ADAMÓW”)

Streszczenie

Wody powierzchniowe i podziemne terenów górniczych tworzą skomplikowany wielofunkcyjny system, który wymaga zintegrowanego sposobu gospodarowania uwzględniającego aspekt wody jako zagrożenia dla eksploatacji złóż, wody jako surowca dla przemysłu energetycznego, a przede wszystkim, wody jako czynnika niezbędnego do prawidłowego i trwałego funkcjonowania środowiska przyrodniczego. W opracowaniu przedstawiono problematykę kształtowania stosunków wodnych

w obszarach górniczych na przykładzie Kopalni Węgla Brunatnego „Adamów”. Na etapie eksploatacji złóż metodą odkrywkową stosunki wodne w obszarach górniczych ulegają przekształceniom związanym z koniecznością dostosowania ich funkcji do potrzeb górnictwa i energetyki. Zmiany te dotyczą głębokiego odwodnienia horyzontów wodonośnych, przekształceń sieci hydrograficznej (likwidacja cieków, przebudowa koryt, budowa kanałów odwadniających), przekształceń rzeźby terenu i szaty roślinnej, czyli podstawowych komponentów, które warunkują kształtowanie się stosunków wodnych krajobrazu. Po zakończeniu eksploatacji działania w zakresie gospodarki wodnej powinny prowadzić do zwiększenia ilości wody w krajobrazie, zwiększenia intensywności jej obiegu, a tym samym do wytworzenia nowej równowagi w antropogenicznych systemach wodnych. Koncepcja racjonalnego i kompleksowego kształtowania stosunków wodnych przedstawiona w opracowaniu, uwzględnia aspekt środowiskowy funkcjonowania gospodarki wodnej (kształtowanie retencji wodnej krajobrazu przez budowę zbiorników wodnych, ograniczenia zrzutów wód z odwodnienia do sieci wód powierzchniowych i zatrzymanie ich w obrębie zlewni) oraz jej wymiar społeczny (rozwój funkcji turystyczno- rekreacyjnych, wypoczynkowych związanych z wodą).

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POST-MINING LANDSCAPE ECOLOGY - ANALYSIS OF SELECTED PROBLEMS, THE CASE OF ADAMÓW BROWN COAL BASIN

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The paper presents the main problems of the development of post-mining area landscapes, which are due to the ignoring or including, to a small extend, the environmental criteria in the process of reclamation. It refers to the newly shaped elements (forests, meadows, reservoirs, arable land), which create the ecological structure of post-mining landscape, and in particular their spatial distribution, structural and functional integrity with the areas not transformed by mining. On this basis, the principles of shaping the ecological structure of post-mining areas were formulated, which should become a code for good reclamation practice.

Keywords: post- mining landsapes, landscape ecology, reclamation

1. INTRODUCTION

The natural environment is a system which combines two basic categories of geographical space: the natural environmental system and anthropogenic environmental system which is formed as a result of human activity. In the precincts of Turku, anthroposphere is mainly the result of processes related to the opencast exploitation of lignite, and the post-mining landscape with its distinctive character (external and internal dump, final excavation) is their visualization. Its structure and functioning depend on the direction and strength of the interaction between post-mining geosystems and system of natural environment. Therefore, the post-mining areas are the element of the system of natural environment and require a systematic approach at all stages of their development. For the geographic space, the stage of reclamation and development is the most important, as it restores the environment bringing

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round the areas which were temporarily out of use and degraded due to exploitation. The policy of reclamation directions defines the types of new elements of landscape structure, which determines the shape and character of the post-mining areas. Mutual relations between the new elements of the structure as well as the relationship between the new elements of the structure and the environment decide how quickly the post-mining area should reach a new secondary equilibrium and take up new environmental, economic and social functions.

Observation of the processes of reclamation and development of post-mining areas in Poland, which have been taking place in recent decades, indicates a high level of adopted solutions of technical and biological reclamation. Optimization of reclamation methods focuses primarily on the criterion of the quality delivered in land use. The result is a full-fledged land, characterized by beneficial physico-chemical properties that create good conditions for the development of crops as well as forests. In the process of reclamation, however, the ecological criteria, to a certain extent, are ignored or taken into account. It refers to the principles of the spatial distribution of the newly emerging structures, their structural and functional integrity. This is particularly important in the case of multi-open-cast mines (KWB "Adams", KWB "Konin"), where the exploitation of lignite is carried out within a few, distributed spatially mining areas.

The purpose of this study is to identify the problems in the development of post-mining areas and an indication on the basis of the principles of the planning system; taking into account the ecological conditions of post-mining landscapes. This issue shall be illustrated by case study examples of reclamation of the post-mining areas of Adamowski Brown Coal Basin, where mining activity has been carried out for more than 50 years now. Opencast lignite exploitation is being carried out within the two mining areas "Adamów", and "Koźmin" while exploitation has been completed in "Bogdałów" and "Władysławów" open-cast mines. Since the beginning of mining until the year 2009, 928 hectares of land were reclaimed for forestry, 2185.00 for farming and 514 hectares for water or other resources [5]. The post-mining area in the precincts of Turek is 3627 hectares (36.27 km^2).

2. THE PROBLEMS OF DEVELOPING POST-MINING AREAS FROM THE POINT OF VIEW OF LANDSCAPE ECOLOGY

Landscape Ecology is a science that studies the components of the landscape and the ongoing relationship between them [8] and in particular spatial relations. Ecology of the landscape assumes that the spatial structure and configuration of the landscape play an important role in the conservation of biological diversity as they determine the possibilities for survival and spread of particular species [9, 4, 2]. Thus, the landscape ecology research focuses on the natural elements of the landscape, and in particular on their size (area), quality, distribution in space and the spatial cohesion resulting from this distribution. Analysis of the structure and configuration of the reclaimed post-mining areas, taking into account the above mentioned features, provides a basis for identifying problems that affect the functioning of post-mining landscapes. The most important ones are the following:

2.1. Limiting the concept of reclamation and management to the degraded areas through the process of exploitation

Post-mining areas with natural structures created by the process of reclamation, with internal and external relationships determining their functioning, are specific post-mining geoecosystems. Post-mining geosystem, even though it is man-made from the "terra nova" point of view, is not to be seen as an individual spatial unit, but as part of a greater whole, a component of the natural environment. In such a system approach, where the relations between particular elements are important, the reclamation plans should be linked with the environment and the spatial structure which surrounds the reclaimed area ("background environment") taken into account. That is because the environment affects various elements of post-mining geosystems and, furthermore, it has impact on the environment. The projects of reclamation of the open-pit mines clearly highlights the problem. The paths of reclamation are outlined within the borders of post-mining areas, while the information on the surrounding is limited to the presentation of situational elements in the form of roads or waterways. Thus, ignoring land cover types important for the functioning of the environment in particular, the elements forming the ecological structure of the area. Such an approach towards the reclamation process of the areas permanently altered by the process of exploitation is not conducive for adaptation in the natural environment, but emphasizes alienation and distinct new forms. It also contradicts the idea of temporary exclusion of the areas from being used and their re-inclusion into the functioning of the natural environment.

2.2. Lack of spatial connectivity of post-mining geoecosystems and the presence of natural geoecosystems in their surroundings

Spatial connectivity of the landscape is defined as the completeness of the natural resources that build ecological structure, enabling the maintenance of functional relationships between particular elements of that structure.

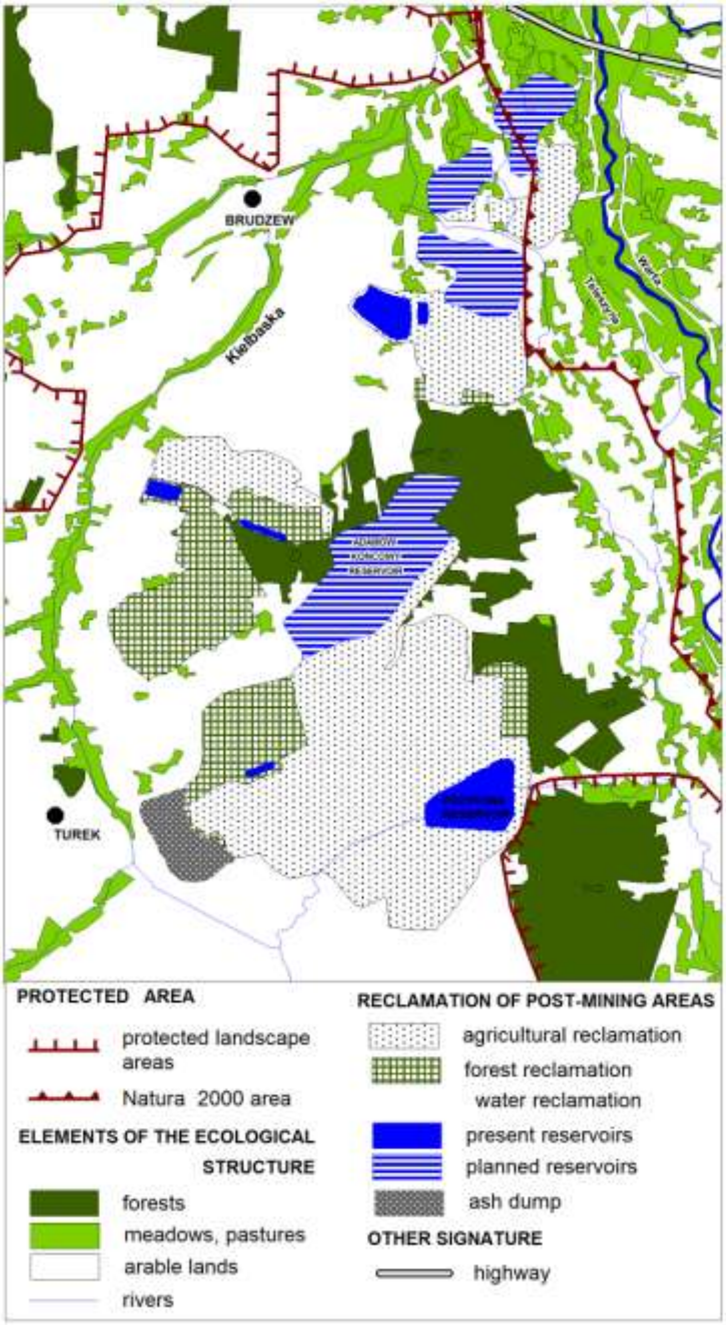

Fig. 1. Spatial distribution of post-mining geosystems against the ecological structure of the Adamów mining area (source: own work)

In the assessment of spatial connectivity of post-mining landscapes it is particularly important to assess the ecological relationships (continuity and discontinuity) between the post-mining geosystems created as a result of reclamation and natural geosystems located in their surroundings.

The basis for this assessment is the analysis of the spatial distribution of post-mining geosystems against the basic forms of land use, particularly important for the preservation of the ecological balance and biodiversity: forests, meadows and pastures, river valleys, reservoirs, protected areas (Fig. 1), occurring in the vicinity of open-pit mines. It allows for the identification of areas that need reshaping in order to restore, or maintain the spatial coherence of the natural system of pre-and post-mining areas. While shaping the post-mining landscapes, one should strive to protect main natural structures (large stands, the major ecological axis). However, if the conditions of deposit exploitation require elimination of such structures, one should, at the stage of reclamation place priority on rebuilding the lost land and its relations, as a result of the exploitation. Not taking into account these principles may result in the deepening of the problem of degradation of habitats and fragmentation of the natural matrix within the post-mining areas. The principles of reclamation of post-mining areas which take into account the issue of reconstruction of the ecological structure and development of ecological connections will be discussed under the example of the "Adamów” open-pit mine in the final part of the paper (Fig. 2).

2.3. The shaping of the structure of using the catchment of newly constructed reservoirs, which is unfavorable for water protection

Reclamation plans for the post-mining area of "Adamów" mine imply water reclamation of about 26% of the excavation area [5]. Three reservoirs Bogdałów, Przykona and Janiszew were given out to be used, and there are plans to build other five reservoirs until the end of exploitation period in this area (2023). For the sake of protecting them, it is important to develop, in the process of multi-direction reclamation, the most favorable structure of catchment use, particularly in the immediate vicinity of the reservoir. Biological reconstruction of the river bank zone by planting herbaceous vegetation, shrubs (willow scrub - alder, willow - poplar) and trees (reforestation) in a system depending on the functions carried out by the particular reservoir will prevent water erosion, which is the cause of the movement of the slime material in the catchment. Foliage around the reservoir creates the so-called biogeochemical barrier, which limits the flow of mineral matter (NPK-fertilizers, plant protection chemicals) into water, which supports its protection against pollution and eutrophication [6, 7].

Around the completed Przykona and Janiszew reservoirs no buffer zones were created. Surrounding the reservoirs is an open space, partly covered by sod of the synanthropic character, and partly devoid of vegetation, where one can observe the intensification of the processes of wind and water erosion. It also applies to the southern part of the Przykona reservoir which is intended for recreational use, where the sandy-grass sunbathing zone goes directly into a zone of allotment gardens and recreational buildings. Subsequent reclamation projects of the built reservoirs (Głowy, Koźmin, Koźmin-końcowy, Adamów) indicate that in their surrounding there will be agricultural land. Neither afforestation nor the creation of buffer zones is planned around the reservoirs. The implementation of water reclamation without taking comprehensive solutions into consideration, does not only have adverse effects on the functioning of the reservoirs, but also on the aspect of the landscape.

2.4. Lack of biological reconstruction of the river valleys, rivers and canals

One of the reasons for the change related to water in the post-mining areas is the transformation of the network of surface waters associated with the necessity of elimination of watercourses, relocation of the river troughs and construction of a number of drainage canals as well as the channels which are the arteries of water transfers (Warta–Kiełbaska Channel). For example, within the "Adamów" open-pit mine, part of the Teleszyn trough was closed-down. The progress of mining activities within the Koźmin deposit forced the replacement of 3.5 km section of the Struga Janiszewska on the eastern edge of the pit and the in-take of the waters by a so called Passive Canal. The need for the water management within the catchment and regulating water relations within its borders, requires technical reconstruction of the water courses and reservoirs in the form of distribution structures (weirs, embankment locks), estuaries (culverts, pipes) and dams. However, no attention is paid to the fact that the watercourses as linear structures, in the natural landscape, serve as ecological corridors, which are migration paths of matter, energy and organisms in the landscape. Moreover, they are also habitats for specific groups of species act as filter (barriers) and they have enriching and regulating (biotic and abiotic) impact on the environment. As a result of mining activities, many of these functions have been lost. Rebuilding of the ecological potential of the watercourses is possible at the stage of reclamation by introducing canals along the river, and biological recovery in the form of shrubs and tree plantings, which will strengthen and enrich the ecological structure. Observation of a new system of hydrographic network in the "Adamów" open-pit mine shows that the issue of renaturalization of the transformed watercourses and built canals as well as the forms of their natural enrichment are marginalized in reclamation project.

2.5. The landscape monotony of the large-scale internal spoil tips reclaimed for farming

Since the beginning of the "Adamów" open-pit mine, 2185 ha of agricultural land has been reclaimed. After the reclamation and agro technical activities the soils reach higher quality classes (III, IV) than the ones occupied for the purpose of mining - poor, sandy soils typical for the region. As a result of reclamation, a valuable land was created, which was efficient for the development of crop and dairy farming. However, while developing these areas, the ecological principles of shaping the agricultural landscape were ignored. As a result, the landscape was dominated by vast sheets of monotonous agricultural land devoid of ecological structure. The ecological structure of agricultural land is created by rows of mid-field woodlots along balks, watercourses and roads. They not only increase the aesthetic value of the landscape, but most of all, they stimulate geodiversity and biodiversity. They are a refuge for plants and animals, acting as a link between patches of forest and, thereby, reducing their isolation. The basic functions of mid-field woodlots are: reduction of wind erosion and water erosion of soil (windproof and waterproof function), shaping the microclimate and water protection [1, 10, 6, 7]. The introduction of mid-field woodlots in the reclamation of areas for agriculture is the most effective tool supporting water management by increasing the retention capacity of the environment (reducing evaporation from the soil surface, facilitating the infiltration of snow accumulation), increasing evapotranspiration, reducing run-off and increasing precipitation. These processes intensify water flow and increase the amount of water recirculating in an agricultural environment contributing to the favorable shaping of the water balance. In the post-mining areas where, after the stage of transition of water relations (dehydration), the reconstruction of water-bearing horizons is inevitable; and the support of this process by the properly shaping the structure of large areas reclaimed towards agriculture, is particularly important.

2.6. Geometric shapes of landscape borders

The borders of natural geosystems are developed (winding) and have a mild course. They form transitional zones called ecotones, within which the characteristic features for one system of components are gradually disappearing, while some typical features for the new system show up [8]. For example, the "full" border of the forest covers forest phytocoenoses – climber – bushes – herbaceous plants and moves into non-forest community (arable land). The borders of the post-mining ecosystems, in accordance with the borders of open-pit excavations, stand out characteristically from its surroundings with straight and sharp lines. They are formed, for instance, by a wall of monoculture forest and arable land. If correction of the shape of borders of post-mining complexes is difficult due to the technology of mining or land ownership, insomuch as the shaping of the borders is possible in the process of reclamation and justified from an environmental point of view, taking into account their spatial development (which is, creating transition zones between anthropogenic and natural geosystems). This is especially true in case of the borders between the land reclaimed into forest and other forms of land use (agricultural land), which ought to be densified with enduring bushy, herb-like vegetation. A well-developed vegetation of forest marginal zone encourages a faster formation of characteristic conditions for the interior of the forest (e.g. microclimate) and creates a barrier to protect the interior of the forest against the ingression of foreign species.

3. CONCLUSIONS

With regard to the above formulated problems and indications a concept for the reclamation of "Adamów" open-pit has been developed, which presents the idea of comprehensive shaping of post-mining landscape on environmental grounds (Fig. 2).

In the surrounding of the Adamów and Bogdałów open-pit mines, the fragments of two areas of protected landscape were listed (Złotogórski Protected Landscape Area and Uniejowski Protected Landscape Area) as well as the area of Natura 2000 "The Valley of the Central Warta." The dominant element in the system of ecological structure is the valley of Warta and Teleszyna as well as Kiełbaska rivers. The valleys of the meridional courses define the main axes of the structure creating ecological corridors which are essential (at regional and local levels) in the implementation of the ecological relationships as they constitute a pathway of migration of substances, energy and organisms in the landscape. The vast majority are a series of meadow-peatbog, forested in small sections. The structure is completed by large forest complexes. In the north, we have woods, which cover an area of 1166 ha (located in the foreland of the open-pit mine and are partly intended for logging) while in the east and south-east there are forest patches covering areas of 371 ha and 2542 ha respectively, which surround the reclaimed parts of the open-pit mine. The complex shaping of this area, which takes into account the environmental conditions, should include:

- harmonious combination of elements of the natural structure of the post-mining areas and the natural areas occurring in their environment
- reconstruction of the forest complex in the northern part of the Adamów open-pit mine. In particular, the creation of greenways along the eastern edge of the Final Adamów Reservoir, which would be a link between the

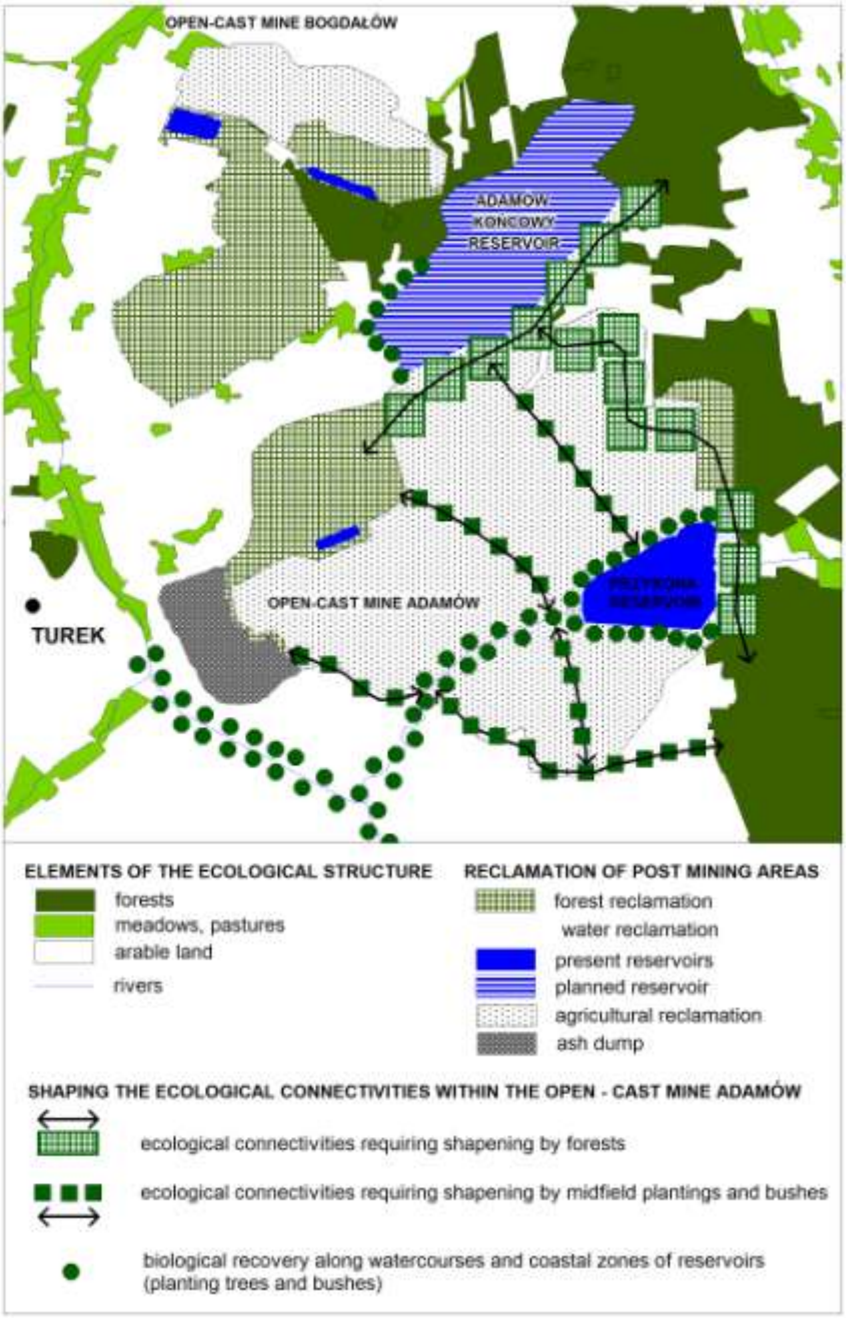

Fig. 2. The concept of shaping the post-mining landscape of Adamów and Bogdałów open-pit mine (source: own work)

reclaimed parts of the internal spoil tip towards the forest and primary forests in the western and eastern part of the open-pit mine. The plantings along the eastern edge of the Przykona reservoir should be the continuation of the greenway, which implements the ecological relationships with a large forest complex surrounding the external spoil tip from the south-east.

- creation, in the form of a network, of links between the existing nodal forest areas and the river valleys of Kiełbaska and Teleszyna by introducing ecological microstructure in the form of midfield plantings and bushes in the area of reclaimed internal spoil tip into agricultural land
- protection of the valleys of Kiełbaska and Teleszyna as well as the Przykona and Adamów reservoirs by introducing biological recovery along the watercourses and coastal zones of the reservoirs (i.e. planting trees and bushes).

4. SUMMARY

The aim of this study was to present the issue of shaping the landscape of post-mining areas in terms of landscape ecology. The basic recommendation resulting from the research is that the planning of reclamation activities cannot be limited to areas degraded by the reclamation process but it must take into account its relationship with the environment. However, the presented principles for shaping the ecological structure of post-mining areas are a kind of code of good practice of reclamation. Reclamation of post-mining areas is a statutory obligation for a mining entrepreneur, who is obliged to secure funds for this purpose (mine closure fund) and carry out the reclamation process. Taking into account that, in the reclamation plans, plantings necessary to fill up or strengthen the natural structure, are therefore not additional financial or executional burden, but has a dimension of ideas, the introduction of which will involve a qualitative change of the reclamation process. Landscaping in the post-mining reclamation process, that harmonizes nature and open-cast mining is now a necessity in the light of requirements of the National Environmental Policy and towards the increasingly environmentally conscious society. It should also be a fundamental factor in the discussions on the design of the exploitation of new deposits.

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EKOLOGIA KRAJOBRAZU POGÓRNICZEGO – ANALIZA WYBRANYCH PROBLEMÓW NA PRZYKŁADZIE KOPALNI WĘGLA BRUNATNEGO „ADAMÓW"

Streszczenie

W opracowaniu przedstawiono problemy kształtowania krajobrazu obszarów pogórniczych, wynikające z pomijania w procesie rekultywacji, lub uwzględniania w niewielkim zakresie, kryteriów ekologicznych. Dotyczy to kształtowanych w procesie rekultywacji nowych elementów (lasy, łąki, zbiorniki wodne, grunty orne) tworzących strukturę ekologiczną krajobrazu pogórniczego, a w szczególności ich rozkładu przestrzennego, spójności strukturalnej i funkcjonalnej z obszarami nie przekształconymi przez górnictwo. Analiza dokonana na przykładzie Adamowskiego Zagłębia Węgla Brunatnego wskazuje, że głównym problemem jest ograniczanie prac rekultywacyjnych do przestrzeni zdegradowanej przez proces eksploatacji, bez uwzględniania jej relacji z otoczeniem. Efektem jest brak spójności przestrzennej pomiędzy geoekosystemami i postępujący proces fragmentacji osnowy przyrodniczej w obrębie obszarów górniczych. Brak wykształconej struktury ekologicznej (obudowa biologiczna zbiorników, cieków,

kanałów, zadrzewienia śródpolne) nie sprzyja funkcjonowaniu geokompleksów pogórniczych i opóźnia proces dochodzenia tych obszarów do nowej, wtórnej równowagi. Wpływa również na fizjonomię krajobrazu podkreślając jej antropogeniczny charakter. Na tej podstawie sformułowano zasady kształtowania struktury obszarów pogórniczych z uwzględnieniem przesłanek ekologicznych, które powinny stać się kodeksem dobrej praktyki rekultywacyjnej. W odniesieniu do nich opracowano koncepcję rekultywacji odkrywki Adamów, która przedstawia ideę kompleksowego kształtowania krajobrazu pogórniczego.

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SPATIAL DISTRIBUTION OF IRON AND ALUMINUM IN PORE WATER AND BOTTOM SLUDGE OF THE MEROMICTIC ACID LAKE NO 54, ŁUK MUŻAKOWSKI, POLAND

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The spatial distribution of iron and aluminum in bottom sludge and pore water of the meromictic acid pit lake no 54 situated in Łuk Mużakowski, Poland were examined. Samples were taken three times from two places located within the meromictic zone and one out of it. Chemical composition of pore water and sludge in vertical profiles were analysed. Two patterns of the distribution of elements between solid and liquid parts depending on the sampling location were found. Samples taken outside meromictic zone had comparable high concentration of iron in the sludge associated with its low amounts in pore water - and on the contrary: low concentration of alum in sludge associated with its high amount in pore water. Samples from the meromictic zone characterized reversed relations.

Keywords: bottom sludge, pore water, meromixis, acid pit lake

1. INTRODUCTION

Meromictic lakes – that are lakes which do not mix completely. This phenomenon is not common in natural lakes, but it often occurs in mine lakes [9]. The following mechanism creates meromixis in pit lakes development: a) formation of a less mineralized mixolimnion by the inflow of less mineralized water to the lake surface, b) enrichment of iron and sulphate due to the transport of secondary minerals from mixolimnion to monimolimnion, c) influence of sea water d) accumulation of substances in the monimolimnion due to biological decay, e) evaporation f) influence of groundwater of high TDS [2]. The deepest part of the meromictic lake water body – monimolimnion – has often a very specific chemical composition: strong anoxia, rich in hydrogen sulphide and

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products of microbial decay. The pH value in monimolimnion has a great influence on the lake chemistry and results in iron and sulphate accumulation in monimolimnion. Higher pH of monimolimnion favorites the precipitation of alum compounds and turns back the stratification of aluminium. The precipitation of iron compounds takes place in mixolimnion. In monimolimnion the minerals dissolute and accumulates in water body in the reduced form [1, 4, 8, 9]

Chemical composition of the sludge the reservoir no 54 were examined by [5, 7] but only in one, the deepest place of the reservoir.

The aim of the research presented below was:

1. to compare the chemical composition of sludge sampled in the meromictic zone and out of it,
2. to describe the differences in chemical composition of sludge in vertical profile (up to 40 cm of depth),
3. to determine the composition of pore water.

It was expected, that the sludge composition would reflect the above described processes in water body. Higher pH and accumulation of aluminium in sludge in the meromictic zone and iron accumulation and lower pH outside was predicted.

2. THE STUDY AREA

Samples from the reservoir no 54, located about 2 km east of Łęknica, 2.3 km west of Przewoźniki and 2 km south of Nowe Czaple 51°32’23.97” and 14°46’27.89” (Fig. 1). The reservoir was generated due to lignite mining in the seventies of the 20-th century. Exploitation was done by means of open cast. The reservoir has never been remediated. The surrounding area is covered with forest. The morphometry of the reservoir is presented in Table 1.

The reservoir has no surface inflows such as streams or other lakes. It results in the fact that the chemical composition of its waters depends mainly on the composition of groundwater and precipitation, and reactions within the water body (biogenic meromixis).

Table 1. Morphometry of the res. no 54

No res.	Water level n.m.p	Surface area	Max length	Extending factor	Max width.	Max depth	Volume	Shore line length	Shoreline development
	m	ha	m	-	m	m	tys.m^2	m	-
54	132,0	20,2	896	1,91	225	21,5	1950	2625	1,65

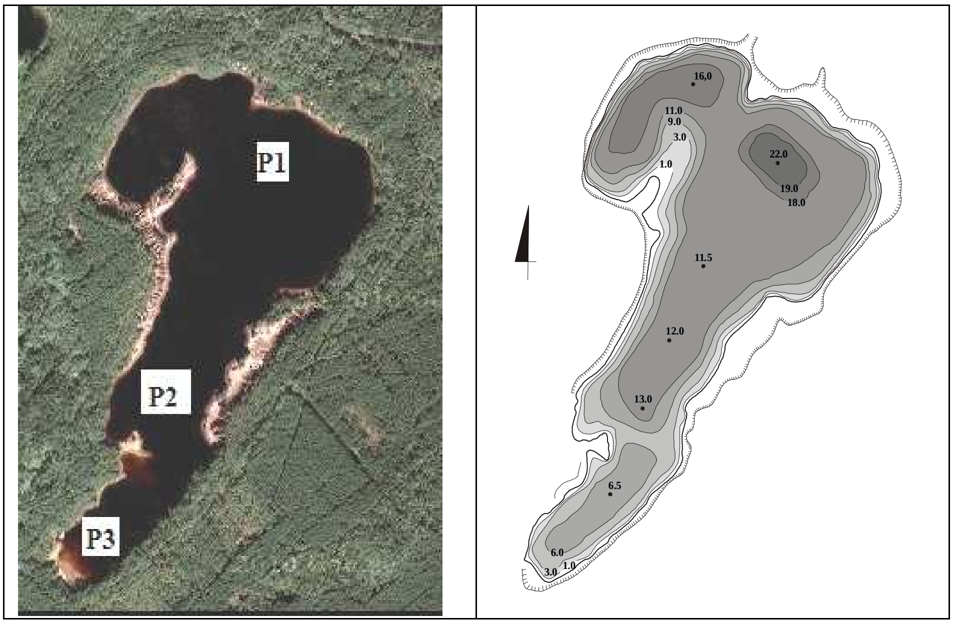

Fig. 1. Bathymetric map of the reservoir no 54 and sampling location

The lake is extremely acidic with a high concentration of iron and sulphur. Chemical composition of reservoir modified significantly during the years of observation. The pH of bottom layer has been increasing systematically and reached in 2008 values of about 4.8-4.9. Iron concentration in the mixolimnion layer was almost steady, but in monimolimnion increased from about 100 to more than 800 mg/dm^3 in the years 1981-88 and, since 1993, to more than 1500 mg/dm^3. Sulphate concentration did not change as rapidly as iron ones. In the years 1981-88 sulphate concentration was almost steady in the upper part of water body (from the surface to 11 m in depth). Deeper, its content increased with depth. The research done later, showed low concentration of sulphate in the layer 0-7 m, and rapid concentration increase between 7 and 11 m to about 3000 mg/dm^3, and then gentle increase to the maximum concentration about 4300 mg/dm^3.

Aluminium concentration had two different profile patterns. In 1981 aluminium concentration increased with depth. Later the concentration of aluminium decreased significantly with depth from the amount of about 35 to less than 10 mg/dm^3.

3. METHODS

Samples were taken three times in September and December 2009 y. and April 2010 y. from three points labeled P1, P2 and P3 (Fig. 1) by the sampler of

Limnos type. The depth of water body was as follows P1 – 21 m, P2 – 10 m, P3 – 4 m. Thermocline layer was situated between 8 and 9 m of depth. Each core was split into three pieces of the following thickness:

- 2 cm – upper layer,
- 5 cm – intermediate layer,
- 9 cm. – the deepest layer.

Two sampling points, P1 and P2 were influenced by meromixis. Point P3 was located out of meromictic zone. To extract pore water samples were centrifuged by 30 min (2000 r/min). Pore water was trickled by 0,45μm drains, and then pH value was measured and acidified. The sludge after dewatering was dried and wet mineralized. Metals were analysed by means of AAS Specr AA 10 Varian.

4. RESULTS

4.1. pH value in pore water

The pH value varied from 2.28 to 4.76. P1 and P2 samples had pH in the range from 3.33 to 4.76. Samples from P3 profile were more acid and had pH from 2.28 to 4.05, but the upper layers had pH from 2.37 to 3.38. No essential variations of pH value in vertical profile were stated. Only in April, in P2 profile pH decreased significantly with depth (Fig. 2).

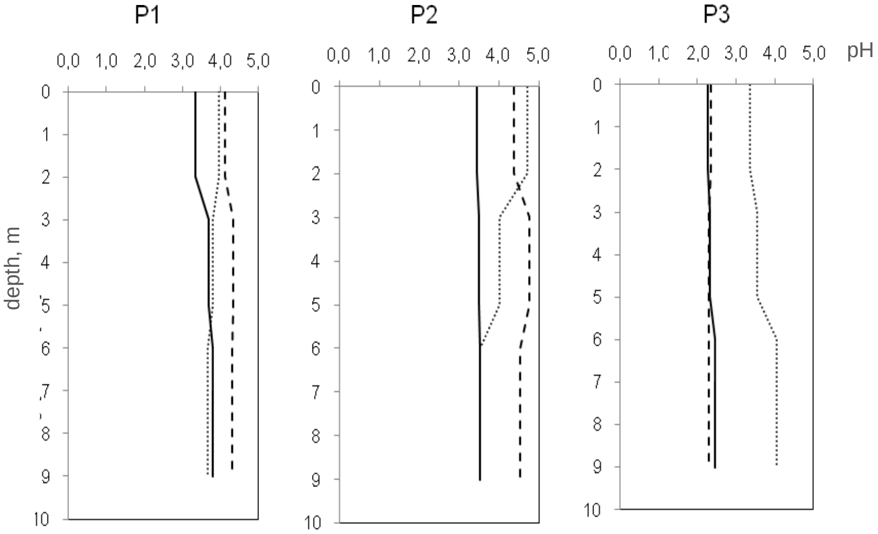

Fig. 2. pH value of pore water in vertical profiles, (dashed line represents results from September, continuous from December and dotted line – April – the same labeling is repeated in the following figures).

4.2. Iron

The concentration of iron in upper layers of the sludge in P1 and P2 profiles ranged from 18 to 43 mg/g dry mass (Fig.3). Much higher iron concentrations, from 80 to 224 mg/g dry mass, were stated in the upper and medium layers of P3 samples. Iron concentration decreased with the depth in P1 and P3 profiles and was almost constant in P2 profile. The abnormal high amount of iron were stated in September P2 sample. It seems, that the “base” concentrations in the ground, before lake water impact was the range from 30 to 50 mg/g dry mass. In the profile P3 iron precipitations were cumulated at the bottom surface.

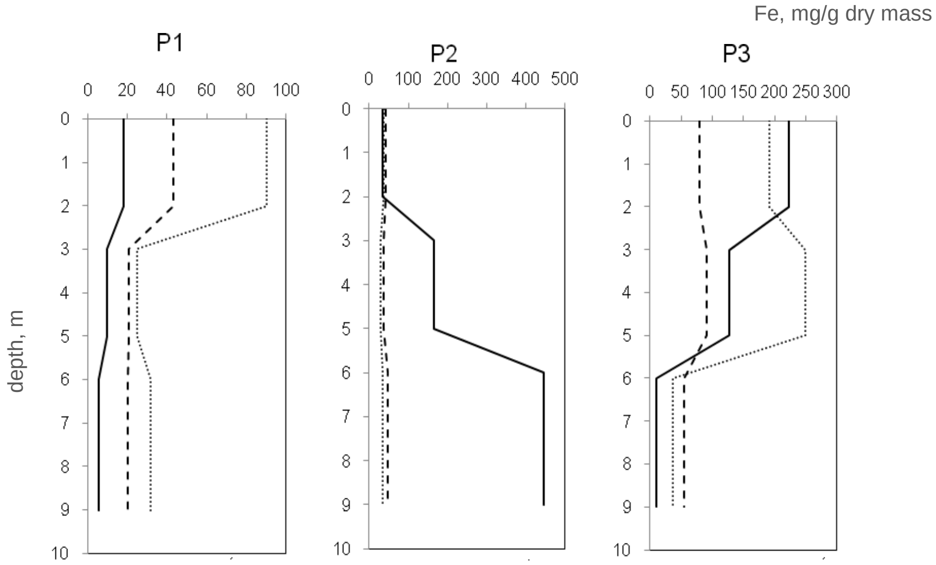

Fig. 3. Vertical variability of iron content in sludge core, mg/g dry mass

The concentration of iron in pore water taken from meromictic zone (P1 and P2) and outside (P3) differed considerably. Pore water in P1 and P3 profiles contained respectively from 995 to 1782 mg/dm^3 and from 465 to 1029 mg/dm^3 and showed no remarkable changes with the depth (Fig.4). In the profile P3 maximal concentration of iron equaled 72 mg/dm^3 and occurred in the upper layers in each period of sampling. The iron content decreased with the depth and reached the minimal value, about 18 mg/dm^3, in the deepest layer. The amount of iron in the profile P3 was ten times lowered, than the concentration detected in other profiles. The comparison of iron amounts in the sludge and pore water points that high iron amounts in bottom sludge are accompanied by low concentration of this element in pore water and inversely.

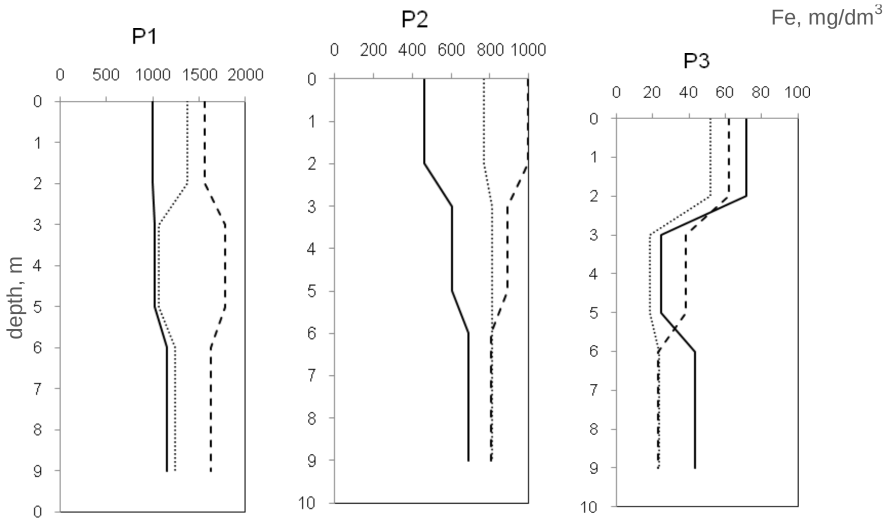

Fig. 4. Vertical variability of iron content in pore water, mg/dm^3

4.3. Aluminium

Aluminium concentration in bottom sludge of the profiles P1 and P2 was on the similar level, from 9 to 18 mg/g dry mass in the upper layer and decreased with depth to at least 2 mg/g dry mass. The sludge in the profile P3 contained aluminium in the range from 0.4 to 4.5 mg/g dry mass depending on sampling period. Its concentration was almost constant in two upper layers and changed deeper (Fig. 5).

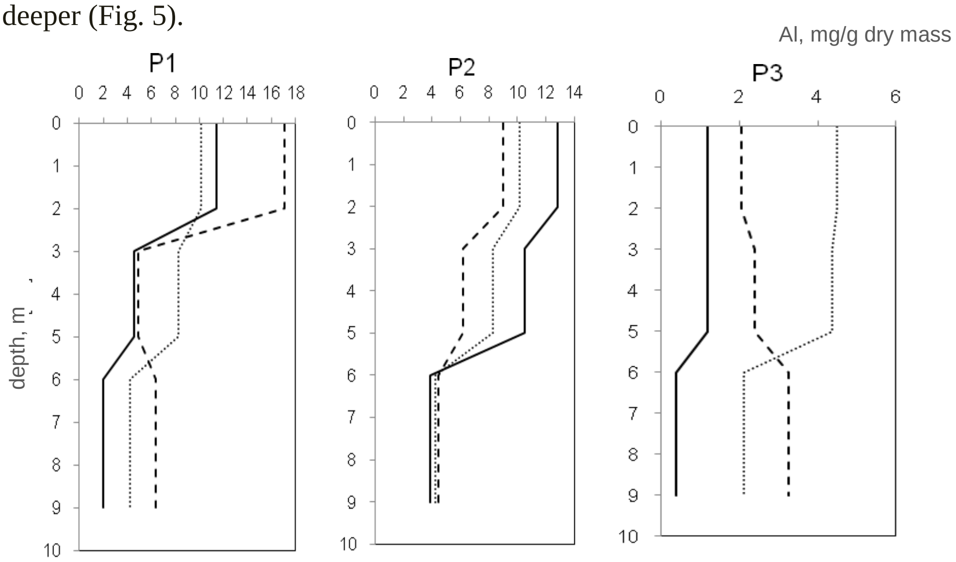

Fig. 5. Vertical variability of aluminum content in sludge core, mg/g dry mass

Aluminium concentration in pore water in P3 profile was higher than in the other profiles. The concentration of the element in pore water in profiles P1 and P2 ranged from 0.32 mg/dm^3 to 24.62 mg/dm^3, whereas in profile P3 ranged from 25.86 mg/dm^3 to 36.09 mg/dm^3. The concentration of aluminum in the profiles P1 and P2 changed according to the sampling period and the depth. The concentration of aluminum in the profiles P3 was almost constant each time and slightly increased with the depth.

5. DISCUSSION OF THE RESULTS

The differences between chemical composition of sludge and pore water coming from meromictic zone (P1 and P2) and outside (P3) were very significant, especially in the upper layer. The chemistry of deeper layers was similar, what suggests that only 5 cm thin, top layer is influenced by the processes in the lake body.

The distribution of the analysed elements between sludge and pore water had two patterns (Table 2):

1. for iron and aluminum the comparable high concentration of element in sludge is associated with its low amounts in pore water
2. on the contrary, low concentration of element in sludge is associated with its high amounts in pore water.

It proved, that these elements take part in geochemical processes in the lake. In meromictic zone pore water is undersaturated with iron and potassium, which cumulate, and are present at low amounts in sludge. On the contrary aluminum precipitate, so its concentration in pore water should be low, but in sludge high. Outside the meromictic zone, there are conditions for iron compound precipitation, so the element is cumulated in the sludge and precipitates from water. Iron is supposed to precipitate as potassium or natrium jarosite, schwertmannite or different hydrous oxides. The accumulation of potassium and natrium can be observed in the pore water in meromictic zone and the sludge outside.

Table 2. The comparison of the composition of bottom sludge and pore water in upper layer of the cores

Parameter		P1	P2	P3
iron	sludge	medium	medium	high
	pore water	high	medium	low
aluminium	sludge	high	high	low
	pore water	low	low/high	high
pH	pore water	3.5-4.5	3.5-4.5	2.5-3.5

The redox reaction with iron and sulphate participation depend mainly on the organic matter aviability. The profiles P1 and P2 cut through coal stratum [3], so higher concentration of organic matter in the sludge samples can be connected with brown coal presence. TOC concentration in pore water in P1 and P2 profiles is higher than in the P3 profile (with exclusion the samples taken in September). In P3 profile the concentration of TOC in pore water and sludge decreased with depth. It suggests that some redox processes can take part in deeper parts of sludge where oxygen recourses had been exhausted.

6. SUMMARY

The studies have confirmed the influence of meromixis phemomena of the iron and aluminium content in bottom sludge and pore water. The greatest differences were observed in the upper layer of sample cores. Samples coming from the meromictic zone consisted comparable low amounts of iron and aluminium in the solid part and their high concentrations in pore water. Sample P3 characterised reversed relationship.

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ZAWARTOŚĆ ŻELAZA I GLINU W WODZIE POROWEJ I OSADACH DENNYCH ACIDOTROFICZNEGO ZBIORNIKA MEROMIKTYCZNEGO NR 54 W ŁUKU MUŻAKOWSKIM, POLSKA

Streszczenie

W publikacji przedstawiono zmiany zawartości żelaza i glinu w wodzie porowej i osadach dennych acidotroficznego zbiornika meromiktycznego nr 54 w Łuku Mużakowskim. Próbki pobierano trzykrotnie z dwóch miejsc w strefie meromiksji i jednego poza nią. Analizowano skład chemiczny osadów i wody porowej w profilu pionowym obranych prób. Stwierdzono dwa wzory rozkładu stężeń badanych pierwiastków między wodą porową i osadami. W próbkach pochodzących spoza strefy meromiksji stosunkowo wysokim stężeniom żelaza w osadach towarzyszyła jego niska zawartość w wodzie porowej, natomiast odwrotną zależność stwierdzono dla glinu, tj. wysokim stężeniom glinu w wodzie porowej towarzyszyła jego niska zawartość w osadach. W próbkach pochodzących ze strefy meromiksji zależności te przebiegały odwrotnie.

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BARRAGE BARTOSZOWICE-OPATOWICE INFLUENCE ON GROUNDWATER STATE IN ADJACENT AREAS IN 1997

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The main idea of this study was to analyze an influence of altering water level, by the barrage Bartoszowice – Opatowice, on the groundwater in adjacent areas. In this paper a physiographic characteristic of the Big Island and characteristics of barrages are presented. A simulation of the influence of a flood wave passing in 1997 on water level in the study area was presented. The simulation included: period before the flood, period of flood wave passing through Wrocław and period after the flood. To carry out model testing previously collected physiographic data and data regarding water levels in 1997. The test were carried out using mathematical model FIZ, that allows modeling of groundwater flow. For hydrotechnical engineers influence of structures altering water level on groundwater is an important issue, because it can disturb foundations of existing structures, adjacent buildings or other objects in close proximity of groundwater influence. It is worth to predict the influence of a hydrotechnical structure on groundwater.

Keywords: ground water, earth water, barrages, computer modelling, water level increase, Big Island, Odra River

1. INTRODUCTION

Hydrographic conditions in the areas adjacent to watercourses and water reservoirs are formed depending on geology, surface water level and groundwater supply conditions. Location of the water table is closely connected with surface water. Groundwater can be recharged by surface water (losing stream) or recharge surface water (gaining stream). Periodic changes from gaining to losing stream are connected with fluctuation of water level in the stream. The Big Island was created by rivers and channels, separating it from the rest of Wrocław. These rivers and channels are: Inundation Channel and

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Shipping Channel from the Northeast, Odra riverbed from the south side and Old Odra River from the west side. In the area of the Big Island are weirs: Bartoszowice, Szczytniki, Opatowice and Psie Pole. A task of these hydrotechnical structures is to alter water level in order to maintain a constant water level in the river. The weirs are also part of the flood control system (Wrocław Power Plant I). Significant fluctuations of water table can be observed in vicinity of weirs. Particular situation can be observed in the area of canalized part of the Odra River in Wrocław (WWW), including the Big Island with quarters: Zacisze, Dąbie, Biskupin, Sępolno, Szczytniki and Bartoszowice.

2. AREA OF RESEARCH

The Big Island in Wroclaw is located in the eastern part of the city by Odra River. It contains housing estates: Bartoszowice, Biskupin, Dąbie, Zacisze, Sępolno and Zalesie, Szczytniki and Sępolno. The name: Big Island was given in 1980 by professor Wanda Kononowicz. For a long time it was an unofficial name, nowadays it is used also by Wrocław City Council. The lands belonging to the Island except Zacisze were located on the left bank of Odra River (in the area between Odra and Oława) until the 16th century. In the following years the construction began, involving digging the riverbed. These settlements lien now on the opposite bank of the Orda river (which were separated by oxbow lakes). There is, however, a connection with the left bank and with the Wrocław city center – bridges: Szczytnicki and Zwierzyniecki. The Big Island has an individual protection – Natural –Landscape Complex being a part of Szczytnicki Natural-Landscape Complex [1], [2], [3], [4], [5].

Barrage Bartoszowice – Opatowice

Barrage Bartoszowice – Opatowice is situated at km 245 + 035 of Odra River. This barrage consists of: weir Bartoszowice, lock Bartoszowice, weir Opatowice, Navigation Channel Opatowice, upper and lower outer harbors of lock Bartoszowice, residential buildings, magazines and outbuildings. It is connected with Navigation Channel Bartoszowice – Zacisze – Różanka, Flood Control Channel, dykes, polders: Blizanowice, Trestno and Oławka and with spillway to Widawa. That barrage has a great significance for the whole Wrocław Water Junction, especially with regard for flood control in the city. The barrage intercepts water flowing to the city and controls its flow.

- ***Weir Bartoszowice*** was built in 1913-1917. It is a weir with a segmental closing. It was built to be a part of Bartoszowice Barrage. Weir Bartoszowice alter water levels of Odra River in upper course. It is situated 0,45 km from the flood control channel. In is a three-span structure of dimensions: 2 x 30,00 [m], 1 x 40,00 [m]. The clear span of the weir is 100,00 m and its length is 108,40 m.

Slope for NPP [m] equals 4,49. Threshold crown in weir Bartoszowice: 117,60 mamsl. Ordinate ”0” of water gauge: 111,188 mamsl.

The weir regulates water level together with the weir Opatowice:

- level of upstream water for lock Bartoszowice and lock Opatowice,
- level of downstream water for lock Janowice.

Fig. 1. Weir Bartoszowice from downstream side – view from left bank

Fig. 2. Weir Bartoszowice from upstream side – view from left bank

- ***Weir Opatowice*** was built in 1977-1985. It is a weir with a sectional closing. The weir consists of: abutment with control room on the right bank, abutment with a fish ladder on the left bank, two piers, threshold with sectional chamber and a passage. The structure made of concrete is a casing for three main steel sectors 2,70 m high and 32,00 m long. Weir Opatowice has a hydraulic system to control these sectors, a defrosting installation that allows its exploitation during the whole year, and washing, draining and ventilation systems. Span lengths are: 3 x 32,00 [m]. The clear span of the weir is 96,00 m and its length is 103,70 m.

Above the weir there is a footbridge that allows also privileged cars to get to the Opatowicka Island. The riverbed below the weir Opatowice is an artificial bump, protected by a riprap lying on a slab mattress of thickness of 1,0 m. Scarps of the riverbed are protected by concrete slabs, supported by a riprap lying on a fascine mattress. The embankment on the right bank is protected by steel sheet piling and on the left bank – by a groin.

The weir regulates water level together with the weir Bartoszowice:

- level of upstream water for lock Opatowice and lock Bartoszowice,
- level of downstream water for lock Janowice.

Fig. 3. Weir Opatowice – view from right bank

Fig. 4. Weir Opatowice – view from left bank

3. NUMERICAL MODEL AND BASIC HYPOTHESES

FIZ software – used in the engineering practice to determine influence of the designed hydrotechnical structures on hydrographic conditions in the adjacent area. FIZ software allows modeling of the groundwater flow and contaminants flow. Basic formula in FIZ software is Boussinesq equation:

$$\frac{\partial}{\partial x}\cdot\left(T_x\cdot\frac{\partial H}{\partial x}\right)+\frac{\partial}{\partial y}\cdot\left(T_y\cdot\frac{\partial H}{\partial y}\right)+W=\mu\frac{\partial H}{\partial t} \tag{1}$$

where:
x, y – spatial variable $(x, y)\ \varepsilon\ \Omega$, Ω – filtration area, t – time,
μ – coefficient of gravity drainage capacity, H – piezometric height,
T_x – hydraulic diffusivity in direction of OX axis, $T_x = k_x (H – a)$,
T_y – hydraulic diffusivity in direction of OY axis, $T_y = k_y (H – a)$,
k_x, k_y – coefficient of hydraulic diffusivity on direction , respectively, OX and OY,
a – ordinate of the bottom of layer,
W – source function.

That is used to describe an unstable groundwater flow in saturated area. In order to solve the equation for unstable filtration it is necessary to specify initial conditions and boundary conditions. Initial conditions indicates distribution of piezometric heights at the present moment (t = 0). Piezometric height values in nodes for the initial moment can be determined on the basis of performed measurements or calculations for steady state [15].

Boundary conditions [16]:

- First-type condition (Dirichlet Boundary Condition) – by piezometric height, it occurs when the values of the function h (x,y,t) are given on the filtration area borders:

$$h = F_1(x, y, t) \tag{2}$$

- Second-type condition (Neumann Boundary Condition) – by intensity of the flow, it occurs when on the border the values of a derivative normal to the border are given, which means that boundary conditions depend on the value of the flow on the borders:

$$Q_n = \int_{C_f} q_n \cdot ds = \int_{C_f} k \frac{\partial h}{\partial n} \cdot ds \tag{3}$$

- Third-type condition (mixed) – it occurs when on the border a linear combination of the values of the function h and its derivative is given:

$$h + A \frac{\partial h}{\partial n} = F_3(x, y, t) \tag{4}$$

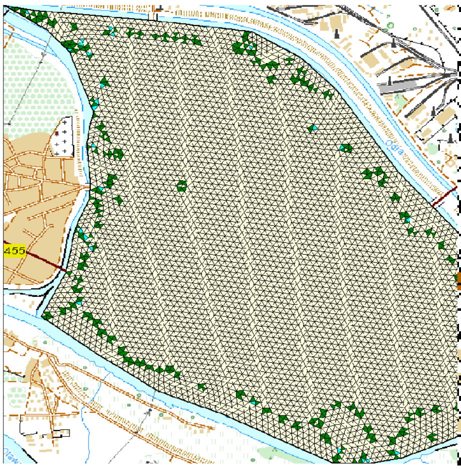
4. RESULTS FROM MODEL TESTING

Model testing for the Big Island

In model testing an influence of surface water on groundwater in adjacent area was determined. The influence of water level of Odra River in 1997 on rise of water level was tested. Mathematical model was used for testing the influence of the flood in 1997 on groundwater level. The studies allowed to determinate changes of water levels when the flood wave was coming, during the flood wave culmination and after the flood wave and estimation of reach of reach of the influence of altering water levels and duration of elevated groundwater level.

Discretization of the selected area

On the study area a triangular finite element mesh was generated. To each element, which is located in the area covered by the study, coordinates of nodes (x,y) were assigned. These nodes are linked together and they allow to solve the assignment problems. Division of the area into smaller elements allows to obtain more accurate calculation results. In my studies the applied mesh is uniform, the triangles are equilateral or similar to equilateral triangles.



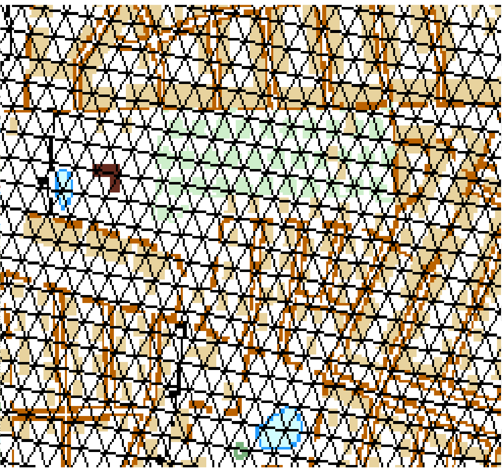


Fig. 5. Discretization mesh

Fig. 6. Part of the mesh

The mesh consists of 4686 nodes and 9091 triangles. The triangles are described with subsequent numbers of nodes. The maximum angle should not exceed a value of 70 degrees. The mesh accuracy is 0.05 %, which means that only 0.05% of triangles are obtuse triangles (marked with red color), in which calculation errors may occur. In the test there is one such triangle, located on northwest.

Theoretical studies have shown that if the triangles are close to equilateral, results of the model testing are more accurate. Blue triangles are similar to right triangles, which angle exceed 80 degrees but not exceed the maximum value of 90 degrees. In the test there are several quasi-right triangles, located on the east side of the study area. Other triangles are similar to equilateral, they are marked with yellow color (angles smaller than 70 degrees) and green color (angles between 70 and 80 degrees) – these triangles give the most accurate results.

Parameters preparation

To each node several values were assigned:

- filtration coefficient along x and y axis – for the study area a mean value of the coefficient k = 10 m/d was assumed (filtration coefficient for medium sand),
- coefficient of gravity drainage capacity μ = 0,16 – calculated using the Bieciński formula

$$\mu = 0{,}117\,\sqrt[7]{k} \tag{5}$$

where:

k – filtration coefficient [m/d]

[5]

- altitudes of the top and the bottom and the ground level, the top altitude is 118 mamsl and the bottom altitude is 112 mamsl [16], [8], [7], [17], [4].

In the model it was assumed that the average rainfall equal to 600 mm/year is equal to evaporation on the study area. Therefore it was assumed that charging by rainwater is equal to 0 mm/day.

Determination of boundary conditions

In the studies the first-type boundary condition (Dirichlet Boundary Condition) was used, on the borders of the filtration area a value of the function h(x,y,t) was assumed:

$$h = F_1(x, y, t) \tag{6}$$

Groundwater level was determined on the border of the area in accordance with water altitudes in the watercourse. In the paper second-type and third-type conditions were not used.

Influence of the barrages on groundwater levels in 1997

The study of the influence of surface water on groundwater in the Big Island in 1997 area was carried out. The research began two months before the culmination of the flood wave – on May 18, 1997, to estimate a distribution of water table rise for groundwater in the study area before the flood, during the flood and after the flood.

May 18, 1997

Simulation studies for period before the flood (May – June, 1997)

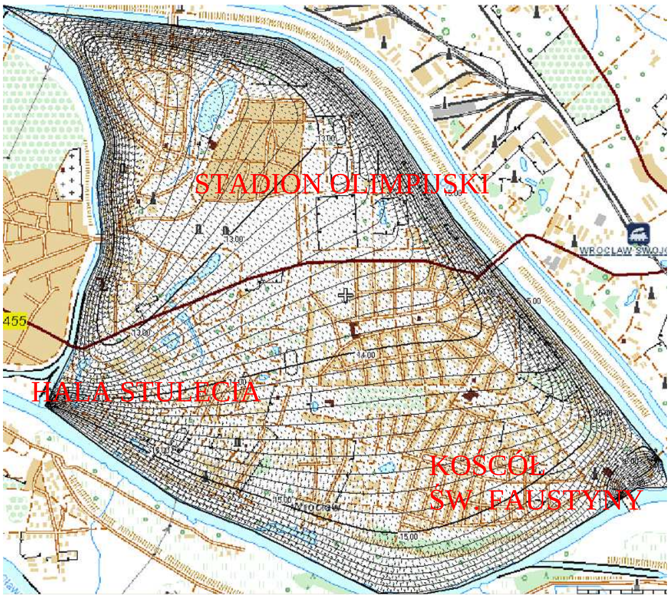


Fig. 7. Hydroisohips and velocity field of 18 May, 1997

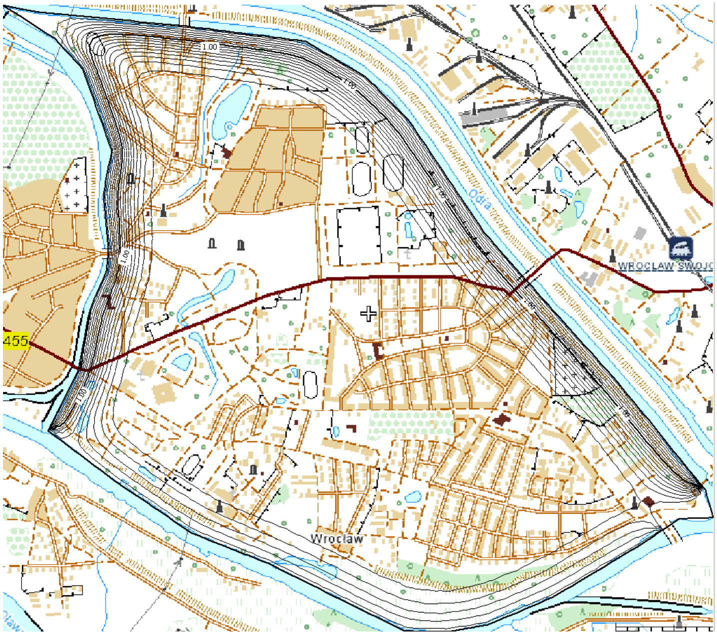


Fig. 8. Rise of groundwater level of 18 May, 1997

June 18, 1997

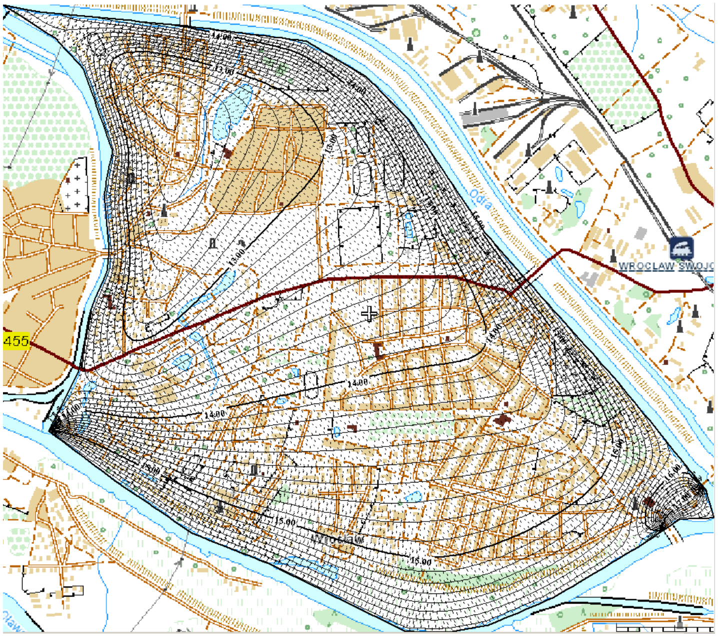


Fig. 9. Hydroisohips and velocity field of 18 June, 1997

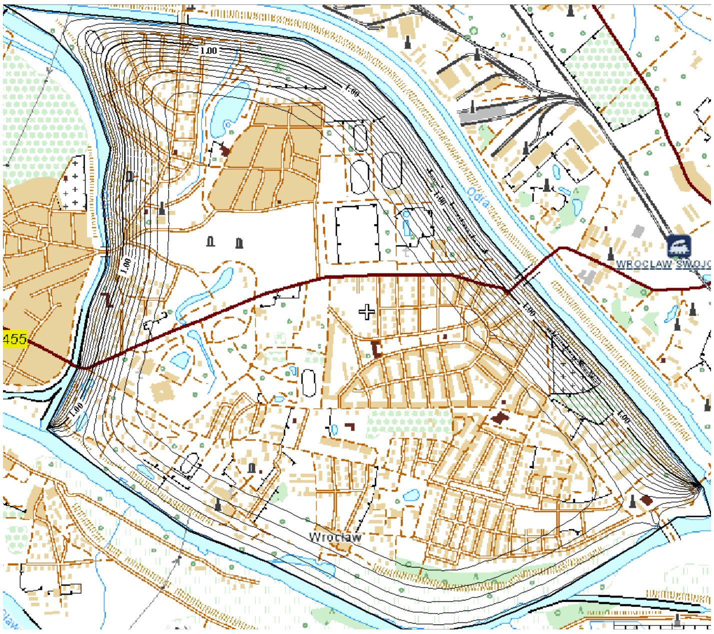


Fig. 10. Rise of groundwater level of 18 June, 1997

July 12, 1997

Simulation studies for period during the flood (July 1997)

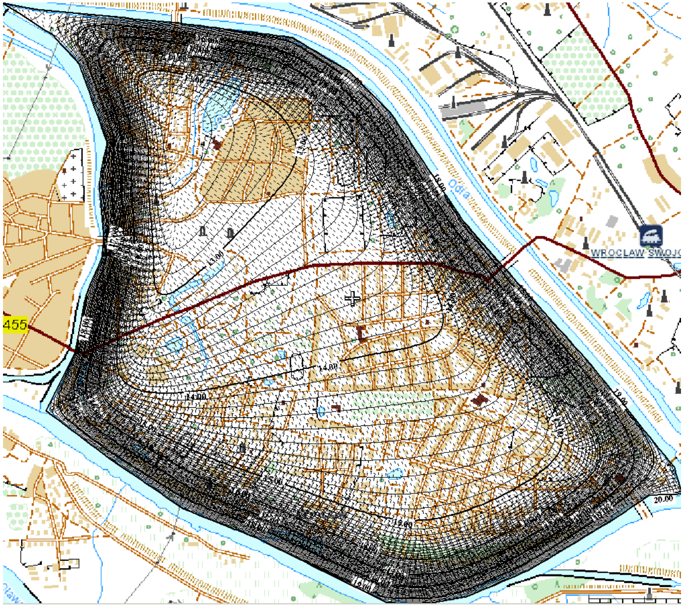
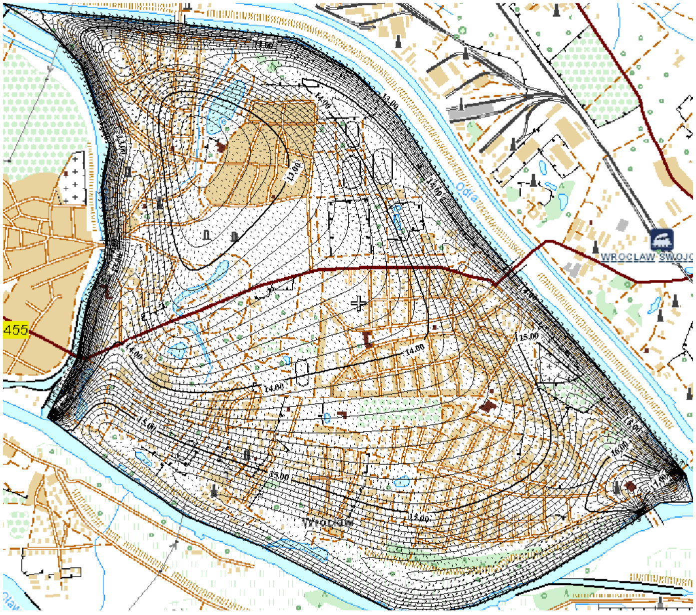


Fig. 11. Hydroisohips and velocity field of 12 July, 1997

Fig. 12. Rise of groundwater level of 12 July, 1997

August 12, 1997

Simulation studies for period after the flood (August, 1997 - April 1998)



Rys. 13. Hydroisohips and velocity field of 12 August, 1997

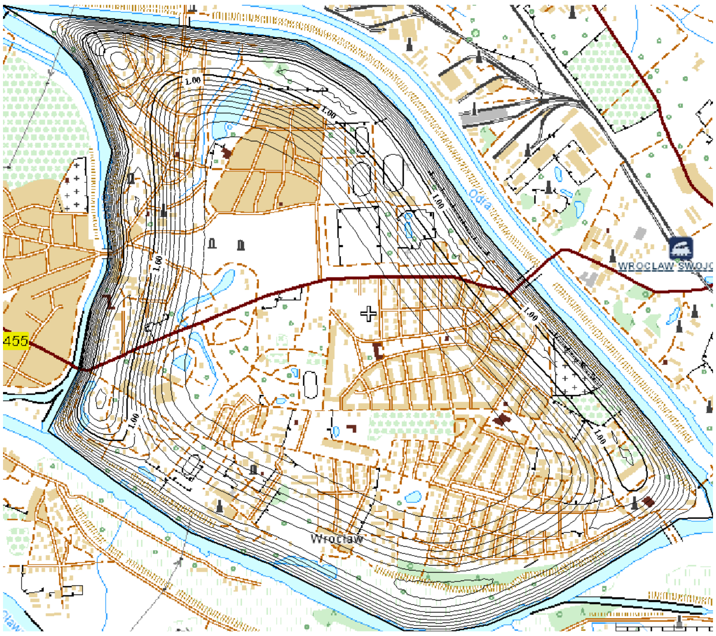


Fig. 14. Rise of groundwater level of 12 August, 1997

October 12, 1997

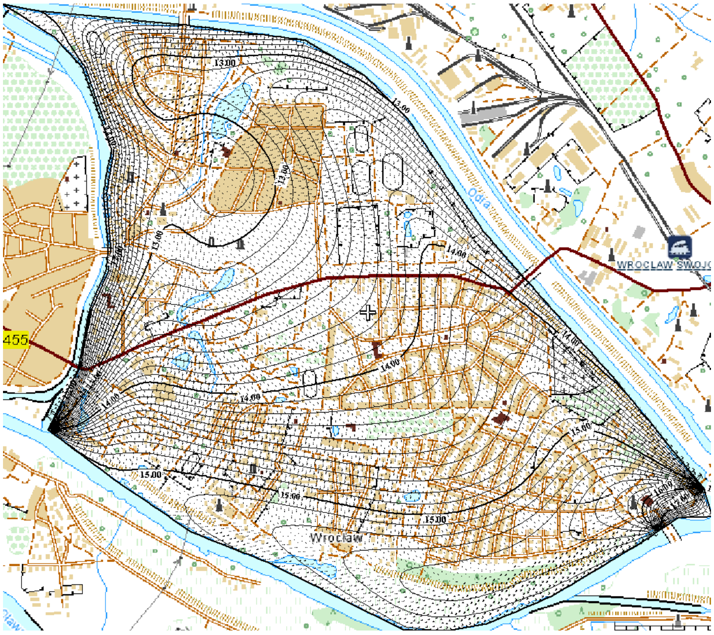


Fig. 15. Hydroisohips and velocity field of 12 October, 1997

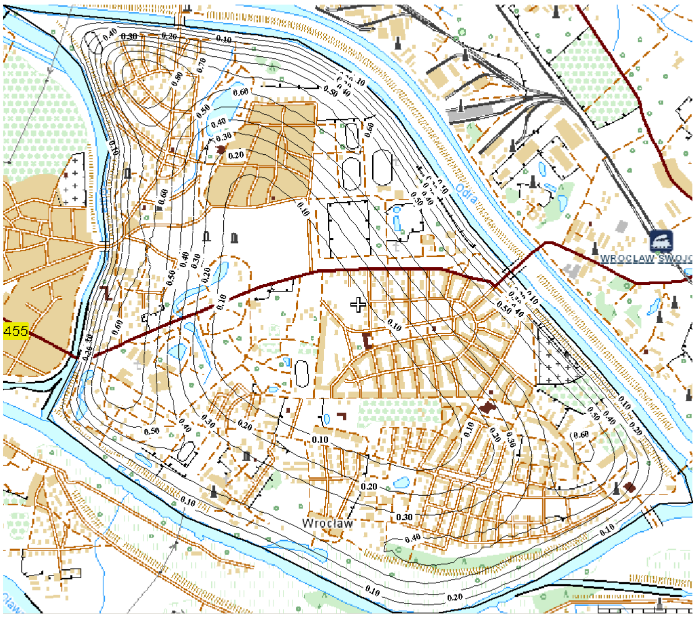


Fig. 16. Hydroisohips and velocity field of 12 October, 1997

April 12, 1998

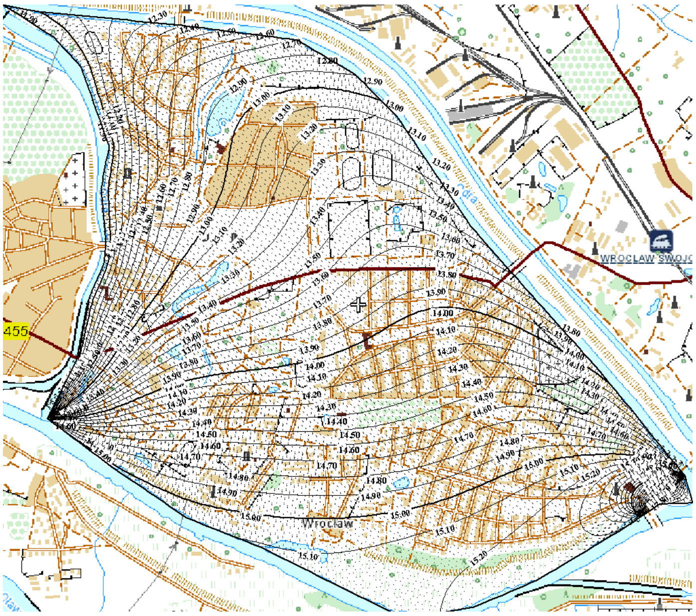


Fig. 17. Hydroisohips and velocity field of 12 April, 1998

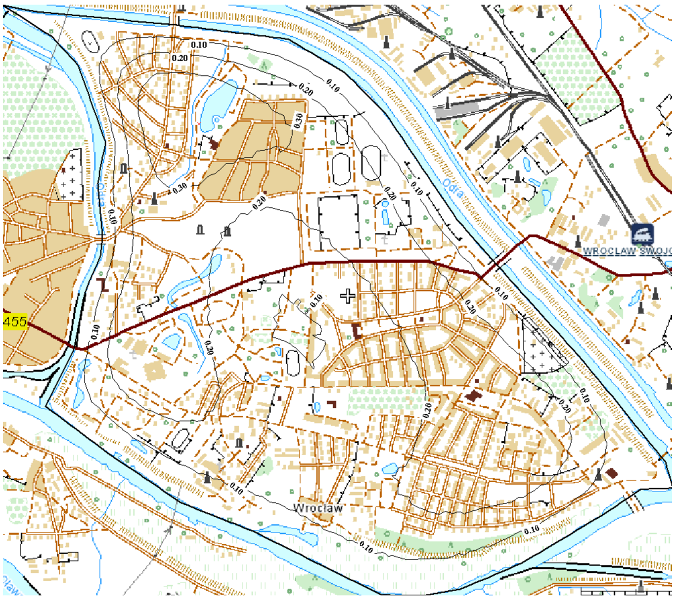


Fig. 18. Hydroisohips and velocity field of 12 April, 1998

5. MODEL TESTING RESULTS ANALYSIS

The simulation was carried out for the period from 18th May, 1997 to 12th April, 1998. The largest area of the influence of surface water on groundwater is located in the north and northeast part if the Big Island, between the Old Odra and the flood control channel, near the weir Psie Pole. Isoline of an increase equal to 0.1 m was located along Józefa Mianowskiego Street, Jana Głogowczyka Street on the east side and to Morskie Oko on the west side. Range of influence of surface water on water table in the Big Island area was about 150 metres from the Odra River toward the center of the study area. The largest rise of the groundwater level occurred near Odra River and it was about 1.5 – 1.8 m.

After thirty days of observation a larger range of the water table rise of 0.1 m was observed, which reached a quarter Zalesie in the northern part of the area and it was distributed proportionally to the whole area from Odra River towards the city center at a distance of about 450 m from watercourses. From the side of a quarter Sępolno an isoline of level rise 0.1 m was located near Piotra Wysockiego Street. In the southern part of the island rise of water levels was equal to 0.5 m and in other areas – between 1.5 and 1.8 m [Fig. 9 – 10].

On the day of culmination of the flood wave (July 12, 1997) groundwater level significantly increased. The maximum increase was in the area of the Old Odra and near the flood control channel. Isoline of level rise 0.1 m was located near Spółdzielcza Street [Fig. 11 – 12].

A month after the culmination of flood wave rises of water levels in the vicinity of the Odra River were significantly reduced. The biggest values of the rises were observed in the zone of 280 m from the Odra River toward the Island center (from Bartoszowice, Sępolno, Zalesie and Szczytniki). However, the range of isoline level rise 0.1 m was moved toward the center of the Big Island, about 800 m from the watercourses [Fig. 13 – 14].

In October in the vicinity of the Odra River water level increase equaled about 0.3 m and in the area situated about 300 m farther from the river toward the center the increase equaled 0.5 m. The range of the area of water level increase was enlarged at 0.1 m. Isoline 0.1 m ran in the proximity of Ludomira Różyckiego Avenue, Walerego Sławika Avenue, Karola Olszewskiego Avenue, reaching Banacha Street and Zaleskiego Bridge [Fig. 15 – 16].

Nine months after the start of the study (12th April 1998) water levels were back to normal levels – before the flood. Near Odra increases from 0.1 to 0.2 m were observed. In the Big Island center the area of groundwater level increase covered also Adama Mickiewicza Street. As can be observed in the following analyses, the flood of 1997 had a huge influence on groundwater level in the area of the Big Island. Even nine months after the flood increased level of groundwater could be observed.

6. SUMMARY AND CONCLUSIONS

In the paper the influence of altering water levels by the barrage Bartoszowice – Opatowice and cooperating weirs Szczytniki and Psie Pole on groundwater in adjacent area during the flood of 1997 was analyzed. The study was carried out using mathematical model FIZ, which allows modeling of the groundwater flow. For model testing previously obtained physiographic data for the Big Island area were used together with data regarding water levels in 1997. After preparation and elaboration all input data they were introduced into the mathematical model. A simulation of the influence of the flood wave in 1997 on water table in the area of the Big Island was carried out. The simulation covered the period before the flood, period of flood duration in Wrocław and period after the flood.

- Performed model test have showed the huge influence of the flood wave on groundwater level in the area of the Big Island. During the Millennium Flood many places in the area of the Big Island were inundated. The cause of the rise were two flood waves that occurred one after the other in a very short time period, caused by high intensity of rainfall. The rises remained constant in the closest vicinity to the Odra River. The highest surface water levels (reaching a value of 120.00 mamsl) were observed on the weirs Bartoszowice, Opatowice and Różanka on 12th July, 1997. That level remained constant for three days. After culmination the flood wave started to subside to 20th July when water level on the weir reached 118.50 mamsl. At the time when flood wave was subsiding, heavy rainfall occurred and caused the second flood wave with a water level of 119.00 mamsl. The range of the influence of surface water on groundwater significantly increased. Isoline of the water level rise equal to 0.1 m covered the area of Adama Mickiwicza Street. Even four months after the culmination of flood wave an increase of the range of influence of isoline 0.5 m in the center of the Big Island was observed. Only in April 1998 values of the groundwater isolines increase came back to pre-flood conditions.

- After the flood in 1997 most of the dikes have been rebuilt and modernized. The dikes surrounding the Big Island have been sealed up. Hydrotechnical structures and devices have been modernized and rebuilt.
- Performed model tests have shown in which areas of the Big Island the largest increase of water table caused by high water level during and after the flood may occur. Obtained data allow to indicate the areas endangered by flooding. In these areas appropriate damp insulation should be applied to building foundation.

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ODDZIAŁYWANIE STOPNIA WODNEGO BARTOSZOWICE – OPATOWICE NA SATNY WÓD PODZIEMNYCH TERENÓW PRZYLEGŁYCH W 1997 ROKU

Streszczenie

Główną ideą pracy była analiza wpływu piętrzenia stopnia wodnego Bartoszowice – Opatowice na wody podziemne terenów przyległych. W niniejszej pracy przedstawiono charakterystykę fizjograficzną Wielkiej Wyspy wraz z charakterystyką stopni wodnych. Zamieszczono symulację oddziaływania przejścia fali powodziowej w 1997r. na kształtowanie się zwierciadła wody na terenie objętym badaniem. Symulacje obejmowały: okres przed wystąpieniem powodzi, okres przejścia fali przez Wrocław i okres po powodzi. Do wykonania badań modelowych posłużyły wcześniej zgromadzone dane fizjograficzne oraz dane dotyczące stanów wody w latach 1997. Badania wykonano przy zastosowaniu modelu matematycznego FIZ, który umożliwia modelowanie przepływu wód podziemnych. Dla inżynierów hydrotechników kwestia wpływu budowli piętrzących na wody podziemne odgrywa istotną rolę, ponieważ może zaburzyć posadowienie istniejących konstrukcji, przyległych budynków, jak i innych elementów w bliskim otoczeniu oddziaływania wód gruntowych, dlatego warto przewidywać, jaki wpływ będzie miała budowla hydrotechniczna na wody podziemne.

Słowa kluczowe: wody podziemne, wody gruntowe, stopnie piętrzące, modelowanie komputerowe, przyrosty stanów wód, Wielka Wyspa, rzeka Odra

CIVIL AND ENVIRONMENTAL ENGINEERING REPORTS

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WASTEWATER TREATMENT IN CONSTRUCTED WETLANDS

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Constructed wetlands are an alternative and economically reasonable way for the wastewater from dispersed development treatment. Existing systems showed that the effectiveness of this treatment is high. The whole treatment process depends on many factors such as time of operation, type of filling, temperature. Constructed wetlands with proper construction and operation are safe for the environment and users.

Keywords: constructed wetlands, hydrophytic wastewater treatment plant

1. INTRODUCTION

Constructed wetlands as a technology of wastewater treatment was developed in Poland from early nineties of the twentieth century, mainly due to low construction cost and maintenance-free operation [9]. The simple design and cost much lower in comparison with conventional construction of wastewater treatment plants resulted in their wide application [11] .

Constructed wetlands is based on many different processes such as sorption, sedimentation, evapotranspiration, chemical properties of wastewater, biological activity of microorganisms and plants (bioaccumulation and biodegradation) [8, 14, 17, 18].

The aim of this paper is a brief discussion of wastewater treatment solutions on constructed wetlands.

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2. THE MECHANISM OF WASTEWATER TREATMENT IN CONSTRUCTED WETLAND

Each wastewater treatment plant should be based on at least two-step purification. The first one should be mechanical f.e. septic tank and the second one – biological [15]. Individual system of wastewater treatment begins in a septic tank. Debris, during the sedimentation process, creates bottoms where facultative and anaerobic bacteria lives. Anaerobic digestion leads to a partial liquefaction of the sediment. As a result of the bacteria more stable organic compounds and gases are formed. Gases from the fermentation are discharged through the ventilation system. Hydrogen sulfide combine with metals contained in the sludge and form insoluble sulphides, which significantly eliminates odors.

This first step in the sewage treatment process in a septic tank takes 2 to 3 days. After this step clarifier effluent with significant decrease content of fat and slurry flow to wetland.

Wastewater treatment in constructed wetland is a biological process that occurs through the involvement of heterotrophic microorganisms and hydrophytes. Porous tissue present in wetland plants supply the reservoir whith atmospheric oxygen, which creates around rhizomes and hydrophytes roots aerobic zones surrounded by anaerobic and anoxic zones [14, 17]. This combination of aerobic and anaerobic zones is settled down with a whole range of various microorganisms. Favorable conditions improve the efficiency and effectiveness of wastewater treatment [17].

3. REQUIREMENTS FOR CONSTRUCTED WETLANDS TREATMENT PLANTS

Hydrophytic treatment plants, due to specifics of their construction, are regulated on three main factors: pollution reduction, location and space.

2.1. Pollution reduction

The maximum values of pollutants at the outlet of the wastewater treatment plant is shown in Table 1. According to Minister of Environment Regulation [6] indicator of pollution, such as BOD_5 must be reduced to 20% and total suspended solids to 50%.

Table 1. The maximum values of pollutants at the outlet of the wastewater treatment plant

Nr.	Indicator, $mg \cdot dm^{-3}$	The maximum allowed value of the indicator for the system below 10,000 PE
1.	BOD_5	40
2.	COD	150

3.	Total suspended solids	50
4.	$N_{tot.}$	30*
5.	$P_{tot.}$	5*

* only in the wastewater discharged directly into lakes and to the artificial water reservoirs

2.2. Location of the septic tank

Location of the septic tank must comply with the conditions defined in [4, 5]:

- it should be located at least 5 meters from the windows and doors fo the inhabited building.
- The tank can be placed in the immediate vicinity of the building, however the venting from the tank will be constructed at least 0.6 meters above the upper edge of the external doors and windows.
- At least 2 meters from the border. It's possible to build it at the border itself, however it must be adjacent to a similar device on a neighboring plot.
- At least 30 m from the wells with drinking water, and 1.5 m from the highest aquifer utility.
- At least 1.5 m of gas pipeline gas.

2.3. The need for space

Area required for the construction of the treatment plant depends on the amount of sewage inflow. Many authors indicate the values from 2 to 20 m^2 for PE [8, 14, 17]. It is assumed that the minimum area requirement for the root system with horizontal flow, is approximately 5 m^2 for PE, which should ensure that the effluent BOD_5 value of 30 $g \cdot m^3$ [16].

2.4. Problems of economic and location

Choosing the right treatment system depends on the type of building and economic aspects. The dispersed development should force the designers and investors to effective, reliable and relatively low-cost technology solutions for the treatment of small quantities of wastewater [12]. Individual sewage treatment systems, the cost of the operation is much lower then in traditional systems and depends on these factors [2]:

- type of wastewater treatment system,
- efficiency of wastewater treatment,
- chemical properties of pollutants.

4. THE CONSTRUCTION OF THE PLANT-SOIL FILTER

The right part of the treatment plant (plant-soil filter) performs several functions [14, 17]:

- it is an environment for the biological treatment processes,

- it is an environment for the development and growth of plants,
- provides a surface for the growth of microorganisms,
- can be a decorative element.

Construction of the tank should be seald. Protection against water infiltration into the soil and ground water can be provide as a seal with an impermeable material such as geomembrane [14].

The minimum thickness of the filter layer should provide free plant growth, however, should not be greater than 1.5 m. The typical thickness of the filter vary from 0.60 to 0.80 m [14].

According to [14] the filter can be divided into the following zones (fig. 1):

- Inflow zone. It’s built of stone, Ø 40 to 80 mm, total length of 2 m.
- Zone I - 2 m (30% of the total length of the filter). It is composed of particulate material which the filtration coefficient of 1% of the rate of filtration of pure material.
- Zone II - 4 m (70% of the total length of the filter). It is made of a material having a grain diameter of 20 to 30 mm, the rate of filtration is the filtration rate of 10% pure material.
- Outflow zone , with a length of 1 m. It’s built (same as inflow zone) of stone with grain sizes 40 to 80 mm.

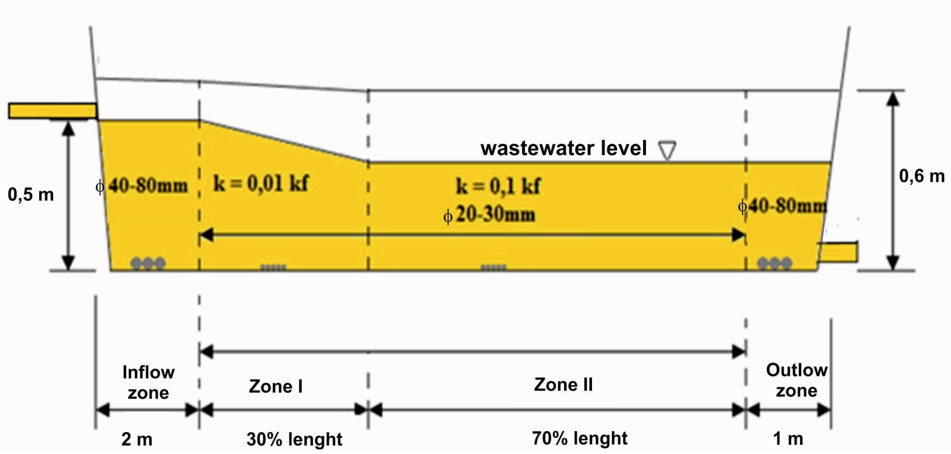

Fig. 1. Selected zones in the constructed wetlands [14]

5. PLANTS

Plants growing on the constructed wetlands are supplied with simple substances by microorganisms. Efficiency of this process reaches 10-15% [17]. In addition to partial assimilation of nutrients, plant also:

- ensure the delivery of oxygen to the microorganisms,
- clears the filter and prevent clogging,
- use water in the process of evapotranspiration.

For soil-plant filter strongly recommended are plants characteristic of wetland ecosystems. They should have the following characteristics:

- vigorous growth throughout the year,
- easily adapt to the environment and climatic conditions,
- resistance to pests,
- developed root system.

The most commonly used plants include *Phragmites australis*, *Glyceria aquatica*, *Typha latifolia*, *Iris pseudoacornus* and *Salix viminalis*.

6. THE EFFICIENCY OF EXISTING SYSTEMS

The efficiency of wastewater treatment systems in constructed wetlands for indicators such as BOD_5 and COD is very high and vary from 80% to 90% [1]. High pollution reduction confirm the publications of other authors [10, 15]:

- BOD_5 - 75 to 97.5 [%]
- COD - 73.2 [%]
- suspended solids - 55 to 83 [%].

Studies carried out in the initial phase of treatment plant (1997-1999) showed average efficiency of BOD_5 and total suspended solid reduction. It was of 60.8% for total suspended solids and 87% for BOD_5 [10]. Decress of the efficiency is the result of the accumulation of organic and inorganic substances in the filter, which reduce water flow and the contact time with the biofilm [7]. Clogging phenomenon does not occur as often in filters filled with gravel, in which the removal efficiency of organic matter is stable in the first years of life [3].

Better effects of pollution reduction can be achived if the vegetation will not be truncated before winter. Plants will form a layer of thermal insulation and space for bacterial flora growing on macrophytes root system [13, 12].

7. CONCLUSIONS

Based on the presented results it can be concluded that:

- hydrophytic wastewater treatment plant for at least 10 years of service, ensure the removal of organic matter from wastewater at the required level.
- The effectiveness of the wetlands systems decreases with time. This is due to clogging of the filter.

- Due to the high demand of the area this solution is recommended to the stand-alone buildings, inhabited by a small number of residents.

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OCZYSZCZANIE ŚCIEKÓW W OCZYSZCZALNI HYDROFITOWEJ

Streszczenie

Oczyszczalnie hydrofitowe są alternatywnym i ekonomicznie uzasadnionym, sposobem na oczyszczanie ścieków pochodzących z zabudowań charakterze rozproszonym. Literatura oraz badania istniejących systemów ze złożem gruntowo roślinnym pokazują, że skuteczność oczyszczania ścieków jest wysoka. Na skuteczność wpływa wiele czynników tj.czasu eksploatacji, rodzaju wypełnienia złoża, temperatury. Hydrofitowe oczyszczalnie ścieków przy odpowiedniej budowie i eksploatacji są bezpieczne dla środowiska oraz użytkowników.

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COD FRACTIONS IN RAW AND MECHANICALLY TREATED WASTEWATER

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The paper presents results of studies concerning the designation of COD fraction in the raw and mechanically treated wastewater in different year seasons. The research object was a mechanical-biological wastewater treatment plant with the output of >40 000 P.E., located in western Poland. The results of COD fraction in the raw wastewater were compared with data received in the ASM models. Methodology for determining the COD fraction was based on the guidelines ATV - A 131. During the research following fractions were determined: particulate slowly biodegradable substrates (X_S), soluble readily biodegradable substrates (S_S), inert particulate organic material (X_I) and inert soluble organic material (S_I). Soluble and particulate components were differentiated by filtration through 0.45μm membrane filters. The percentage of each fraction in total COD determined on the real concentration in raw wastewater are different from data reported in the literature.

Keywords: raw wastewater; COD fractions; ASM models; organic substances biodegradable and non-biodegradable

1. INTRODUCTION

The diversity of unit biochemical processes occurring in integrated removal of contaminants from wastewater has had an impact on the application of computer simulations based on various mathematical models in designing [5,13,19]. The application of these methods requires, however, more detailed data on the wastewater content, as compared to the values of conventional indices, such as BOD_5, COD_{Cr}, COD_{Mn}, TOC or ignition loss. Also the knowledge of many kinetic parameters of kinetic unit processes is required. In the design and optimisation of biological wastewater treatment processes, it is very important

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to determine the biodegradability of contaminants with taking into account the ratios of contained by them compounds responsive and resistant to decomposition, and the influence of wastewater constituents on the course of unit processes. Detailed characterisation of organic contaminants is of increasing significance also in sludge stabilisation processes and problems related to sludge liquors forming in wastewater treatment plants [5,11,12,17]. The index BOD_5, so commonly used in designing technology wastewater treatment systems, only provides information about easily biodegradable contaminant content, however, it does not, take into account the amount of non-biodegradable contaminants which lower the effectiveness of biological wastewater treatment. The index COD, with division into fractions, is currently presented as the most appropriate for the characterisation of organic substrates present in wastewater, because it makes it possible to obtain information on biodegradability of organic contaminants, both in dissolved and suspension form [1,3,15,23,24].

According to the IAWQ (*International Association on Water Quality)* nomenclature, dissolved constituents are marked with the symbol S and undissolved ones with the symbol X [8]. Depending on the form of compounds, total COD will be the sum of:

$$COD_{tot.} = S_{COD} + X_{COD}, gO_2 / m^3 \tag{1.1}$$

where: S_{COD} – the sum of dissolved organic substances, gO_2/m^3
X_{COD} – the sum of organic substances in suspension, gO_2/m^3.

The percentage ratio of the suspension fraction in total COD of raw household wastewater is 65÷79% and dissolved – 21÷35. It is also assumed that the percentage ratio of suspensions in household wastewater is about 57% COD and colloids and dissolved substances about 43% in total [4,6,16,18].

2. COD FRACTION CONCENTRATIONS IN BIOKINETIC ASM MODELS

The IAWPRC (*International Association on Water Pollution Research and Control*) work group, currently *International Water Association* (IWA), was appointed in 1982, in order to develop a universal mathematical model for designing the activated sludge process with the removal of nitrogen and phosphorus compounds [6,7,15,25].

The preliminary version of the model named (*Activated Sludge* Model No.1) was published in 1987 [10,15]. ASM1 model enables the simulation of the processes of removal of organic compounds and nitrogen compounds from wastewater, with taking into account unit processes which occur both in wastewater, as well as active sludge [7,10,14].

The model includes eight unit processes which are divided into 3 groups:

- hydrolysis processes involving:
  - organic compound hydrolysis under non-limiting oxygen conditions,
  - organic compound hydrolysis under oxygen-free conditions,
  - organic nitrogen hydrolysis,
- organic substance decomposition processes occurring in the presence of heterotrophic bacteria (X_H):
  - heterotrophic biomass growth under non-limiting oxygen conditions,
  - heterotrophic biomass growth under anoxic conditions,
  - heterotrophic biomass decomposition,
- processes conducted by autotrophic bacteria (nitrificants) (X_A):
  - autotrophic biomass growth under non-limiting oxygen conditions,
  - autotrophic biomass decomposition.

The constituents of total COD according to the ASM1 model are presented by the equation:

$$COD_{tot.} = S_S + S_I + X_S + X_I + X_H + X_A + X_P, gO_2/m^3 \tag{2.1}$$

where:

S_I – inert soluble organic material, gO_2/m^3
S_s – soluble readily biodegradable substrates, gO_2/m^3
X_I – inert particulate organic material, gO_2/m^3
X_S – particulate slowly biodegradable substrates, gO_2/m^3
X_H – heterotrophic organisms, gO_2/m^3
X_A – autotrophic nitrifying organisms, gO_2/m^3
X_P – decay products, gO_2/m^3.

Unless the biomass fraction is included, this model is simplified to the form:

$$COD_{tot.} = S_S + S_I + X_S + X_I, gO_2/m^3 \tag{2.2}$$

ASM1 modifications have led to the creation of subsequent versions: ASM2, ASM2d and ASM3 [2,6,7,8,9,15]. Thus, the ASM1 model, which describes only the removal of organic compounds and nitrogen compounds, has been expanded to a version covering advanced phosphorus removal processes. A novelty in the ASM2 model is the isolation from the group of active sludge microorganisms (PAO’s) ones with the ability of phosphorus cumulation by polyphosphate storage [6,8,10].

The concentrations of the individual COD fractions according to the ASM1 and ASM2 models are the following [4,6,8,9,10]:

ASM1

$COD_{tot} = 400\ gO_2/m^3$

X_S particulate slowly biodegradable substrates:	**280**gO_2/m^3
S_S soluble readily biodegradable substrates:	**60** gO_2/m^3
X_I inert particulate organic material:	**40** gO_2/m^3
S_I inert soluble organic material:	**20**gO_2/m^3

ASM2

$COD_{tot} = 263\ gO_2/m^3$

X_S particulate slowly biodegradable substrates:	**125**gO_2/m^3
S_F fermentable, readily biodegradable organic substrates:	**30** gO_2/m^3
X_I inert particulate organic material:	**25** gO_2/m^3
S_I inert soluble organic material:	**30** gO_2/m^3
S_A fermentation products (acetate):	**20** gO_2/m^3
X_H heterotrophic organisms:	**30** gO_2/m^3
X_A autotrophic nitrifying organisms:	**1** gO_2/m^3
X_{PAO} Phosphorus Accumulating Organisms PAO:	**1** gO_2/m^3
X_{PHB} cell internal storage product of PAO's:	**1** gO_2/m^3

The division of organic substances in the ASM2 model is much more complex than in the ASM1 version, because it takes into account 19 constituents used in wastewater and active sludge characterisation. Ten of them relate to insoluble constituents, nine to soluble ones [6,9,10].

The models assume that in raw wastewater fractions X_s and S_s are dominant, whereas in lower concentrations two other fractions occur: S_I and X_I. The percentage ratios of the individual fractions assumed by the ASM1 and ASM2 models are presented below:

ASM1

X_S particulate slowly biodegradable substrates:	**70 %**
S_S soluble readily biodegradable substrates:	**15 %**
X_I inert particulate organic material:	**10 %**
S_I inert soluble organic material:	**5%**

ASM2

X_S particulate slowly biodegradable substrates:	**35 ÷75 %**
S_S soluble readily biodegradable substrates:	**12÷30 %**
X_I inert particulate organic material:	**10÷15 %**
S_I inert soluble organic material:	**5÷10%**

The ASM1 model assumes constant values of the percentage ratio of the individual fractions, whereas the ASM2 model gives ranges of percentage ratios of the individual fractions in total COD of raw wastewater.

3. METHODOLOGY OF COD FRACTION DETERMINATION

The methodology of COD fraction determination has been developed on the basis of the ATV-A131 guidelines [20,21,22,26]. The methodology for the determination of the fractions involves the characterisation of COD and BOD_5 in filtered and non-filtered samples of raw and treated wastewater.

- The dissolved, non-biodegradable fraction S_I is termed as COD in filtered treated wastewater.

- The dissolved, easily biodegradable fraction S_S is calculated from the difference of the concentration of dissolved organic contaminants S_{COD} determined in filtered raw wastewater and the concentration of the dissolved non-biodegradable fraction (S_I):

$$S_S = S_{COD} - S_I, gO_2/m^3 \tag{3.1}$$

- The slowly biodegradable organic suspension, fraction X_S is defined as the difference of total BOD (BOD_T), calculated based on the BOD_5 of non-filtered raw wastewater and biochemical decomposition coefficient (k_1) and the dissolved easily biodegradable fraction S_S:

$$X_S = \frac{BOD}{k_1} - S_S, gO_2/m^3 \tag{3.2}$$

for household wastewater, it is assumed that k_1=0.6, 1/d.

- Non-biodegradable organic suspension X_I is calculated from the dependence:

$$X_I = X_{COD} - X_S, gO_2/m^3 \tag{3.3}$$

where: X_{COD} is total concentration of dissolved organic substances in suspension.

- Total COD of raw wastewater as the sum of the fractions is determined with the equation:

$$COD_{tot.} = S_S + S_I + X_S + X_I, gO_2/m^3 \tag{3.4}$$

Soluble and particulate components were differentiated by filtration through 0.45μm membrane filters.

4. THE GOAL AND SCOPE OF THE RESEARCH

The goal of the research was to determine the actual concentrations of COD fractions in raw wastewater flowing into a municipal wastewater treatment plant with the output of 15000 m^3/d. The results and calculations obtained have made it possible to determine percentage ratios of the individual fractions in total COD and compare the results obtained with the assumptions of the biokinetic ASM1 and ASM2 models. It was also investigated the effect of mechanical treatment in grit chamber into the COD fractions changes. This part of the study was to test how the process of mineral suspended solids separate will affect on the participation of the COD fractions.

4.1. The characteristic of the research subject

The research object was a municipal wastewater treatment plant with the output of >40 000 P.E., located in western Poland. It is a mechanical-biological wastewater treatment plant with the function of the nitrogen and phosphorus compounds removal.

During the research following wastewater samples were collected: raw wastewater, wastewater after grit chamber and treated wastewater. The technology diagram of the research object is presented in Fig. 1.

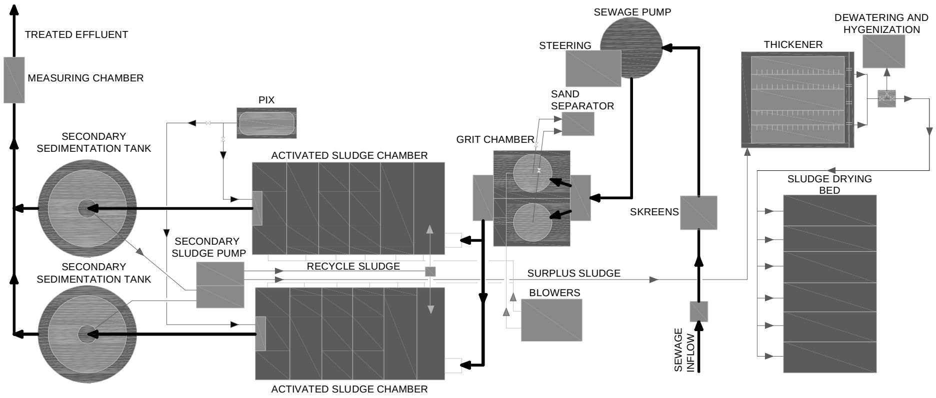

Fig. 1. The technology diagram of the WWTP

4.2. Testing methodology

Raw and treated wastewater samples were taken in accordance with PN-ISO 5667-10:1997.

The scope of physical-chemical analyses of wastewater samples included the characterisation of:

- Chemical oxygen demand, COD – with the potassium dichromate method, as per PN-74/C-04578.03, PN-ISO 6060:2006,
- Biochemical oxygen demand, BOD - with the manometric method, using the OxiTop Control OC110 measurement system made by WTW,
- Total organic carbon, TOC – using the total organic carbon analyser TOC-V CSN made by Shimadzu,
- Dissolved organic carbon, DOC – using the total organic carbon analyser TOC-V CSN made by Shimadzu, in a sample of wastewater filtered through a 0.45μm filter.

The characterisations were conducted in three repetitions, in raw wastewater samples and samples filtered through a 0.45μm filter.

The obtained research results were statistically analyzed using Statistica 9.0. Determined following statistical values: the arithmetic mean, median, maksiumum value, minimun value and standard deviation.

5. TEST RESULTS

In the testing period, the organic contaminant values in raw wastewater were: COD = 868.0-1428.0 gO_2/m^3, BOD_5 = 456.0-730.0 gO_2/m^3, TOC = 212.0-290.0 gC/m^3, while in the wastewater after grit chamber were: COD = 566.0-920.0 gO_2/m^3, BOD_5 = 288.0-494.0 gO_2/m^3 and TOC = 135.8-234.1 gC/m^3.

The test results of raw wastewater composition and its changes after grit chamber as mean values are presented in Table 1.The test results correlated in Table 1 suggest that in the analysed period encompassing different seasons, the composition of raw wastewater flowing into the WWTP did not vary significantly.

Table 1. Organic contaminants in raw wastewater and in wastewater after grit chamber

Wastewater samples	**COD,** gO_2/m^3		**BOD_5,** gO_2/m^3		**TOC** Unfiltred samples	**DOC** Filtred samples
	Unfiltred samples	Filtred samples	Unfiltred samples	Filtred samples	gC/m^3	
Raw wastewater	1143.3±187.1	401.3±62.0	595.8±98.9	301.3±75.7	252.6±29.2	151.8±26.7
Wastewater after grit chamber	775.8±127.4	354.5±82.2	401.5±75.1	201.9±69.3	194.4±34.3	104.0±15.9

The wastewater was characterised by a mean COD value of 1143.3±187.1 gO_2/m^3 and a mean BOD_5 value of 595.8±98.9 g O_2/m^3. Wastewater treatment in grit chamber resulted in a decrease concentration of organic pollutants average of 30%.

In accordance with the procedure for determining the COD fraction given in point 3, the concentrations of the individual fractions in the effluent and mechanically treated wastewater in analysed wastewater treatment plant have been calculated. The results showing the concentrations of the individual fractions are presented in Table 2.

Table 2. The COD fraction concentrations in raw wastewater (P1) and in wastewater after grit chamber (P2)

Season of the year		**COD fractions, gO_{2}/m^3**			
		S_I	**S_S**	**X_S**	**X_I**
Spring	P1	30.0±2.8	317.0±24.0	549.5±70.0	109.5±98.3
	P2	30.0±2.8	277.0±15.6	281.5±95.5	75.5±24.7

Summer	P1	26.0±8.5	409.0±41.0	683.0±217.8	111.0±76.4
	P2	26.0±8.5	445.0±38.2	356.5±40.3	71.5±19.1
Autumn	P1	30.0±2.8	407.0±114.6	726.0±43.8	229.0±22.6
	P2	30.0±2.8	330.0±31.1	395.0±107.5	102.0±52.3
Winter	P1	32.0±0.0	354.0±14.1	522.0±161.2	138.0±25.5
	P2	32.0±0.0	248.0±28.3	339.5±21.9	63.5±17.7

S_I inert soluble organic material, **S_S** soluble readily biodegradable substrates, **X_S** particulate slowly biodegradable substrates, **X_I** inert particulate organic material

During the research found a high variability of wastewater parameters, which reflect the values of the standard deviation.

The test results show that in raw wastewater, the most concentrated are fractions X_S and S_S. Definitely lower are the concentrations of fractions X_I and $S_{I.}$ The highest concentrations among the calculated fractions characterised the undissolved, slowly biodegradable organic fraction (X_S). In raw wastewater, its concentration was between 408 and 837gO_2/m^3. In raw wastewater, biodegradable fractions (S_S+X_S) constituted over 80% of total COD.

As a result of mechanical treatment wastewater in grit chamber, concentration of suspended solids, fractions X_I and X_S, were reduced average about 34 – 43% and the S_S fraction about 13%.

The determined percentage ratio of the individual fractions in raw wastewater dependent on the season is presented in Fig. 2. Among biodegradable fractions, fraction X_S which characterises slowly degradable suspensions and constitutes between 43.4 and 64.1 % of total COD is predominant. The ratio of fraction S_S (easily biodegradable organic contaminants) in total COD of the wastewater was between 24.0 and 38.0%. The percentage content of fraction X_I was at 4.4 – 18.1%. The lowest ratio, at 1.7 ÷ 3.4% in total COD of the tested raw wastewater, was that of fraction S_I.

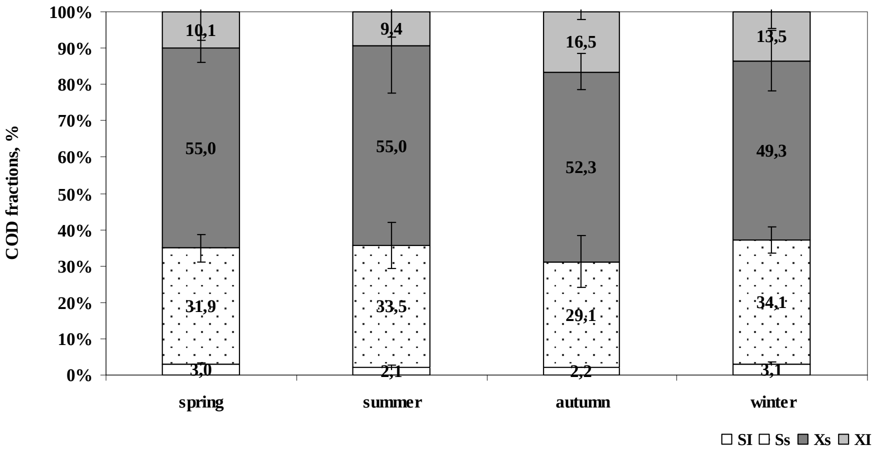

Fig. 2. The average percentage ratio of the individual fractions in total COD of raw wastewater in different seasons

Changes in the percentage of COD fractions in wastewater after grit chamber dependent on the season are shown in Fig. 3. The data show that in the wastewater after grit chamber percentage of S_S fraction was higher than in raw wastewater and ranged from 34.2 to 53.0%.

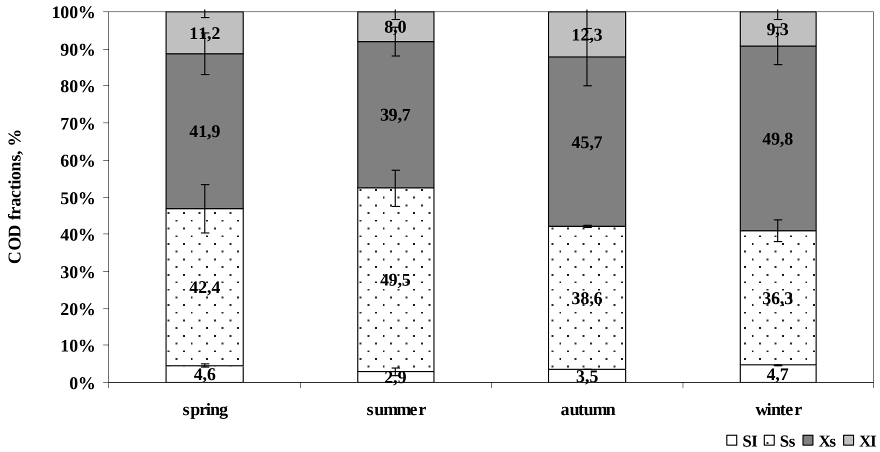

Fig. 3. The average percentage ratio of the individual fractions in total COD of wastewater after grit chamber in different seasons

The other hand the percentage of particulate slowly biodegradable substrates – fraction X_S was lower than in raw wastewater and ranged from 36.9 to 53.3% In the wastewater after grit chamber biodegradable fractions (S_S+X_S) constituted still over 80% of total COD.

6. DISCUSSION AND CONCLUSIONS

The test results with the average percentage ratios of the individual fractions in raw wastewater and in wastewater after grit chamber are presented in Fig. 4.

Both in raw wastewater and in wastewater after grit chamber, over 80% of total COD constituted biodegradable fractions (X_S+S_S). The presented results show that in raw municipal wastewater the average percentage ratio of the individual COD fractions was as follows: X_S=52.9±6.7%, S_S=32.2±4.6%, X_I=12.4±5.3% and S_I=2.6±0.6%, while in the wastewater treated in grit chamber was respectively: X_S=44.2±6.0%, S_S=41.7±6.3%, X_I=10.2±3.5% and S_I=3.9±0.9%.

The study found that, the percentage ratios of X_S and X_I fractions in the wastewater after grit chamber relative to the value in raw wastewater has decreased, while the percentage ratios of S_S and S_I fractions has increased. The obtained results may indicate of the hydrolysis of suspended solids fraction already in the mechanical part of the plant. This is confirmed by the reduction in the mechanical treatment the percentage of X_S fraction with a parallel increase in the percentage of S_S fraction. This changes are particularly evident in the spring and summer.

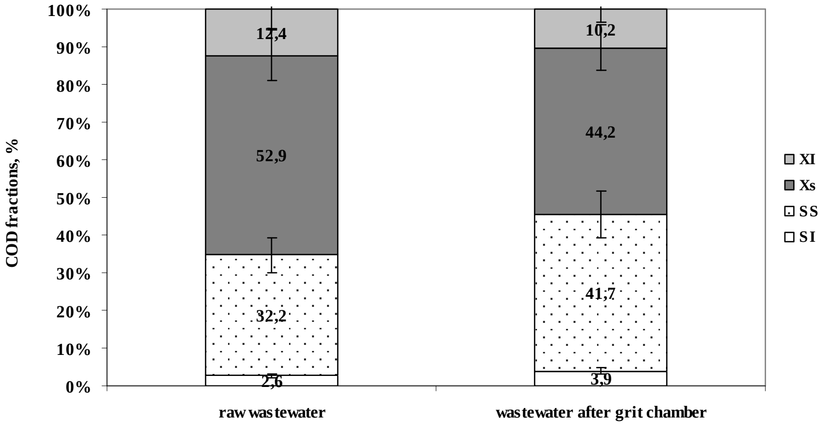

Fig. 4. The average percentage ratio of the individual fractions in total COD of raw wastewater and of wastewater after grit chamber

The research has shown that the fraction occurring in the highest concentration in raw wastewater is X_S, followed by S_S, X_I and S_I. Such an order is present in the biokinetic models (Tab. 3). Significant differences between actual research and model assumptions pertain to the content range of the individual fractions. The research has revealed higher percentage ratios of fractions X_I and S_S, as compared to the assumptions of the ASM1 and ASM2 models, and lower percentage ratios of fractions S_I and X_S in the raw wastewater.

Table 3. The percentage COD fraction ratio in raw wastewater according to own research and the assumptions of the ASM1 and ASM2 models

COD fractions,%	**WWTP with the output >40 000 P.E.**	**in ASM1 model**	**in ASM2 model**
	raw wastewater		
S_I	1.7 – 3.4	5.0	5.0 – 10.0
S_S	24.0 – 38.0	15.0	12.0 – 30.0
X_I	4.4 – 18.1	10.0	10.0 – 15.0
X_S	43.4 – 64.1	70.0	35.0 – 75.0

The presented test results are a basis for the formulation of final conclusions:

The concentrations and percentage ratios of the individual COD fractions in raw wastewater determined in real conditions differ from the values assumed by the ASM models. The real concentrations and percentage ratios of the individual COD fractions in raw wastewater should be a basis for the calibration of models used in the modelling and control of the operation of wastewater treatment plants.

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FRAKCJE CHZT W ŚCIEKACH SUROWYCH I MECHANICZNIE OCZYSZCZONYCH

Streszczenie

W artykule przedstawiono wyniki badań dotyczące frakcji ChZT w ściekach surowych i mechanicznie oczyszczonych w piaskowniku. Badania prowadzono w mechaniczno-biologicznej oczyszczalni ścieków o wielkości>40 000 RLM, zlokalizowanej w zachodniej Polsce. Próbki do badań pobierano w różnych porach roku. Metodyka wyznaczania frakcji ChZT została opracowana w oparciu o wytyczne ATV-131. Podczas badań określono następujące frakcje: substancje organiczne w zawiesinie, biologicznie wolno rozkładalne (X_S), rozpuszczone substancje organiczne, biologicznie łatwo rozkładalne, (S_S), substancje organiczne w zawiesinie, biologicznie trudno rozkładalne (X_I) i rozpuszczone substancje organiczne, biologicznie nierozkładalne (S_I). Rozdziału frakcji rozpuszczonych i w zawiesinie dokonano przez filtrację próbek ścieków przez filtry membranowe o wielkości porów 0,45 μm. Wyniki badań wykazały, że zarówno w ściekach surowych jak i oczyszczonych mechanicznie udział frakcji biodegradowalnych wynosił ok. 80% całkowitego ChZT. Oczyszczanie ścieków w piaskowniku spowodowało obniżenie stężenia zanieczyszczeń ogranicznych o ok. 30% oraz wpływało na zmiany w udziale frakcji rozpuszczonych i w zawiesinie. Wartości procentowego udziału frakcji X_S i X_I w ściekach po piaskowniku zmalały, podczas gdy wartości procentowego udziału frakcji S_S i S_I wzrosły, w stosunku do ich udziału w ściekach surowych. Udział procentowy frakcji ChZT w ściekach surowych wyznaczony w badaniach różni się od danych zawartych w modelach ASM1 i ASM 2.

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EMISSION AND DISTRIBUTION OF AMMONIA FROM TURKEY FARM

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The objective of the study was to determine the emissions of ammonia and the extent of its impact on the environment. On the farm there are two livestock buildings. The ammonia emission was calculated on the basis of the emission ratio per 1 m^2 of the usable area of the building, for females determined at 1.38 kg per annum [9]. The volume of emission and the dispersion of ammonia was calculated at the height of 0.0 m and 6.5 m above ground level with the KOMIN and RWW programs. Regardless of the height at which the calculation was done, the highest of the maximum concentrations was observed 16 m from the emitters situated in the roof ridge and 1 m from the emitters in the sidewall. The values of average annual concentrations and maximum 1-hour concentrations were higher for calculations at 0.0 m than 6.5 m. Within the area where the reference values were exceeded there is a compact rural residential area, whose west part is subject to very high above-standard ammonia concentrations much more frequently.

Keywords: livestock facility, emitter, ammonia emission, the extent of the impact of ammonia

1. INTRODUCTION

Animal production is one of the main sources of pollution harming the basic elements of environment, especially the atmosphere [12].

Poultry farms, beside pig farms, rank as the biggest emitters of gas pollution released in the air, including ammonia [4]. Ammonia is generated in large amounts in livestock facilities as a result of bacterial and enzymatic processes taking place in animal manure [1].

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The greatest ammonia loss occurs with the deep litter systems of managing animals. The gas, because of its physicochemical properties may cause significant decrease in the animals' productivity as well as health problems [13]. Therefore, depending on climatic conditions and the birds' requirements, poultry facilities must be ventilated naturally and mechanically. In Poland the mechanical supply and exhaust system of ventilation is commonly used with the ventilation chimneys distributed in the roof, the endwall or the sidewall [9]. Regardless of the design approach, the basic task of ventilation systems is to remove the polluted air out of the building.

The pollution emitted into the atmosphere undergoes numerous chemical transformations, whose products have a negative environmental impact [2,4,8,10,13,18,19]. Such chemical compounds as NH_3, CH_4, H_2S, ketones and mercaptans present in the air in livestock buildings and their surroundings not only cause discomfort to local residents, who have reason to complain about the odour nuisance but they may also become a serious health hazard to human health and the state of the environment [11,16].

The atmospheric air is the medium least resistant to pollution and is also characterized by the fastest pace and dynamics of its expansion into the other elements of the environment (water, soil) [3,14,15].

The problem of environment protection during animal production has not yet been solved despite numerous regulations by law such as acts, regulations and provisions. The Regulation of the Minister of the Environment [6] of 13.05.1995 requires that investment projects related to animal breeding with the stocking density of over 50 DJP, and 100DJP for litter rearing, be considered an environmental hazard. Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC imposes an obligation to make an assessment of environmental impact of intensive rearing of poultry for installations with more than 40 000 places, including turkey broilers.

The Regulation of the Minister of the Environment of 26 January 2010 on the reference values for certain substances in the air [7] includes the referential methodology of modelling of levels of substances in the air as well as reference values for air pollutants, including ammonia.

Ammonia is not a greenhouse gas but it contributes to rain acidification and even more so to the photochemical smog. When it settles on the ground, it is oxidized to nitric acid, which acidifies the lithosphere and hydrosphere.

The objective of this study is to determine the extent of the impact of the above-standard concentrations of ammonia emitted from livestock facilities in which turkeys are grown and fattened.

2. MATERIALS AND METHODS

The computer simulation of the dispersion of ammonia around livestock buildings was carried out for a poultry farm situated south-west of compact rural residential area and about 50 m from the nearest residential buildings.

There are two livestock buildings on the poultry farm (B1 and B2), each with the usable area of 1100 m^2. The ventilators in B1 and B2 have the same technical parameters: ventilator output - 5 000 $m^3 \cdot h^{-1}$; the inner diameter - 0.55 m; the geometric height of the ventilation chimney outlets in the roof ridge is 3.5 m and in the sidewall - 1.0 m. The exhaust gas velocity for ventilation chimneys in the roof ridge in B1 and B2 is 5.85 $m \cdot h^{-1}$ whereas in the sidewall it is 0.0 $m \cdot h^{-1}$ [7].

The calculation of emission volumes and the modeling of ammonia dispersion in the atmospheric air around the farm was made in compliance with the referential methodology specified in the Regulation of the Minister of the Environment of 26 January 2010 on the reference values for certain substances in the air [7].

To calculate the levels of ammonia emission and to visualize the extent of its impact, the following assumptions were used:

- the maximum composite average emission for one hour $E_{g\ max}$. calculated on the basis of the emission ratio per 1 m^2 of the usable area of the building, for females determined at 1.38 kg per annum [9]
- the pollutant background - for ammonia - 5 $\mu g \cdot m^{-3}$
- meteorological data: the statistics of steady states of the atmosphere, wind velocity and direction accepted for the weather station in Zielona Góra
- the average temperature of the atmospheric air in the calculation period - one year - 281.2K
- the temperature of exhaust gases from the emitter - 293.2K
- the calculations of substance levels in the air for sets of emitters were done on a geometric network of points with the coordinates X_p i Y_p
- the emitters' coordinates are set as Xe i Ye. The x-axis faces east and the y-axis faces north
- the contours of B1 and B2 were set in quadrant I of the Cartesian coordinate system XOY
- the aerodynamic terrain roughness coefficient z_0 = 0.5 m [7]

In accordance with the Regulation of the Minister of the Environment, to calculate the dispersion of the pollution plume the Pasquill formula was applied, which is a simplified solution of a differential equation of atmospheric diffusion of pollution in moving gaseous medium. The model disregards the appearance of inversion, stillness, the absorption of pollution by the ground and precipitation, chemical transformations of pollutants and the turn of wind at higher altitudes. For so determined conditions the equation describing the dispersion of pollution looks as follows:

$$S_{xyz} = \frac{E_g}{2\pi \bar{u}\, \sigma_y \sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2} \right) \left\{ \exp\left[-\frac{(z-H)^2}{2\sigma_z^2} \right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2} \right] \right\} \cdot 1000 \quad \left[\mu g / m^3 \right]$$

S – the concentration of the gas substance at a point with the coordinates Xp, Yp, Zp
E_g – maximum emission of substance, mg·s^{-1}
u – the wind velocity, m·s^{-1}
σ_y, σ_z – horizontal and vertical atmospheric dispersion coefficients, m
H – the effective height of the release, m
z – the height for which the concentration of substance in the air is calculated, m.

The range of calculations of substance levels in the air includes the calculations of the distribution of maximum concentrations of the substance averaged for one hour including the statistics of meteorological conditions to ensure that at every point of the terrain surface the following condition was met:

$$S_{mm} \leq D_1$$

where:
S_{mm} – the highest of maximum substance concentrations in the air, μg·m^{-3}
D_1 – the reference value of the substance in the air or the permissible level of substance in the air averaged for one hour, μg·m^{-3}.

The calculations for B1 and B2 were done in a network with 5-metre intervals at the height of 0.0 m at ground level and 6.5 m above ground level. The calculation part of this paper was done by means of the KOMIN program whereas the graphic component illustrating the dispersion in the atmosphere of ammonia emitted in the turkey farm was done with the RWW program.

3. RESULTS AND DISCUSSION

The calculation results obtained with the KOMIN program are presented in Table 1.

Table 1. The volume of ammonia emission, the values of maximum average annual and 1-hour concentrations and the incidence of exceedance of annual and 1-hour concentrations depending on the height at which calculations were done.

Parameter	Height at which calculation was done Z [m]	Livestock facilities	
		B1, B2	B2
		Emitters in roof ridge	Emitters in wall
Highest of maximum ammonia concentrations [μg·m^{-3}]	0.0	225.9	72804.4
	6.5	225.9	72804.4
Distance of emitter from point of concentration [m]	0.0	16	1
	6.5	16	1
Maximum of average annual concentrations [μg·m^{-3}]	0.0	6894.5	
	6.5	1594.5	
Maximum of max. 1-hour concentrations [μg·m^{-3}]	0.0	75433.4	
	6.5	30994.7	
Maximum of percentile S99.8	0.0	74552.3	
	6.5	30857.7	
Maximum incidence of concentration exceedance 50.0 μg·m^{-3} [%}	0.0	83.3	
	6.5	77.8	
Maximum incidence of concentration exceedance 400.0 μg·m^{-3} [%]	0.0	77.1	
	6.5	63.6	

Source: autor's calculations

As the data in Table 1. show, regardless of the height at which the calculations were done, the highest of maximum concentrations was 225.9 μg·m^{-3} and was observed 16 m from the emitters in the roof ridge.

Very high values of the highest of maximum concentrations were found at emitters along the sidewall in B2 and regardless of the height at which the calculations were done, the concentrations were 72804.4 $\mu g \cdot m^{-3}$ and were found at the distance of 1 m from the emitters.

The values of maximum of average annual concentrations calculated at the height of 0.0 m were much higher than those calculated at the height of 6.5 m above ground level. The difference was 5300 $\mu g \cdot m^{-3}$.

The highest of maximum 1-hour concentrations calculated at 0.0 m were higher by 44438.7 $\mu g \cdot m^{-3}$ as compared to those calculated at 6.5 m AGL.

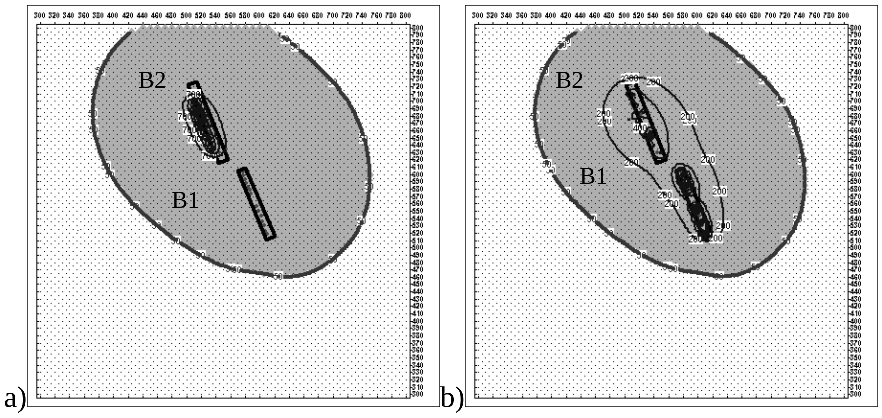
The calculation results showed that the maximum of percentile S99.8 for the height of 0.0 m was higher by 43694.6 $\mu g \cdot m^{-3}$ than that calculated for the height of 6.5 m AGL.

The maximum incidence of reference value exceedance for one year (50 $\mu g \cdot m^{-3}$) was higher by 5.6 percentage points for the calculation height of 0.0 m than for 6.5 m AGL.

The observed maximum incidence of reference value exceedance for one hour (400 $\mu g \cdot m^{-3}$) were higher by 13.5 percentage points for the calculation height of 0.0 m than for 6.5 m AGL.

The annual volume of ammonia emission from the farm was 85.03 tons.

Figures 1 - 6 present computer simulations illustrating the dispersion of ammonia from the farm buildings (B1 and B2) corresponding to the calculation height of 0.0 m and 6.5 m AGL. The rectangles represent the livestock facilities. The shadowed area represent the zone where the ammonia concentrations exceed the averaged reference values for a calendar year (50 $\mu g \cdot m^{-3}$) and for one hour (400 $\mu g \cdot m^{-3}$).

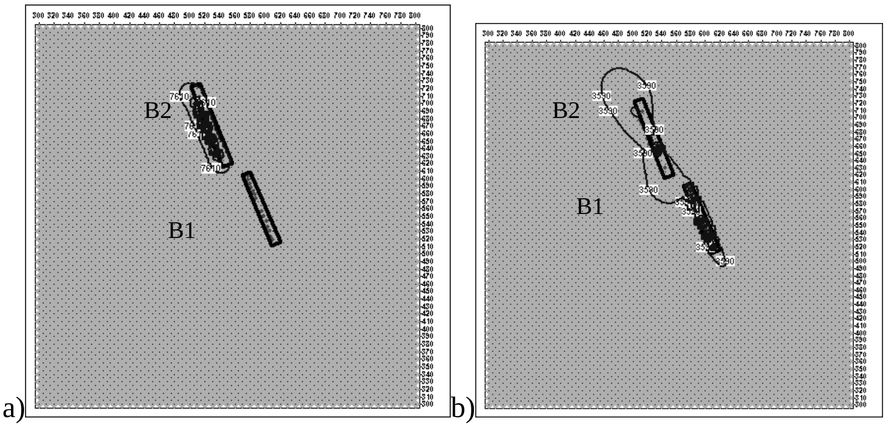


Source: author's calculations

Fig. 1. The distribution of average annual concentrations from the farm at 0.0 m (a) and 6.5 m AGL (b)

The distribution of contour lines presented in Fig. 1a) and b) shows that the area of above-standard average annual concentrations covers the farm area. For the calculation height of 0.0 m AGL very high concentrations (700 µg·m^{-3}) occur only around the building B2. A likely reason for such distribution of ammonia concentrations is the location of 10 emitters along the sidewall of B2.

The distribution of contour lines for calculations done at the height of 6.5 m AGL shows that also at this height there are high concentrations (400 µg·m^{-3}) around B2. The contour line representing 200 µg·m^{-3} covers a smaller area around B1 than B2. The impact zone of the above-standard average annual concentrations from B1 and B2 covers the west part of the compact rural residential area.



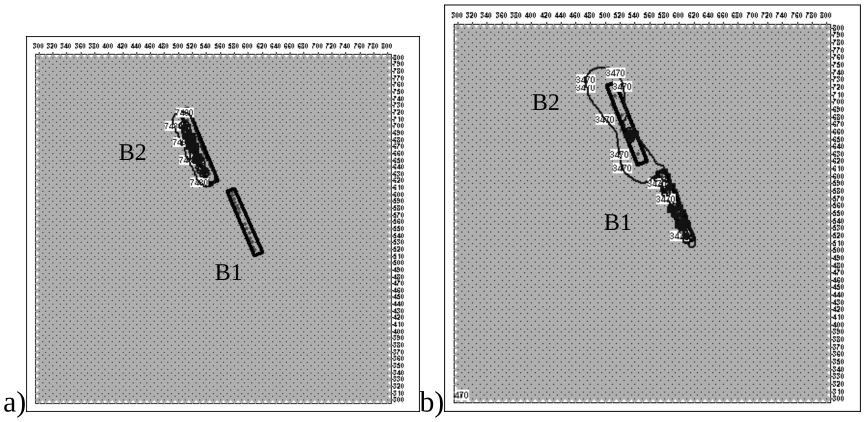
Source: author’s calculations

Fig. 2. The distribution of maximum 1-hour concentrations from the farm at 0.0 m (a) and 6.5 m AGL (b)

Figure 2a) and b) shows that the extent of impact of above-standard 1-hour maximum concentrations is very large (the shadowed area) and covers the compact rural residential area. The distribution of contour lines shows that for calculations done at the height of 0.0 m the impact area of very high concentrations (7610 µg·m^{-3}) occurs only around B2. The position of contour lines for calculations done at the height of 6.5 shows that the extent of the impact of high concentrations (3590 µg·m^{-3}) covers B1 and B2, but is larger around B2.

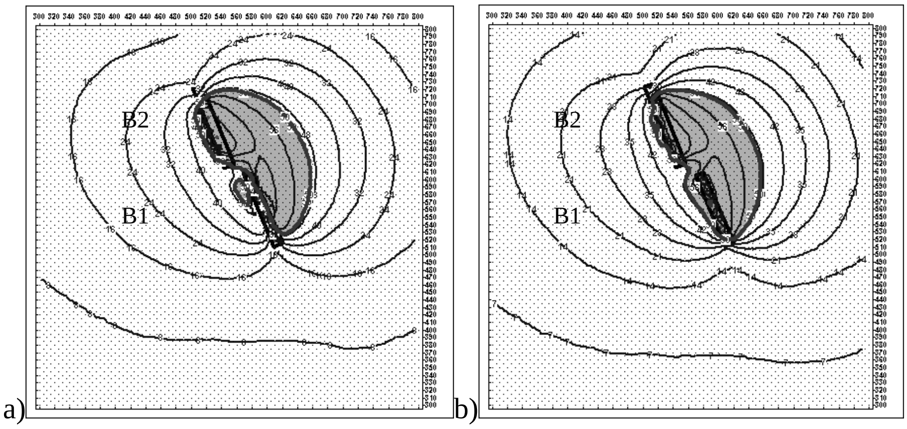
Figure 3a) and b) the contour lines illustrating the distribution of the maximum of percentile S99.8 show that the reference values were exceeded many times both for calculations at 0.0 m and 6.5 m AGL. For the calculation height of 0.0 m the contour line representing the highest value of percentile (7480 µg·m^{-3}) covered the area around B2 whereas for the calculation height of 6.5 m AGL the contour line representing the highest value of percentile (3470 µg·m^{-3}) covered B1 and B2.

The distribution of contour lines as presented in Fig. 4a) and b) show that both within the area of the farm and north-east of it the maximum incidence of the exceedance of concentration 50 μg·m^{-3} are very high. The maximum incidence of the exceedance of this concentration for calculations done at the height of 0.0 m and 6.5 m AGL were 83.33% and 77.77% respectively.



Source: author's calculations

Fig. 3. The maximum of percentile S99.8 at 0.0 m (a) and 6.5 m AGL (b)

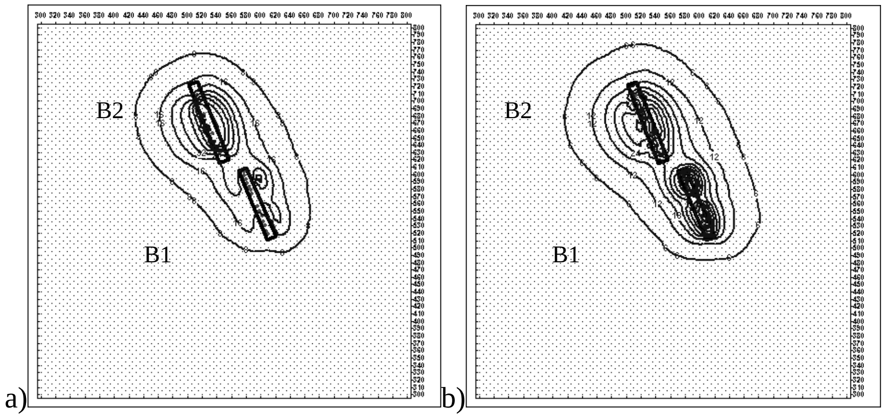


Source: author's calculations

Fig. 4. The maximum incidence of the exceedance of concentration 50 μg·m^{-3} at 0.0 m (a) and 6.5 m AGL (b)

The distribution of contour lines shows that within the compact rural residential area (north-east of the farm as presented in Fig. 4) the exceedance of the reference value for one year are much more frequent at the height of 0.0 m (16%) than at 6.5 m AGL (14%).

The contour lines illustrating the distribution of the incidence of exceedance show that the maximum incidence of the exceeded levels of concentration 400 $\mu g \cdot m^{-3}$ within the area of the farm are high and equalled 77.1% and 63.6% for the heights of 0.0 m and 6.5 m AGL respectively.



Source: author's calculations

Fig. 5. The maximum incidence of the exceedance of concentration 400 $\mu g \cdot m^{-3}$ at 0.0 m (a) and 6.5 m AGL (b)

The distribution of contour lines indicates that in the west part of the compact rural residential area the reference values for one hour are exceeded more frequently at the height of 0.0 m (8%) than at 6.5 m AGL (6%).

4. SUMMARY

The above calculations show that even a small poultry farm consisting of two livestock buildings emits considerable amounts of ammonia into the atmosphere per annum (85.03 tons).

The analysis of calculation results conducted with the Komin program showed that regardless of the height at which the calculation was done, the highest of the maximum concentrations was observed 16 m from the emitters situated in the roof ridge. Very high values of concentrations were also found at the distance of only 1 m from the emitters located in the sidewall.

The maximum average annual concentrations and the maximum 1-hour concentrations were higher for calculations done at 0.0 m AGL than 6.5 m AGL. A likely reason for such differences in the values of concentrations calculated at various heights is the location of 10 emitters along the sidewall of B2, from which the high concentration plume quickly reaches the ground surface. This is a highly unfavourable phenomenon as high concentrations of ammonia have a negative influence on animals and people in the building and around it. The distribution of ammonia concentrations shows that it is more beneficial to locate ventilation chimneys in the roof ridge of the livestock building.

The conducted analysis of the contour lines distribution showed that the impact area of the above-standard average annual concentrations of ammonia covers the area of the farm and the west part of the rural residential area. However, the extent of the impact of the above-standard maximum 1-hour concentrations is very large and covers a compact rural residential area. The contour lines illustrating the distribution of the maximum of percentile S99,8 show the reference values were exceeded many times regardless of the height of the calculation.

Within the area of the farm and north-east of it the maximum incidence of the exceedance of concentration 50 $\mu g \cdot m^{-3}$ are very high regardless of the height of the calculation.

The analysis of the distribution of contour lines shows that within the compact rural residential area the reference values for one year are exceeded more frequently for calculations done at the height of 0.0 m than 6.5 m AGL.

The contour lines illustrating the distribution of the incidence of exceedance showed that within the area of the farm 1-hour concentrations are high and more frequent for calculations done at the height of 0.0 m than 6.5 m AGL.

In view of the above analysis, it can be said that the area of the exceeded reference values covers the compact rural residential area, whose west part is more frequently exposed to the impact of the above-standard ammonia concentrations emitted from the buildings on the farm.

There should be no residential buildings within the area where permissible values are exceeded.

Dz. U. [5] of 2001 includes a provision which affirms that residential buildings owned by the party operating the installation may be located within the area exposed to above-standard impact of ammonia as long as they are situated in an area to which the party holds a legal title.

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EMISJA I ROZPRZESTRZENIANIE AMONIAKU Z FERMY INDYCZEJ

Streszczenie

Celem pracy jest określenie emisji amoniaku i zasięgu jego oddziaływania na środowisko. Na fermie znajdują się dwa budynki inwentarskie, w B1 jest 14. emitorów jest w kalenicy, w B2 4. emitory są w kalenicy a 10 w ścianie podłużnej. Parametry emitorów są takie same. Emisję amoniaku obliczono korzystając ze wskaźnika emisji z 1

m^2 powierzchni użytkowej budynku wynoszącym dla samic 1,38 kg rocznie [9]. Wielkości emisji i rozprzestrzenianie amoniaku wykonano dla wysokości 0,0 m i 6,5 m n.p.t. przy pomocy programów KOMIN i RWW. Niezależnie od wysokości obliczeń najwyższe ze stężeń maksymalnych wystąpiło 16 m od emitorów znajdujących się w kalenicy, oraz 1 m od emitorów w ścianie podłużnej. Maksymalne stężenia średnie roczne oraz stężenia maksymalne 1-godz były wyższe dla obliczeń na 0,0 m. niż na 6,5m. W zasięgu występowania przekroczeń wartości odniesienia znajduje się zwarta zabudowa a jej zachodnia część jest częściej narażona na oddziaływania bardzo wysokich ponadnormatywnych stężeń amoniaku. W obszarze występowania przekroczeń wartości dopuszczalnych nie powinny znajdować się budynki mieszkalne.

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GASIFICATION PROCESS AS A COMPLEX METHOD OF SEWAGE SLUDGE TREATMENT

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Today, there is a rising interest in many countries in “traditional” (e.g. agro and forest) biomass and waste biomass (e.g. sewage sludge) utilization processes (e.g. combustion, co-combustion, gasification and pyrolysis). During the last twenty years, there has been a major change in the way that sludge is disposed. For example, in the European Union (EU) landfill or water deposition of the sewage sludge with the e.g. higher heating value (HHV) equal to 6 MJ/kg will be prohibited. In light of there is a large and pressing need for the development of thermal methods for the disposal of sewage sludge. Gasification has several advantages over traditional combustion process. This work investigates sewage sludge gasification in a fixed bed gasifier. The effects of operating conditions on the gasification process were investigated.

Keywords: gasification, sewage sludge, fixed bed reactor, gasification gas parameters

1. INTRODUCTION

The quantity of sludge production in Europe [2, 8, 16, 17] varies widely over different countries (16-94 g/(person·day)). As population increases, there is an increase in the production of sewage sludge. Moreover, the final of sewage sludge disposal depends on the sludge treatment methods used on the wastewater treatment plant (anaerobic or aerobic digestion, drying, thermal utilization etc.). In the European countries anaerobic stabilization is more popular (in 24 countries) than aerobic countries (in 20 countries) [8]. Unfortunately, the most popular way of final sewage sludge management is storage. In countries that are technologically less developed, direct agricultural application or storage is typical pathways to safely dispose of stabilized sludge from wastewater treatment plants. In countries where policy makers practically forbade such solutions (e.g., the European Union), only thermal disposal methods are available [4-7]. The thermo-chemical conversion of sewage sludge consists of four main processes: combustion, co-combustion, pyrolysis and gasification. One of the promising thermo-chemical conversion technologies that can be used to convert sewage sludge to useful energy forms suited for small to medium size throughput is gasification. Gasification has attracted attention as one of the most efficient methods for utilizing biomass as CO_2 emission has become an important global issue. This process has several advantages over a traditional combustion process [13]. First of all, as a consequence of the reducing atmosphere in the gasifier (amount of the oxidizer is much less than the stoichiometric amount), gasification prevents emissions of sulphur and nitrogen oxides, heavy metals and the potential production of chlorinated dibenzodioxins and dibenzofurans. Due to it most of sulphur, nitrogen, chloride and fluoride in sewage sludge may be released as H_2S, NH_3, HCl and HF. Secondly, a less volume of gas is produced compared to the volume of flue gas from combustion [1, 3, 9-11, 14, 15].

This article reports on experimental investigations of fixed-bed gasification of sewage sludge. In Poland, several industrial fixed bed gasifier plants using "traditional" biomass (mainly agricultural) are in operation. Nevertheless, there is a lack of experimental research on locally available sewage sludge feedstock. Considering that only 1% of the sewage produced in Poland is currently thermally decomposed and given the advantages of the gasification process, the analysis presented here is especially important. Analysis of influence of the gasification process operating conditions and sewage sludge feedstock composition on the gasification gas parameters is presented.

2. METHODOLOGY

2.1. Sewage sludge properties

Two types of sewage sludge feedstock were analysed. Sewage sludge no. 1 (SS1) was taken from Polish wastewater treatment plant operating in the mechanical-biological system and sewage sludge no. 2 (SS2) was taken from mechanical-biological-chemical wastewater treatment plant with phosphorus precipitation. In both analysed cases, sewage sludge is stabilized by anaerobic digestion and dehydration. After anaerobic digestion, sewage sludge is dried. In the case 1 (SS1) sewage sludge was dried in cylindrical dryer with heated shelf. The temperature of hot air was equal to $260^{o}C$ (high temperature). In the case 2 (SS2) air belt dryer was used. The temperature of hot air in this case was equal to $150^{o}C$ (low temperature). As a consequence, in the case 1 form of the dried sludge is similar to granulate and in the case 2 to “noodles”. Table 1 summarizes the main physical and chemical properties of sewage sludge. The main components in the sewage sludge were determined using automatic infrared (IR) analyzers. The moisture content of the sewage sludge was obtained following standard PN-EN 14774-3:2010. The sludge volatile content was determined according to standard PN-EN 15402:2011. The sludge ash content was obtained using PN-EN 15403:2011. Lower Heating Value was calculated on the basis of hydrogen content on dry basis.

Table 1. Sewage sludge properties used in the gasification tests

	Symbol of sewage sludge	
	SS1	SS2
Proximate analysis, % (as received)		
Moisture	5.30	5.30
Volatile matter	51.00	49.00
Ash	36.50	44.20
Ultimate analysis, % (dry basis)		
C	31.79	27.72
H	4.36	3.81
N	4.88	3.59
O (by difference)	57.07	63.04
S	1.67	1.81
F	0.013	0.003
Cl	0.22	0.03
Calorific value		
LHV, MJ/kg (on dry basis)	12.96	10.75

Analysing ultimate analysis results it can be concluded that sewage sludge from mechanical-biological-chemical wastewater treatment plant with phosphorus precipitation (SS2) in comparison to the sewage sludge from mechanical-biological wastewater treatment plant (SS1) characterized lower amounts of C, H, N, F and Cl. This feature indicates on lower utility such sludge to thermal treatment. Additionally, this feature proves that in-depth waste treatment configuration has a direct impact on the sewage sludge calorific value (expressed by lower heating value LHV) of received derived fuel from sewage sludge. The LHV of SS2 is lower than SS1. Nevertheless, in both analysed cases, is lower than 6 MJ/kg what is the limit value for possibility of sewage sludge storage on waste landfill (based on the Polish criteria for the storage of sewage sludge in a non-hazardous waste landfill) [12].

2.2. Experimental instalation

The sewage sludge gasification tests were conducted using a fixed bed gasification facility [18]. The main system component was a stainless gasifier with a 150-mm internal diameter and a total height of 300 mm. The reactor was well insulated to prevent major heat loss. In this study, the granular sewage sludge was fed into the top of the gasifier. The gasification air was fed from the bottom by a blower. The sewage sludge was circulated in a countercurrent direction to the process gases. There were four zones in the gasifier. In the first zone (the drying zone), water was evaporated to form sewage sludge. In the second zone (the pyrolysis zone), the sewage sludge was thermally decomposed into volatiles and solid core. In the third zone, carbon was converted to the main combustible components of syngas. In the last zone, the remaining char was combusted. The combustion zone provides a source of energy for the gasification reactions in the upper zones. The gasification reactions are mainly endothermic. The internal reactor temperature was measured by six N-type thermoelements integrated with an Agilent temperature recording system. The thermocouples were located along the vertical axis of the reactor. The gasification gas temperature was also measured at the outlet of the reactor. The gasification air flow rate and the syngas flow rate were measured by flow meters. The syngas was transported from the gasifier by a gas pipe. The syngas was cleaned by a cyclone, a scrubber and a drop separator. The volumetric fractions of the main syngas components were measured online using a Fisher Rosemount and ABB integrated set of analyzers. The system was also equipped with a sampling port to collect gas for chromatographic analysis by an Agilent 6890N gas chromatograph.

A scheme of the installation is shown in Figure 1.

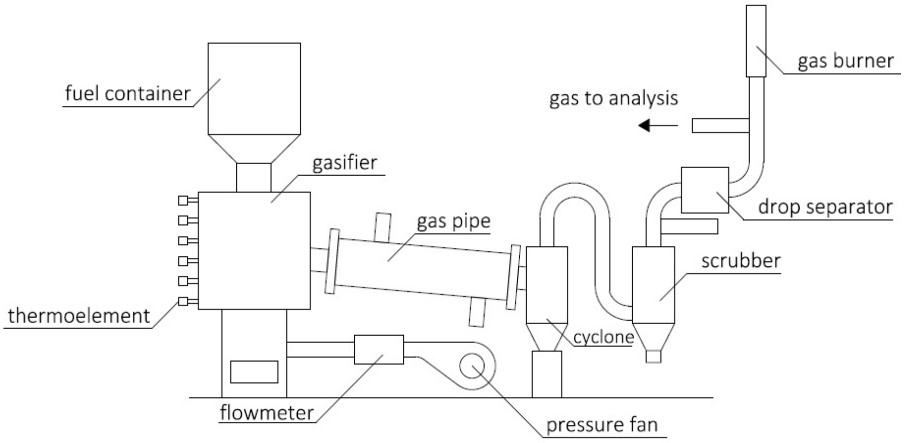

Fig. 1. Scheme of fixed bed gasifier installation

3. RESULTS

The study included the effect of the amount of supply air gasification on the composition of the gas from gasification.

The gasification process occurs in three major steps. The first step is associated with the initial decomposition of sewage sludge via the thermo-chemical processes that produce tar, volatiles and char residues. The second step involves reacting the volatiles. The last step comprises the heterogeneous reactions of the remaining carbonaceous residues with the gaseous producer gas and the homogeneous reactions of carbon monoxide, carbon dioxide, hydrogen, vapor and hydrocarbon gases.

Figure 2 and 3 shows the evolution of the H_2 and CO concentrations in gasification gas with varying air excess ratios for both analysed sludge (SS1 and SS2).

Analysing Figures 2 and 3 it can be confirmed that throughout the range of analysed air excess ratio (λ=0.12-0.27) volumetric fraction of main combustible components of gasification gas (CO and H_2) are higher in the case of the sewage sludge 1 (positive aspect) in comparison to SS2. This is mainly caused by the composition (as an effect of wastewater treatment configuration) of sewage sludge. Mechanical-biological-chemical (in-depth) wastewater treatment causes that sewage sludge is characterized by a lower utility to thermal treatment.

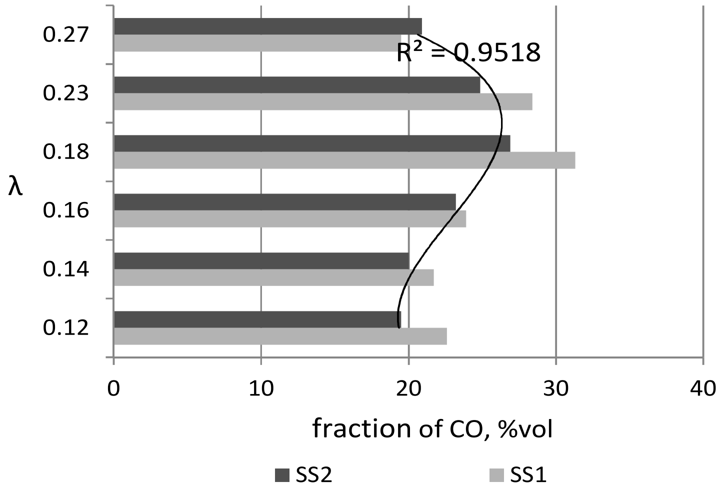

Fig. 2. Volumetric fraction of CO for different values of air excess ratio

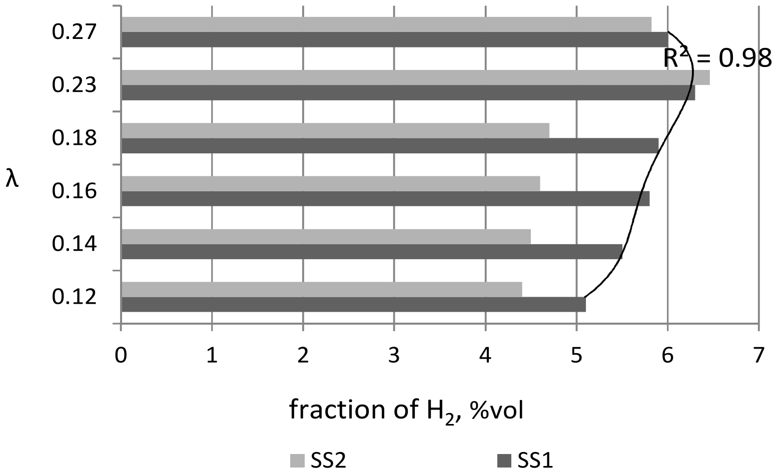

Fig.3. Volumetric fraction of H_2 for different values of air excess ratio

Figure 4 shows the evolution of the lower heating value of the both analysed sewage sludge feedstock gasification gas.

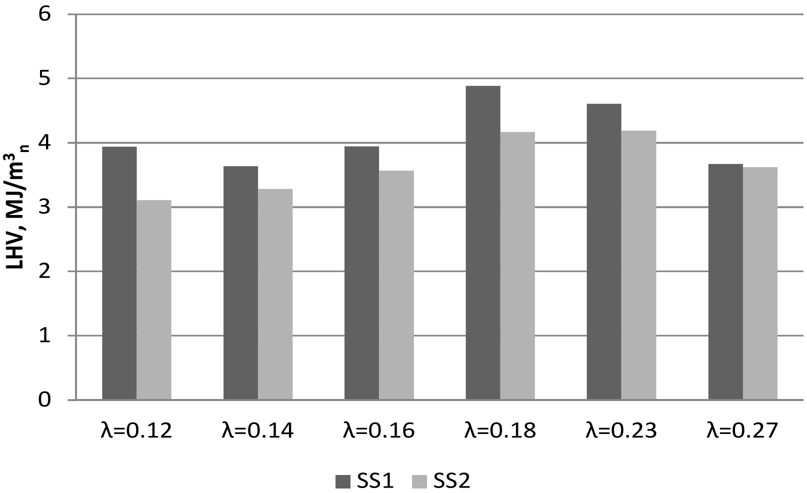

Fig. 4. Evolution of the LHV of the gasification gas with varying air excess ratios for both analysed sludge

Analysing the data presented in Figure 4 it can be concluded that taking into consideration the lower heating value LHV of the gasification gas there is the optimum value of the air excess ratio equal to 0.18 in which the LHV takes its maximum value. It is true irrespective of the sewage sludge type. Above that optimal value, the thermo-chemical process could be shifted from gasification to combustion.

4. CONCLUSIONS

The main conclusions from the study are as follows:

1. Original experimental results on sewage sludge gasification are presented in this study. Air gasification of sewage sludge was investigated, and a fixed bed reactor was used. Experiments have not been previously conducted on Polish sewage sludge used as a feedstock in the gasification process. The results obtained showed that it is technically feasible gasification of sewage sludge in fixed bed gasification installation.
2. Sewage sludge has a high economic potential due to its extremely low price.
3. The operating conditions (amount of the gasification agent) of the sewage sludge gasification process greatly influence the syngas composition distribution.
4. Higher values of the main components (especially C and H) in the sewage sludge plant affect on the increase of the LHV of gasification gas. 5. Throughout the range of analysed air excess ratio (λ=0.12-0.27) volumetric fraction of main combustible components of gasification gas (CO and H_2) are higher in the case of the sewage sludge 1 (positive aspect) in comparison to SS2.
5. Taking into consideration the lower heating value LHV of the gasification gas there is the optimum value of the air excess ratio equal to 0.18 in which the LHV takes its maximum value.

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ZGAZOWANIE JAKO KOMPLEKSOWA METODA ZAGOSPODAROWANIA OSADÓW ŚCIEKOWYCH

Streszczenie

W wielu krajach obserwuje się rosnące zainteresowanie termicznym przekształcaniem (spalanie, współspalanie, zgazowanie i piroliza) tradycyjnej (typu "agro" i leśną) biomasy a także biomasy odpadowej. W ostatnim dwudziestoleciu zaszły duże zmiany w sposobie zagospodarowania osadów ściekowych. Na przykład w kracjach Unii Europejskiej składowanie osadów, które charakteryzują się ciepłem spalania równym przynajmniej 6 MJ/kg jest (lub będzie w ciągu najbliższych trzech lat) zakazane. W związku z tym istnieje duża potrzeba rozwoju termicznych metod utylizacji osadów ściekowych. Zgazowanie posiada w stosunku do tradycyjnego spalania wiele zalet. Praca zawiera rezultaty badań procesu zgazowania osadów ściekowych w reaktorze ze złożem stałym. Przeanalizowano wpływ parametrów procesowych na proces zgazowania osadów.

CONTENTS

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