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VARIA

ECOLOGICAL CHEMISTRY AND ENGINEERING A

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Mariusz DUDZIAK[1]

DEVELOPMENT AND VALIDATION OF A GC-MS METHOD FOR THE SIMULTANEOUS QUANTITATION OF ZEARALENONE AND ITS METABOLITES IN WATER

OPRACOWANIE I WALIDACJA METODY GC-MS DO RÓWNOCZESNEGO OZNACZANIA ZEARALENONU I JEGO METABOLITÓW W WODZIE

Abstract: The method of simultaneous determination of zearalenone and its metabolites in water with use of GC-MS chromatography was evaluated. The solid phase extraction SPE was used for analytes separation from water and as an enrichment method. The influence of compounds concentration and water sample volume on analytes recovery was investigated. The chromatographic analysis was preceded by conversion of compounds to trimethylsilyl ethers derivatives. The developed SPE-derivatization-GC/MS method allow to separate quaternary mixture of mycoestrogens with the quantitative analysis in water, when their concentration is greater than 0.2–0.5 ng/dm^3. The repeatability of the results was from 1 to 8 %. The recovery of compounds exceeded 60 % for samples contains from 50 to 200 ng/dm^3 of mycotoxins. The concentration of analytes and volume of the sample (100–500 cm^3) did not have an influence on the extraction output. The developed method can be applied to analyze water samples containing mycoestrogens at the level of ng/dm^3.

Keywords: zearalenone, metabolites, mycoestrogens, SPE, GC-MS, determination, water analysis

The group of biologically active organic micropollutants effected aqueous environment has recently been widened with mycotoxins, which, despite of toxic properties, demonstrate also an estrogenic activity [1]. This is the reason they are also named mycoestrogens. In literature, the most commonly described toxin is zearalenone (ZON) (toxin F-2), which is produced by fungi of kind *Fusarium* living on grains, especially on corn and products, which are produced from it [2]. The increase of feminizing effect of ZON is observed among animals, when the mycotoxin concentration in fodder is greater than 0.06 mg/kg of animal body mass/day [3]. Analogically, the consumption of the toxin with food and water may also have an influence on humans.

The modified form of zearalenone produced via fermentation is zearalanone (ZAN). The compound is used in USA as an anabolic, which stimulates the mass growth of

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cattle [1]. Zearalanone can also be applied as a regulator for plant growth [4]. However, in Europe, including Poland, ZAN is totally forbidden to be used. However, *in vivo* studies on animals and humans have revealed the possibility of direct transformation of natural zearalenone into zearalanone [5–6]. In analyzed urine samples metabolites of ZON were identified, including α-zearalenol (α-Zol) and β-zearalenol (β-Zol) (primary metabolites of ZON) and α-zearalanol (α-Zal) (zeranol) and β-zearalanol (α-Zal) (taleranol) (secondary metabolites of ZON) [6]. Compounds from the group of secondary ZON metabolites can be transformed into ZAN. The transformation pathways of zearalenone are presented in Fig. 1.

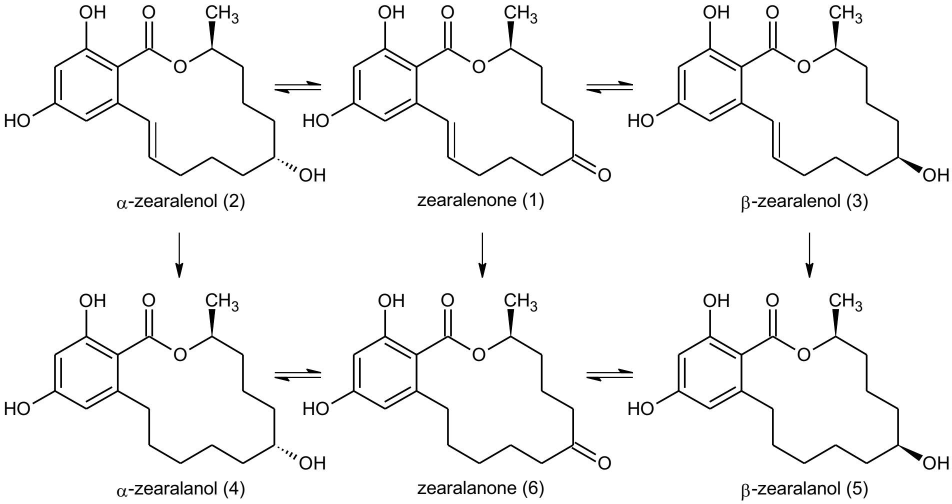

Fig. 1. Structures of zearalenone and its metabolites [1]

The presence of zearalenone, zearalanone and their metabolites is restrictively checked in food and fodder samples [3]. However, the data about the appearance of those compounds in aqueous environment is very limited. There are several papers which discuss the presence of ZON and ZAN in surface water [1–2, 7–8], as well as in influent and effluent streams of municipal wastewater treatment plants [1–2, 8–9]. The concentration of those compounds in aqueous environment was estimated at the level from 0 to 60 ng/dm^3 [1–2, 7–9]. In Poland, according to the study of Gromadzka et al [2] the concentration of zearalenon in selected water samples did not exceed 43.7 ng/dm^3.

The qualitative and quantitative analysis of mycoestrogens in water environment is based on chromatographic techniques, among which liquid chromatography tandem mass spectrometry (LC-MS-MS) is the most popular [1, 7–9]. The aim of the study was the development of a procedure of parallel indication of zearalenone and its metabolites (α-Zol, β-Zol and ZAN) in water by means of solid phase extraction (SPE) and gas chromatography-mass spectrometry (GC-MS). The chromatographic analysis was preceded by the conversion of compounds into trimethylsilyl ethers derivatives.

Materials and methods

Apparatus, materials, reagents

Zearalenone (ZON), zearalanone (ZAN), α-zearalenol (α-Zol), β-zearalenol (β-Zol), mirex (IS), *N*,*O*-bis(trimethylsilyl)trifloroacetamide (BSTFA), trimethylchlorosilane (TMCS) and dithioerythritol (DTE) were purchased from Sigma-Aldrich (Poland). Methanol and acetonitrile, both of reagent grade, were supplied by POCH S.A. (Poland). SPE Supelclean^{TM} ENVI-18 Supelco tubes (6 cm^3, 1 g of the phase) and a Varian SPE chamber were used during the solid phase extraction.

Their base and working solutions of mycoestrogens had concentrations of 1 mg/cm^3 and 10 ng/mm^3 (μL), respectively, and they were added to deionized water and tap water in selected amounts.

Solid Phase Extraction SPE

The separation of mycoestrogens from a water sample (of volume 100–500 cm^3) was carried out in SPE C_{18} extraction tubes (Supelclean^{TM} ENVI-18), which were firstly washed with (5 cm^3) of acetonitrile (ACN) and conditioned with water (5 cm^3). The extract was eluted with 4 cm^3 of ACN. The removal of solvent from the eluate was made by nitrogen stripping and the conversion of analytes was performed.

Silylation reaction

The silylation reaction of mycoestrogens was made with the use of ternary mixture of BSTFA/TMCS/DTE composed in ratio of 1000:10:2 (v/v/w). The reaction took 5 min under the temperature of 90 °C. Conditions of the reaction were selected according to Kinani et al studies [10].

GC-MS analysis

The analysis was made with the use of gas chromatograph with mass detector GC-MS of ion trap type (model Saturn 2100 T by Varian). The device was equipped with VF-5ms column of dimensions 30 m × 0.25 mm × 0.25 μm (the film thickness). The detailed parameters of the chromatographic analysis are represented in Table 1.

Table 1

GC-MS conditions for mycoestrogens analysis

Instrument	Varian Saturn 2100T GC-MS
Parameters for GC	
Carrier gas	Helium (purity > 99.999 %)
Carrier gas flow rate	1.4 cm^3 min^{-1}
Injector temperature	300 °C

Table 1 contd.

Instrument	Varian Saturn 2100T GC-MS
Injected volume Injection mode Oven program	3 mm^3 splitless Initial temperature of 140 °C, hold 0.5 min, 20 °C min^{-1} to 280 °C, hold 5.5 min
Parameters for MS	
Ionization	Electron Ionization EI, 70 eV
Ion trap temperature Ion source temperature	200 °C

Results and discussion

The analytical method was based on the selected ions monitoring (SIM) presented in Table 2. More than two ions were selected for registration of particular compounds in order to increase the sensitivity of identification. The chromatogram of the mixture of standards of mycoestrogenes derivatives is displayed in Fig. 2.

Table 2

Selected ions for derivatives [m/z] in SIM and retention time

Compound	Ions for derivatives [m/z]	Retention time [min] (t_R ± *SD**, n = 12)	*C.V.*** (%, n = 12)
Mirex (IS)	272, 235, 187, 119	9.2506 ± 0.023	0.246
ZAN	449, 432, 406, 308	10.462 ± 0.026	0.245
ZON	444, 430, 306, 150	10.903 ± 0.027	0.249
α-Zol	446, 432, 414, 306	10.964 ± 0.178	0.620
β-Zol	446, 432, 414, 306	11.173 ± 0.030	0.265

* Standard deviation; ** Coefficient of variation.

Conditions applied for the chromatographic analysis allowed to separate all silyl derivatives of mycoestrogens present in the mixture. Chromatographic peaks corresponding to particular components of the mixture had different times of retention (Table 2, Fig. 2).

The crucial parameter of the qualitative analysis is the retention of peak derived from the sample and from the standard, that is retention time. The very precise identification method is the comparison of retention times coming from sample analysis with those obtained for standards. The variation of retention times, which were obtained during many chromatograph analyses, was insignificant. That could be confirmed by low values of standard deviation of this parameter for all investigated compounds as well as by the high precision of measurements certificated by values of variability coefficient (*C.V.*), which varied from 0.245 to 0.620 % (Table 2).

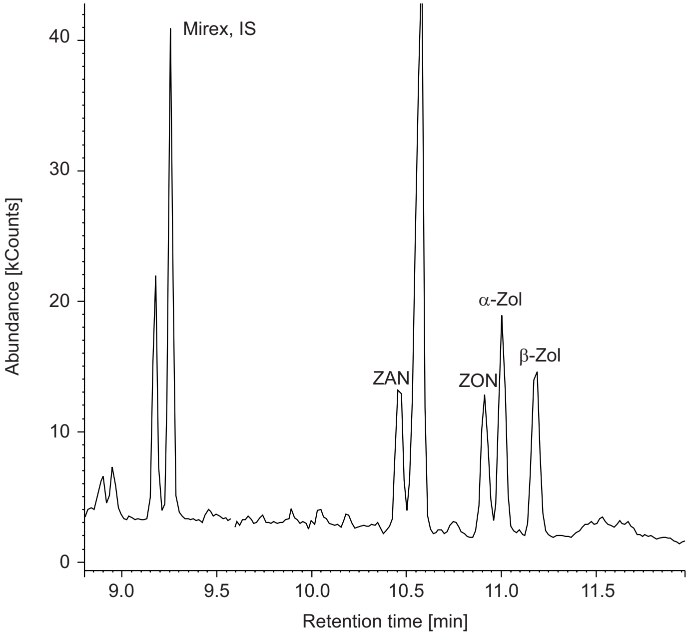

Fig. 2. Chromatogram GC-MS derivatives of mycoestrogens after SPE (concentration of the compounds 50 ng/dm^3, volume of the sample 500 cm^3)

In the quantitative analysis of mycoestrogens content in water the repeatability of results is very important. This analysis was made using peaks areas of mass ions (m/z) of mycoestrogens derivatives (Table 2), which were corrected with areas obtained for the constant content of the internal standard (IS-mirex). The precision of the response of the mass detector was calculated for two different concentrations of mycoestrogens derivatives introduced onto the chromatographic column (Table 3). The *limit of detection* (*LOD*) as well as linear response of the mass detector were also determined for mycoestrogens concentrations in the range from 1 ng/3 mm^3 to 15 ng/3 mm^3.

Table 3

The limit of detection, precizion and linearity of mass detector response

Compound	Limit of detection (*LOD*)* [ng/μg]	Concentration		Correlation coefficient (R^2)**
		3 ng/3 mm^3	12 ng/3 mm^3	
		C.V. [%]		
ZAN	0.3	10	2.0	0.980
ZON	0.1	10	0.3	0.982
α-Zol	0.1	5.5	1.9	0.997
β-Zol	0.1	0.5	0.1	0.998

* Defined as the mass of analyte injected producing a peak with a signal-to-noise ratio (*S*/*N*) of 3; ** Linear ranges of the calibrations curve: 1 ng/3 mm^3 to 15 ng/3 mm^3.

The repeatability (expressed as *C.V.*) of most of GC-MS analysis results varied from 0.1 to 5.5 %, what confirmed the good precision of the measurements. However, during the analysis of ZON and ZAN the obtained repeatability was equal to 10 % for the lower concentration of these compounds, what is shown in Table 3. Linear correlation coefficients (R^2) of calibration curves exceeded 98 % for all investigated compounds. The limit of detection of the method was estimated at the level of 0.1 ng/μg except from ZAN, for which it was equal to 0.3 ng/μg.

Values of parameters characterizing the quantitative analysis using the SPE-derivatization-GC/MS procedure are presented in Table 4.

Table 4

Efficiency of mycoestrogens extraction and accuracy of the SPE-derivatization-GC/MS method

Compound	Sample	Concentrations [ng/dm^3]						Limit of quantification LOQ** [ng/dm^3]
		200		100		50		
		Recovery [%]*	*RSD** [%]*	Recovery [%]*	*RSD** [%]*	Recovery [%]*	*RSD** [%]*	
ZAN	Deionized water	61	8	63	4	62	1	0.5
	Tap water	69	1	68	1	75	3	0.5
ZON	Deionized water	69	4	71	4	77	4	0.5
	Tap water	62	7	76	8	80	8	0.3
α-Zol	Deionized water	80	3	60	2	83	5	0.3
	Tap water	60	3	63	1	72	1	0.2
β-Zol	Deionized water	92	1	64	1	68	2	0.3
	Tap water	62	1	65	1	64	1	0.3

* Relative standard deviation; ** *S/N* > 10, The recoveries and precision were examined by replicates analysis (n = 4, volume of the sample 500 cm^3).

The efficiency of extraction and measurements precision were determined by quadruple repetition of the whole procedure in which two types of water (deionized and tap water) were used. The concentration of mycoestrogens varied from 50 to 200 ng/dm^3. Obtained results allowed to determine the efficiency of the extraction of mycoestrogens. Values of this parameter were in the range from more than 60 % to more than 90 % depending on the compound extracted. The precision of the method can be noted as good. The influence of the impurities content in water on the extraction efficiency was negligible. Similarly, the volume of the water sample from which compounds were extracted did not effected the extraction process, what is presented in Table 5. The repeatability (expressed as *relative standard deviation*, *RSD*) of the results obtained during the developed method was satisfying. The calculated *RSD* values were in the range from 1 to 8 %. The lower limit of analysis of mycotoxins concentration in water varied from 0.2 to 0.5 ng/dm^3 depending on the investigated matrix.

Table 5

The effect of sample volume on the recovery of mycoestrogens

Compound	Concentration [ng/dm^3]	Sample volume [cm^3]		
		500	250	100
		Recovery (*RSD*) [%]*		
ZAN	200	61 (*8*)	63 (*4*)	62 (*1*)
ZON		69 (*4*)	68 (*3*)	64 (*8*)
α-Zol		80 (*3*)	80 (*2*)	93 (*5*)
β-Zol		92 (*1*)	94 (*1*)	98 (*2*)

* The recoveries and precision were examined by replicates analysis (n = 4).

Conclusions

1. The applied chromatographic conditions are suitable to separate compounds in quaternary mycoestrogenes mixture and to run the effective qualitative and quantitative analysis. The limit of detection of the GC-MS method was estimated at the level of 0.1 ng/mm^3 except from zearalenone for which it was equal to 0.3 ng/mm^3.

2. The developed SPE-derivatization-GC/MS method allow to determine the concentration of mycoestrogens in water at the level from 0.2 to 0.5 ng/dm^3, depending on the applied matrix (deionized and tap water). The carried out analysis of water samples containing from 50 to 200 ng/dm^3 of mycoestrogens characterized with satisfied value of results repeatability equal from 1 to 8 %. The recovery of mycoestrogens exceeded 60 % and the compounds concentration and volume of the sample did not have an influence on the value of investigated parameter.

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OPRACOWANIE I WALIDACJA METODY GC-MS DO RÓWNOCZESNEGO OZNACZANIA ZEARALENONU I JEGO METABOLITÓW W WODZIE

Instytut Inżynierii Wody i Ścieków
Politechnika Śląska

Abstrakt: Ocenie poddano metodę równoczesnego oznaczania zearalenonu i jego metabolitów w wodzie z użyciem chromatografii GC-MS. Ekstrakcja do fazy stałej SPE wykorzystana została jako metoda wydzielania i wzbogacania analitów z wody. Badano wpływ stężenia i objętości próbki wody na odzysk związków. Z kolei przed chromatograficznym oznaczeniem mykoestrogeny przeprowadzono w etery trimetylosiliowe. Metoda SPE-*derywatyzacja*-GC/MS umożliwia rozdział czteroskładnikowej mieszaniny mykoestrogenów i ich ilościowe oznaczenie w wodzie na poziomie stężeń 0,2–0,5 ng/dm^3. Powtarzalność oznaczeń była w zakresie 1–8 %. Wyznaczony odzysk związków dla stężenia w zakresie 50–200 ng/dm^3 przekraczał 60 %. Nie obserwowano znacznego wpływu stężenia analitów jak i objętości próbki wody (100–500 cm^3) na wydajność ekstrakcji. Przedstawioną metodykę można więc zastosować do kontroli analitycznej obecności mykoestrogenów w środowisku wodnym na poziome stężeń ng/dm^3.

Słowa kluczowe: zearalenon, metabolity, mykoestrogeny, SPE, GC-MS, oznaczanie, analiza wody

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Jolanta BOHDZIEWICZ[1], Mariusz KUGLARZ[2] and Bożena MROWIEC[2]

ASSESSMENT OF KITCHEN BIOWASTE AND SEWAGE SLUDGE SUSCEPTIBILITY TO METHANOGENIC CO-DIGESTION IN BATCH TESTS

OCENA PODATNOŚCI BIOODPADÓW KUCHENNYCH I OSADÓW ŚCIEKOWYCH DO KOFERMENTACJI PROWADZONEJ W WARUNKACH STATYCZNYCH

Abstract: The article presents the results of a study meant to establish the most favourable proportion of source-sorted kitchen biowaste undergoing mesophilic methane fermentation along with waste activated sludge (WAS). The optimum combination of substrates was supposed to ensure the stability of the process in a batch mode. An attempt was made to replace a part of sludge with waste foam floating periodically on the surface of the aeration tank. The assessment of the various combinations of substrates was based on the following criteria: total biogas production and biogas yield, degree of organic matter decomposition and indices of process stability (VFA, VFA/TA). It was established that the co-digestion of kitchen biowaste with sewage sludge influenced the quantity and quality of the biogas produced as well as organic matter biodegradation in a positive way. The optimum kitchen biowaste proportion in digestion mixtures amounted to 60 % TS, which is tantamount to about 25 % if expressed as wet weight proportion. Under those conditions, the total biogas production increased more than three times and the process exhibited the greatest biogas yields. Moreover, the addition of kitchen biowaste did not deteriorate the stability of the process. In case of optimum kitchen biowaste and sewage sludge co-digestion run, the replacement of a part of sewage sludge by waste foam did not impact the effectiveness as well as the stability of the process. However, the addition of waste foam had a positive impact on the biogas production rate

Keywords: methane fermentation, co-digestion, biogas, sewage sludge, sewage sludge foaming, kitchen biowaste

The main by-product of municipal and industrial wastewater treatment is sewage sludge, which amount is steadily increasing. It is estimated that the amount of sewage sludge generated in municipal wastewater treatment plants will amount to 700 000 Mg

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in 2015, which is 23 % more than the equivalent amount in 2008 [1]. One of the most popular methods used for wastewater treatment is activated sludge method, which allows to remove both organic and biogenic substances. Excess biomass, ie *waste activated sludge* (WAS), generated as a by-product of wastewaters treatment, is periodically removed from bioreactor's chamber. The method was proved to generate foam layer on the surface of the bioreactors. It hinders wastewaters aeration and has a negative impact on the effectiveness of their treatment [2–3]. The main factors behind the negative process of sewage sludge foaming are: excessive growth of zoogloea bacteria, activated sludge swelling caused by excessive amounts of polysaccharides as well as disturbances of the treatment process. Most methods meant to counteract sewage sludge foaming consist in a permanent monitoring of activated sludge conditions as well as adding chemical substances which suppress foaming. The chemicals, however, very often work only for a limited period of time. In practice, the foam is frequently removed mechanically from the bioreactor's chambers and requires to be utilized [2–4].

Similarly, excessive sewage sludge, needs to be treated. It is usually stabilized in anaerobic conditions in the process of methane fermentation. Despite high investments costs and seasonally occurring technological problems, the anaerobic digestion for biogas production is considered to be an attractive method of wastes utilization. The main advantage of the process is the possibility to generate renewable energy in the form of biogas, which in turn allows to meet energy demands of the wastewater treatment plants, especially in winter. Co-digestion of wastewaters treatment by-products with substrates containing a higher easily-biodegradable organic matter seems to an interesting alternative allowing their utilization as well as enhancement of the biogas production.

The literature contains multiple accounts of successful treatment of a primary or/and surplus activated sludge combined with: source-sorted or mechanically separated *organic fraction of municipal solid waste* (OFMSW) [5–10], livestock wastes [11–12] as well as industrial organic wastes, predominantly from food industry [13–14]. However, cases concerning integrated co-digestion of wastewater treatment by-products in the form of waste activated sludge (WAS) and waste foam together with source-sorted kitchen biowaste are very scarce. Besides, increasing popularity of the municipal solid waste collection at the place of origin as well as growing environmental awareness of the society are important factors behind the fact that source-sorted kitchen biowaste – exhibiting a high content of easily-biodegradable organic matter – is considered as a valuable substrate in biogas plants. Poland generates about 10 mln Mg of solid municipal wastes, whose one of the main fraction is just kitchen biowaste [1].

The article presents the results of a study meant to establish the most favourable proportion of kitchen biowaste undergoing anaerobic digestion for biogas production along with excess activated waste (WAS). In case of the optimum combination of kitchen biowaste and sewage sludge, an attempt was made to replace a part of the activated sewage sludge with foam floating seasonally on the surface of the wastewater treatment chambers. The assessment of various combinations of substrates was based on the following criteria: total biogas production and biogas yield, degrees of organic matter decomposition and indices of process stability.

Materials and methods

Kitchen biowaste referred to as *kitchen biowaste* (KB) below, thickened waste activated sludge (WAS) referred to as sewage sludge below and foam floating on the surface of the nitrification chamber of the bioreactor treating municipal wastewater referred to as *waste foam* (WF) below were used as a digestion feedstock. The kitchen biowaste was collected selectively from households as well as institutions (restaurants, school canteens etc) located in the vicinity of the wastewater treatment plant which provided the sewage sludge. A domestic food blender was used to homogenize the various components of biowaste into granules smaller than 2 mm in diameter. Then, it was stored in a refrigerator at 5 °C. The sewage sludge was taken after thickening from a full-scale municipal treatment plant based on *Enhanced Biological Nutrients Removal* (EBNR), operated on the activated sludge method. The digested sludge taken from the same wastewater treatment plant which provided the thickened sludge was used as an inoculum. It was a full-scale continuous process operated in mesophilic conditions. Characteristics of the substrates used is presented in Table 1.

Table 1

Characteristics of the digestion feedstock

Indicator	Kitchen biowaste (KB)	Waste activated sludge (WAS)	Waste foam (WF)	Inoculum
pH [-]	4.65 (0.15)	6.44 (0.11)	6.19 (0.10)	7.76 (0.09)
TS [%]	23.44 (0.98)	5.20 (0.21)	5.82 (0.15)	3.09 (0.17)
VS [%]	21.64 (0.82)	3.57 (0.16)	4.05 (0.12)	1.73 (0.11)
$C_{org.}$ [% d.m.]	55.18 (0.32)	38.44 (0.47)	33.22 (0.99)	31.02 (0.89)
$N_{tot.}$ [% d.m.]	2.94 (0.02)	4.98 (0.06)	4.23 (0.04)	3.28 (0.04)
NH_4^+ [mg/dm^3]	—	18.3 (1.5)	20.5 (2.5)	1 850 (124)
COD [mgO$_2$/dm^3]	—	292 (70)	158 (62)	1 620 (212)

In the bracket standard deviation values.

The process was carried out in a set of digesters with a working volume of 3 dm^3. Digesters were maintained at a constant temperature of 36°C (±0.5) for 35 days. Their contents were mixed periodically – 5 minutes in every 3 hours. The experiment was divided into two parts. In the first one, digestion process was carried out for a sewage sludge as well as mixtures of kitchen biowaste and sewage sludge – based on the *following total solids* (TS) ratio: 20:80; 40:60; 50:50; 60:40 and 70:30. During the second part of the experiment, for the most favourable co-digestion mixture of substrates (kitchen biowaste + sewage sludge), 10 % TS and 20 % TS of the sludge undergoing digestion was replaced by waste foam. The digestion feedstock was mixed with the inoculum at the weight ratio of 1:2, which was established as an optimum, based on preliminary tests. The criterion for assessing the optimum substrates-to-inoculum ratio was total biogas production. The biogas production from the inoculum itself was subtracted from biogas production of all digested samples. All samples were prepared in duplicates. The characteristics of the digestion input is presented in Table 2.

Table 2

Characteristics of the digestion input

Indicator	Digestion mixtures composition [% TS]							
	KB:WAS						KB:WAS(WF)	
	0:100	20:80	40:60	50:50	60:40	70:30	60:40(10)	60:40(20)
pH [-]	7.25	7.21	7.19	7.16	7.01	6.81	7.08	7.12
TS [%]	3.77	4.22	4.67	4.88	5.33	5.83	5.54	5,56
VS [%]	2.36	2.77	3.23	3.48	3.93	4.43	3.94	3.96
C:N [-]	7.7	8.9	10.3	10.9	11.7	12.6	11.8	11.9

The scope of the analyses conducted encompassed: pH value measurement as well as determinations of total solids (TS), volatile solids (VS), chemical oxygen demand (COD), total volatile fatty acids (VFA), total alkalinity (TA), ammonia-nitrogen (NH_4^+) as well as total organic carbon (C) and total Kjeldahl nitrogen (TKN). The biogas produced was stored in a plexus tube containing 5 % NaOH solution. The recorded amounts of biogas were adjusted to the volume at standard temperature (0°C) and pressure (1 atm). The biogas was periodically analysed for CH_4 content (% vol.) [15].

Results and discussion

As the assays were undergoing digestion, the daily biogas production was recorded – Fig. 1. As expected, co-digestion mixtures produced more biogas than sewage sludge itself. The highest biogas production, ie 13.19 dm^3 was recorded for the digestion mixture containing 60 % TS from kitchen biowaste, which is almost three times more than in case of sample containing exclusively sewage sludge (3.58 dm^3). It was established that further increase in kitchen biowaste proportion in digestion trials led to the significant decrease of biogas production which might have been caused by VFAs accumulation. In the most favourable combination of digested substrates, ie 60 % TS of kitchen biowaste and 40 % TS of sewage sludge, a part of sewage sludge treated was replaced with periodic foam floating on the surface of the wastewater treatment chambers. Similar amounts of biogas were generated irrespective of the amount of waste foam added. Adding 10 % TS and 20 % TS of waste foam led to the biogas production of 13.30 m^3/m^3 d and 13.16 m^3/m^3 d, respectively. Both above – mentioned amounts of biogas were comparable with the amount of biogas generated by trial without waste foam addition, ie 13.19 m^3/m^3 d. However, foam addition had a positive impact on the biogas production rate. Digestion mixtures containing waste foam reached biogas production peak already in the fourth day of the experiment, ie 1.63 $m^3/m^3 \cdot d$ (10 % of foam) and 1.53 $m^3/m^3 \cdot d$ (20 % of foam). Whilst the biogas production peak for digestion trials without foam was reached on the 12th day of the process. Dependency of the composition of digestion mixtures on the biogas production was illustrated in Fig. 1 and 2.

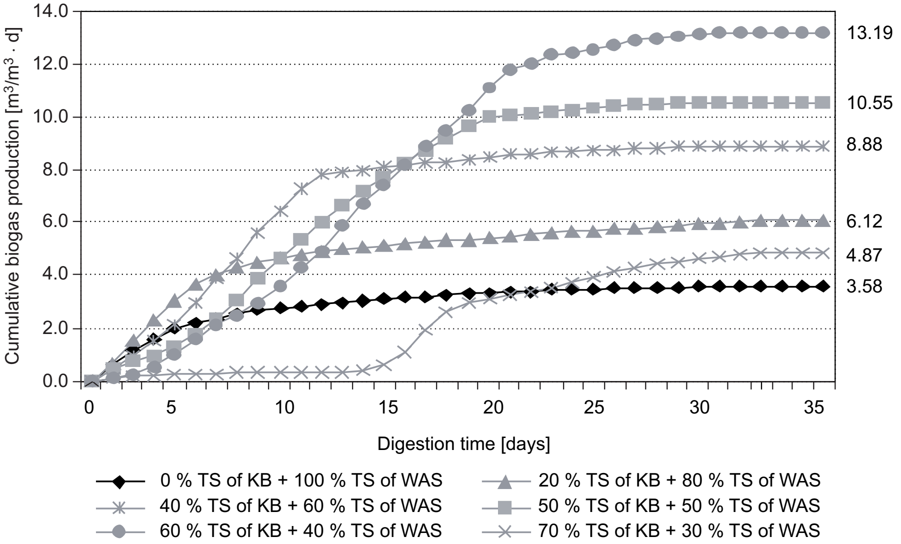

Fig. 1. Influence of kitchen biowaste addition on the amount of biogas produced

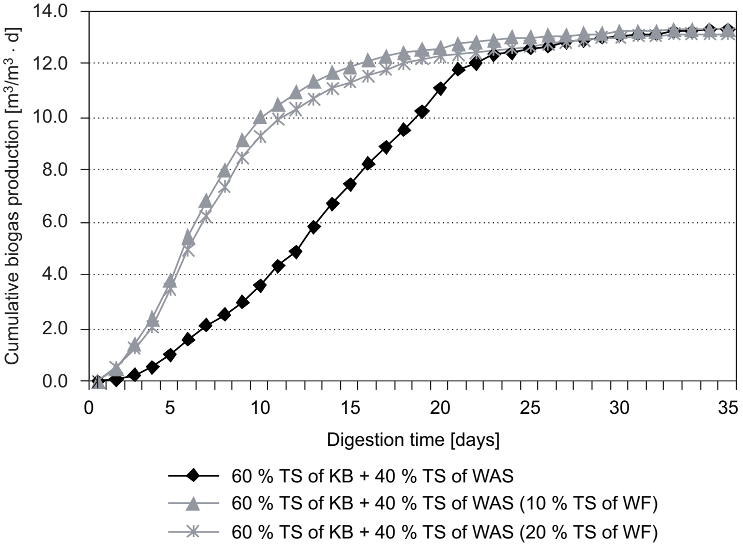

Fig. 2. Influence of waste foam addition on the amount of biogas produced.

On the one hand, the amount of biogas generated depends primarily on the amount of biodegraded organic matter. On the other hand, the composition of the biogas produced is conditioned by the feedstock chemical structure, ie the content of proteins, fats and carbohydrates and their derivatives. Accordingly, the study was not focused exclusively on the amount of biogas generated but also on its methane content. The average methane content measured in a stable state of the process for the run containing sewage sludge without kitchen biowaste amounted to 56 %. By contrast, the amount of methane in the co-digested runs fluctuated between 67 and 72 %. The addition of waste foam to the digestion feedstock did not have any influence on the CH_4 content. A relative increase of CH_4 concentration in kitchen biowaste-loaded trials may be caused by the introduction of a substrate rich in proteins and fats [16–17].

During multi-step process of anaerobic digestion macromolecular substances are converted into simpler compounds. One of the most common parameters to measure the bioconversion is the degree of volatile matter (VS) reduction. Compared with the run containing sewage sludge exclusively (42.8 %), all co-digested samples exhibited a higher degree of VS reduction (45.8–63.6 %) – Table 3. Accordingly, it allows to conclude that more varied composition of the digested mixtures positively impacts the efficiency of bioconversion, mainly by improving the C/N ratio. In our case, the C/N ratio of the analysed sludge amounted to 7.7 (Table 1). The optimal value of the ratio reported in the literature varies widely. It is frequently mentioned to fluctuate between 10:1 and 25:1 [18]. The addition of biowaste as a co-substrate allowed to increase the C/N ratio to the level of 8.9–12.6. Whilst introducing the waste foam in mixtures undergoing anaerobic digestion did not impact both C/N of the digestion feedstock and degrees VS reduction (Tables 2 and 3).

Table 3

Organic matter reduction

Indicator	Digested mixtures [% TS]							
	KB:WAS						KB:WAS(WF)	
	0:100	20:80	40:60	50:50	60:40	70:30	60:40(10)	60:40(20)
TS [%]	2.59	2.80	3.02	3.04	2.82	3.27	3.23	3.22
VS [%]	1.35	1.50	1.67	1.63	1.43	1.69	1.51	1.55
TS reduction [%]	31.3	33.6	35.3	37.7	47.1	43.9	41.7	42.1
VS reduction [%]	42.8	45.8	48.3	53.2	63.6	61.9	61.7	60.9

In order to assess the influence of co-substrates addition, biomethanization results were recalculated and expressed in terms of biogas yield – Fig. 3.

The highest value of the parameter in terms of VS added (0.336 m^3/kg VS) as well as degraded (0.527 m^3/kg VS) was achieved for sample containing 60 % of TS from kitchen biowaste. The above values are about 121 % and 49 % higher than those recorded for sewage sludge without kitchen biowaste addition respectively. Similarly to the biogas production and degrees of organic matter reduction, the adition of waste foam did not change significantly values of biogas yields.

Finally, the influence of the kitchen biowaste and foam addition on the stability of the methane fermentation was taken into consideration. Due to excessive production of VFAs, uncontrolled introducing of substrates rich in easily-biodegradable organic matter in anaerobic condition may cause a significant decrease in pH value beyond the range ensuring an appropriate growth and development of methane generating bacteria [18–19]. Optimum concentration of VFA in a bioreactor amounts to about 500 mg CH_3COOH/dm^3, while, the critical value, which indicates some instability in the

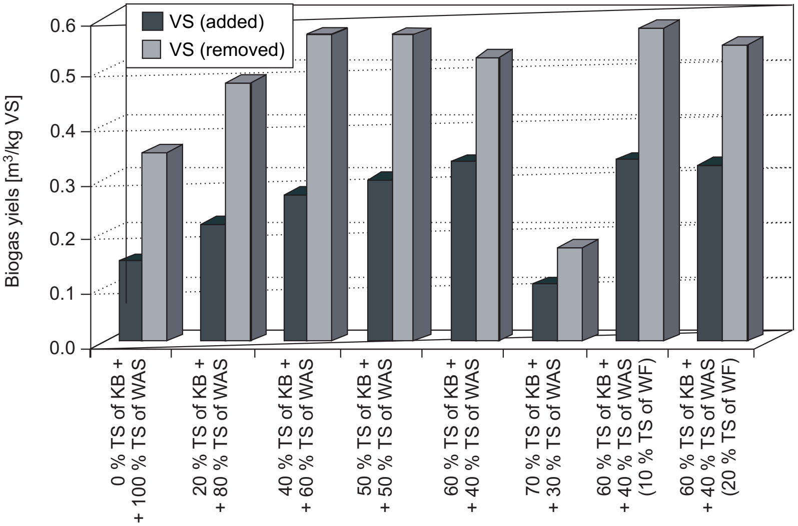

Fig. 3. Efficiency of the methane fermentation, expressed as biogas yields

process oscillates at the level of 2000 mg CH_3COOH/dm^3 [19]. The latter value was only exceeded (2600 mg CH_3COOH/dm^3) in case of a digestion run including the highest content of kitchen biowaste, ie 70 % TS. However, the accumulation, which occurred was not related to a significant decrease in pH value (7.6) – Table 4. The fact is not very unexpected, mainly because of high content of proteins in kitchen biowaste. Due to mineralization of proteins in anaerobic conditions, the ammonia concentration increases, which in turn counteracts to a some extend the decrease of pH value in spite of significant VFAs accumulation.

Table 4

Factors affecting the stability of the methane fermentation

Indicator	Digested mixtures [% TS]							
	KB:WAS						KB:WAS(WF)	
	0:100	20:80	40:60	50:50	60:40	70:30	60:40(10)	60:40(20)
pH [-]	7.8	7.9	7.8	7.9	7.9	7.6	7.9	7.8
NH_4^+ [mg/dm^3]	1370	1390	1410	1490	1870	2160	1765	1864
VFA [mg CH_3COOH/dm^3]	690	890	1030	1060	890	2600	790	815
Total alkalinity [mg $CaCO_3/dm^3$]	6182	6846	6059	6438	9865	4333	9655	9456
VFA/TA [-]	0.11	0.13	0.17	0.16	0.09	0.60	0.08	0.09

Taking into account the fact that significant changes in pH value caused by VFAs accumulation usually occurs after the collapse of the process and when the acid phase dominates in the bioreactor; a more reliable stability indicator seems to be a volatile fatty acids to total alkalinity, ie VFA/TA ratio. If the latter exceeds the threshold of 0.3–0.4, it is believed to have an inhibitive effect on the process stability and may even lead to the collapse of the biogas production [19–20].

On the basis of the – above mentioned ratio, we can figure out that the process exhibited stable conditions for digestion mixtures containing the kitchen biowaste in the range of 20–60 % TS. In case of run containing the largest kitchen biowaste proportion (70 % TS), the value of the parameter (VFA/TA = 0.60) exceeded significantly the critical value. The addition of waste foam to the optimum co-digestion mixture comprising of sewage sludge and kitchen biowaste did not deteriorate stability of the process (Table 4).

Conclusions

1. The addition of kitchen biowaste to the mesophilic digestion of sewage sludge had a positive effect on the quantity and quality of the biogas produced as well as organic matter biodegradation. The optimum kitchen biowaste proportion in digested mixtures ensuring stable conditions of the process amounted to 60 % TS, which is tantamount to 25 % if expressed as wet weight proportion. Under those conditions, the total biogas production increased more than three times and the process exhibited the greatest biogas yields.

2. The addition of a co-substrate in the form of waste foam to the optimum co-digestion mixture comprising of 60 % TS from kitchen biowaste and 40 % TS from sewage sludge did not impact the effectiveness as well as the stability of the process. Whilst the waste foam addition had a positive impact on the biogas production rate.

3. Biogas plants allows both to produce energy and utilize wastes impacting the natural environment in a negative way. Taking into account the fact that the capacity of biogas facilities at wastewater treatment plants are frequently exceeding the amount of sewage sludge treated, the introduction of additional co-substrates, eg in the form of kitchen biowaste would increase the energy balance of the facility.

4. The co-digestion of kitchen biowaste and sewage sludge may be a promising solution of their utilization. According to the European Council Directive on the landfill of waste (1999/31/EC), the member states are obliged to reduce gradually the amount of biodegradable waste deposited at municipal dump sites [21].

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OCENA PODATNOŚCI BIOODPADÓW KUCHENNYCH I OSADÓW ŚCIEKOWYCH DO KOFERMENTACJI PROWADZONEJ W WARUNKACH STATYCZNYCH

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Abstrakt: Przedstawiono wyniki badań dotyczące ustalenia najkorzystniejszego udziału selektywnie zbieranych bioodpadów kuchennych poddawanych procesowi mezofilowej fermentacji z nadmiernym osadem czynnym. Wyznaczony optymalny skład mieszaniny kofermentacyjnej miał zapewnić stabilność prowadzonego procesu w warunkach statycznych. Podjęto również próbę zastąpienia części osadu czynnego poddawanego fermentacji metanowej pianą występującą okresowo na powierzchni komory napowietrzania. Jako kryterium oceny prawidłowości doboru składu poszczególnych mieszanin substratów, zapewniającego optymalny przebieg beztlenowego procesu rozkładu substancji organicznych przyjęto: sumaryczną oraz jednostkową produkcję biogazu; stopień usunięcia suchej masy organicznej oraz stabilność procesu (LKT; LKT/Zasadowości). Wykazano, że kofermentacja bioodpadów kuchennych i osadów ściekowych wpłynęła pozytywnie na ilość i skład produkowanego biogazu oraz stopień usunięcia materii organicznej. Najkorzystniejszy udział bioodpadów kuchennych wyniósł 60 % s.m., co w przeliczeniu na udział mas odpowiadało około 25 % mas. Wykazano, że dla najkorzystniejszego składu mieszaniny kofermentacyjnej (60 % s.m. bioodpady kuchenne + 40 % s.m. osad ściekowy) uzyskano ponad trzykrotny wzrost sumarycznej produkcji biogazu, w porównaniu z ilością biogazu generowanego w procesie fermentacji metanowej osadu nadmiernego. Nie zaobserwowano również znaczącego pogorszenia stabilności procesu (LKT/Zasadowości). Zastąpienie części osadu ściekowego pianą osadu czynnego nie wpłynęło negatywnie na efektywność oraz stabilność kofermentacji bioodpadów kuchennych i osadów ściekowych. Natomiast dodatek piany wpłynął pozytywnie na dynamikę produkcji biogazu.

Słowa kluczowe: fermentacja metanowa, kofermentacja, biogaz, nadmierny osad czynny, pienienie osadu czynnego, bioodpady kuchenne

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SORPTION CAPACITY OF SEWAGE SLUDGE FOR IONS OF SELECTED METALS

ZDOLNOŚCI SORPCYJNE WYBRANYCH METALI PRZEZ OSADY ŚCIEKOWE

Abstract: The study was conducted to determine the sorption capacity of excessive and fermented sewage sludge with respect to nickel(I) and lead(II). The sorption capacity of the sludge was found to be dependent on the content of organic matter and the iodine adsorption value. Samples of fermented sludge exhibited higher sorption capacity for both metals.

Keywords: waste sludge, sorption, heavy metals

Sewage sludge produced from the treatment of municipal wastewater amounts to approximately 400 000 Mg d.m. per year [1]. Treated sludge is classified as waste, and the principles of waste management are applied. One of the options to manage sludge is land application, when sludge is released into the environment.

As can be seen from the data provided in [2], sewage sludge shows considerable sorption capacity for halogens. It is desirable to establish whether sludge will show sorption capacity for ions of heavy metals. If the answer is positive, sludge can be used as a substance immobilizing heavy metal ions in the environment and limiting their migration.

This study focused on the sorption capacity of sludge for the ions of two selected metals: nickel and lead. Since the sorption capacity of natural sorbents such as soils is dependent on the content of organic matter [3], the analysis was conducted for sewage sludge material differing in the content of organic matter.

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Experimental part

1. Material

The sewage sludge samples used in the tests were obtained from different municipal wastewater treatment plants. Two types of sludge were analyzed: surplus sludge from sites I and II, and stabilized and fermented sludge from site III.

2. Determining the sludge properties

2a. Determining the content of organic matter

The content of organic matter was determined using the Tiurin method [4].

The sludge samples of 0.25 g were dried in the air prior to testing. Then, they were ground in a mortar, passed through a 0.25 mm sieve and placed in a flask. Each sample was submerged in 15 cm^3 of 0.4 N $K_2Cr_2O_7$ to which 0.1g of Ag_2SO_4 was added. The flask content was heated to boiling for five minutes under a reflux condenser. After cooling, the samples were transferred quantitatively into conical flasks, dissolved in 250 cm^3 of distilled water and titrated with 0.2 N solution of Mohr salt in the presence of diphenylamine.

The carbon content was calculated applying the following formula:

$$\% C = \frac{(V_1 N_1 - V_2 N_2) \cdot 0.003}{p} \cdot 100$$

where: V_1 – volume of $K_2Cr_2O_7$ added to the sample,
N_1 – $K_2Cr_2O_7$ titre,
V_2 – volume of Mohr salt used for titration with surplus $K_2Cr_2O_7$,
N_2 – Mohr salt titre,
0.003 – carbon milligram equivalent,
p – weighed amount of sludge [g].

The carbon content was then converted into the content of organic matter $\% I_{om}$, using the following relationship:

$$\% I_{om} = \% C \cdot 1.724$$

where: 1.724 – conversion coefficient.

2b. Determining dry residue and water content

Dry residue and water content were determined following the EN 12 880:2000 standard [5]. Sludge samples of 5 g were dried in a dryer at 105 ^{o}C. The samples were dried until the material attained dry mass.

The content of dry residue, w_{dr} [%], was calculated from the following relationship:

$$w_{dr} = [(m_c - m_a) / (m_h - m_a)] \cdot 100$$

and the content of water, w_w [%], was calculated from

$$w_w = [(m_h - m_c) / (m_h - m_a)] \cdot 100$$

where: m_a – mass of an empty evaporator [g],
m_b – mass of an evaporator with a non-dried sludge sample [g],
m_c – mass of an evaporator with a dried sludge sample [g].

2c. Determining the iodine adsorption value

The iodine adsorption value was determined according to the PN-83/C-97 515.04 [6] standard adjusted to sewage sludge.

A sample of non-dried sludge in the amount equivalent to 0.2 g of dry mass was treated with 4 cm^3 of 1 M HCl solution and 20 cm^3 of 0.2 M iodine solution. The sample submerged in the solutions was shaken for five minutes using a laboratory shaker (300 rev./min). Once the sludge was mechanically separated from the solution, iodine was titrated with 0.1 M solution of sodium thiosulphate using a starch indicator. The iodine (adsorption) value, *LJ*, was calculated from the following relationship:

$$LJ = \frac{(V_0 - V_1) \cdot c_1 \cdot 126.92}{m} \quad \text{[mg/g d.m.]}$$

where: V_0 – volume of the 0.1 M $Na_2S_2O_3$ solution used for a blank titration [cm^3],
V_1 – volume of the 0.1 M $Na_2S_2O_3$ solution used for titration of a sample [cm^3],
c_1 – concentration of the $Na_2S_2O_3$ solution [M],
126.92 – mass of 1 mol of (1/2 I_2) iodine [g],
m – mass of a sludge sample converted into dry mass [g].

3. Analyzing the sorption capacity of the sludge material for nickel(II) and lead(II)

3a. Determining the sorption kinetics for nickel(II) and lead(II) ions

The analysis was conducted under static conditions. Sewage sludge samples 5 g were placed in eight flasks and treated with 50 cm^3 of 0.1 M solution of lead nitrate(V) or nickel nitrate(V). The samples were then shaken in a GFL-3005 shaker at a rotational speed of 300 rev./min. The shaking time ranged from 5 minutes to 20 hours. The solutions of metal salts separated from the sludge were tested for the concentration of lead(II) and nickel(II). The metal equilibrium concentration was determined using a spectrophotometric method included in Merck's procedures [7,8]. The spectrophotometric measurements were taken by means of a Merck Nova 60.

The sorption capacity was calculated using the following expression:

$$A = \frac{v(c_0 - c)}{m}$$

where: A – proper sorption [mg/g],
c_0 – initial concentration of the metal salt solution [mg/dm^3],
c – equilibrium concentration of the metal salt solution [mg/dm^3],
v – volume of solution [dm^3],
m – sorbent mass [g].

3b. Determining the sorption isotherms

The sorption isotherms for nickel(II) and lead(II) were determined under static conditions. Five sewage sludge samples, 2.0, 5.0, 7.5, 10.0 and 12.5 g, were placed in five conical flasks, respectively. Each was treated with 50 cm^3 of 0.1 M solution of lead nitrate(V) or nickel nitrate(V). The samples were shaken in a laboratory shaker for four hours. The next steps were the same as in section 3a.

Results and discussion

The first objective of the analysis was to determine selected physical and chemical properties of the sewage sludge samples (Table 1).

Table 1

Properties of the sewage sludge material

Treatment plants	Content of organic matter [%]	Content of water [%]	*LJ* [%]	Content of dry residue [%]
I N	46.96	81.06	412	18.94
II C	41.12	86.13	424	13.87
III P	57.25	48.63	473	51.37

The fermented sludge (sample III) showed the highest content of dry residue (51.37 %) and the highest amount of organic matter (57.25 %). The surplus sludge (sample II), on the other hand, had the lowest content of dry residue (13.87 %) and organic matter (41.12 %). The changes in the content of dry residue and organic matter were represented by the iodine adsorption value. The iodine (adsorption) value, which was used for determining the sorption capacity of the sludge material, was the highest for the fermented sludge (sample III) with the highest amount of organic matter and dry residue. The iodine adsorption value, ranging from 412 to 473 mg I/g d.m., was several times lower for soil samples (approx. 100–150 mg I/g d.m.) and twice as low as those for WD-extra activated carbon (920 mg I/g d.m.) [9, 10]. The iodine (adsorption) value showed that the sewage sludge material possessed relatively high sorption capacity.

The next objective was to determine the sorption kinetics for nickel and lead salts. As can be seen from the sorption curves in Figs. 1 and 2, the sorption equilibrium was achieved after four hours. The contact time was determined from the sorption isotherms (Figs. 3 and 4). For lead, the highest sorption capacity, ie 385 mg/g, was obtained for the samples fermented in a closed fermentation chamber. The sorption capacity was reported to be lower for the surplus sludge samples; it was 54 mg/g for sample I and 86 mg/g for sample II. For nickel, the best sorption of 266 mg/g was observed also for the

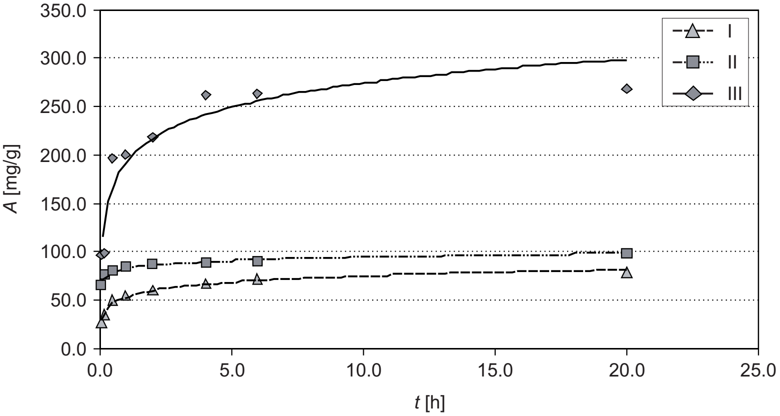

Fig. 1. Adsorption vs time for nickel

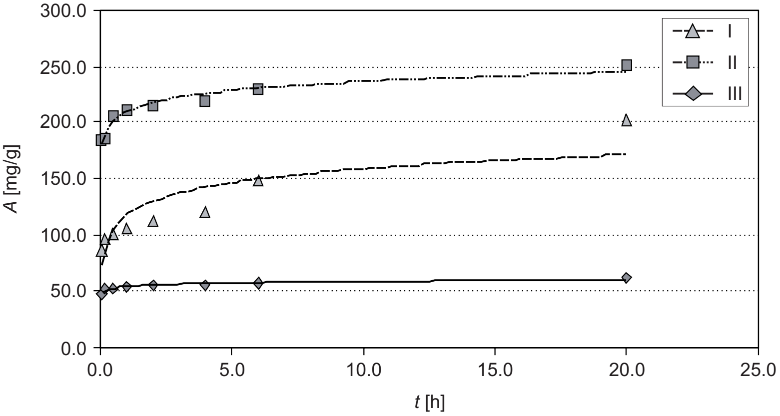

Fig. 2. Absorption vs time for lead

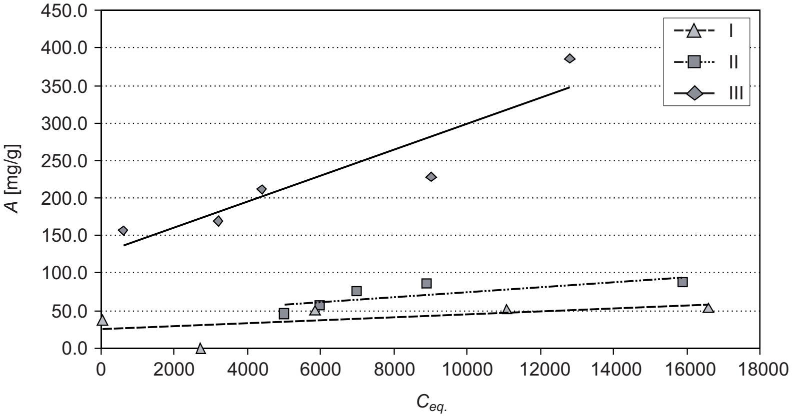

Fig. 3. Nickel sorption isotherms

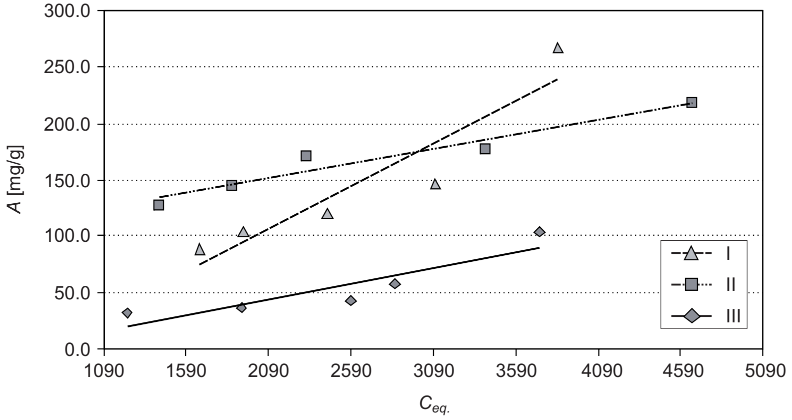

Fig. 4. Lead sorption isotherm

material fermented in a closed fermentation chamber; the surplus sludge had a sorption of 218 (sample II) and 104 (sample I).

The changes in the sorption capacity were consistent with the data provided in the literature [3, 9]. The highest sorption of nickel and lead was reported for the sludge samples with the highest content of organic matter and the highest iodine (adsorption) value. The sorption equilibrium was described through the Freundlich isotherm, $A = \mathrm{k} \cdot c_{\mathrm{eq.}}{}^{1/n}$ [11], which, as Weber suggests [3], well describes the sorption of hydrophobic substances in soil assuming that it occurs mainly for an organic fraction of soil. Parameter k reflects the sorption capacity of a sorbent for a sorbate, while $1/n$ reflects the energy of binding of the sorbent by the sorbate.

Table 2 presents the values of parameters k and n and the coefficient of determination calculated by using version 7.0 of STATISTICA. The values of the coefficient of determination higher than 0.9 confirm that the Freundlich isotherms were suitable for describing the test results.

Table 2

Estimators of the parameters of the function $A = k \cdot c^{1/n}$ describing the Freundlich isotherms used in the analysis

Treatment plants	Pb			Ni		
	R	K	*n*	R	K	*n*
I	0.9237	9.287	5.354	0.9451	0.022	0.897
II	0.8425	0.357	1.703	0.9687	6.845	2.462
III	0.9126	43.194	5.375	0.8944	0.021	0.997

Conclusions

1. The sludge material demonstrated good sorption capacity for ions of heavy metals such as nickel and lead.
2. From the analysis it is clear that sewage sludge can be used as a substance immobilizing heavy metal ions in the environment.
3. The sorption capacity of a sludge material is dependent on the content of organic matter; the higher the amount of organic matter, the higher the sorption capacity.
4. The sorption capacity of sludge can be assessed using the iodine (adsorption) value.

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ZDOLNOŚCI SORPCYJNE WYBRANYCH METALI PRZEZ OSADY ŚCIEKOWE

Wydział Budownictwa i Inżynierii Środowiska
Politechnika Świętokrzyska w Kielcach

Abstrakt: Zbadano zdolności sorpcyjne jonów niklu(II) i ołowiu(II) przez osady ściekowe nadmierne i przefermentowane. Stwierdzono, że zdolności sorpcyjne osadów zależą od zawartości w nich materii organicznej i od wartości liczby jodowej. Wyższe zdolności sorpcyjne dla obu metali miały próbki osadów przefermentowanych.

Słowa kluczowe: osady ściekowe, sorpcja, metale ciężkie

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SORPTIVE AND CATALYTIC PROPERTIES OF ACTIVATED CARBON USED FOR THE REMOVAL OF CRYSTAL VIOLET FROM AN AQUEOUS SOLUTION IN THE PRESENCE OF HYDROGEN PEROXIDE

SORPCYJNO-KATALITYCZNA ROLA WĘGLA AKTYWNEGO W PROCESIE USUWANIA FIOLETU KRYSTALICZNEGO Z ROZTWORU WODNEGO W OBECNOŚCI NADTLENKU WODORU

Abstract: Activated carbons play an important role in the processes of purifying waters, wastewaters and gases. While analyzing the effectiveness of these processes mainly the sorptive properties of the activated carbons are considered, taking no account of their catalytic abilities. According to the data presented in the literature, activated carbons catalyze the decomposition of oxidants such as hydrogen peroxide or ozone creating the hydroxyl radical, which is the strongest oxidating factor. This reaction may be used to oxidate the organic impurities in the aqueous solutions. In the activated carbon – oxidant – organic impurities system most probably both the processes of sorption and catalytic oxidation of the organic compounds take place.

In this paper the effectiveness of removing the crystal violet from the aqueous solution in the presence od various activated carbons and hydrogen peroxide was examined (C_d = 20 mg/dm^3, $C_{H_2O_2}(1)$ = 375 mg/dm^3, $C_{H_2O_2}(2)$ = 3750 mg/dm^3, m_{ac} = 0.5 g, t = 160 min). In the research the commercial activated carbon WDex, activated carbon WDex oxidated with hydrogen peroxide and activated carbon WDex saturated with crystal violet and regenerated with Fe^{2+}/H_2O_2 and Fe^{2+}/Ox (sorption – oxidation of adsorbed compounds) were used.

It has been observed that in specified conditions the effectiveness of removing the dye in the presence of carbon and oxidant is greater (72 mg/g) than the sorptive abilities of the activated carbons (34 mg/g). It has been also concluded that the efficiency of the process depends on the type of the activated carbon used, the amount of the hydrogen peroxide and the method of carrying out the process.

It has been also show that the effectiveness of removing crystal violet from the aqueous solution is greater when the process is carried out in the activated carbon – crystal violet – hydrogen peroxide system than in case of removing the dye by the sorption on activated carbon – regeneration of the activated carbon – subsequent regeneration (56 mg/g). The results of the research confirm both the sorptive and catalytic properties of the activated carbons in the analyzed process.

Keywords: activated carbon, oxidation, sorption, crystal violet, hydrogen peroxide

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Activated carbon, characterized by a large surface area and specific chemical properties resulting from a highly porous structure, is commonly used for treating water, wastewater and gases [1]. Its sorptive capacity is reported to be particularly useful in processes involving the removal of impurities from a liquid or gaseous phase. The catalytic properties are considered to be of less importance; however, when combined with the sorptive capacity, their role in the removal process increases. Activated carbon (AC) can be used, for instance, to remove organic compounds by means of the AOP method, where organics are oxidized using hydroxyl radicals OH^* generated in the reaction system of hydrogen peroxide and/or ozone in the presence of UV irradiation as well as Fenton's reagent (ie H_2O_2 and Fe^{2+} ions) in the presence or absence of UV irradiation [2–7]. Hydroxyl radicals OH^* forming in the reaction system are characterized by a high oxidizing potential (2.7 mV), which makes them the most effective oxidants. As shown in [7] and [8], hydroxyl radicals also form in a reaction system containing hydrogen peroxide or ozone in the presence of activated carbon according to the following equations:

$$\begin{aligned}
&AC - OH + H_2O_2 \longrightarrow AC - OOH + H_2O\\
&AC - OOH + H_2O_2 \longrightarrow AC - OH + H_2O + O_2\\
&AC + H_2O_2 \longrightarrow AC^+ + OH^- + \underline{OH}^*\\
&AC^+ + H_2O_2 \longrightarrow AC + HO_2^* + H^+
\end{aligned}$$

The AOP process can be applied to oxidize the organic compounds present in the solution and those adsorbed on the surface of the activated carbon.

An example application of the sorptive and catalytic properties of activated carbon is the removal of organic impurities from textile dye effluents, which contain not only dyes but also hydrogen peroxide used for bleaching [9–11]. Such industrial wastewater can be treated by sorption on activated carbon as well as by oxidation using hydroxyl radicals.

In this analysis, the sorptive and catalytic properties of activated carbon were used for removing crystal violet from an aqueous solution by sorption and oxidation with hydrogen peroxide in the presence of virgin and regenerated WD-extra carbons. The regeneration of activated carbon saturated with crystal violet was conducted using classic Fenton's reagent, Fe^{2+}/H_2O_2, or modified Fenton's reagent, Fe^{2+}/Ox, with the latter containing an oxidant which becomes an alternative source of hydrogen peroxide. Once introduced into a reaction system, the reagent ensures gradual formation and a more effective use of hydroxyl radicals. The aim of the study was to compare the effectiveness of sorption with that of oxidation in removing a dye from a solution. It was also essential to assess the effectiveness of the analyzed method of carbon regeneration and the possibility of carbon reuse.

Methodology

The materials used for the analysis were:

– commercial activated carbon produced by Gryfskand, Hajnowka, PL (WD-extra), commonly used as a sorbent,

– commercial activated carbon subjected to preliminary oxidation (WD-extra /H_2O_2),

– commercial activated carbon saturated with crystal violet, which was then regenerated with classic Fenton's reagent, (WD-extra/Fe^{2+}/H_2O_2),

– commercial activated carbon saturated with crystal violet, which was then regenerated with modified Fenton's reagent, Ox, (WD-extra/Fe^{2+}/Ox).

Sorption of crystal violet on activated carbons

0.1 g, 0.2 g, 0.5 g, 1.0 g and 1.5 g samples of different activated carbons, WD-extra, WD-extra/Fe^{2+}/H_2O_2, and WD-extra/Fe^{2+}/Ox, were placed in 300 cm^3 conical flasks to be treated with an aqueous solution of crystal violet, the concentration of which was C_{fk} = 20 mg/dm^3. The flasks were shaken for 12 hours, the time being determined on the basis of the sorption kinetics analysis. The sorption isotherms for crystal violet are shown in Fig. 1.

Oxidation of virgin activated carbon with hydrogen peroxide

Accurately weighed 0.5 g samples of maiden activated carbon, WD-extra, were placed in 300 cm^3 conical flasks and treated with distilled water and an H_2O_2 solution in the amount necessary to obtain a concentration of 3750 mg H_2O_2/dm^3. After being stirred vigorously for 160 minutes, the solution over the activated carbon was decanted. The oxidation procedure was repeated twice. Finally, the activated carbon was rinsed with distilled water (4 × 200 cm^3). The activated carbon prepared in this way is represented by the symbol WD-extra/H_2O_2.

Regeneration of WD-extra activated carbon saturated with crystal violet

After sorption, the WD-extra carbon saturated with crystal violet was separated from the solution. No drying time was selected. The carbon was placed in a beaker of distilled water. 300 mg/dm^3 of H_2O_2 or Ox was then introduced at pH = 3–4. Subsequently, iron(II) sulphate(VI) ($FeSO_4 \cdot 7H_2O$) was added, the weight ratio being Fe^{2+}/H_2O_2 or Ox = 1:4. The reactor content was stirred for 20 min at room temperature. The carbon was rinsed with distilled water (5 × 100 cm^3). The activated carbons regenerated in this way are represented by the symbols WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox, respectively.

Removal of crystal violet from an aqueous solution by sorption and oxidation

0.5 g samples of different activated carbons, ie WD-extra, WD-extra/H_2O_2, WD-extra/Fe^{2+}/H_2O_2, and WD-extra/Fe^{2+}/Ox, were placed in 300 cm^3 conical flasks and treated with 200 cm^3 of the dye solution with a concentration of about 20 mg/dm^3 and an H_2O_2

solution until the concentration 3750 mg H_2O_2/dm^3 was achieved. The samples were stirred vigorously for 160 minutes. The dye concentration in the reaction mixture was determined at time intervals. After 160 minutes, the solution over the activated carbon was decanted. The carbon was then treated with a subsequent portion of the crystal violet solution with a concentration of about 20 mg/dm^3 and the hydrogen peroxide solution. The procedure was repeated many times until the decolourization efficiency declined considerably.

Analysing the changes in the concentration of crystal violet

The concentration of crystal violet in the aqueous solution was determined using a Marcel Media UV/VIS spectrophotometer with wavelength λ = 590 nm.

Measuring the pH of the water extract of the activated carbons

1.0 g of carbon was treated with 20 cm^3 of distilled water, shaken for one hour, and stored at room temperature for 24 hours until used to measure the pH of the solution in contact with activated carbon.

Discussion of results

The first stage of the analysis focused on assessing the sorptive efficiency of WD-extra activated carbon used for removing crystal violet from an aqueous solution. As can be seen from Fig. 1, the dye sorption exhibited Langmuir behaviour up to

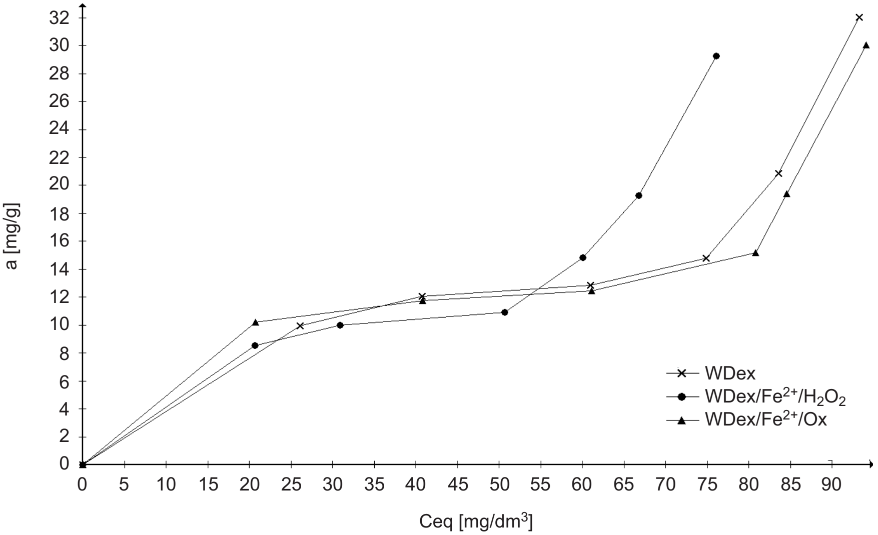

Fig. 1. Sorption isotherms of crystal violet on maiden and regenerated activated carbons, WD-extra, WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox

12 mg/g; then it increased and reached a maximum, which was 32 mg/g. The sorptive efficiency did not rise even if the sorption time was increased up to 24 hours.

Activated carbon saturated with a dye becomes waste, which needs to be disposed of properly. One of the methods of disposal is regeneration by chemical oxidation of the adsorbed substances. In this analysis, WD-extra activated carbon saturated with crystal violet was subjected to chemical regeneration using classic or modified Fenton's reagent, Fe^{2+}/H_2O_2 and Fe^{2+}/Ox, respectively. When classic Fenton's reagent was used, the adsorbed substances (ie crystal violet) decomposed in the presence of hydrogen peroxide and Fe^{2+} ions introduced into the system in an acidic environment. On the other hand, during the regeneration with modified Fenton's reagent, hydrogen peroxide formed gradually and directly in the reaction system. In either case, the forming hydroxyl radicals were responsible for the decomposition of the organic substances. However, the decomposition process was more effective when modified Fenton's reagent was applied.

The effectiveness of the regeneration process was determined by studying the sorptive capacities of the regenerated activated carbons, WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox. The static sorption isotherms in Fig. 1 show that the sorptive capacity and the mechanism of sorption on maiden activated carbon, WD-extra, were similar to those obtained for the activated carbon regenerated with Fenton's reagent. The sorption of crystal violet on the regenerated activated carbons exhibited Langmuir behaviour up to 10–12 mg/g, then it increased significantly to 30 mg/g. The isotherms suggest that there was a change in the spatial orientation of the sorbed particles after they had covered a certain surface area of both the maiden and the regenerated activated carbon (using specific active centres) and/or the presence of another type of interactions between the activated carbon and the dye.

The static sorption on the maiden activated carbon, WD-extra, and the regenerated activated carbons, WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox, shows that sorption is an effective method for removing crystal violet from an aqueous solution. The results indicate that the procedure applied to regenerate activated carbon saturated with crystal violet was effective and that it allowed recovery and reuse of the sorbent. It should be noted, however, that although the sorption on activated carbons is a suitable method for removing impurities from an aqueous solution, this process requires long contact time of the sorbent with the sorbate. It was thus essential to analyze the behaviour of the crystal violet – activated carbon system after hydrogen peroxide was introduced. Sanchez-Polo et al have pointed out [3] that activated carbon catalyzes the decomposition of hydrogen peroxide to form hydroxyl radicals. Thus, under desired conditions, the solution should decolourize more rapidly.

For this reason, the solution of crystal violet was treated with hydrogen peroxide in the amount sufficient to achieve a concentration of 3750 mg/dm^3. The measurement results in Figure 2 show that despite its oxidizing properties, hydrogen peroxide did not cause any changes in the dye concentration. This means that there was no oxidation reaction in the crystal violet – hydrogen peroxide system. When hydrogen peroxide and WD-extra activated carbon (C_{fk} = 20 mg/dm^3, $C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3, $m_{WD\text{-}extra}$ = 0.5 g) were introduced into the dye solution, the decolourization efficiency

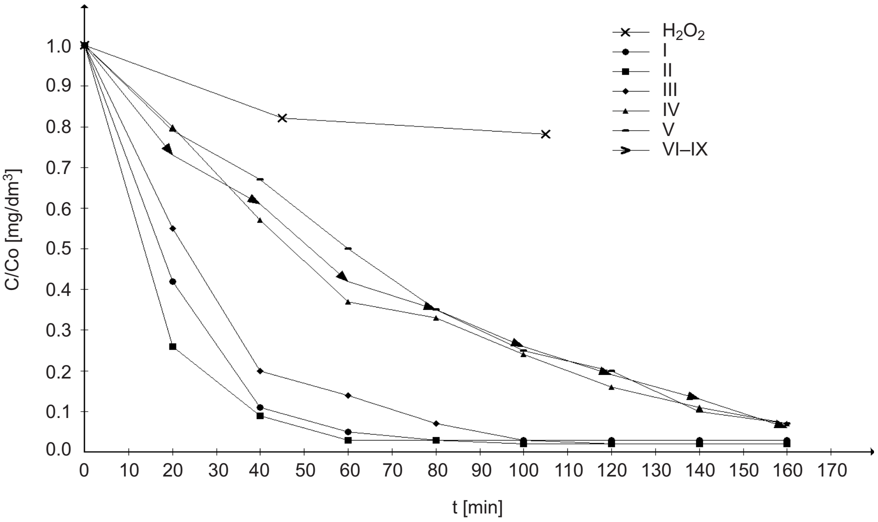

Fig. 2. Rate of change in the concentration of the subsequent portions of crystal violet in the presence of hydrogen peroxide ($C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3) and WD-extra activated carbon

was much higher than during sorption (Fig. 2). Under such conditions, the dye concentration was reduced to 80 % as early as after 20 minutes; the total decolourization of the solution was achieved about 120 minutes after the reaction was initiated. When the same sample of activated carbon was treated with a new portion of crystal violet and hydrogen peroxide twice, the decolourization of the solution was equally effective. This suggests that some oxidizing agent responsible for the decomposition of crystal violet formed in the reaction system. The agent was most probably hydroxyl radicals forming during the reaction between the activated carbon and hydrogen peroxide, and the activated carbon is the reaction catalyst. When the same sample of activated carbon was treated with subsequent portions of the dye and the oxidant, the oxidation process slowed down slightly. Under such conditions, a 50 % reduction in the dye concentration was observed after approximately 80 minutes. Even though there was a decrease in the rate of decolourization of the crystal violet solution, 32 mg/g of crystal violet per 1 g of WD-extra activated carbon was removed by sorption. In the presence of WD-extra carbon and hydrogen peroxide, the amount of the dye removed was as much as 72 mg/g (Table 1). It is important, however, that the process involved a 3.6 % loss of mass of the activated carbon.

As it was necessary to explain the changes in the decolourization rate for the subsequent portions of the crystal violet solution in the presence of activated carbon and hydrogen peroxide, first the carbon was subjected to preliminary oxidation, and then it was used to remove the dye from the solution under the same conditions as in the previous experiments. The results in Fig. 3 show that the changes in the concentration of crystal violet in the subsequent portions of the solution were similar to those obtained for maiden activated carbon, WD-extra, starting with the fourth portion of the solution

Table 1

Comparing the efficiency of activated carbons used to remove crystal violet from an aqueous solution by sorption and upon oxidation with H_2O_2 ($C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3)

Methodology	Activated carbon			
	WD-extra	WD-extra/H_2O_2	WD-extra/Fe^{2+}/Ox	WD-extra/Fe^{2+}/H_2O_2
Sorption [mg/g]	32	—	30	30
Amount of dye removed in the presence of H_2O_2 [mg/g]	72	48	56	24
Loss of mass of activated carbon [%] [Δ_m]	3.6	5.3	5.3	10

being decolourized (see Fig. 2). The results indicate that the preliminary oxidation of the surface of the WD-extra activated carbon by using hydrogen peroxide was not favourable for the dye decomposition. This justifies the high treatment efficiency of virgin activated carbon (WD-extra) in the activated carbon – crystal violet – hydrogen peroxide system as well as the loss of the sorptive and catalytic properties of the carbon because of its contact with hydrogen peroxide. It should be noted that the total amount of the dye removed from the solution was 48 mg per 1 g of the activated carbon and that it was higher than that obtained by sorption on the maiden activated carbon, WD-extra (Table 1). Of importance is also the fact that the oxidation of the dye was accompanied by the oxidation of the carbon matrix, the evidence of which was a 5.3 % loss of mass of the activated carbon.

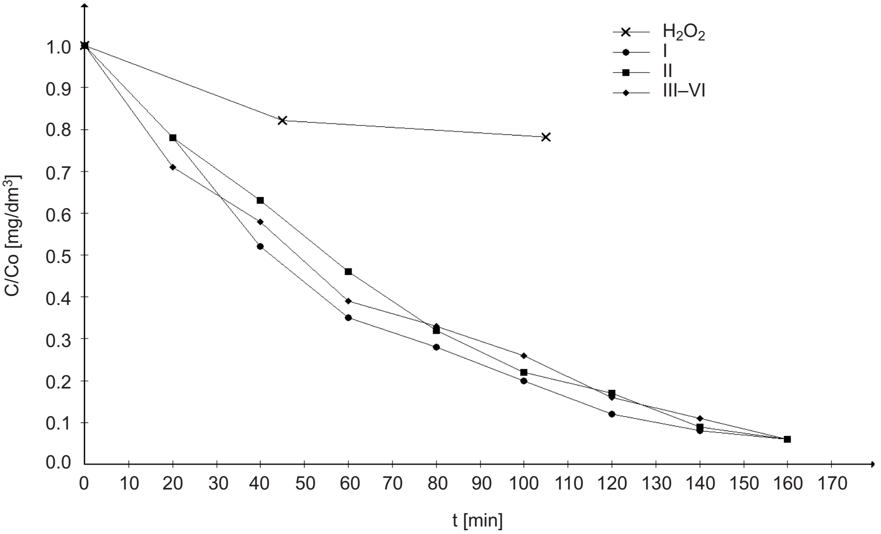

Fig. 3. Rate of change in the concentration of the subsequent portions of crystal violet in the presence of hydrogen peroxide ($C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3) and activated carbon subjected to preliminary oxidation, WD-extra/H_2O_2

The regenerated carbons, WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox, were used to determine how the properties of activated carbon affected the efficiency of removal of crystal violet from an aqueous solution. Figure 1 shows that the sorptive capacities of these carbons were similar to that of virgin carbon, WD-extra. As can be seen from Figs. 4 and 5, the treatment efficiency of the chemically regenerated carbons introduced into the crystal violet – H_2O_2 system was similar to that of maiden activated carbon subjected to preliminary oxidation, WD-extra/H_2O_2, despite the fact that the solution decolourized as a result of the dye decomposition. It should be noted that under predetermined conditions, the total amount of the dye removed in the presence of the WD-extra/Fe^{2+}/Ox carbon was 56 mg/g and it was higher than that obtained during sorption. The overall efficiency of the dye oxidation process in the presence of activated carbon regenerated with Fenton's reagent, WD-extra/Fe^{2+}/H_2O_2, was considerably lower – only 24 mg/g. The results confirm the previous conclusion that the dye was removed from the solution in the crystal violet – H_2O_2 – activated carbon system not by sorption but by oxidation, and the reaction catalyst was the activated carbon. The efficiency of the analyzed process was lower than that achieved in the presence of maiden carbon, WD-extra. It should be noted that the change in the chemical character of the carbon surface due to the contact with the oxidant did not affect its sorptive capacity for crystal violet; however, it reduced its catalytic capacity for the decomposition of hydrogen peroxide and the formation of hydroxyl radicals. Because of the presence of ash in the analyzed carbons, the functional groups, and accordingly, the chemical character of the carbon surface could not be determined. It was possible to establish only the pH of the water extracts of the activated carbons. Thus, the pH of the maiden activated carbon, WD-extra, was basic (8.60), the pH of the water extract of

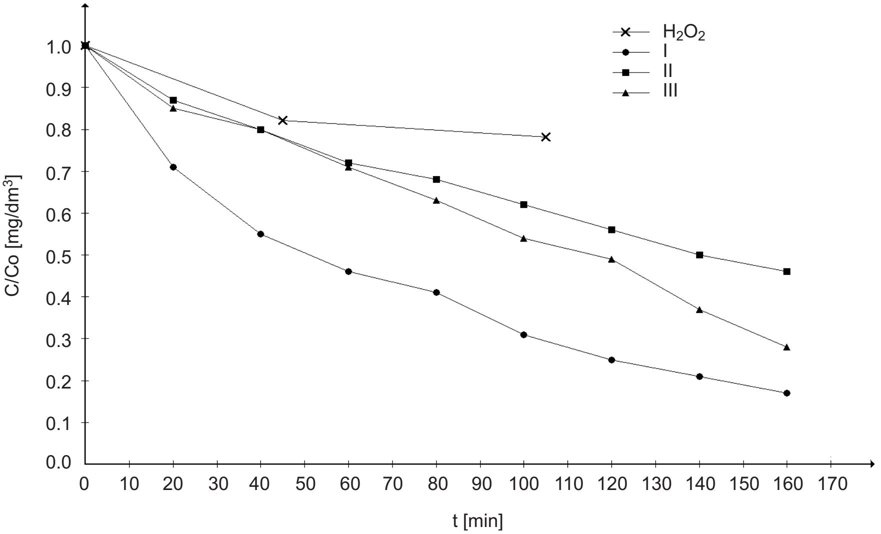

Fig. 4. Rate of change in the concentration of the subsequent portions of crystal violet in the presence of hydrogen peroxide ($C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3) and WD-extra activated carbon saturated with a crystal violet solution, and then regenerated with classic Fenton's reagent

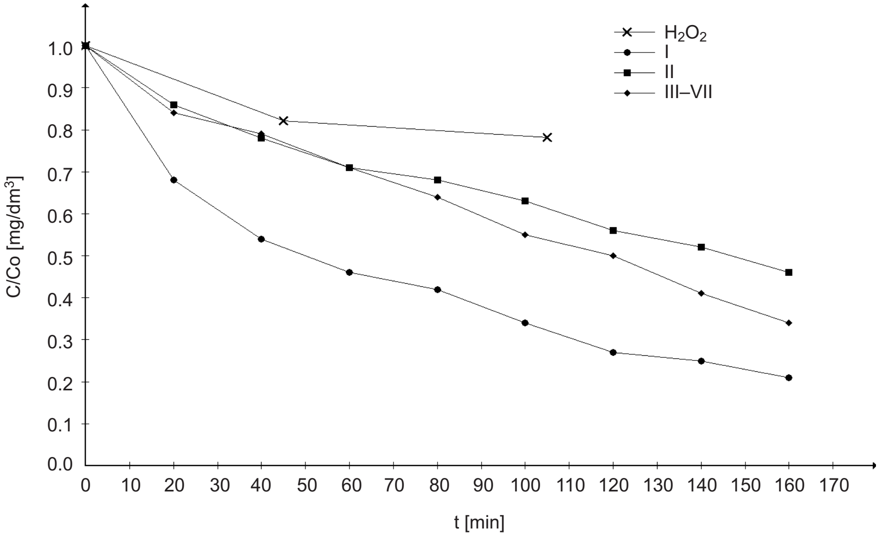

Fig. 5. Rate of change in the concentration of the subsequent portions of crystal violet in the presence of hydrogen peroxide ($C_{H_2O_2}$ = 3750 mg H_2O_2/dm^3) and WD-extra activated carbon saturated with a crystal violet solution, and then regenerated with modified Fenton's reagent

the activated carbon after regeneration with classic Fenton's reagent was acidic (4.0), and, finally, the pH of the water extract of the activated carbon regenerated with modified Fenton's reagent was almost neutral (6.5), despite the fact that the regeneration was performed in a solution with pH 3.0. This suggests that the catalytic removal of crystal violet from an aqueous solution was more effective in the basic environment, whose source can be both the surface of the activated carbon as well as the ash and other substances introduced during the regeneration with modified Fenton's reagent.

It should be noted that the oxidation of crystal violet in the solution was accompanied by a mass loss of the activated carbon. The loss, however, was varied. The smallest loss of mass, ie 3.6 %, was reported for the maiden activated carbon, WD-extra, at the highest efficiency of dye oxidation. The mass losses for WD-extra/H_2O_2 and WD-extra/Fe^{2+}/Ox resulting from the oxidation of crystal violet were comparable (5.3 %). Since the mass loss of the activated carbon regenerated with Fenton's reagent, WD-extra/Fe^{2+}/H_2O_2, reached as much as 10 %, it was impossible to reuse the carbon. The results suggest that the hydroxyl radicals forming in the dye – oxidant – activated carbon system reacted not only with the organic substance present in the solution but also with the carbon matrix, which caused a change in the chemical character of the activated carbon surface and a complete oxidation of the carbon material.

Conclusions

The experimental results show that WD-extra activated carbons are suitable for the sorptive removal of crystal violet from an aqueous solution. Moreover, this sorbent can be effectively regenerated using classic or modified Fenton's reagent. The sorptive capacities of the regenerated activated carbons, WD-extra/Fe^{2+}/H_2O_2 and WD-extra/Fe^{2+}/Ox, were comparable to those of the maiden carbon, WD-extra. It was found that the removal of crystal violet from an aqueous solution using WD-extra activated carbon was more effective in the presence of hydrogen peroxide (72 mg/g) than in its absence (32 mg/g). This indicates that the reaction system contained an oxidizing agent, other than hydrogen peroxide, which was responsible for the decomposition of crystal violet. The hydroxyl radicals formed by the reaction of activated carbon with hydrogen peroxide were probably the agent, while the activated carbon was the reaction catalyst. Another finding was that the oxidation of the dye present in the solution was accompanied by the oxidation of the carbon surface, the result of which was a change in its chemical character. The oxidation of the carbon surface was not favourable, because it caused a reduction in the catalytic capacity of the activated carbon for the decomposition of hydrogen peroxide and the formation of hydroxyl radicals, and also a significant loss of the carbon mass.

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SORPCYJNO-KATALITYCZNA ROLA WĘGLA AKTYWNEGO W PROCESIE USUWANIA FIOLETU KRYSTALICZNEGO Z ROZTWORU WODNEGO W OBECNOŚCI NADTLENKU WODORU

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Politechnika Świętokrzyska w Kielcach

Abstrakt: Węgle aktywne odgrywają ważną rolę w procesach oczyszczania wód, ścieków oraz gazów. Analizując efektywność tych procesów, bierze się pod uwagę głównie właściwości sorpcyjne węgli aktywnych, pomijając ich zdolności katalityczne. Dane literaturowe wskazują, że węgle aktywne katalizują reakcję rozkładu utleniaczy, takich jak nadtlenek wodoru czy ozon z utworzeniem najsilniejszego czynnika utleniającego jakim jest rodnik hydroksylowy. Reakcja ta z powodzeniem może być wykorzystana do utleniania zanieczyszczeń organicznych w roztworach wodnych. W układzie węgiel aktywny – utleniacz – zanieczyszczenia organiczne, najprawdopodobniej mają miejsce zarówno procesy sorpcji, jak i katalitycznego utleniania substancji organicznych.

W pracy podjęto badania nad efektywnością usuwania fioletu krystalicznego z roztworu wodnego w obecności różnych węgli aktywnych i nadtlenku wodoru (C_d = 20 mg/dm^3, $C_{H_2O_2}(1)$ = 375 mg/dm^3, $C_{H_2O_2}(2)$ = 3750 mg/dm^3, m_{ac} = 0,5 g, t = 160 min). W badaniach wykorzystano handlowy węgiel aktywny WDex, węgiel aktywny WDex utleniany nadtlenkiem wodoru oraz węgiel aktywny WDex nasycony fioletem krystalicznym i poddany regeneracji za pomocą Fe^{2+}/H_2O_2 i Fe^{2+}/Ox (sorpcja – utlenianie zaadsorbowanych substancji).

Zaobserwowano, że w zadanych warunkach skuteczność usuwania barwnika w obecności węgla i utleniacza jest większa (72 mg/g) w stosunku do sorpcyjnych zdolności węgli aktywnych (34 mg/g). Stwierdzono również, że wydajność tego procesu zależy od rodzaju zastosowanego węgla aktywnego, jak i od ilości nadtlenku wodoru oraz sposobu realizacji procesu.

Wykazano, że efektywność usuwania fioletu krystalicznego z roztworu wodnego jest większa w przypadku realizacji tego procesu w układzie węgiel aktywny – fiolet krystaliczny – nadtlenek wodoru, w porównaniu do usuwania barwnika poprzez sorpcję na węglu aktywnym – regeneracja węgla aktywnego – ponowna regeneracja (56 mg/g). Uzyskane wyniki badań potwierdzają zarówno sorpcyjne, jak i katalityczne właściwości węgli aktywnych w analizowanym procesie.

Słowa kluczowe: węgiel aktywny, utlenianie, sorpcja, fiolet krystaliczny, nadtlenek wodoru

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CONCENTRATION OF SELECTED PRIORITY SUBSTANCES IN KLODNICA RIVER CATCHMENT

ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KŁODNICY

Abstract: The paper presents results of research on concentrations of selected priority substances in the Klodnica River catchment. Two metals were selected: cadmium and mercury, as well as six polycyclic aromatic hydrocarbons (PAHs): anthracene, benzo[a]pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene. Mercury was determined with the method of cold vapor atomic absorption spectrometry (CV AAS) using RA-915$^+$ analyzer with RP-91 attachment produced by Lumex. Cadmium was determined with the method of direct electrothermal atomic absorption (ET ASS) using AAnalyst 600 appliance produced by Perkin Elmer. PAHs were analyzed with high-performance liquid chromatography method with fluorescence detection (HPLC-FLD) using liquid chromatograph HP 1050 produced by Hewlett Packard. The research was carried out in 2008 in four measurement campaigns, once every quarter. In all campaigns 28 measurement points, located in the Klodnica River catchment, were examined. The obtained results were compared with permissible concentration values for priority substances in surface waters included in the proposal of the UE concerning Environmental Quality Standards, and with requirements determined by the Polish legislation as limit values of water quality indicators.

Keywords: priority substances, river catchment, screening study

Upper Silesia is the biggest industrial district in Poland. In this area there are 21 mines, which belong to "Katowicki Holding Weglowy" and "Kompania Weglowa". There are also many coal mines which do not function nowadays but which in the past contributed to degradation of natural environment of the Upper Silesia Industrial Region (GOP). In the vicinity of energy sources many other branches of industry also appeared, eg metallurgical industry, power industry, engineering industry and chemical industry. The Klodnica River is the longest river flowing through the region of GOP. It is one of

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the right-bank tributaries of the Odra River. It is over 75 km long, 40 km of which are within GOP. The spring of the Klodnica River is situated in the southern part of Katowice, in Murckowski Forests. The river flows through the biggest cities of the Upper Silesia, such as: Katowice, Ruda Slaska, Mikolow, Zabrze, Bytom, Gliwice and ends its course in Kedzierzyn-Kozle flowing into the Odra River [1]. The most important tributaries of the Klodnica River are: Bielszowicki Brook, Czarniawka Brook, Bytomka Brook, Drama Brook, Toszecki Brook (right-bank), and Jamna Brook and Gieraltowicki Brook (left-bank). In the course of the river three big dam reservoirs are located: Dzierzno Duze Lake on the Klodnica River, Dzierzno Male Lake on the Drama River and reservoir Plawniowice on the Toszecki Brook. The biggest pollution discharge is drained to the Klodnica River in its main course, where the river and its tributaries flow through densely populated and industrially most active areas of the Upper Silesia. The main sources of pollution of the Klodnica River are: precipitation sewage and thawing sewage flowing down from industrial and post-industrial areas, sewage flowing into the river from the areas where industrial and municipal landfills are located, discharge of mine water containing a lot of salt and untreated household sewage from cities and communes where there are no sewage treatment plants, or where sewage cannot be treated properly with the currently applied technology. In the catchment of the Klodnica River there are 23 sewage treatment plants, 11 of which function, 2 are to be modernized and three are planned to be built in the future [2]. As far as the efficiency is concerned these plants can be divided into small and big. Small sewage treatment plants are located mainly on the tributaries of the Klodnica River, and these are sewage treatment plants of the efficiency of several thousand m^3/day. Middle and big sewage treatment plants are located on the Klodnica River and their efficiency is several dozen m^3/day. Most of them are mechanical-biological sewage treatment plants.

Polish and European regulations regarding priority substances

According to regulations of the Water Framework Directive (WFD) established by the European Parliament and the Council of Europe on 23 October 2000, Poland, as a Member State, has to undertake actions that will guarantee protection of inland surface waters, passing waters, coastal waters and groundwaters. One of the main principles of the WFD is to achieve good chemical status of waters, that is assessed by taking into consideration the presence of substances that are proved to have or are highly probable to have a harmful influence on ecosystems and water organisms as well as on human health (the so called “priority substances”). The main act regulating protection of waters in Poland is the act of 21 April 2001, Environmental Protection Act, with its further amendments and executive regulations [3, 4]. A full list of priority substances can be found in Annex X of the WFD [5] and in the Regulation of the Minister of the Environment dated 10 November 2005 on register of priority substances in the field of water policy (DzU 05.233.1987) [6, 7]. The Regulation of the Minister of the Environment on ways of classifying the state of uniform parts of surface waters, that came into force in 2008, defines limit values of water status indicators [8]. Using these indicators it is possible to unequivocally interpret results of the carried out research. Implementation of the principles of the WFD means that good chemical status of waters will be achieved by 2015, establishing at the same time the year 2025 as a deadline for elimination of substances recognized as priority hazardous substances from group of priority substances. As a support for implementing the WFD the European Union has started a project "Source Control of Priority Substances in Europe" (SOCOPSE), which was realized under EU FP6 in the period of 2006–2009. Under this project Institute for Ecology of Industrial Areas (IETU), as one of the participants, was obliged to make a case study and prepare reports on effective possibilities for reduction of the emission of mercury, cadmium and polycyclic aromatic hydrocarbons [9].

This paper presents results of screening research of the content of selected priority substances in the catchment of the Klodnica River. Two heavy metals: mercury and cadmium were selected for research as well as compounds from the group of polycyclic aromatic hydrocarbons: anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene. The obtained contents of mercury, cadmium and PAHs in surface waters were compared with regulations of the EU Environmental Quality Standards (EQS) [6], and with regulations of the Polish legislation [8]. Acceptable contents of mercury, cadmium and PAHs according to EQS and according to the Polish legislation are presented in Table 1.

Table 1

Allowable concentrations of mercury, cadmium and selected PAH by EQS [6], and by Polish legislation [8]

Priority substances	EQS		DzU 2008, no. 162, issue 1008	
	Annual average concentration [μg/dm^3]	Maximum allowable concentration [μg/dm^3]	Annual average concentration [μg/dm^3]	Maximum value of concentration [μg/dm^3]
Mercury and its compounds	0.05	0.07	—[3]	0.07
Cadmium and its compounds	0.08–0.25[1]	0.45–1.5[1]	—[3]	0.45–1.50[2]
Anthracene	0.10	0.40	—[3]	0.40
Benzo[a]pyrene	0.05	0.10	—[3]	0.10
Σ Benzo[b]fluoranthene + Benzo[k]fluoranthene	0.030	not applicable	0.030	—
Σ Benzo[g,h,i]perylene + Indeno[1,2,3-cd]pyrene	0.002	not applicable	0.002	—

[1] Depending on water hardness classes [6]; [2] Depending on water hardness classes [8]; [3] No available data.

Properties of selected priority substances

Mercury

Elemental mercury, its inorganic salts and organic compounds belong to the group of metals responsible for trace but dangerous pollution of the environment. The toxicity of these compounds has been known for many years. Mercury can accumulate in various parts of living organisms and cause enzymatic disturbances and mutagenic lesions in DNA, which may result in many medical complications and diseases [10]. Mercury shows high chemical and biological activity, variability of phase states (liquid, gaseous and solid). Mercury compounds of different physico-chemical properties occur in different natural cycles, the most important of them being atmospheric and hydrobiological cycles. Mercury is introduced to the environment from many anthropogenic and natural sources. The natural sources of mercury emission to the environment are volcanic eruptions, reemission from soil and rock surface and natural processes of biomass combustion. The anthropogenic sources of mercury are combustion of coal, waste combustion, cement production, chlor-alkali manufacturing industry and non-ferrous metal production. Mercury infiltrates into water as a result of atmospheric precipitation deposition as well as surface and groundwater run-off. Its chemical form depends mainly on oxidation-reduction conditions. In water, where oxidation conditions are prevailing, the most popular mercury compounds are $HgCl_4^{2-}$ and $HgOH^+$. However, in places where reduction conditions are dominant the most popular are CH_3HgS^- and HgS^{2-} [11]. In water where redox conditions change, mercury can be observed mainly in the form of CH_3HgCl and CH_3Hg^{2+}. Mercury compounds have the ability to accumulate in bottom sediments, therefore the increase of their concentrations is a good indicator of pollutant inflow to water ecosystem. The content of this metal in water is scattered and may vary depending on the type of water and its origin [12–18]. It was assumed that the average content of Hg in the sea and ocean water was at the level of 0.005 μg/dm^3, and in the river water – at the level of 0.01 μg/dm^3 [11].

Cadmium

Cadmium is an element which might pose a serious threat to health as it can be easily absorbed by living organisms. This element when absorbed by organisms can create complexes with proteins, which may result in its accumulation in liver and kidneys. Cadmium strongly interacts with iron, zinc, copper and selenium. Increased concentration of these elements decreases toxic activity of cadmium. The toxicity of cadmium consists in disorders of reproductive functions, abnormal functioning of liver and kidneys and may cause hypertension and cancer [10, 11]. Cadmium is present in high dispersion in rocks. The natural source of cadmium emission to the environment is reemission from soil and rock surface. The main anthropogenic source of cadmium is production of non-ferrous metals and phosphorus fertilizers. The natural concentration of cadmium in waters is estimated at 0.1 ppb level. It is mainly shaped by anthropogenic factors. Generally, this element does not remain long in solution, because it is quickly precipitated in form of carbonates or absorbed by loams, hydroxides and metal oxides. In rivers the cadmium concentration is relatively low, it reaches the level of 10–500 ng/dm^3, whereas in the sea and ocean waters it is even lower (0.5 to 10 ng/dm^3) [19, 20].

PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) constitute a large group of compounds which contain a few aromatic circles in a particle. Physico-chemical properties of individual aromatic hydrocarbons are different and depend mainly on their molecular masses. Some of PAHs have toxic, cancerogenic and mutagenic properties. Among them the most severe ones are those of compounds which contain in their structure a circle system of benzo[a]anthracene eg: benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene and others. Anthropogenic emission of PAHs is stronger than the emission from natural sources. The anthropogenic sources of PAHs are: combustion of coal and fuels as well as heavy industry based on processing of coal and petroleum [21, 22]. Most of PAHs because of their nonpolarity and high molecular masses are badly soluble in water. Therefore, in water environment PAHs do not undergo hydrolysis but gradually degrade. PAHs combine with colloids and suspensions, and during their sedimentation go into sediments, which explains low concentration of PAHs in water column in comparison with their concentration in sediments. PAHs are introduced to water environment mainly through industrial discharge, surface flows and failures during transportation of liquid fuels. Another important source is deposition of dust coming from burning of the fossil fuels and biomass.

Study of area

Research on the content of priority substances (mercury, cadmium and PAHs) in the catchment of the Klodnica River were conducted in four measurement campaigns in 2008, with sampling frequency once a quarter. The first campaign was made on the 24th of January 2008, the second on the 9th of April 2008, the third between 11th and 12th of September 2008 and the fourth one on the 11th of December 2008. Eight measurement points were examined in four campaigns. The points were situated from the spring of the Klodnica River in Brynow (district of Katowice), through inlets of sewage and run-offs of sewage treated in sewage treatment plants placed in the course of the river next to the mouth of the most important tributaries, right up to the inlet of the Klodnica River to the dam reservoir – Dzierzno Duze and the inlet of the river to the Odra River in Kedzierzyn-Kozle. The register of measurement points of all four campaigns is presented in Fig. 1 and Table 2.

Methods and sample preparation

To determine mercury concentration in waters of the Klodnica River and its tributaries a multifunctional analyzer of mercury RA-915$^+$ has been used. Its work is based on Zeeman atomic absorption spectroscopy with the use of modulation with high polarization of light (ZAAS-HFM), together with RP-91 attachment. The attachment is used to determine the concentration of mercury in liquid samples using the technique of "cold vapor", which is produced as a result of reduction of Hg(II) to atomic form.

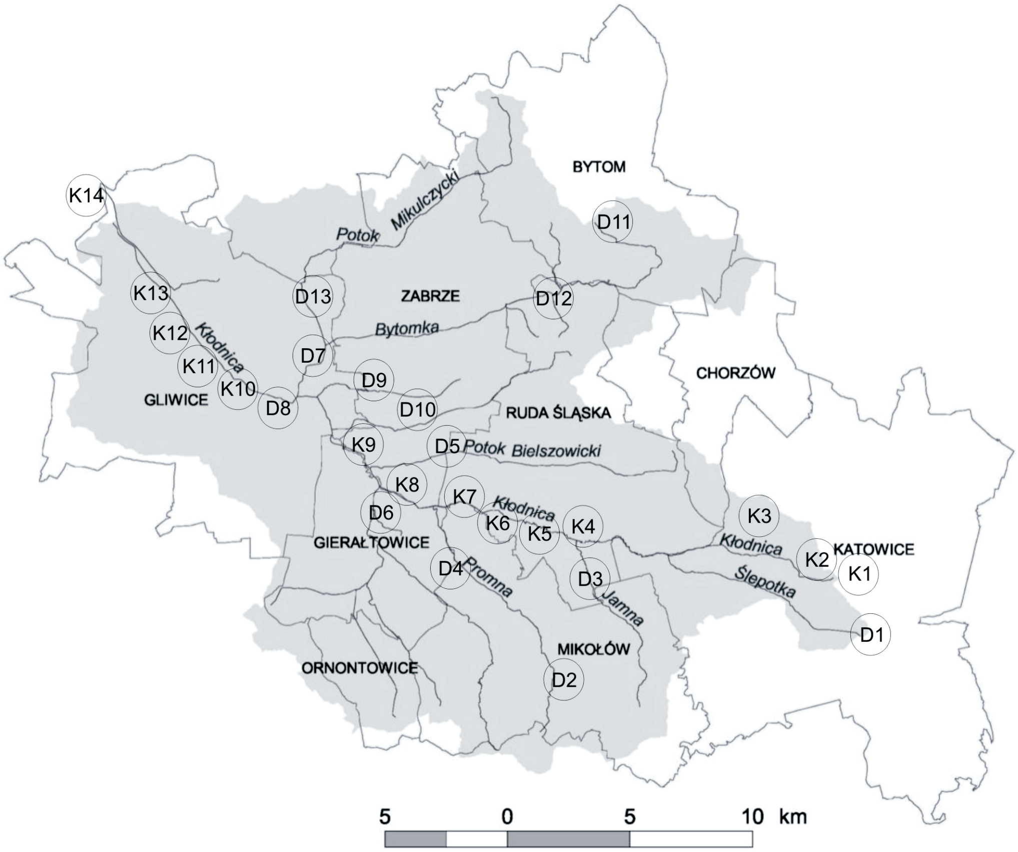

Fig 1. Chart of sampling points in the catchment of Klodnica River [2]

Table 2

List of sampling points in the catchment of Klodnica River

Mark of the sampling points	Entitle of the sampling points	Session I 24.01.2008	Session II 9.04.2008	Session III 11–12.09.2008	Session IV 11.12.2008
"K1"	Inlet of Klodnica River to city of Katowice, 74 km of river	–	+	+	–
"D1"	Slepiotka Stream, left inflows of Klodnica River	–	+	–	–
"K2"	Inlet of sewage to sewage treatment plants – mechanical- -biological type	–	–	+	–
"K3"	Outlet of sewage to sewage treatment plants – mechanical--biological type	–	+	+	–
"D2"	Jamna Stream, left inflows of Klodnica River	–	+	–	–
"D3"	Jamna Stream, left inflows of Klodnica River, before outlet to Klodnica River, 64.5 km of river	–	+	–	–
"K4"	Klodnica River after outlet of discharges waters "Halemba--Wirek" Colliery, 63 km of river	–	+	+	–
"K5"	Klodnica River, Ruda Slaska water-gauge, 63.8 km of river	+	+	+	+
"K6"	Inlet of sewage to sewage treatment plants – mechanical--biological-chemical type	–	–	+	–
"K7"	Outlet of sewage to sewage treatment plants – mechanical--biological-chemical type	–	+	+	–
"D4"	Promna Stream, left inflows of Klodnica River, before outlet to Klodnica River, 58.6 km of river	–	–	+	–
"K8"	Klodnica River after outlet of Promna Stream, 55 km of river	–	+	–	–
"D5"	Bielszowicki Stream, 54.4 km of river	–	+	+	–
"D6"	Outlet Jasienica Stream to Klodnica River, 1.3 km of river	–	–	+	–
"K9"	Klodnica after outlet Bielszowicki Stream, 53.8 km of river	–	+	–	–
"D7"	Bytomka Stream – Gliwice water-gauge, 2.7 km of river	+	+	+	+
"D8"	Bytomka Stream – Gliwice, before outlet to Klodnica River	–	+	–	–
"D9"	Discharges waters of "Sosnica-Makoszowy" Colliery	–	+	+	–

Table 2 contd.

Mark of the sampling points	Entitle of the sampling points	Session I 24.01.2008	Session II 9.04.2008	Session III 11–12.09.2008	Session IV 11.12.2008
"D10"	Czarniawka Stream after "Makoszowy" Colliery	–	+	+	–
"D11"	Bytomka Stream	–	–	+	–
"D12"	Bytomka Stream – Ruda Slaska	–	–	+	–
"D13"	Mikulczycki Stream outlet to Bytomka Stream, 0.3 km of river	–	+	–	–
"K10"	Klodnica River – Gliwice, 50.5 km of river	–	+	–	–
"K11"	Klodnica River – Gliwice water-gauge, 47.2 km of river	+	+	+	+
"K12"	Inlet of sewage to sewage treatment plants – mechanical-biological-chemical type	–	+	+	–
"K13"	Outlet of sewage to sewage treatment plants – mechanical-biological-chemical type	–	+	+	–
"K14"	Klodnica River outlet to barrage reservoirs Dzierzno Lake, 38.6 km of river	–	+	+	–
"K15"	Klodnica River – Kedzierzyn-Kozle-outlet to Odra River, 0 km of river	–	+	–	–

Samples of water were dripped through membrane filters (cellulose nitrate) with the diameter of 47 mm (diameter of pores 0.45 μm). 1 cm^3 of nitric acid and 1 cm^3 of solution of potassium chromate(VI) were added to the obtained filtrate. Then, the samples were mineralized for 2 hours in water steam-baths in the temperature of 95 ^oC, in oxidizing mixture consisting of $KMnO_4$, HNO_3, H_2SO_4, $K_2S_2O_8$ [23]. Detection limit of the applied method is 0.002 $\mu g/dm^3$. Cadmium in waters was determined using Electrothermal Atomic Absorption Spectrometry (ET-AAS) and AAnalyst 600 spectrometer produced by PerkinElmer. Samples of water were dripped in the same way as samples of mercury. 1 cm^3 of nitric acid was added to the obtained filtrate. Limit of detection of the applied method is 0.2 $\mu g/dm^3$. In order to determine concentrations of PAHs the samples of water were extracted with SPE technique and octadecyl(C_{18}) phase. Extracts were analyzed with the technique of High Performance Liquid Chromatography with Fluorescence Detection (HPLC-FLD), using liquid chromatograph HP 1050 produced by Hewlett Packard. Separation was conducted on Bakerbond PAH 16-Plus column, using gradient elution with mixture methanol and water. Limit of detection of the applied method is different depending on the determined compound and is, as follows: anthracene 0.009 $\mu g/dm^3$, benzo[a]pyrene 0.003 $\mu g/dm^3$, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) 0.004 $\mu g/dm^3$, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) 0.003 $\mu g/dm^3$. Laboratory glassware and all other utensils used during the analysis were washed in a laboratory dishwasher (Miele G7883, Ontario). Solutions were prepared with the use of deionized water of high cleanliness Milli-Q (Millipore, Bedford, MA, USA). All reagents used to determine metals had a certified concentration of mercury and cadmium (pro analysis, Merck, Germany). HPLC reagents of cleanliness produced by Baker were used to determine PAHs.

Results and discussion

Concentrations of mercury, cadmium and selected PAHs for the Klodnica River and its tributaries, obtained in four measurement campaigns are shown in Tables 3 and 4.

In most cases the results of particular measurement campaigns for the same measurement points were different. This difference probably results from the fact that weather and water conditions differed during particular measurement campaigns. It may also result from the amount of inflowing pollutants coming from rainwater and household sewage coming to the river from industrial plants and households located in its course. The second measurement campaign was carried out in spring when the river level was high and rainfall in March and at the beginning of April 2008 came to 80 mm. Such a quantity of rainfall could cause that a part of water, and therefore also pollutants, which got into the Klodnica River, came from rainwater flushing. The third measurement campaign was conducted in autumn after heat-wave, when the volume of rainfall from 15th August to 12th September was barely 20.14 mm and as a result the river level was relatively low on its whole length. The remaining two measurement campaigns were conducted in January and December 2008. In both periods the average monthly rainfall was around 40 mm and the river level was medium. The obtained concentrations of mercury for the entire catchment of the Klodnica River in all four measurement campaigns ranged from 0.010 to 0.893 $\mu g/dm^3$, whereas concentrations of cadmium varied from < 0.200 to 1.010 $\mu g/dm^3$. The lowest concentrations were observed in points where the river and its tributaries were not polluted by discharge of water from factories and households. The lowest concentrations of mercury ranging from 0.010 to 0.100 $\mu g/dm^3$ were noticed in left tributaries of the Klodnica River (Slepiotka, Jamna, Promna and Gieraltowicki Brooks) as well as in the Klodnica River itself, near its source. The lowest concentrations of cadmium ranging from < 0.200 to 0.300 $\mu g/dm^3$ were recorded in left tributaries of the Klodnica River (Slepiotka, Jamna, Promna). In the third measurement campaign the concentrations of cadmium in all examined points were not bigger than 0.380 $\mu g/dm^3$, which was probably the result of low river level in this period. The biggest concentration of mercury ranging from 0.296 to 0.893 $\mu g/dm^3$ was obtained for points K4 and D9 located near the outlets of mine water from hard coal mines. High concentrations of mercury were also obtained for measurement points D5 and D10 located on right tributaries of the Klodnica River, such as Czarniawka and Bielszowicki Brook. The highest concentrations of cadmium ranging from 0.650 to 1.010 $\mu g/dm^3$ were obtained for points K4 and D9, as well as for point D10. High concentrations of mercury and cadmium in these points may be caused by the fact that rivers in those regions are supplied mainly with waters coming from rainfall, sanitary sewage and commercial wastes and mine waters from hard coal mines located in this area.

Table 3

Concentrations of mercury and cadmium for Klodnica River and its side streams which were obtained in four measurement sessions [μg/dm^3]

Entitle of sampling point	Hg [μg/dm^3]				Cd [μg/dm^3]			
	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV
"K1"	—	0.086	0.100	—	—	1.01	0.20	—
"D1"	—	0.016	—	—	—	< DL	—	—
"D2"	—	0.010	—	—	—	0.37	—	—
"D3"	—	0.048	—	—	—	0.22	—	—
"K4"	—	0.266	0.707	—	—	0.65	< DL	—
"K5"	0.137	0.182	0.458	0.108	< DL	0.50	0.38	0.51
"D4"	—	—	0.070	—	—	—	< DL	—
"K8"	—	0.236	—	—	—	0.33	—	—
"D5"	—	0.146	0.893	—	—	0.46	0.34	—
"D6"	—	—	0.069	—	—	—	< DL	—
"K9"	—	0.339	—	—	—	0.22	—	—
"D7"	0.163	0.190	0.084	0.083	< DL	< DL	0.22	< DL
"D8"	—	0.129	—	—	—	< DL	—	—
"D9"	—	0.189	0.296	—	—	0.65	0.30	—
"D10"	—	0.402	0.244	—	—	0.69	< DL	—
"D11"	—	—	0.052	—	—	—	< DL	—
"D12"	—	—	0.053	—	—	—	< DL	—
"D13"	—	0.354	—	—	—	< DL	—	—
"K10"	—	0.142	0.066	—	—	< DL	< DL	—
"K11"	0.131	0.337	0.075	0.369	0.6	0.59	< DL	< DL
"K14"	—	0.475	0.088	—	—	0.53	< DL	—
"K15"	—	0.179	—	—	—	< DL	—	—

Table 4

Concentrations of chosen PAHs for Klodnica River and its side streams witch were obtained in four measurement sessions [μg/dm^3]

Entitle of sampling points	Anthracene [μg/dm^3]				B[a]P^1 [μg/dm^3]				Σ B[b]F +B[k]F^2 [μg/dm^3]				Σ B[g,h,i]P +IP^3 [μg/dm^3]			
	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV	Session I	Session II	Session III	Session IV
“K1”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
“D1”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
“D2”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< 0.004	—	—
“D3”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—
“K4”	—	< DL	< DL	—	—	< DL	0.005	—	—	< DL	< DL	—	—	< DL	0.006	—
“K5”	< DL	< DL	< DL	0.011	0.003	< DL	< DL	0.015	0.004	< DL	< DL	0.021	0.002	0.004	< DL	0.018
“D4”	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
“K8”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	0.004	—	—
“D5”	—	< DL	< DL	—	—	0.018	0.018	—	—	0.014	< DL	—	—	0.028	0.011	—
“D6”	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
“K9”	—	< DL	—	—	—	0.004	—	—	—	< DL	—	—	—	0.011	—	—
“D7”	< DL	< DL	0.012	< DL	0.007	0.006	0.003	0.014	0.009	0.011	< DL	0.018	0.010	0.008	0.004	0.022
“D8”	—	< DL	—	—	—	0.007	—	—	—	0.014	—	—	—	0.012	—	—
“D9”	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—
“D10”	—	0.052	0.013	—	—	0.011	0.010	—	—	0.013	0.006	—	—	0.009	0.006	—
“D11”	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—
“D12”	—	—	0.010	—	—	—	0.006	—	—	—	0.006	—	—	—	0.004	—
“D13”	—	< DL	—	—	—	0.003	—	—	—	0.007	—	—	—	0.005	—	—
“K10”	—	< DL	< DL	—	—	0.006	0.004	—	—	< DL	< DL	—	—	0.010	0.003	—
“K11”	< DL	< DL	0.012	0.031	0.004	< DL	< DL	0.058	0.005	< DL	0.006	0.078	0.007	0.004	0.010	0.091
“K14”	—	< DL	< DL	—	—	< DL	< DL	—	—	< DL	< DL	—	—	0.004	< DL	—
“K15”	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—	—	< DL	—	—

Table 5

Concentrations of mercury, cadmium and concentrations of chosen PAHs, which were obtained on inlets and outlets of three sewage treatment plants draining treated sewage to Klodnica River [µg/dm^3]

Priority substances		Sewage treatment plants mechanical-biological type	Sewage treatment plants mechanical--biological-chemical type	Sewage treatment plants mechanical--biological-chemical type
Hg	Inlet of sewage [µg/dm^3]	0.458	0.476	0.283
	Outlet of circumcised sewage [µg/dm^3]	0.257	0.123	0.093
Cd	Inlet of sewage [µg/dm^3]	0.33	< DL	< DL
	Outlet of circumcised sewage [µg/dm^3]	< DL	< DL	< DL
Anthracene	Inlet of sewage [µg/dm^3]	< DL	0.010	0.066
	Outlet of circumcised sewage [µg/dm^3]	< DL	< DL	< DL
B[a]P	Inlet of sewage [µg/dm^3]	0.004	< DL	0.023
	Outlet of circumcised sewage [µg/dm^3]	< DL	< DL	< DL
Σ B[b]F + + B[k]F	Inlet of sewage [µg/dm^3]	0.056	< DL	0.032
	Outlet of circumcised sewage [µg/dm^3]	< DL	< DL	< DL
Σ B[g,h,i]P + + IP	Inlet of sewage [µg/dm^3]	< DL	< DL	0.023
	Outlet of circumcised sewage [µg/dm^3]	< DL	< DL	< DL

[1] B[a]P – Benzo[a]pyrene; [2] B[b]F + B[k]F - Σ Benzo[b]fluoranthene + Benzo[k]fluoranthene; [3] B[g,h,i]P + IP – Σ Benzo[g,h,i]perylene + Indeno[1,2,3-cd]pyrene.

Concentrations of PAHs in the Klodnica River and its tributaries obtained in four measurement campaigns ranged as follows: anthracene from < 0.009 to 0.066 μg/dm^3, benzo[a]pyrene from < 0.003 to 0.058 μg/dm^3, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) from < 0.004 to 0.056 μg/dm^3, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) from < 0.003 to 0.028 μg/dm^3. In most measurement points concentrations of PAHs in the analyzed water samples were below the detection limit of the applied analytical method. Concentrations of PAHs were higher and could be determined only in points K4, D5, D9, D10, located behind the outlets of mine water collectors and on right tributaries of the Klodnica River (Czarniawka and Bielszowicki Brook). Sums of contents of six assayed PAHs in points with the highest concentration of these substances were 0.035 μg/dm^3 for point D10 in the third measurement campaign and 0.086 μg/dm^3 in the second one. The sum of concentrations of six PAHs was 0.144 μg/dm^3 for point K11 in the third measurement campaign. Points located on inlets and outlets of three sewage treatment plants draining treated waste to the Klodnica River were examined during the third measurement campaign. The obtained contents of mercury, cadmium and PAHs on inlets of waste and outlets of treated waste from sewage treatment plants are presented in Table 5. Two of the examined sewage treatment plants were of mechanical-biological-chemical type and one was a mechanical--biological one. In all three cases a definite improvement of water quality concerning cadmium, mercury and PAHs in points located on outlets of the examined sewage treatment plants can be noticed.

Conclusions

1. Concentrations of mercury, which were obtained in the carried out research in all points and four measurement campaigns range from 0.010 to 0.893 μg/dm^3. According to the Environment Quality Standards EQS [6] and the Regulation of the Minister of the Environment on ways of classifying the status of uniform parts of surface waters [8] the maximum permissible content of mercury in surface waters should not exceed 0.07 μg/dm^3. Concentrations of mercury did not exceed the limit values only on left-side tributaries of the Klodnica River in points D1, D2 and D3. Concentrations of mercury near to the maximum permissible value were observed in points D4, D6 and D11. In the rest of the examined points the permissible value was considerably exceeded.

2. Concentrations of cadmium obtained in all examined points and four measurement campaigns range from < 0.200 to 1.010 μg/dm^3. Polish legislation as well as European Environment Quality Standards accept the increased content of cadmium up to 1.5 μg/dm^3 depending on the class of water hardness. In 2007 the Voivodeship Inspectorate for Environmental Protection located fifteen points of operational monitoring [6] on the Klodnica River. On this basis waters of the Klodnica River in nine points were classified as class "V" – water of bad quality, and in six points as class "IV" – water of unsatisfying quality. Assuming that waters of the Klodnica River belong to "IV" class of quality, the concentration of cadmium according to EQS [5] and Polish legislation [4] should not exceed 0.9 μg/dm^3. This condition was not fulfilled only in point K1. Assuming that waters of the Klodnica River belong to "V" class of quality, the

concentration of cadmium according to EQS [5] and Polish legislation [4] should not exceed 1.5 μg/dm^3. This condition was fulfilled in all examined points.

3. Concentrations of PAHs determined for the Klodnica River and its tributaries for both measurement campaigns range as follows: anthracene from < 0.009 to 0.066 μg/dm^3, benzo[a]pyrene from < 0.003 to 0.0180 μg/dm^3, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) from < 0.0045 to 0.032 μg/dm^3, sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) from < 0.0025 to 0.0275 μg/dm^3. In most of the examined points concentrations of PAHs were on the level unabling their determination with the applied measurement method and comparing these concentrations with values of European Environment Quality Standards EQS [5] or limit values of priority substance concentrations described in the Regulation of the Minister of the Environment [4]. Only few measurement points located near collectors of mine waters from hard coal mines and points located on the inlets of sewage treatment plants operating on the Klodnica River slightly exceeded the permissible concentrations. These are: sum (benzo[b]fluoranthene and benzo[k]fluoranthene) and sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene).

4. The research confirms that there are three "hot points" [2], ie places of considerable exceedence of permissible concentrations of dangerous substances, in the Klodnica River catchment. The first of them is point K4. In this point the concentration of mercury was 0.707 μg/dm^3 in the third measurement campaign and the concentration of cadmium was 0.650 μg/dm^3 in the second measurement campaign. The next "hot point" is point D5, where mercury concentration was 0.893 μg/dm^3 in the third campaign and cadmium concentration was 0.460 μg/dm^3 in the second one. In this point also small excess of PAHs was noticed. The third "hot point" was point D10. The concentration of mercury in this point was 0.402 μg/dm^3 and cadmium concentration was 0.690 μg/dm^3.

5. Points located near inlets of sewage and outlets of treated sewage from three sewage treatment plants operating in the Klodnica River catchment were also examined. In all three cases the comparison of pollutant concentrations on inlets and outlets of sewage, both for mercury, cadmium and PAHs, showed considerable improvement of water quality on outlets of treated sewage.

6. The carried out screening research proved that in waters of serious anthropogenic changes the exceeded permissible concentrations of mercury, cadmium, sum (benzo[b]fluoranthene and benzo[k]fluoranthene) and sum (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene), defined by the European Environment Quality Standards and Polish legislation may be expected.

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ZAWARTOŚĆ WYBRANYCH SUBSTANCJI PRIORYTETOWYCH W ZLEWNI RZEKI KŁODNICY

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Abstrakt: Przedstawiono wyniki badań zawartości wybranych substancji priorytetowych w zlewni rzeki Kłodnicy. Do badań wybrane zostały dwa metale: kadm i rtęć oraz sześć związków z grupy wielopierścieniowych węglowodorów aromatycznych (WWA): antracen, benzo[a]piren, benzo[b]fluoranten, benzo[k]fluoranten, benzo[g,h,i]perylen, indeno[1,2,3-cd]piren. Rtęć oznaczana była techniką zimnych par absorpcyjnej spektrometrii atomowej (CV AAS) za pomocą analizatora RA-915$^+$ z przystawką RP-91 firmy Lumex, kadm oznaczano metodą absorpcyjnej spektrometrii atomowej z elektrotermiczną atomizacją próbki (ET AAS) za pomocą urządzenia AAnalyst 600 firmy PerkinElmer, WWA analizowano techniką wysokosprawnej chromatografii cieczowej z detekcją fluorescencyjną (HPLC–FLD), przy użyciu chromatografu cieczowego

HP 1050 firmy Hewlett Packard. Badania przeprowadzone zostały w 2008 roku, w czterech sesjach pomiarowych, z częstotliwością raz na kwartał. Łącznie we wszystkich sesjach przebadano dwadzieścia osiem punktów pomiarowych zlokalizowanych w obrębie całej zlewni rzeki Kłodnicy. Otrzymane wyniki badań porównano z dopuszczalnymi stężeniami substancji priorytetowych w wodach powierzchniowych zawartych w propozycji Unii Europejskiej dotyczących standardów jakości środowiska – Environmental Quality Standards (EQS), oraz z wymaganiami określanymi przez polskie prawodawstwo jako wartości graniczne chemicznych wskaźników jakości wód.

Słowa kluczowe: substancje priorytetowe, zlewnia rzeczna, badania screeningowe

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HEAVY METALS IN SOIL FROM COAL MINE DUMP IN GLIWICE

METALE CIĘŻKIE W GLEBIE Z HAŁDY POGÓRNICZEJ W GLIWICACH

Abstract: The aim of this work was to carry out investigation on heavy metal content: Cu, Zn, Mn, Pb, Ni, Cd and Fe in samples of soil collected from the coal mine dump in Gliwice and evaluation of their bioavailability. Each sample was subjected to sequential extraction according to Tessier's method. Five fractions were separated: I – exchangeable; II – carbonate; III – bound to Mn and Fe oxides; IV – bound to organic matter and V – residue. The content of Cu, Zn, Mn, Pb, Ni and Fe in particular fractions was analysed by atomic absorption spectrometry (AAS) with flame atomization, whereas Cd by AAS with electrothermal atomization.

On the basis of carried out experiments it was found that in examined samples of soil the contents of metals are higher than admissible values and also higher than geometric mean reported for this region. The greatest amounts of heavy metals have been found in oxide, organic and residue fractions, in forms less available for plants. Smaller amounts were determined in more available exchangeable and carbonate fractions. It is advisable to monitor such deposits as coal mine dumps, due to the potential threat for the environment.

Key words: heavy metals, sequential extraction, soil

Coal mine tailings in Gliwice, in Pszczynska street, have been deponed near the former mine and the coke plant in Gliwice. Additionally, this area is prone to dusts settlement from the coal combustion in the coke plant, as well as the products of car exhaust emissions from outlet of high street.

Heavy metals can be leached from the heaps of deponed material to surface and groundwater, and then contaminate arable soil from which they can be accumlated by plants growing on them. In this way they can be hazardous also to people.

Heavy metals in trace amounts are necessary for proper functioning of life forms, participating in many important metabolic processes, but both their excess and deficiency can turn out to be toxic, therefore monitoring their concentration in the environment is important. Heavy metals can be accumulated in different organs of alive

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organisms but effects of their action can appear after many years. Their presence causes the enzymatic disorders the most often. Damaging the root system, slowing down the growth of plants, appearance of chlorosis and necrosis are the most frequent symptoms of heavy metals contamination. In the forest soil heavy metals are accumulated mostly in the forest litter, and in the arable soil mostly in humus layer [1, 2].

Materials and methods

Sampling of soils

5 soil samples were collected from the Gliwice dump: 3 samples were taken from the side of the former coke plant (samples No. 3, 4 and 5), and 2 samples were taken from the other side of the dump, eg from the side of Pszczynska street (samples No. 1 and 2). For comparison of results two samples were collected from the allotment in the center

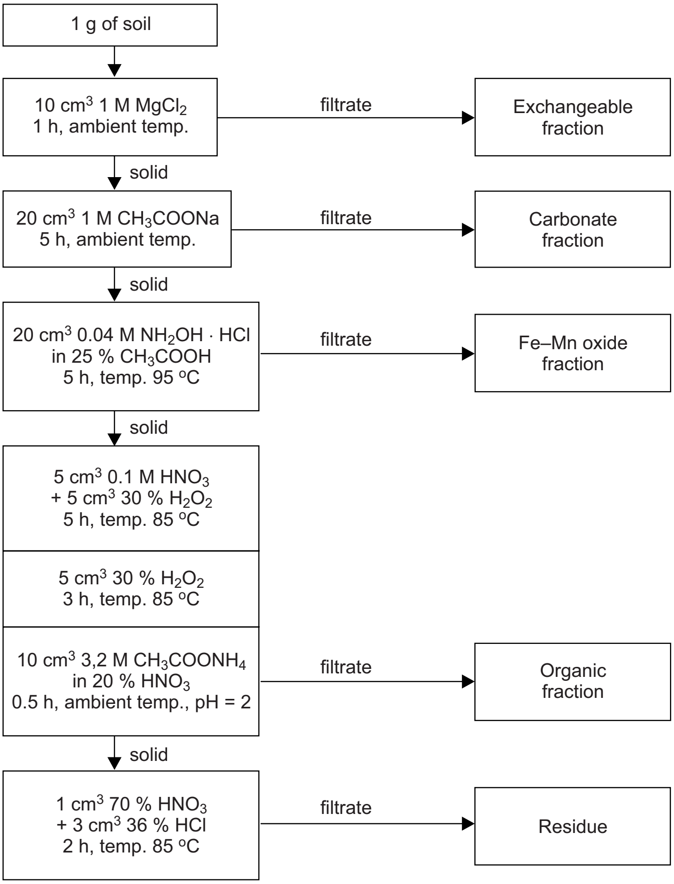

Fig. 1. Flow diagram of the Tessier’s method of sequential extraction of heavy metals from the soil [3]

of Gliwice (sample No. 6) and from the unpolluted area near Zawada village in the Małopolskie province (sample No. 7).

Methods of analysis

Dried off to the state air dry the samples of soils (< 0.75 mm) were subjected to Tessier's method of the sequential extraction. Applied procedure and used reagents are described in Fig. 1. For each sample six replicates have been analysed. Content of Cu, Zn, Mn, Pb, Ni and Fe in each fraction have been determined using the FAAS spectrometer, Carl Zeiss Jena while Cd by the ETAAS technique. Additionally a pH of each soil solution was determined according to the Polish Standard PN-ISO 10390:1997.

Results and discussion

Content of metals in each fraction of sequential extraction of soil samples has been gathered in Table 1. Percentage of individual metals in fractions of the examined soil samples has been shown in Fig. 2–8, whereas in Table 2 total contents of determined metals, being a sum of values obtained for each fraction and the pH of the corresponding soil solutions have been presented.

On the basis of carried out analyses, it was found that copper in examined samples is present mainly in the forms associated with organic matter. Amounts below limit of detection of analytical technique were observed in the exchangeable fraction while in the carbonate fraction small amounts of copper were found. In four samples collected from the dump the amount of copper was higher than the natural level (according to IUNG, Pulawy) and the threshold limit values (according to the Dutch List) [4]. In the soil from the side of the former coke plant the obtained values were even 1.5–2 times higher than in the samples collected from the side of Pszczynska street.

Contents of zinc distribute relatively evenly among four last fractions, but the contribution of this element into the oxide fraction is the greatest. The content of zinc in other fractions of soils varies among samples. Small amounts of zinc were found in the exchangeable fraction. Two last fractions obtained from soil samples from the side of coke plant contained much higher amount of Zn than other samples. In all samples of soil from the dump the contents of zinc were higher than the natural level (according to IUNG) and exceeded threshold limit values (in soil 4 and 5 even twice) (according to the Dutch List).

In the examined soil the greatest amount of manganese appeared in the oxide and carbonate fraction, constituting essentially about 80 % of the total content. The smallest amounts of manganese were found in the exchangeable fraction. In the soil samples collected from the side of the coke plant the content of Mn was about 1.5 times greater than in the samples collected from the side of Pszczynska street.

It was found that the content of lead in particular fractions differed considerably for each sample. Significant amount of Pb was found mainly in organic fraction (except samples No. 5 and 6) and in residue (the greatest amount in the sample No. 5).

Table 1

Content of metals in each fraction of sequential extraction of soil samples

Soil	Fraction	Mean value ± SD [µg/g] n = 6						
		Cu	Zn	Mn	Pb	Ni	Cd	Fe
1	Exchangeable	< 0.4	3.74 ± 0.27	3.71 ± 0.16	4.10 ± 0.23	6.80 ± 0.09	—	8.42 ± 0.17
	Carbonate	5.43 ± 0.41	45.09 ± 0.99	81.40 ± 2.77	< 4	14.80 ± 0.31	$(0.39 \pm 0.04) \cdot 10^{-1}$	63.75 ± 1.48
	Oxide	10.47 ± 0.40	57.78 ± 1.95	142.83 ± 2.52	< 4	9.75 ± 0.49	0.88 ± 0.10	3588 ± 70
	Organic	22.95 ± 2.23	16.65 ± 0.79	13.04 ± 0.61	17.93 ± 1.38	3.64 ± 0.35	$(0.46 \pm 0.05) \cdot 10^{-1}$	1276 ± 63
	Residue	7.59 ± 0.68	30.79 ± 0.82	33.55 ± 1.91	8.24 ± 0.22	6.71 ± 0.46	0.26 ± 0.03	12530 ± 637
2	Exchangeable	< 0.4	6.80 ± 0.16	6.05 ± 0.04	11.05 ± 0.57	< 0.4	—	8.41 ± 0.11
	Carbonate	< 0.8	77.20 ± 1.75	114.59 ± 3.32	12.39 ± 1.02	3.80 ± 0.22	$(0.43 \pm 0.02) \cdot 10^{-1}$	76.43 ± 4.22
	Oxide	< 0.8	88.82 ± 2.42	148.77 ± 8.88	< 4	7.34 ± 0.19	1.29 ± 0.13	2616 ± 58
	Organic	22.16 ± 0.75	32.79 ± 1.62	11.72 ± 0.30	13.40 ± 0.89	1.45 ± 0.07	$(0.95 \pm 0.05) \cdot 10^{-1}$	991 ± 14
	Residue	7.65 ± 0.26	39.48 ± 1.81	41.39 ± 1.76	3.29 ± 0.23	13.87 ± 0.30	2.12 ± 0.05	8442 ± 401
3	Exchangeable	< 0.4	5.66 ± 0.19	5.79 ± 0.07	3.54 ± 0.10	< 0.4	—	9.15 ± 0.17
	Carbonate	1.39 ± 0.04	3.64 ± 0.33	12.62 ± 1.20	< 4	6.48 ± 0.30	$< 0.08 \cdot 10^{-1}$	16.54 ± 0.47
	Oxide	< 0.8	78.84 ± 1.34	266.50 ± 3.09	15.02 ± 1.29	12.28 ± 0.24	1.63 ± 0.14	3762 ± 60
	Organic	54.93 ± 2.41	108.79 ± 1.66	87.71 ± 1.12	47.76 ± 2.40	18.42 ± 0.99	0.24 ± 0.01	15659 ± 554
	Residue	6.08 ± 0.13	29.93 ± 1.14	20.45 ± 1.02	3.74 ± 0.17	12.39 ± 0.61	0.79 ± 0.12	6611 ± 301
4	Exchangeable	< 0.4	5.34 ± 0.25	4.82 ± 0.08	13.22 ± 0.18	< 0.4	—	4.38 ± 0.17
	Carbonate	4.51 ± 0.20	35.67 ± 1.41	176.57 ± 3.13	8.87 ± 0.44	4.46 ± 0.16	$(0.36 \pm 0.04) \cdot 10^{-1}$	260 ± 14
	Oxide	1.24 ± 0.05	88.02 ± 1.39	209.30 ± 4.74	37.31 ± 1.04	10.58 ± 0.32	0.84 ± 0.08	3535 ± 57
	Organic	37.29 ± 0.61	56.91 ± 1.64	20.19 ± 0.59	32.68 ± 0.60	5.39 ± 0.25	0.47 ± 0.01	2871 ± 38
	Residue	13.96 ± 0.30	96.01 ± 3.38	56.47 ± 0.91	24.09 ± 0.55	16.26 ± 0.27	1.27 ± 0.04	11923 ± 271

Table 1 contd.

Soil	Fraction	Mean value ± SD [μg/g] n = 6						
		Cu	Zn	Mn	Pb	Ni	Cd	Fe
5	Exchangeable	< 0.4	3.01 ± 0.14	5.78 ± 0.27	8.69 ± 0.45	< 0.4	—	7.97 ± 0.26
	Carbonate	3.95 ± 0.13	49.86 ± 2.46	180.23 ± 8.23	8.41 ± 0.52	2.83 ± 0.12	$(0.30 \pm 0.02) \cdot 10^{-1}$	373 ± 36.7
	Oxide	2.84 ± 0.04	74.62 ± 2.12	189.75 ± 7.37	6.16 ± 0.23	9.08 ± 0.32	1.42 ± 0.08	3044 ± 72
	Organic	35.37 ± 0.85	59.30 ± 2.97	26.62 ± 1.14	5.61 ± 0.45	4.40 ± 0.20	0.26 ± 0.01	2710 ± 188
	Residue	13.35 ± 0.60	108.67 ± 1.74	66.02 ± 1.17	30.06 ± 1.19	16.60 ± 0.23	0.83 ± 0.03	14018 ± 144
6	Exchangeable	< 0.4	22.92 ± 0.98	34.98 ± 0.46	10.80 ± 0.28	6.40 ± 0.24	—	8.52 ± 0.41
	Carbonate	2.40 ± 0.14	10.57 ± 0.50	15.91 ± 1.19	< 4	13.16 ± 0.25	$(0.52 \pm 0.05) \cdot 10^{-1}$	21.47 ± 1.06
	Oxide	< 0.8	25.04 ± 1.18	144.18 ± 6.01	< 4	4.98 ± 0.22	1.27 ± 0.04	1274 ± 23
	Organic	< 0.8	14.88 ± 0.67	25.25 ± 1.17	< 4	8.07 ± 0.36	$(0.54 \pm 0.05) \cdot 10^{-1}$	1388 ± 50
	Residue	0.68 ± 0.03	7.07 ± 0.35	15.45 ± 1.10	< 2	2.86 ± 0.14	$(0.31 \pm 0.02) \cdot 10^{-1}$	931 ± 40
7	Exchangeable	< 0.4	3.60 ± 0.19	7.27 ± 0.17	4.92 ± 0.24	< 0.4	—	6.15 ± 0.14
	Carbonate	2.56 ± 0.15	21.59 ± 0.57	130.31 ± 2.32	4.27 ± 0.29	< 0.8	$(0.11 \pm 0.02) \cdot 10^{-1}$	32.40 ± 1.03
	Oxide	1.82 ± 0.08	41.40 ± 0.93	212.65 ± 4.66	< 4	5.03 ± 0.18	0.70 ± 0.05	1422 ± 36
	Organic	18.56 ± 0.91	19.34 ± 0.63	10.59 ± 0.44	15.17 ± 1.00	< 0.8	0.23 ± 0.01	1015 ± 37
	Residue	4.30 ± 0.12	19.81 ± 0.33	34.13 ± 1.09	5.47 ± 0.30	10.10 ± 0.40	$(0.47 \pm 0.04) \cdot 10^{-1}$	4709 ± 119

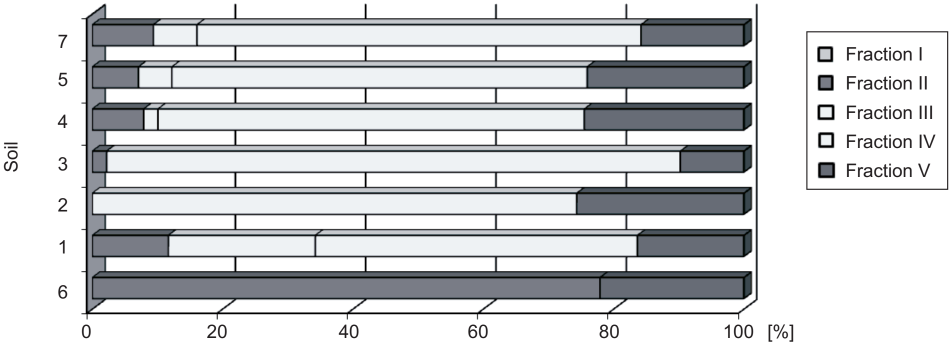

Fig. 2. Percentage of copper in fractions for every soil

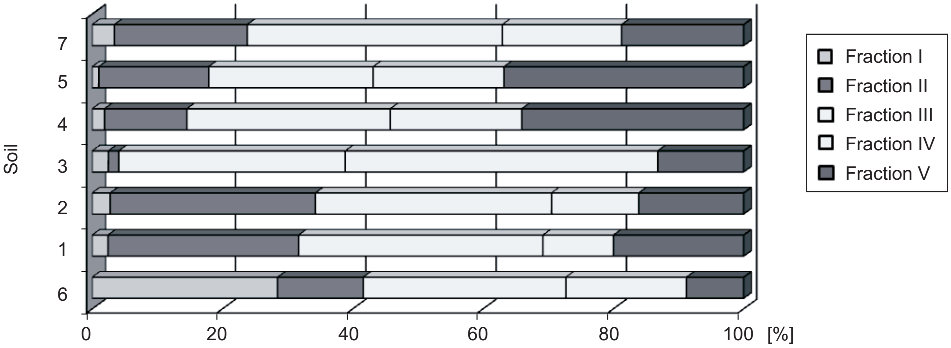

Fig. 3. Percentage of zinc in fractions for every soil

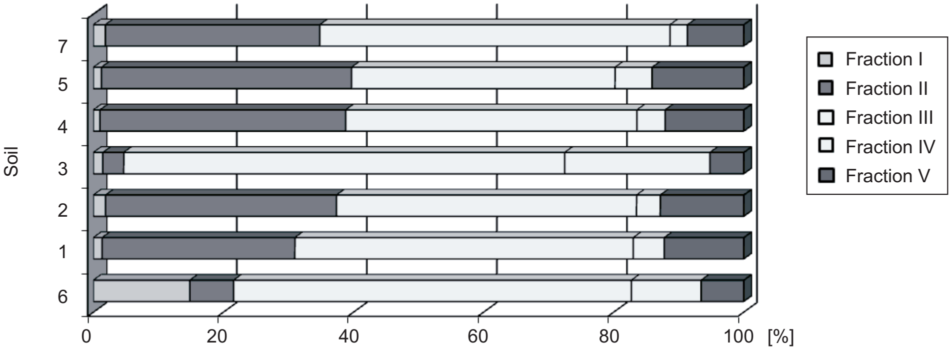

Fig. 4. Percentage of manganese in fractions for every soil

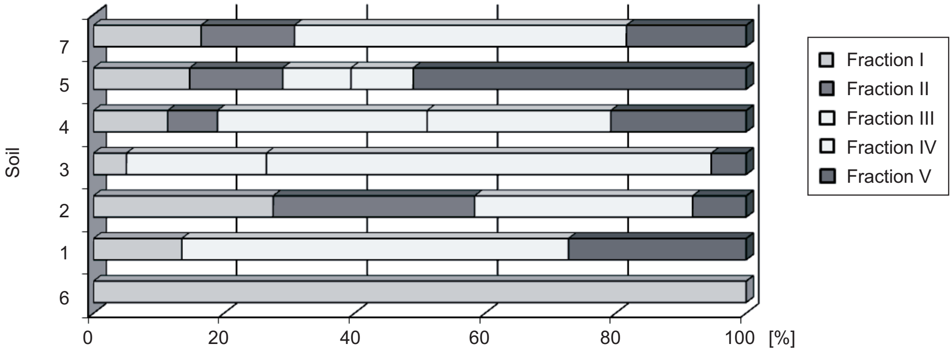

Fig. 5. Percentage of lead in fractions for every soil

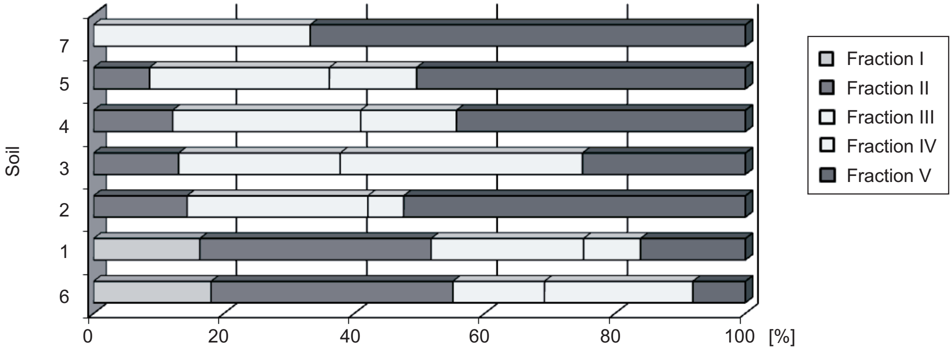

Fig. 6. Percentage of nickel in fractions for every soil

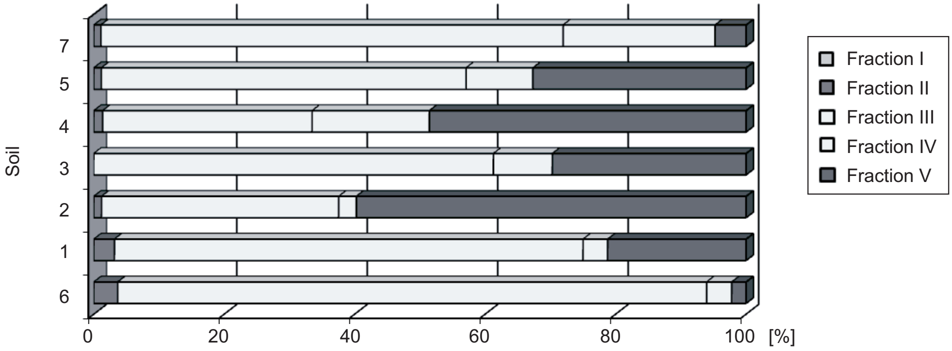

Fig. 7. Percentage of cadmium in fractions for every soil

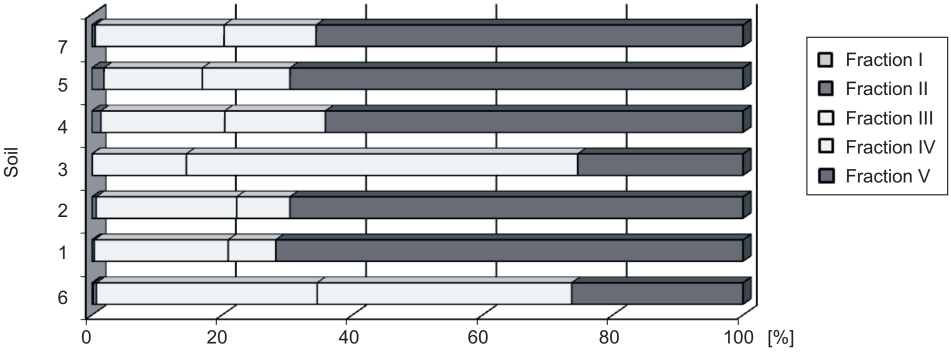

Fig. 8. Percentage of iron in fractions for every soil

Relatively great amount of lead is found in exchangeable fraction. In the samples No. 3 and 4 the content of lead was higher than the natural level (according to IUNG), and in the sample No. 4 an admissible amount was also exceeded (according to the Dutch List).

Table 2

Total content of heavy metals in μg/g of the soil in all examined fractions and corresponding pH values

Soil	Element [μg/g]							pH
	Cu	Zn	Mn	Pb	Ni	Cd	Fe	
1	46.44	154.05	274.53	30.27	41.70	1.23	17466	5.5
2	29.81	245.09	322.52	40.13	26.46	3.55	12133	5.0
3	62.40	226.86	393.07	70.06	49.57	2.66	26058	5.3
4	57.00	281.95	467.33	116.17	36.69	2.62	18593	5.5
5	55.51	295.46	468.40	58.93	32.91	2.54	20153	5.2
6	3.08	80.48	235.77	10.80	35.47	1.41	3551	3.5
7	27.24	105.74	394.95	29.33	15.13	0.99	7185	4

In examined soil samples nickel was found mainly in the oxide fraction, organic fraction and residue. Significant amounts were analysed also in the carbonate fraction. In the samples No. 1 and 6 the great amount of nickel was found also in the exchangeable fraction, what perhaps is connected with the presence of manganese which causes immobilization of nickel in the soil [4]. All examined samples of the soil had the natural content of nickel.

The greatest amount of cadmium was found in the oxide fraction and in the residue. Small amounts are observed in the organic fraction, and trace amounts in the carbonate fraction. The cadmium content in the exchangeable fraction was not analysed due to the interferences coming from $MgCl_2$ presence. In all soil samples from the dump, cadmium contents were higher than the natural level (according to IUNG) and exceeded the thresholds limit values (in soil 2, 3, 4 and 5 even 3–4 times) (according to the Dutch List and PIOŚ [Polish State Inspectorate of Environmental Protection]).

It results from conducted experiments that about 60 % of total content of leachable iron is present in residue (except sample 3 and 6), the rest part of iron was found in the oxide fraction and smaller amount associated with organic matter. Much lower amounts of iron were analysed in carbonate and exchangeable fractions. The content of iron in the soil from the side of the coke plant is about two times higher than in samples from the side of Pszczynska street.

Conclusions

The content of analysed elements in all examined samples of the soils varies significantly but obtained results are within the range of concentrations published for the soils coming from Poland and the Silesia province. It is worth underlying that the total amounts of analysed elements are higher than the geometric mean for Silesia. The sum of the content of elements in four fractions the most easily accessible for plants, for samples coming from the dump is 4–5 times higher than average values for Silesia for copper, 2 times higher than average for zinc, up to 2 times higher for lead, over 2 times higher for nickel and about 2 times higher for cadmium [6].

Samples collected from the side of the coke plant contained greater amount of iron (2–5 ×), copper (more than 2 ×), manganese (1.5 × or more), lead (more than 2 ×x) and cadmium a little bit more. Amounts of remaining elements: of zinc and nickel were similar in samples collected on both sides of the dump.

Comparing the results with those obtained for samples collected from the allotment in Gliwice and from the unpolluted area from Malopolska province, it was found that the content of iron was 3 times smaller, zinc over 2 times smaller, copper about 4 times smaller. The content of remaining elements did not differ markedly from their content in the soil from the dump. It is noticeable that content of zinc and the manganese in exchangeable fraction in the soil No. 6 (from allotment) was 5 times grater than in other samples, what can correlate with fertilizing this soil and its acidity.

High contents of heavy metals in samples of the soil coming from the dump in Gliwice show the constant need for monitoring of their amount, due to the possible leaching of elements to groundwater, uptake by plants, being the part of the food chain, at the end of which is the human being.

It seams to be advantageous to protect area adjacent to the dump by planting hyper accumulating plants or trees which can be used for fitoremediation of contaminated areas.

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METALE CIĘŻKIE W GLEBIE Z HAŁDY POGÓRNICZEJ W GLIWICACH

Katedra Chemii Analitycznej
Politechnika Śląska

Abstrakt: Celem pracy było zbadanie zawartości metali ciężkich: Cu, Zn, Mn, Pb, Ni, Cd i Fe w próbkach gleby z hałdy w Gliwicach oraz określenia ich biodostępności. Dla każdej próbki gleb przeprowadzono frakcjonowanie sekwencyjne metodą Tessiera, podczas której zostaje wydzielonych 5 frakcji metali: frakcji I wymiennej, frakcji II związanych z węglanami, frakcji III związanych z tlenkami, frakcji IV związanych z materią organiczną oraz frakcji V pozostałości. Zawartość Cu, Zn, Mn, Pb, Ni i Fe w poszczególnych frakcjach oznaczono za pomocą absorpcyjnej spektrometrii atomowej z atomizacją w płomieniu, a zawartość kadmu za pomocą absorpcyjnej spektrometrii atomowej z elektrotermiczną atomizacją.

Z przeprowadzonych badań wynika, że w badanej glebie znajdują się duże zawartości oznaczanych metali, często większe niż dopuszczalne, oraz większe od średnich geometrycznych dla tego terenu. Największe ilości metali ciężkich występują we frakcji tlenkowej, organicznej i w pozostałości, a więc w formach mało dostępnych dla roślin. Małe ilości występują w formach biodostępnych czyli we frakcji wymiennej i węglanowej. Pomimo to monitoring takich miejsc powinien być prowadzony, gdyż stanowią one potencjalne zagrożenie ekologiczne.

Słowa kluczowe: metale ciężkie, ekstrakcja sekwencyjna, gleba

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EXPERIMENTAL INVESTIGATIONS OF LARGE-SCALE SOLAR COLLECTOR INSTALLATIONS IN AN INHABITED CLOISTER: A 6-YEAR CASE STUDY

BADANIA EKSPERYMENTALNE WIELKOSKALOWEJ INSTALACJI KOLEKTORÓW SŁONECZNYCH W KLASZTORZE – 6-LETNIE STUDIUM PRZYPADKU

Abstract: In consideration of limited fossil fuel resources and the prevention of pollutant emissions heating installations are preferred which use renewable energy sources. One such solution involves hot water preparation for large buildings using solar collectors. In this work, the results of a six year experimental investigation of a large-scale system of solar flat collectors are introduced. These collectors are located on the roof of a Cloister of Redemptorists in Tuchow, Poland. On average, the installed collectors covered 37 % of the annual thermal requirement for hot water; for the winter half-year 15.9 % and for the summer half-year 56.5 %. The costs of the hot water preparation in the installation with and without collectors were analysed. The Simple Pay Back Time of investment cost was calculated. Special attention was paid to factors which influence the coverage of thermal needs by the solar installation. The reduction in pollutant emissions from combustion of natural gas resulting from the use of solar collectors, was also calculated.

Keywords: cloister, solar thermal systems, large-scale collector system, hot water preparation.

In the face of exhaustible conventional energy resources and the consequences of fossil fuel combustion more and more often renewable energy sources are being promoted. In fact, they are among the most suitable instruments to solve these problems [1]. One such solution is the installation of solar collector systems supporting heating or hot water preparation; the prices of such units has fallen gradually over the last 30 years, while the prices of oil and gas fluctuate incessantly [2]. Much research has already been carried out on both small and large-scale solar [3–5] installations [6,7]. However, new findings and analyses are constantly necessary, both in relation to solar radiation, analysed recently in [8, 9], methods of defining the solar energy potential for

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hot water production in a selected area [10]. Further, the education and training of specialists, able to design, install and service such systems is also crucial to the success of such ventures – a point also made in [11]. On this score alone it is important that future specialists understand the minutiae of existing installations obtained on the basis of experimental research [12]. Therefore, the aim of this work was to demonstrate the long term operation of a large-scale solar collector installation sited in a specific building. The building selected was the world famous Cloister of Redemptorists in Tuchow, Poland.

Material and methods

Research was carried out in the Cloister of Redemptorists in Tuchow, Poland, where a large-scale solar collector installation for hot water preparation has been implemented. The installation was completed in 2001. It was planned for the preparation of hot water of about 45 ^{o}C. The individual demand for hot water can reach 70 dm^3 per day and person. Flat solar collector panels (70 pieces; total surface area of 127 m^2) were applied in the installation. Collectors were installed on two roof surfaces, as two independent batteries. The first battery of collectors was oriented toward the South-East and inclined to the ground plane at an angle of 60^{o}. The second one is directed South and inclined to the ground plane at the angle of 45 ^{o}C (Fig. 1).

Fig. 1. South oriented solar collectors on a roof at the Cloister of Redemptorists, Tuchow, Poland

In this case collectors prepare the hot water bivalently, requiring support from a gas boiler (power: 90 kW). This boiler was put into action during periods of insufficient solar radiation. Hot water generated by the system (Fig. 2) was transferred to accumulation tanks (total capacity ca 8.000 dm^3).

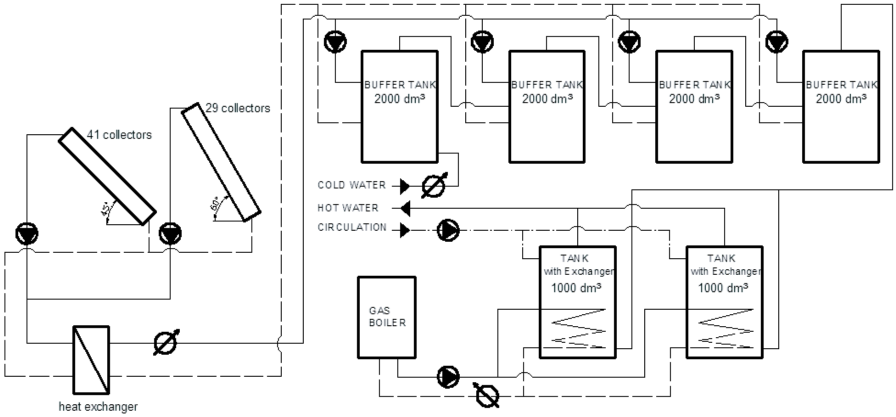

Fig. 2. Scheme of the solar installation at the Cloister of Redemptorists in Tuchow

Measurements were performed everyday at ca 21.45 from November 2001 to November 2007 and included, among other parameters, the following:

– the hot water consumption in m^3;

– the amount of energy (GJ) delivered to the hot water preparation system by the gas boiler.

– the amount of energy (GJ) delivered to the hot water preparation by the solar collectors;

– the amount of energy (GJ) lost during the circulation of hot water in the building.

In consideration of the vast amount of data collected, mean values were used in the further analysis.

Results and discussion

Solar energy in the total energy on hot water preparation

The solar panel installation used in bivalent model for hot water preparation reduces the total energy consumption, delivered from conventional sources. This can be expressed for the individual years of the measuring period by the ratio of the heat delivered from collectors to the total heat used for hot water preparation in % (Fig. 3).

On the basis of Figure 3, it is easily seen that, in the large-scale system using solar collectors for hot water preparation, the *contribution of solar collectors* (SPT) is in the range 24.2–47.8 %. For this reason, it is not easy to establish a mean annual level of the contribution of solar collectors over extended periods. Their dependence on ambient weather conditions, particularly the insolation, thwarts such calculations. In Fig. 3, the average daily hot water consumption in the analysed installation is also presented. Clearly no great influence on SPT on an annual scale is evident.

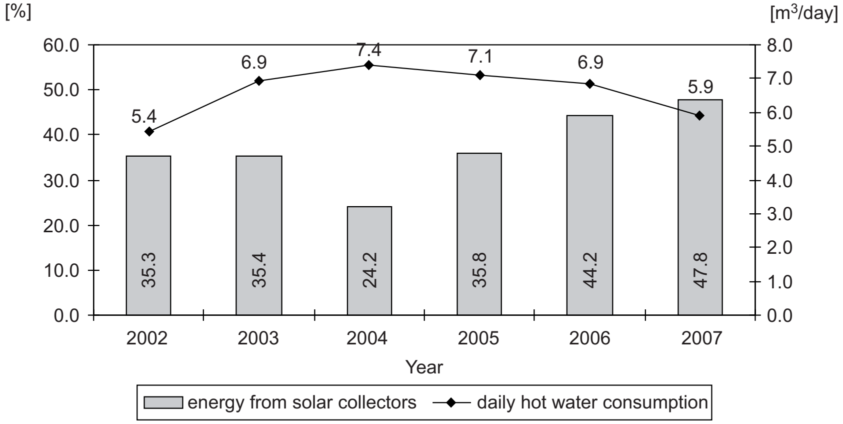

Fig. 3. The average annual level of coverage of thermal needs for hot water preparation by solar collectors for the measuring period (November 2001 to November 2007)

Another factor which did have an influence on SPT on an annual scale was the amount of energy required for the preparation of 1 m^3 of hot water, (see Fig. 4.).

Figure 4 shows that the amount of energy for hot water preparation declines – this has a considerable influence on the value of the SPT indicator.

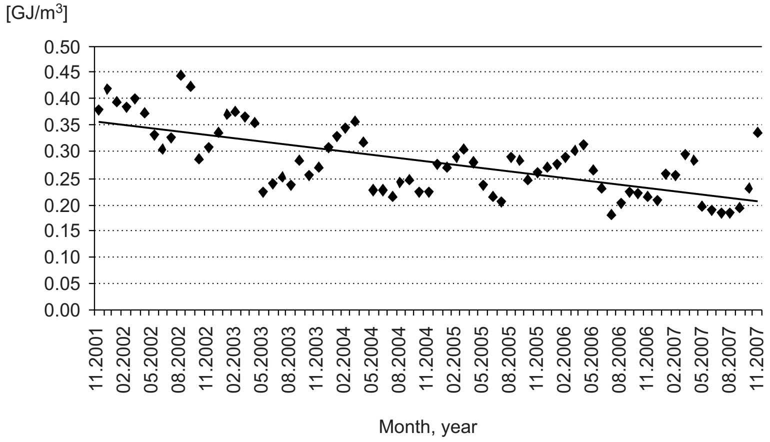

Fig. 4. The coefficient of the heat demand for the preparation of $1m^3$ of hot water in the measuring period November 2001 – November 2007

This decrease in energy consumption resulted from renovation of the thermal isolation of the distribution and hot water circulation pipes. Besides, the required or given temperature on the outflow at the recipient has an influence on the energy required for preparation $1m^3$ of hot water. The smaller the required temperature, the larger the SPT indicator.

To facilitate a more detailed analysis, Fig. 5 provides seasonal data on the system. The summer season is defined as the three months June, July and August. The

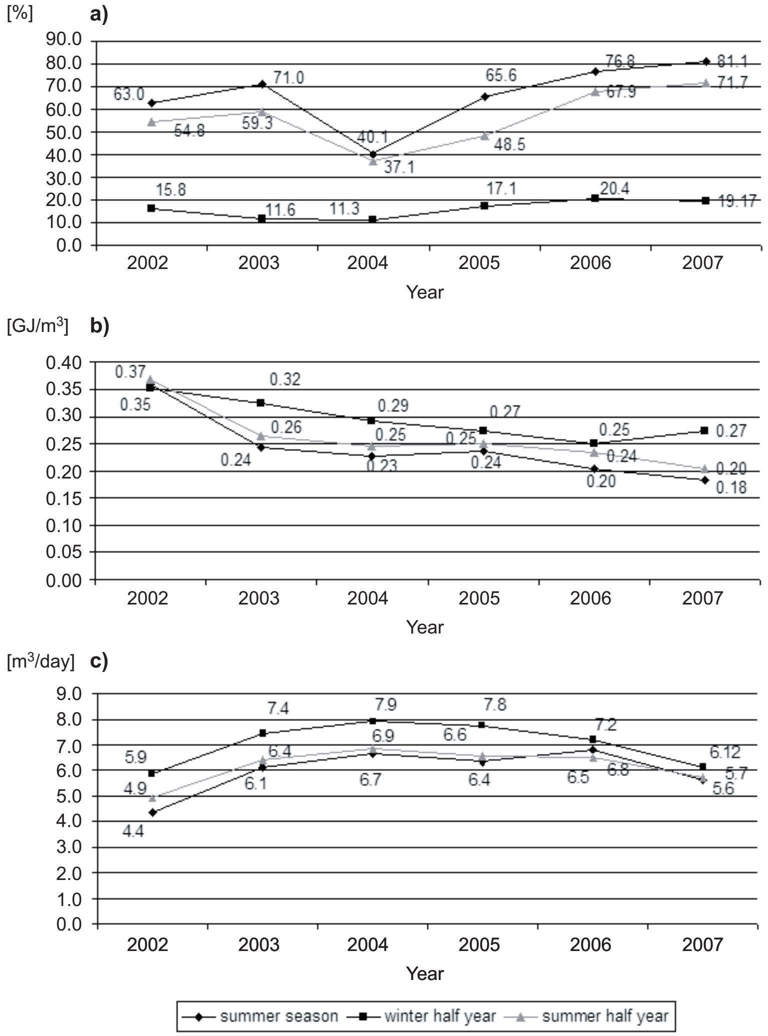

Fig. 5. Characteristics of the investigated installation in the summer and the winter and the summer half-years: a) SPT; b) the coefficient of the energy consumption for the preparation of 1 m^3 hot water; c) the average daily hot water requirement

winter-half-year is the period from October to January, and the summer-half-year lasts from April to September.

The SPT coefficient reaches 66.25 % in summer season and is > ca 9.7 % of the SPT for the summer half-year and ca. 50.34 % in comparison with the winter half-year. For the winter half-year, the SPT coefficient assumed the equal mean value of 15.91 %, which indicates that supporting hot water preparation by the solar collectors in the winter half-year, exists. It was also noted that the value of the coefficient of required heat quantity for hot water preparation was greatest in the winter-half-year amounting to

0.29 GJ/m^3. This is caused, among other things, by enlarged heat losses in the circulation of hot water and increased demand on useful hot water in the winter half-year (Fig. 5c).

It should also be noted that on occasions in which the large-scale installation is able to cover thermal needs of the hot water preparation to a greater degree (the summer season), this demand on hot water drops. This is very important at the design stage as it determines whether a hot water installation design will work at maximum efficiency or lower. This problem often appears in schools or higher colleges, which are closed in summer and in multi-family buildings, where a fall of the hot water consumption can be observed during holidays due to the absence of residents. In the analysed object, the above case was observed in August (Fig. 6), when the average daily hot water consumption fell to 4.2 m^3 per day, because in this period a large number of the occupants left the cloister.

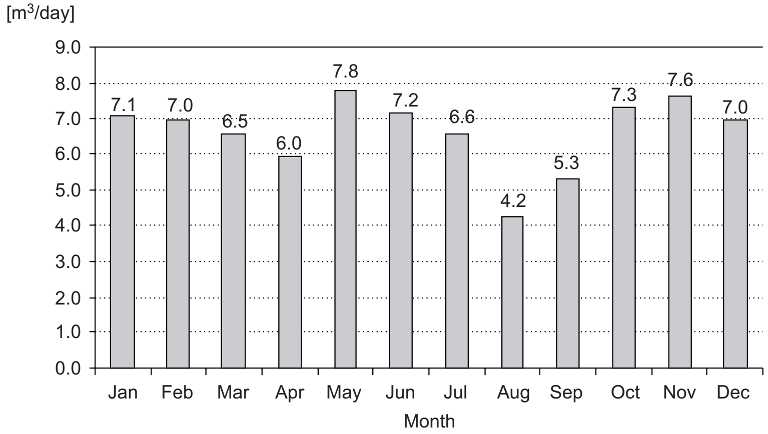

Fig. 6. Average daily hot water consumption during the months of the measuring period

The SPT for individual months of the measuring period together with the monthly average number of solar hours are shown in Fig. 7. August is characterized by the highest average SPT coefficient (75.5 %) in the analyzed period of six years and January, the least (6.9 %).

Such diversity in the values of the SPT is not only a result of weather conditions eg the number of solar hours per month, but also heat losses due to circulation of hot water as presented in Fig. 8. Situations like this occur because the greater heat loss and the greater is the required water temperature on the outflow from the storage tank. This results in a reduction of SPT, which is especially notable for the months of the winter-half-year.

It should be remembered that in using solar collectors to the hot water preparation, it is necessary to be aware that, although the average level of coverage for a given month may be high, days can occur in which thermal requirements can only be covered by the conventional source. For our installation this is shown in Fig. 9.

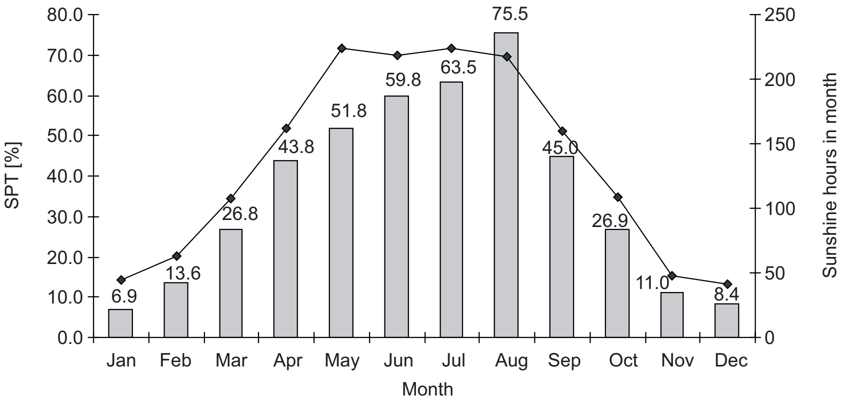

Fig. 7. The SPT coefficient during the months of the measuring period

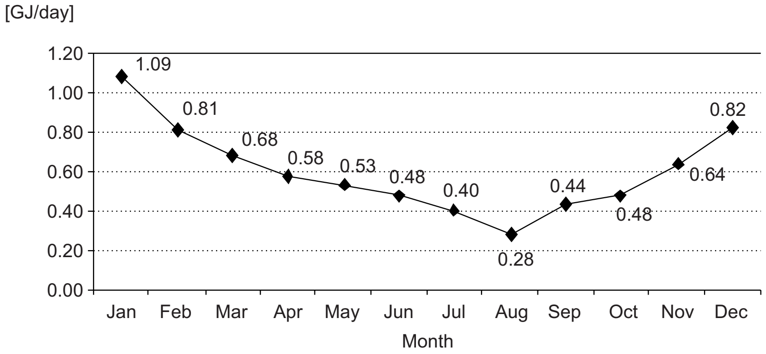

Fig. 8. Average daily heat losses in circulation during the measuring period

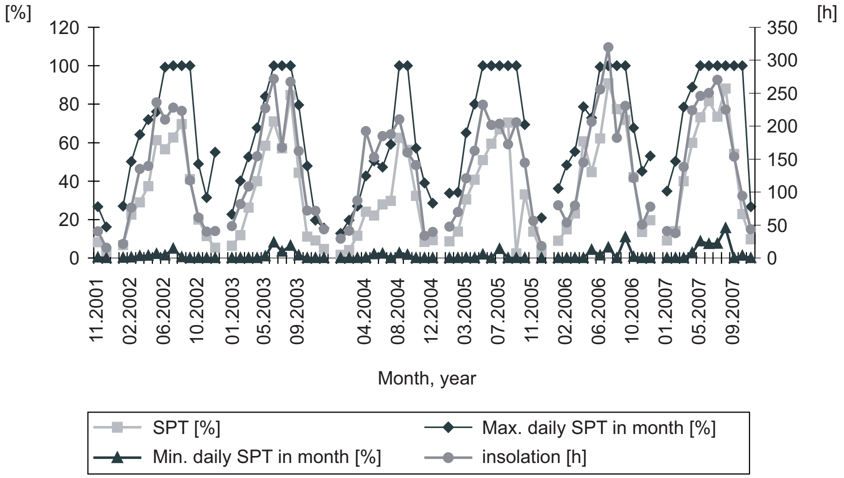

Fig. 9. The average, maximum and minimum daily SPT coefficient during a measuring period together with average monthly insolation

Therefore it is essential to examine the deviations of the average value of the SPT coefficient in Fig. 10. The deviation values of the mean value were calculated by Equations 1 and 2.

$$\sigma = [(1/(n-1)\cdot \Sigma (d_i - d_{śr})^2]^{0.5} \tag{1}$$

$$\sigma_{śr} = \sigma / n^{-2} \tag{2}$$

where: n – is the number of measurements used in the statistical analysis; d_i – the value of i-measurement; $d_{śr}$ – the mean value from measurements taken for the statistical analysis.

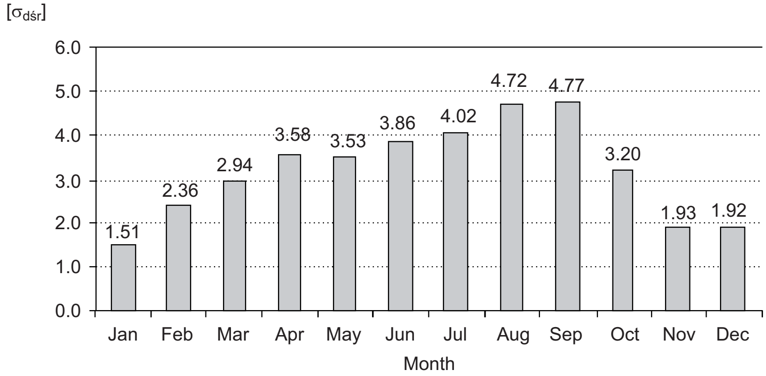

Fig. 10. Values of the deviation from the mean value during the months of the measuring period

Figure 10 shows that the installation was most stable in January, because the value of the deviation from the mean value assumed the value of 1.51. The installation worked was least stable in September, when this deviation from the average value amounted to 4.77, while the average for the measuring period reached 3.19.

Economic and environmental advantages

Investors who decide to purchase solar collectors for hot water preparation hope, among other things, they will save money. Such savings could be noticed when analyzing the cost of hot water preparation in an installation equipped with solar collectors and without them. The data for the cloister are shown in Fig. 11. The cost of hot water preparation in the installation with solar collectors is lower when energy is delivered from collectors, than if it had to be produced from conventional energy. We estimated the savings (S) obtained from the lower natural gas consumption using formulas (3) and (4).

$$V = Q/(Wg \cdot \eta) \tag{3}$$

where: V – the quantity of saved natural gas in m^3; Q – the quantity of heat saved thanks to solar collectors in MJ; Wg – the heat value of natural gas, equal Wg = 31 MJ/m^3; η – the efficiency of gas boiler, whose power amounted to 90 kW, $\eta = 0.7$.

$$S = V \cdot K \tag{4}$$

where: K – the cost of natural gas, K = 0.32 euro/m^3.

From Figure 11 it can be seen that the cost of hot water preparation in the installation with solar collectors is on average about 1.84 times smaller than the cost of hot water preparation using only the gas boiler. The greatest difference in costs is in the summer months the cost is ca 2.98 times less in the case of the solar collector installation.

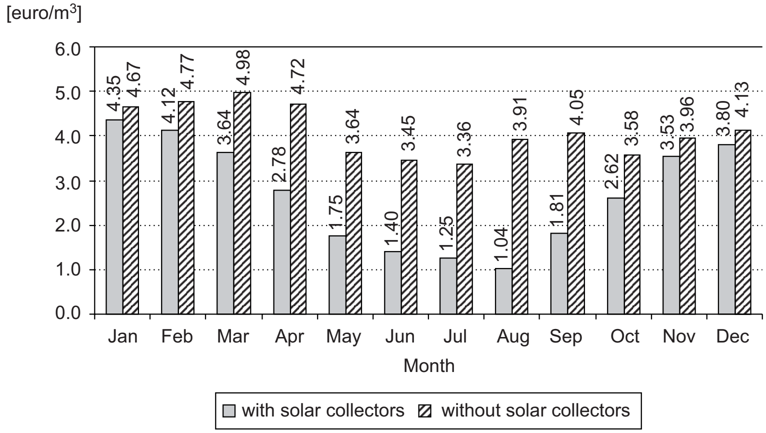

Fig. 11. Installations with and without solar collectors: comparison of monthly costs of preparation of 1 m^3 of hot water during the months of the measurement campaign

In the case of solar collectors it is important, especially for investors, that the installation costs amortize as soon as possible. Therefore, we calculated the Simple Pay Back Time – (SPBT) for our installation, using the Equation 5.

$$SPBT = N/S_a, \text{ years} \tag{5}$$

where: N – the investment costs in euro; S_a – the sum of annual savings with relation to the reference case in euro/per year.

The investment costs for the modernization of the complete hot water installation including the boiler room amounted to 113,902 euro and the average savings of conventional fuel, resulting from use of solar energy were 3155 euro/per year. However, the cost of the solar installation (including instrumentation) amounted to 65,853 euro, yielding an SPBT value of 20.9 years. Additionally the average rise in energy prices during the campaign time was taken as 8 % per year. Taking these facts into account the SPBT will then amount to almost 7 years. Moreover, the investment was refinanced at a rate of 87 %, therefore only 13 % of the total investment sum was actually paid by the

Cloister. For this case, resources invested by the Cloister into the entire modernization of the installation of the hot water and the boiler room (113,902 euro) were returned only 4.7 years after the completion of the installation. It should be pointed out that the solar energy – friendly policy in the country in the form of grants, tax concessions and similar are, and will be, very important in encouraging wider acceptance of solar installations, a view also shared by [13, 14].

Another point worth mentioning in the estimation of SPBT is that additional costs arising from, for example environmental remediation or the costs of pollution-related illnesses to society as a whole were not considered. The use of solar collectors can also result in the diminution of the pollutant emissions to the atmosphere [15–17]. The amount of pollutants avoided by delivering energy for hot water preparation from the solar collectors instead of from the gas boiler is presented in Table 1.

Table 1

A comparison of the annual amount of gas saved [m^3] and resulting abatement in pollutant emission for the installation at Tuchow, Poland

Year	Saved gas	Emission [kg/a]			
		NO_2	CO	CO_2	Dust
2002	11 004	14.1	4.0	21 611.2	0.2
2003	10 470	13.4	3.8	20 563.2	0.2
2004	6 871	8.8	2.5	13 494.6	0.1
2005	10 546	13.5	3.8	20 712.5	0.2
2006	11 136	14.3	4.0	21 871.0	0.2
2007	9 136	11.7	3.3	17 943.9	0.1

Conclusions

Analysis of six years of operational data from the large-scale solar collector installation in the Cloister of Redemptorists at Tuchow showed that the use of solar collectors could cover 37 % of the annual thermal needs for hot water preparation. August provided the greatest coverage level amounting to 75.5 %. August was also the month in which the highest financial savings were evident. At that time 1 m^3 of solar generated hot water cost 3.78 times less than that supplied by the gas boiler.

The feasibility of supporting the preparation of hot water by solar collectors even during the winter period when their contribution was only 15.91 %, was also demonstrated.

For large installations with solar collectors, the Simple Pay Back Time (20.9 years) of the investment is not particularly encouraging. However, taking the increase in fuel price as 8 % per year, the SPBT lowered to 7 years. Moreover, when dealing with large installations for which financial support allowing the inclusion of the investment costs into the total modernization of the hot water installation (including boiler room) is available, the SPBT reduces to 7 years.

Installations using solar collectors for hot water preparation not only generate financial savings, but also play an important part in improving the environment. Thus, they may provide an alternative to existing conventional installations for hot water preparation especially in the light of the global moves to reduce emissions of greenhouse gases to the atmosphere.

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BADANIA EKSPERYMENTALNE WIELKOSKALOWEJ INSTALACJI KOLEKTORÓW SŁONECZNYCH W KLASZTORZE – 6-LETNIE STUDIUM PRZYPADKU

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Abstrakt: W obecnych czasach preferuje się rozwiązania instalacji grzewczych wykorzystujących odnawialne źródła energii, z uwagi na ograniczone zasoby paliw kopalnych oraz zapobieganie emisji zanieczyszczeń do atmosfery. Jednym z takich rozwiązań są instalacje przygotowania ciepłej wody w dużych budynkach wspomagane kolektorami słonecznymi. W pracy przedstawiono wyniki 6-letnich badań eksploatacyjnych wielkoskalowej instalacji kolektorów słonecznych płaskich zlokalizowanych na dachu klasztoru redemptorystów w Tuchowie w Polsce.

Kolektory słoneczne pokrywały średnio 37 % potrzeb cieplnych instalacji ciepłej wody w skali roku, w półroczu zimowym 15.9 %, a w półroczu letnim 56.5 %. Przeanalizowano koszty przygotowania ciepłej wody w instalacji z kolektorami i bez, oraz obliczono czas zwrotu nakładów inwestycyjnych. Zwrócono uwagę na czynniki mogące wpływać na stopień pokrycia potrzeb cieplnych przez instalację słoneczną oraz obliczono redukcję ilość zanieczyszczeń powstających przy spalaniu gazu ziemnego, dzięki zastosowaniu kolektorów słonecznych.

Słowa kluczowe: badania eksperymentalne, klasztor, wielkoskalowy system solarny, przygotowanie ciepłej wody

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APPLICATION OF THE ALTERNATIVE ENERGY SOURCES IN HEATING AND AIR-CONDITIONING INSTALLATIONS

WYKORZYSTANIE ALTERNATYWNYCH ŹRÓDEŁ ENERGII W INSTALACJACH GRZEWCZO-KLIMATYZACYJNYCH

Abstract: One of the most important problems of last years is the development of society, which is not compatible with environment protection. Total consumption of energy does not reflect already the degree of economic development. The index of scientifical and technical progress is nowadays the minimization of the energy consumption and its ecological cleanness. Additionally growing prices of energy carriers, the environmental degradation and climate changes make alternative energy sources interesting. Alternative energy sources can be used not only for room heating but also for its cooling. The connection these both functions by means of 4 different ideas of the heating and air-conditioning installation for the existing auditorium is presented. In the first idea main devices are solar collectors, air-compressor heat pump, the underground heat magazine filled with stones and a water, and ground probes. The second solution introduces the connection into one system of solar collectors, the air-compressor heat pump, the triple hydraulical coupling and ground probes. Into the third solution entered ground probes, solar collectors, absorptive heat pump and the gas boiler. The main elements of the fourth solution are compact heating and cooling devices and solar collectors, which work with warm water tank. The technological schema with well-chosen devices are presented and the special attention on advantages and disadvantages of each solutions is paid. Besides for solution III and IV capital costs, the annual conventional fuel consumption on needs of the heatings, emissions of pollutions to the atmosphere and savings resulting from the use of alternative sources energy were calculated.

Keywords: alternative energy sources, solar collectors, absorptive heat pump, air-compressor heat pump, the ground probe

The renewable energy source are more frequently used in modern building, where the investor decides to join heating and air-conditioning installations into one single system, which may decrease the capital costs. The basic elements of such installations are the heat pumps which derive the energy from bottom source (usually air, ground, ground or surface water or even waste water) [1]. There are many solutions that enable heat derivation from above-mentioned bottom sources, however, it is necessary to take into consideration local conditions and temperature stability in annual and daily cycle. Many

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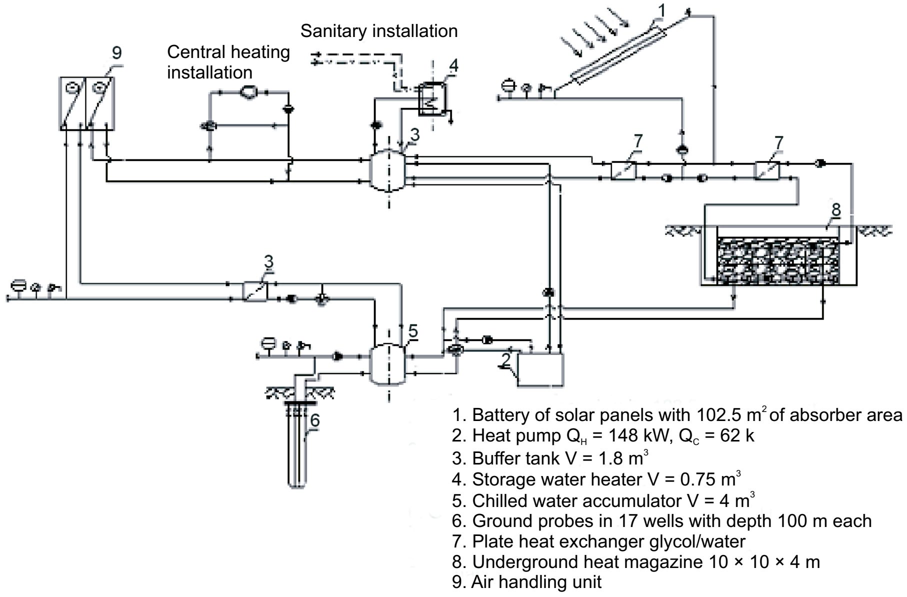
researches have been lead in the world [2–4], which purposes were to show the capability of alternative energy source used in HVAC installation.

Material and methods

The subject of the analysis are the four ideas of HVAC installations in the auditorium of the Faculty of Environment Engineering, which derive the energy from renewable sources. Heat demand for central heating ($Q_{c.o.}$ = 54 kW), hot water ($Q_{c.w.u.}$ = 10 kW) and ventilation ($Q_{c.t.}$ = 84 kW) for auditorium amounts 148 kW, however cold requirement is up to the level 62 kW. For the above-mentioned parameters with the consideration of a local conditions, series of analysis have been made, which were the basis for the elaboration of HVAC installation projects.
Details of individual solutions and their description are presented below.

I Conception

The installation (Fig. 1) consists of a heat pump with rated output 148 kW of heating power and 62 kW of cooling power and solar collectors with 102.5 m^2 of absorber area. Most of the energy acquired from the solar collectors in summer period is directed to underground heat magazine with dimensions 10 × 10 × 4 m filled with stones and water. This underground reservoir serves as a bottom energy source for heat pump in winter period, and after its depletion the bottom source becomes a ground probe. The chill in summer period is acquired from the ground probes [5] and is stored in a chilled water accumulator with capacity of 4 m^3, where from is derived by a chillers of handling units.



1. Battery of solar panels with 102.5 m^2 of absorber area
2. Heat pump Q_H = 148 kW, Q_C = 62 k
3. Buffer tank V = 1.8 m^3
4. Storage water heater V = 0.75 m^3
5. Chilled water accumulator V = 4 m^3
6. Ground probes in 17 wells with depth 100 m each
7. Plate heat exchanger glycol/water
8. Underground heat magazine 10 × 10 × 4 m
9. Air handling unit

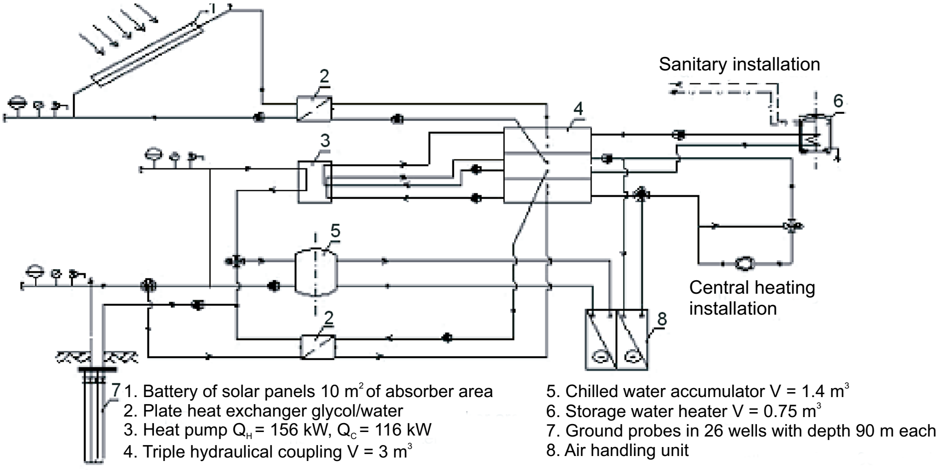
Fig. 1. The flow sheet of the I concept for heating and air-conditioning installation in auditorium of FEE

During chill acquisition from the ground probe, the heat simultaneously accumulates in ground. The advantage of this solution is a high temperature of the bottom heat source, which automatically increases COP (coefficient of performance) of heat pump and decreases the energy consumption in winter. Besides, there are high capabilities to store of solar energy surpluses in the underground heat magazine of 400 m^3 capacity. Disadvantages of this solution are a high costs of underground heat magazine structures and extensive area of solar panels which is the effect of forced finance conditions. Additionally in summer period heat regeneration of the ground takes place, which causes the increase of chill temperature from 7 to 14 ^{o}C at the end of the summer period [6].

II Conception

The basic elements of this solution are: heat pump Hibernatus type W29G3x2 with total heating power of 156 kW and chilling power 116 kW [7] and solar panels Viessmann Vitosol 200 with 10 m^2 of absorber area. In the installation a triple hydraulical coupling is employed, which serves as a tank for hot water with two perforated membranes [8]. These membranes together with two condensers implemented in the heat pump allow to maintain a 3 different temperature zones of upper heat source: $t > 55$ ^{o}C, 35 ^{o}C $< t < 55$ ^{o}C and $t < 35$ ^{o}C. In summer period there is a possibility to change the chill source from ground probes to chilled water accumulator and obtain a chilled water with 6 ^{o}C temperature. The redundant heat from the upper heat source through hydraulical coupling, heat exchanger and 3-way valve is directed to the ground probes. Then takes place the energy accumulation in the ground, which increases the COP coefficient of the heat pump [9]. In summer season the energy for heating purposes is derived by the heat pump, which discharges then ground heat accumulator, which consists of 26 ground probes with length about 90 m each.

This solution (Fig. 2) allows to accumulate waste heat from the air conditioning processes through ground probes and afterwards acquire this energy for heating



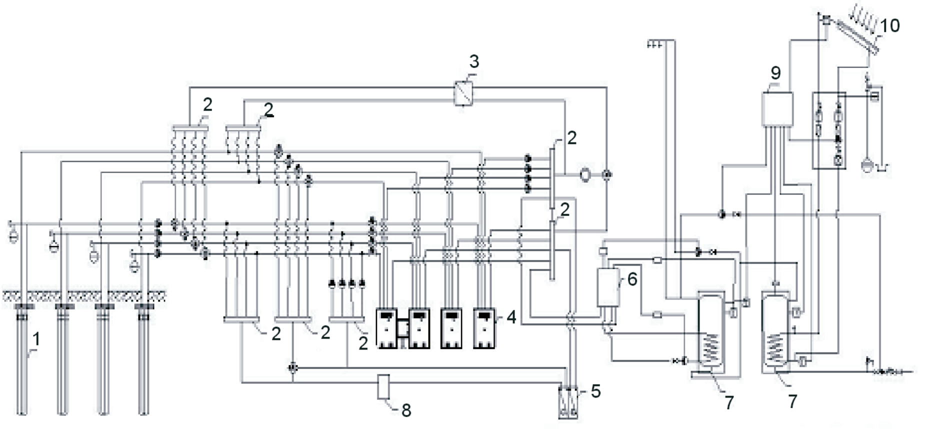
1. Battery of solar panels 10 m^2 of absorber area
2. Plate heat exchanger glycol/water
3. Heat pump Q_H = 156 kW, Q_C = 116 kW
4. Triple hydraulical coupling V = 3 m^3
5. Chilled water accumulator V = 1.4 m^3
6. Storage water heater V = 0.75 m^3
7. Ground probes in 26 wells with depth 90 m each
8. Air handling unit

Fig. 2. The flow sheet othe the II concept for heating and air-conditioning installation in auditorium of FEE

purposes in winter season. The disadvantages of this conception are high costs of structures of ground probes and the consumption of useful area for buffer tank (hydraulical coupling) and chilled water accumulator.

III Conception

The installation described by Walaszek [10] consists of 4 absorptive heat pumps type GAHP-W Robur with heating power of 35.4 kW and cooling power 13.5 kW each. In the installation, there is also employed gas boiler Vitopend 200 with rated output 24 kW [11] as a conventional heat source. At the beginning of summer season the chilled water is derived directly from the ground probes until the preliminary charge of ground accumulator occurs which is revealed through the increasing temperature of chilled water. Subsequently the absorptive heat pumps are turned on and the heat source is shifted from ground probes to chilled water installation. Simultaneously the charging processes follow from the ground accumulator with a heat from generating process of chilled water in plate heater exchanger. The hot tap water is prepared in the solar panels with 6 m^2 of absorber area along with gas boiler. In winter season the energy for heating purposes is derived from 4 heat pomps and in case of higher heat requirement from gas boiler.



1. Ground probes with length l = 90 m each
2. Hydraulical collectors
3. Plate heat exchanger
4. Heat pumps Q_H = 35.4 kW, Q_C = 13.5 kW each
5. Air handling unit
6. Gas boiler
7. Storage water heater V = 0.5 m^3
8. Chilled water accumulator V = 0.35 m^3
9. Controller
10. Battery of solar panels

Fig. 3. The flow sheet of the III concept for heating and air-conditioning installation in auditorium of FEE

The main advantage of this solution is a fact, that energy carrier for heat pumps is a gas, which causes the decrease of exploitation costs in comparison with the unit with compressor and decreasing load of electrical energy network. In the installation are not employed buffer tanks and big chilled water containers. Due to lower chilling power in winter period, the amount of ground probes is smaller and this prolongs discharge of ground accumulator in winter. This installation is characterized by high cost of investment and lack of exploitation experience, because this is a rare and rater not typical.

IV Conception

Installation consists of 4 heating-cooling units Robur [12] type RTYF 240-476/2. Each of them consist of gas boiler rated output 32.5 kW of heating power and from chiller with 17.5 kW of cooling power. In summer period the hot tap water is prepared in solar panels with 6 m^2 of absorber area and in gas boilers.

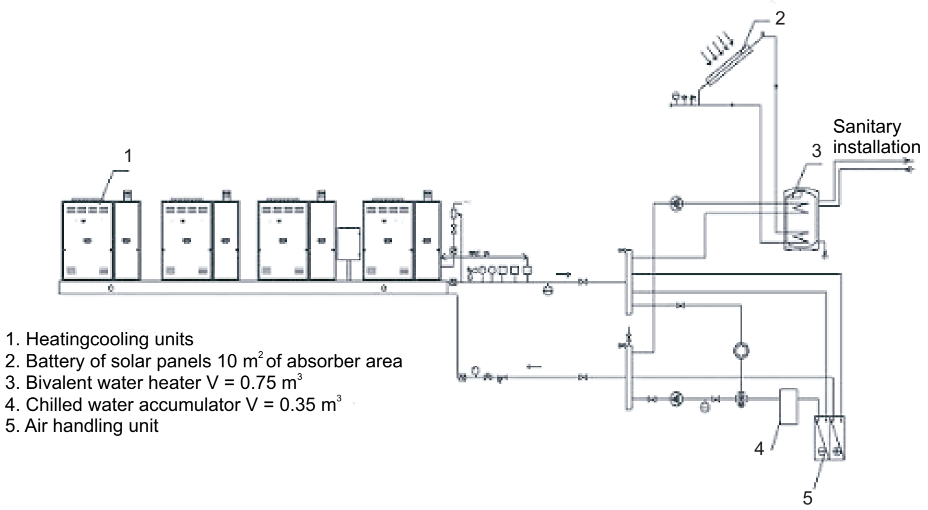


Fig. 4. The flow sheet of the IV concept for heating and air-conditioning installation in auditorium of FEE

The advantage of this solution is lack of necessity of expensive ground collectors and buffer tanks application. Besides, there is a possibility of placing the heat and chill source outside the building onto a common frame, which safes the room useful area. In case of outdoor air temperature decrease below – 20 ^{o}C, the problems with rooms heating may occur.

Results and discussion

In consideration of 4 specifications of heating-cooling system it can be noticed that technical possibilities of the application of renewable energy sources in heating and air-conditionig installations can exist. This contributes to the environment protection. However for the purpose of the detailed estimation its influence on the environment, solutions III and IV, were chosen. For this solutions capital costs were put together. The diminution of the unrenewable annual fuel consumption on each aim and the diminution of gaseous and dust emission, which are introduced to the atmosphere from the energy-combustion of fossil fuels, is defined. If depends on capital costs, in which one seized prices of basic devices, then they are put together it in Table 1 and Table 2.

Table 1

Capital costs of installation number III

Item	Type	Quantity	Price [PLN]
Absorptive heat pump	GAHP-W Robur	4	160000
Gas boiler	Viessmann Vitopend 200, Q = 24 kW	1	65000
Capacitive water heater	Viessmann Vitocell 300-B Vn = 500 m^3	2	27000
Solar Divicon set	Viessmann	1	2600
Pump of bottom source	WILO VeroLine-IP-E 80/140-4/2R1	4	11200
Pump of upper source	WILO VeroLine-IP-E 80/140-4/2R1	4	11200
Pump of iced water	WILO VeroLine-IP-E 80/140-4/2R1	4	11200
Solar collector	Viessmann Vitosol 200-T 6m^2	1	18000
Ground collector	U-pipe l = 90 m	16	100800
		Sum	348500

Table 2

Capital costs of installation number IV

Item	Type	Quantity	Price [PLN]
Heating-colling devices	RTYF-240-476/2	4	183920
Solar collector	Viessmann Vitosol 200-T 6 m^2	1	18000
Capacitive water heater	Viessmann Vitocell 360-M Vn = 750 m^3	1	15300
Solar Divicon set	Viessmann	1	2600
		Sum	219 820

Assuming that the energy source for this building is individual gas boiler, annual consumption of natural gas (GZ-50) for each purpose, can be calculate by means of formulas (1)–(3) [13, 14].

– annual consumption of fuel for central heating:

$$B_a^{c.o} = (24 \cdot 3600 \cdot Q_{c.o.} \cdot SD_{20}) \cdot (Q_i^r \cdot \eta_k \cdot \eta_{inst.c.o.} \cdot (t_i - t_e))^{-1},\ [m^3 \cdot a^{-1}] \quad (1)$$

– annual consumption of fuel for hot water preparation:

$$B_a^{c.w.u.} = (24 \cdot 3600 \cdot Q_{c.w.u.} \cdot 36) \cdot (Q_i^r \cdot \eta_k \cdot \eta_{inst.c.w.u.})^{-1},\ [m^3 \cdot a^{-1}] \quad (2)$$

– annual consumption of fuel for ventilation (technological heat):

$$B_a^{c.t.} = (24 \cdot 3600 \cdot Q_{c.t.} \cdot 180\ ) \cdot (Q_i^r \cdot \eta_k \cdot \eta_{inst.c.t.})^{-1},\ [m^3 \cdot a^{-1}] \quad (3)$$

where: $Q_{c.o.}$ is computational heat demand on central heating ($Q_{c.o.}$ = 54 kW); SD_{20} is numer of degree-day and for the city Lublin amounts SD_{20}= 3957.4 K · d · a^{-1}; Q_i^r is calorific value of natura gas GZ-50 and amounts Q_i^r = 36000 kJ · $(m^3)^{-1}$; η_k is the efficiency of gas boiler, assumed η_k = 0.9; $\eta_{inst.c.o.}$ is the efficiency of central heating installation running, assumed $\eta_{inst.c.o.}$ = 0.85; t_i is computational temperature of internal air, assumed t_i = 20 °C; t_e is computational temperature of external air, assumed for Lublin city t_e = –20 °C; $Q_{c.w.u.}$ is computational heat demand on hot water preparation ($Q_{c.w.u}$ = 10 kW); $\eta_{inst.c.w.u.}$ is the efficiency of hot water installation running, assumed $\eta_{inst.c.w.u.}$ = 0.7; $Q_{c.t.}$ is computational heat demand on ventilation ($Q_{c.t.}$ = 84 kW); $\eta_{inst.c.t.}$ is the efficiency of technological heat installation running, assumed $\eta_{inst.c.t.}$ = 0.7.

However the consumption of unrenewable fuels on each aims for the installation number III and number IV was calculated. These calculations were made on the basis of burners characteristics of components devices of investigated installations and also on the basis of the fuel consumptions for the gas boiler. The results of these calculations are presented in Table 3.

Table 3

Fuel consumptions on each aims

Heat source	$B_a^{c.o.}$	$B_a^{c.w.u.}$	$B_a^{c.t.}$	B_a
Gas boiler	16761	13905	57600	88266
Conception III	6185	5131	21254	32570
Conception IV	13325	11054	45792	70171

On the basis of Table 3 one can, ascertain that the installation number IV uses up about 20.5 % less fuels in comparison with the individual gas boiler, and the installation number III till 63.1 % less. By use of the formula No. 4 [15] average yearly emissions of individual pollutions from individual gas boiler, installation No. III and No. IV, were evaluated. Results of these investigations are placed in Table 4.

$$E_{zan} = B_a \cdot u_{zan}^j \text{ [kg/a]} \tag{4}$$

where: B_a is yearly consumption of natural gas GZ-50, $m^3 \cdot a^{-1}$; u_{zan}^j is index of unit sling of polluting substances from the emission source, for NO_2: $u_{NO_2}^j$ = 1280 · 10^{-6} kg · $(m^3)^{-1}$, for CO: u_{CO}^j = 360 · 10^{-6} kg · $(m^3)^{-1}$, for CO_2: $u_{CO_2}^j$ = 1964000 · 10^{-6} kg · $(m^3)^{-1}$, for dust: u_D^j = 15 · 10^{-6} kg · $(m^3)^{-1}$.

Table 4

Average yearly emissions

Heat source	E_{NO_2}	E_{CO}	E_{CO_2}	E_D
Gas boiler	113.0	31.8	173354.4	1.32
Conception III	41.7	11.7	63967.8	0.49
Conception IV	89.8	25.3	137815.8	1.05

Then by utilization of the formula No. 5, yearly savings [in PLN], received thanks use of alternative energy sources in installations No. III and IV in comparison with the individual gas boiler, were calculeted.

$$\Delta O = \Delta B \cdot K^j \; [\mathrm{PLN} \cdot \mathrm{a}^{-1}] \tag{5}$$

where: ΔB are yearly savings of the fuel consumption in comparison with the individual gas boiler [kg/a]; K^j is unit cost of fuel, for natural gas GZ-50 assumed $K^j = 1.31 \text{ PLN} \times \times (\mathrm{m}^3)^{-1}$.

One received yearly savings thank utilization of the installation No. III on the level $72962 \text{ PLN} \cdot \mathrm{a}^{-1}$, and through the utilization of the installation No. IV up to the level of $23704 \text{ PLN} \cdot \mathrm{a}^{-1}$. Besides one should remember that the additional savings are geting out of the diminutions of charges for the use of environment and costs on forests revitalisations or on the purchase of medicines for allergy.

Conclusions

1. The utilization of renewable energy sources in heating and air-conditioning installations, in the form of gas absorptive heat pumps, allows the diminution of the unrenewable fuels consumption even about 63 % in comparison with conventional parley.

2. Use of heating devices using alternative sources of energy allows CO_2 emission reduction to the atmosphere, minimally about 20 % in the scale of the year.

3. In consideration of the existing possibilities to use renewable energy sources in heating and air-conditioning installations which contribute to the environment protection across the diminution of loads of pollutions emitted to the atmosphere. Every one should promote their utilization in new, as and modernized objects especially in the face of obligatory for Europe regulations “3×20”.

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WYKORZYSTANIE ALTERNATYWNYCH ŹRÓDEŁ ENERGII W INSTALACJACH GRZEWCZO-KLIMATYZACYJNYCH

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Abstrakt: Jednym z ważniejszych problemów ostatnich lat jest pogodzenie rozwoju cywilizacyjnego społeczeństwa ze środowiskiem naturalnym. Globalne zużycie energii nie odzwierciedla już dziś stopnia rozwoju gospodarczego, a wręcz odwrotnie. Wyznacznikiem postępu naukowo-technicznego danego kraju jest obecnie minimalizacja zużycia energii i jej ekologiczna czystość. Dodatkowo ciągle rosnące ceny nośników energii, degradacja środowiska naturalnego oraz zmiany globalne klimatu doprowadziły do wzrostu zainteresowania alternatywnymi źródłami energii. Alternatywne źródła energii można wykorzystywać zarówno do ogrzewania, jak i chłodzenia pomieszczeń. Połączenie tych obu funkcji zaprezentowano za pomocą 4 różnych koncepcji instalacji grzewczo-klimatyzacyjnych dla sali wykładowej. W pierwszej koncepcji głównymi urządzeniami są kolektory słoneczne, sprężarkowa pompa ciepła, podziemny magazyn ciepła wypełniony kamieniami i wodą oraz sondy gruntowe. Drugie rozwiązanie przedstawia połączenie w jeden układ kolektorów słonecznych, sprężarkowej pompy ciepła, trójdzielnego sprzęgła hydraulicznego oraz sond gruntowych. W skład trzeciego rozwiązania weszły sondy gruntowe, kolektory słoneczne, absorpcyjna pompa ciepła oraz kocioł gazowy. Natomiast głównymi elementami czwartego rozwiązania są kompaktowe urządzenia grzewczo-chłodzące, kolektory słoneczne współpracujące z biwalentnym podgrzewaczem wody. Zaprezentowano schematy technologiczne z dobranymi urządzeniami oraz zwrócono uwagę na wady i zalety poszczególnych rozwiązań. Ponadto dla rozwiązania III oraz IV obliczono koszty inwestycyjne, roczne zużycie paliwa konwencjonalnego, emisje zanieczyszczeń do atmosfery oraz oszczędności, które wynikają z wykorzystania odnawialnych źródeł energii.

Słowa kluczowe: alternatywne źródła energii, kolektory słoneczne, absorpcyjna pompa ciepła, sprężarkowa pompa ciepła, sonda gruntowa

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INFLUENCE OF CONDUIT GEOMETRICAL CHARACTERISTICS ON SEWAGE FLOW PARAMETERS

WPŁYW CHARAKTERYSTYK GEOMETRYCZNYCH KANAŁU NA PARAMETRY PRZEPŁYWU ŚCIEKÓW

Abstract: The shape of sanitary conduits consistently defines the cross-section of the wastewater stream, which influences the basic parameters of flow hydrodynamics. The most important of these parameters are wetted perimeter and hydraulic radius, the values commonly used in sanitation systems designing and their work condition modeling. The determination of these parameters is quite simple in case of new conduits in a good technical condition, without the sediments. During the determination of old channels discharge capacity and their work modeling the providing for the sediments deposition is necessary. Deposits covering the bottom of sanitation conduits influence the hydraulic resistance of flow in three different ways: decreasing the cross-section area of the stream, increasing the roughness of the side walls and bottom of the pipe and decreasing the kinetic energy of the stream. The simulation of sanitary network working conditions concerning sediments may have a very important practical meaning. The storm spillways deliveries of the pollutant load included in sediments are, in some cases equal to yearly mean value of pollution contained in treated wastewater delivered to the rivers were observed. Additionally, the variable load of sediments causes non-uniform strain of wastewater treatment plants. The conducted in situ research showed that the height of deposited sediments sometimes was higher than the height of an active area of the stream. The analysis of changes in channel characteristics caused by sedimentation process and their influence on sewage flow parameters were presented. The gained results of calculations showed that sediments bed deposited in the 0.4, 0.5, 0.6 and 0.8 m diameter pipe caused maximum decrease of its wetted perimeter equal to 23.6 %, 22.9 %, 22.3 %, 21.6 % and 39.6 %, 38.7 %, 38.3 %, 37.9 % reduction of actual hydraulic radius value, respectively. The further research concerning other diameters and different shapes of sewer conduits should be conducted.

Keywords: gravitational sewer system, parameters of flow hydrodynamics, calibration of sewer system hydraulic model

The geometrical shape of sanitary conduits cross-section and its wall material roughness directly influence the basic hydrodynamics parameters of the sewage flow. The flow rate and flow velocity distribution in the cross-section of the stream are

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directly connected to wetted perimeter and hydraulic radius of the conduit as well as the coefficient of roughness. These parameters are commonly used in sanitation systems designing and their work condition modeling [1, 2]. Despite the fact that the conduits of sanitation systems may be produced with use of different materials and formed in different shapes, the wetted perimeter and hydraulic radius calculations are quite easy for the brand new, freshly assembled pipes. The flow resistance in this case originates only from the pipe wall roughness. During the long-lasting use of sanitation system the process of sediments deposition appears. Sediments are often defined as any type of settleable particulate material which may be found in sewage and is able to form bed deposits in sewers and their appurtenances [2]. The sediments deposited along the sanitation pipe and creating the bed of different forms [3] clearly influence the parameters of sewage flow. When sediment bed appears in the sanitation conduit, the sewage flow may be influenced by the new types of resistance, besides the pipe material itself – resistance from the sediment grains and resistance from the sediment bed recently formed. The other sources of energy loss may also appear during the sanitation exploitation ie aging effect, construction failures of pipes and biological film development on the pipe wall. The sediments thus influence the hydraulic condition of sewage flow in three different ways: decrease of effective cross section of a flowing stream, increment of the roughness of the side walls and bottom (surface of the sediment bed) of the pipe and decrease the kinetic energy of the stream used to separate sediments particles from the bed [3, 4]. The in situ research conducted by us showed that the height of deposited sediments sometimes was higher than the height of active area of the stream. The sediments in gravitational sewer systems affect not only the hydraulic conditions of flow but also the pollutant management in the network. The storm spillways in combined sanitation systems deliver the pollutant load included in sediments equal to yearly mean value of pollution contained in treated wastewater delivered to the receivers. Additionally, the variable load of sediments causes the non-uniform strain of wastewater treatment plants. The surface of sediment bed may form the following types of arrangement: ripples, dunes and plane bed. Both, ripples and dunes are prone to transformations and further depositions thus the plane bed in case of high sediment load remains stable. The shape of sediment bed surface is directly dependent to the value of dimensionless Froude number comparing inertial and gravitational forces in moving fluid.

Recently the computer modeling of sanitation systems becomes a very useful tool in designing and exploitation of sanitation and combined sewer systems as the example of environmental systems [5]. The computer modeling allows variable, optional design of considered layout of sanitation and its short- and long-term efficiency in different conditions. The choice of the most suitable solution in aspect of hydraulic conditions is also possible due to the numerical calculations. The model of existing sewer network makes the analysis of adding new parts of systems and new users possible. In this case the system operational conditions may be considered taking into account the additional wastewater discharge from the newly designed parts of network. But the quality and accuracy of the computer modeling in reflecting the real conditions, despite its proper mathematical description, are directly connected to the introduced input data [6]. When the geometrical parameters and pipe material roughness for the new, unused material are input the results of flow parameters calculation may differ from the real values. The calibration of computer model becomes necessary [1, 3, 7]. The real shape of the sewage stream cross-section, its wetted perimeter and hydraulic radius as well as resultant roughness coefficient describing additionally resistance after sediments deposition and type of sediments have to be reflected.

This paper presents the results of changes in channel characteristics caused by sedimentation process and their influence on sewage flow parameters. The main objects of analysis were stream geometry, its wetted perimeter and hydraulic radius as well as resultant roughness coefficient of the circular sanitary conduit with different sediments deposition.

Basic equations

The basic description of unsteady flow in open channels may be given by a simplified form of Saint Venant's formula [8]:

$$\frac{\partial Q}{\partial t}+\frac{\partial}{\partial x}\left(\frac{\beta Q^2}{A}\right)+gA\,\frac{\partial h}{\partial x}+g\,\frac{n^2}{R_h^{4/3}}\,\frac{|Q|Q}{A}=0, \qquad \frac{\partial A}{\partial t}+\frac{\partial Q}{\partial x}=0$$

where: R_h – hydraulic radius [m],
A – stream cross sectional area [m^2],
Q – flow rate [m$^3 \cdot$ s^{-1}],
β – dimensionless velocity coefficient [-],
n – roughness coefficient [s$^1 \cdot$ m$^{-1/3}$].

The empirical equation for the friction slope in unsteady flow can be written in the following manner [1]:

$$S_f=\frac{1}{C_{CH}^2}\,\frac{1}{R_h^{2a}}\,\frac{Q|Q|}{A^2}$$

where: S_f – friction slope [m $\cdot$ m $^{-1}$],
C_{CH} – empirical resistance coefficient,
a – empirical exponent [-].

The hydraulic radius is described as follow:

$$R_h=\frac{A}{P_w}$$

where: P_w – wetted perimeter [m].

The empirical roughness coefficient may be presented as Darcy-Weisbach equation:

$$C_{CH} = \left(\frac{8g}{\lambda}\right)^{\frac{1}{2}}$$

where: λ – friction factor [-].

The dimensionless friction factor may be calculated after the Prandtl-Colebrook formula:

$$\frac{1}{\sqrt{\lambda}} = -2\log\left(\frac{2.51}{\mathrm{Re}\sqrt{\lambda}} + \frac{k/D}{3.71}\right) = -2\log\left(\frac{2.51}{\mathrm{Re}\sqrt{\lambda}} + \frac{1}{3.71} + \frac{k}{4R_h}\right)$$

where: D – pipe diameter [m],
k – wall sand roughness [m],
Re – dimensionless Reynolds number [-].

The α angle [rad] is the central parameter in the flow geometry mathematical description. Its definition was shown at Fig. 1 and it may be calculated as:

$$\alpha = \cos^{-1}[(D/2 - d_{\max})/(D/2)]$$

where: $d_{\max}$ – maximum water depth [m].

The α angle can be also determined as follows [1]:

$$h/D = 1/2(1 - \cos\alpha)$$

where: h – actual water depth [m].

In the designing practice the flow description is often reduced to the steady flow equation (mass conservation):

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = 0, \quad Q = C_{CH}\ R_h^{1/2}\ s^{1/2}\ A$$

In this description of steady flow the inclination of water surface s is parallel to the friction slope S_f.

The empirical roughness coefficient in this case is represented by Manning equation:

$$U = \frac{1}{n} R_h^{2/3}\ s^{1/2}$$

where: U – mean flow velocity in steady conditions [m · s^{-1}].

The presented mathematical description of water flow in open channels clearly shows that despite the flow state, hydraulic parameters such as hydraulic radius, wetted perimeter and material roughness coefficient are the most important factors in the analysis.

Material and methods

The presented study was based on hydraulic parameters like wetted perimeter and hydraulic radius changes caused by sediments deposition in the cross section of a sanitation pipe. The analysis of n coefficient changes was also conducted. The calculations were conducted for the 0.4, 0.5, 0.6 and 0.8 m diameter circular pipe with different height of sediments bed. The mentioned diameters were chosen in connection to the parallel field research on gravitational sanitation system in Chelm, Poland.

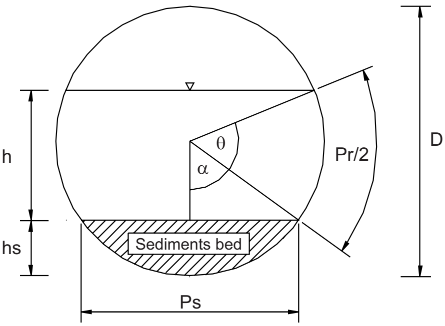

Fig. 1. Studied circular pipe

The resultant roughness coefficient n for the studied pipe was calculated as follows [9]:

$$n = \left(\frac{P_r n_r^2 + P_s n_s^2}{P_w} \right)$$

where: P_r – wetted perimeter of pipe wall [m],
n_r – pipe wall material roughness coefficient [$s^1 \cdot m^{-1/3}$],
P_s – wetted perimeter of sediment bed [m],
n_s – sediments bed surface coefficient of roughness [$s^1 \cdot m^{-1/3}$].

The resultant roughness coefficient was calculated for 0.4, 0.5, 0.6 and 0.8 m pipes and variable sediments bed height – h_s from 5 to 40 cm. In the presented calculations n_s was assumed as equal 0.025 $s^1 \cdot m^{-1/3}$, n_r as like for the new PE pipe – 0.0125 $s^1 \cdot m^{-1/3}$ [9–13]. The length of wetted perimeter for pipe material and sediments bed surface was obtained by standard geometrical calculations.

Results

The results of water flow hydraulic parameters calculations are presented at Fig. 2 and Fig. 3. Figure 2 shows the wetted perimeter of 0.4, 0.5, 0.6 and 0.8 m circular pipe as a function of water depth and in dependence to the height of sediments bed. The decrease of wetted perimeter at the same water depth caused by the increase of sediments bed level is clearly visible. For instance, the wetted perimeter for the new

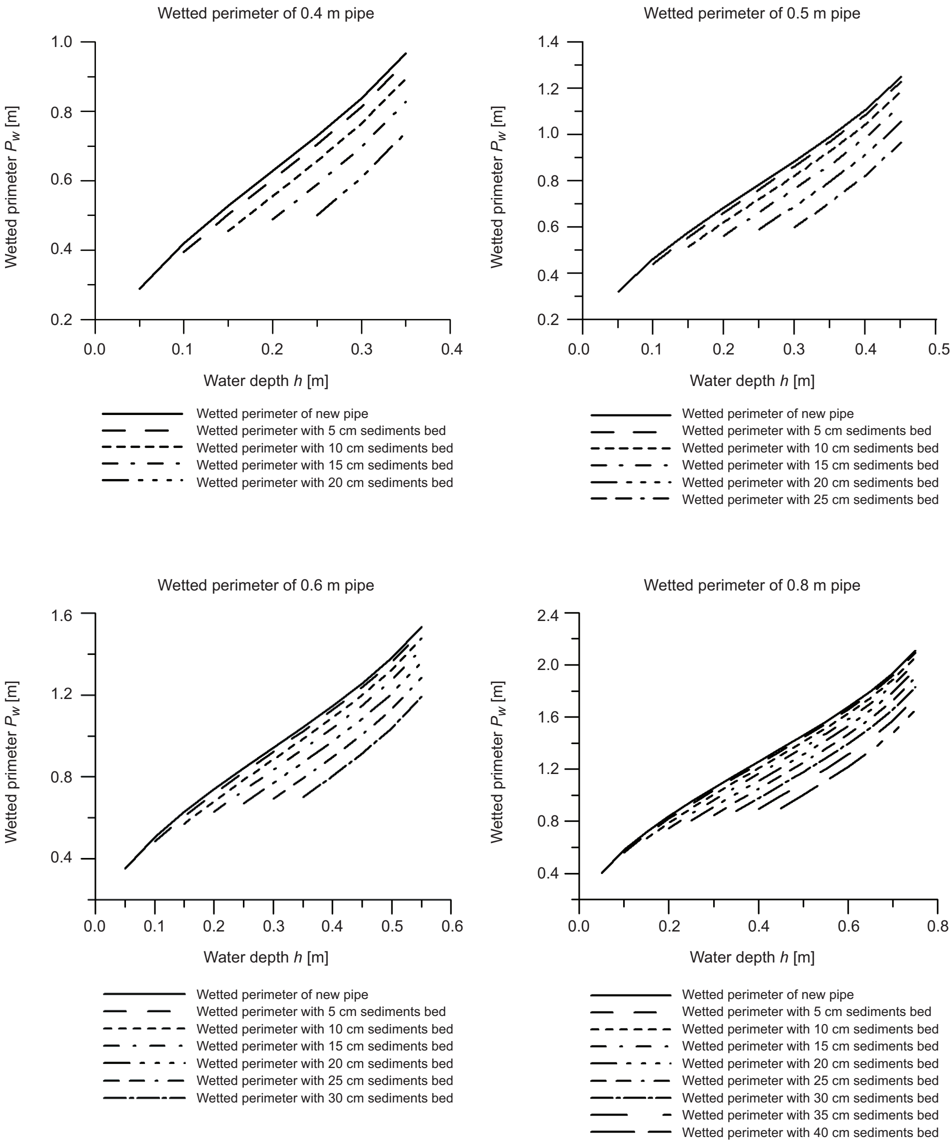

Fig. 2. Wetted perimeter of circular pipe as a function of water depth

pipe 0.5 m, with water depth $h = 0.45$ m, without sediment deposition was calculated as 1.125 m when the obtained wetted perimeter with sediments bed height equal to 25 cm was 0.9636 m. The difference of nearly 22.8 % has significance in water flow rate calculations. In case of the other studied pipes the wetted perimeter length decrease of 23.6 %, 22.3 % and 21.6 % was noted for 0.4, 0.6 and 0.8 m diameters consequently.

Figure 3 presents the results of hydraulic radius of 0.4 m, 0.5 m, 0.6 m, as well as 0.8 m circular pipes calculations as a function of water depth for different level of sediments deposition. The influence of sediments bed height on actual value of hydraulic radius is visible – the higher sediments bed, the lower value of hydraulic radius. The minimum value of R_h was obtained for sediments bed height $h_s = 0.2$ m – it was equal to 0.1042 m, when the hydraulic radius for the new pipe, at the same h was

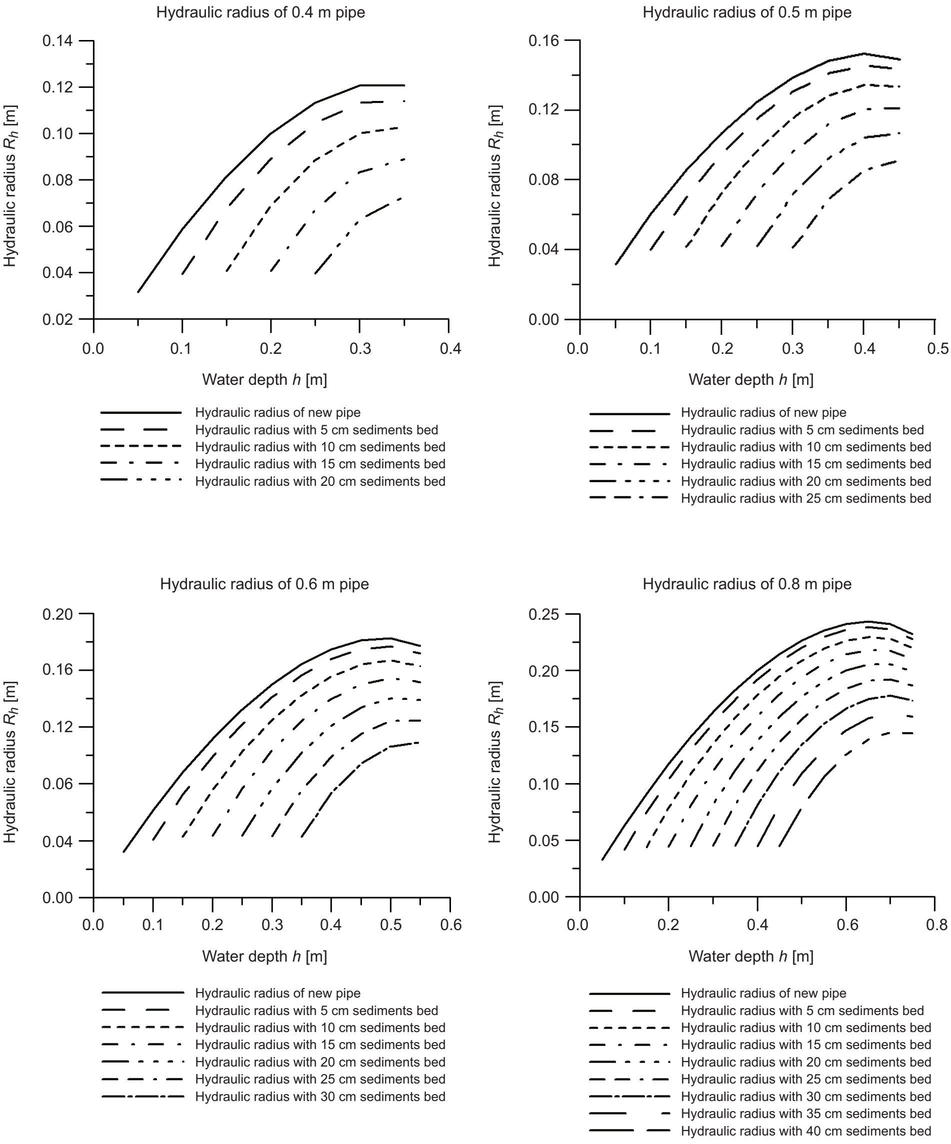

Fig. 3. Hydraulic radius studied pipes as a function of water depth

calculated as 0.1524 m. The maximum observed decrease of hydraulic radius length reached the level of 39.6–37.9 % for all studied cases. This means the notable influence on the flow rate in considered pipes.

The results of resultant roughness coefficient calculations for different water levels and various sediments bed heights are presented in Fig. 4. The obtained results show that deposited sediments clearly cause the additional resistance of water/sewage flow in the studied circular pipes. The higher sediments bed the higher flow resistance,

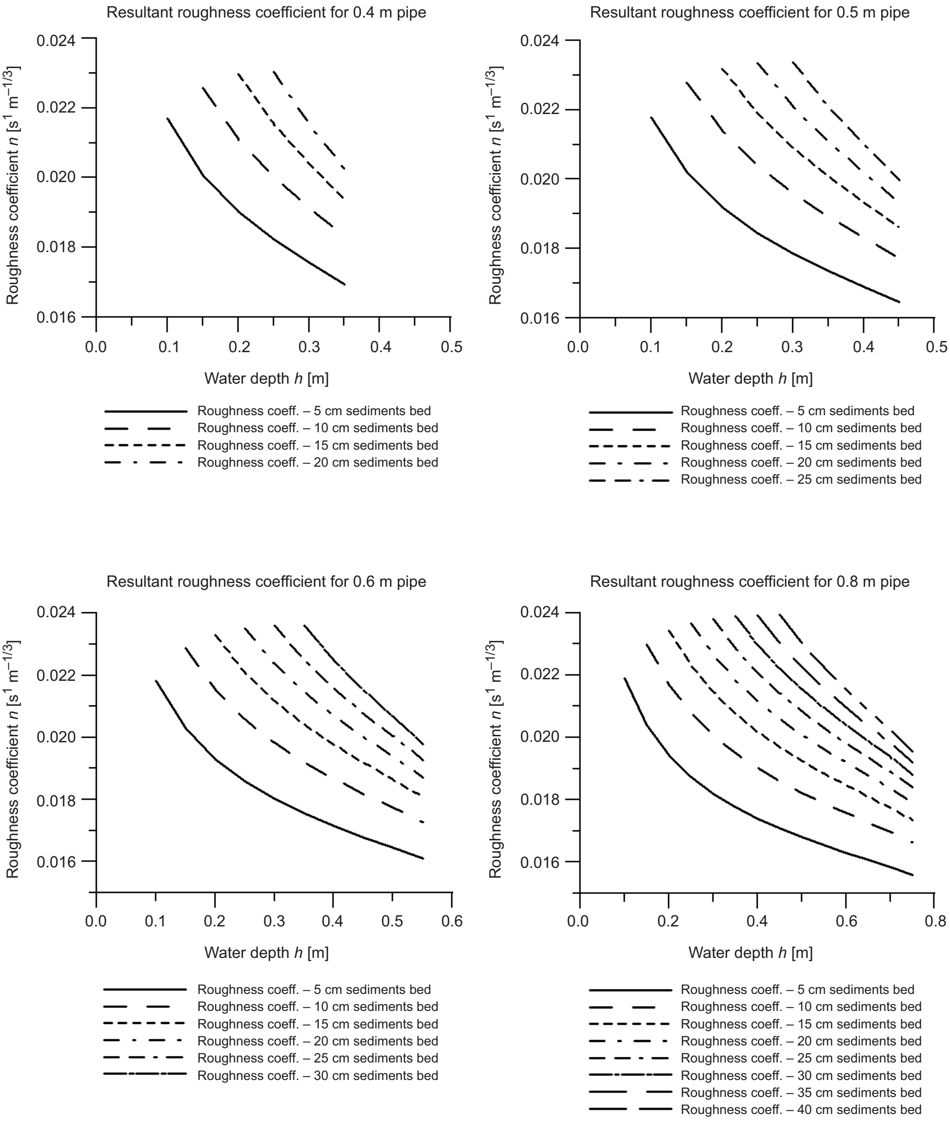

Fig. 4. Resultant roughness coefficient for studied pipes as a function of water depth

especially at low water depth. The maximum calculated resultant roughness coefficient for polymer pipe with sediments bed reached the level of $n = 0.0203–0.0239\ \mathrm{s}^{1} \cdot \mathrm{m}^{-1/3}$ for $h_s = 0.5\ D$ and sewage depth $h = 5$ cm. It means the maximum 62.4–91.2 % increase of n value for the mentioned cases.

The exploitation practice shows that so high sediments deposition is possible only inside wrongly designed sanitation conduits but our calculations show that serious increase of additionally resistance was obtained for all studied sediments bed heights.

The presented research results showed that calibration of numerical model including changes in wetted diameter, hydraulic radius and additionally flow resistance caused by deposited sediments is necessary. Otherwise, the design errors and exploitation problems are possible.

Conclusions

1. Sediments deposited along the sewage pipes clearly influence the hydraulic conditions of flow.
2. Sediments bed deposited in the 0.4, 0.5, 0.6 and 0.8 m diameter pipe caused maximum decrease of its wetted perimeter equal to 23.6 %, 22.9 %, 22.3 %, 21.6 % and 39.6 %, 38.7 %, 38.3 %, 37.9 % reduction of actual hydraulic radius value respectively.
3. The maximum calculated increase of resultant roughness coefficient for polymer pipe with sediments bed reached the level 91.2 % for the studied pipes.
4. The obtained results of calculation showed that calibration of sanitation systems models considering sediments and their influence on hydraulic conditions of fluid movement is necessary.
5. The results of our studies may be directly used in sanitation systems designing, computer modeling and models calibration.
6. The further research concerning other diameters and different shapes of sewer conduits should be conducted.

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WPŁYW CHARAKTERYSTYK GEOMETRYCZNYCH KANAŁU NA PARAMETRY PRZEPŁYWU ŚCIEKÓW

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Abstrakt: Kształt kolektora kanalizacyjnego w sposób jednoznaczny definiuje przekrój poprzeczny strumienia ścieków, który z kolei wpływa na podstawowe parametry związane z hydrodynamiką przepływu. Najważniejsze z tych parametrów to obwód zwilżony i promień hydrauliczny, czyli wielkości standardowo wykorzystywane w pracach projektowych systemu kanalizacyjnego oraz przy symulacjach komputerowych pracy tych systemów. Wyznaczenie tych parametrów jest stosunkowo proste w przypadku wspomnianych nowych kolektorów w dobrym stanie technicznym, bez złogów osadów. Przy określaniu przepustowości starych kanałów oraz modelowaniu ich pracy niezbędne staje się uwzględnianie osadów odkładających się na dnie kanałów oraz narastających na ściankach. Osady zalegające na dnie przewodów kanalizacyjnych mają wpływ na opory hydrauliczne przepływu na trzy różne sposoby, a mianowicie: zmniejszają przekrój wewnętrzny kanału, zmieniają szorstkość ścian i dna oraz podczas rozmywania nagromadzonych złogów zmniejszają energię strumienia przepływających ścieków. Symulacja pracy sieci kanalizacyjnej z uwzględnieniem odkładających się osadów wydaje się mieć duże znaczenie praktyczne, z uwagi na fakt odprowadzania z sieci ogólnospławnych przez przelewy burzowe do wód odbiornika ładunku zanieczyszczeń zawartego w osadach, którego wartość średnia w skali rocznej odpowiada ładunkowi odprowadzanemu z oczyszczalni wraz z oczyszczonymi ściekami. W przypadku sieci rozdzielczej okresowo wymywane osady wpływają także na nierównomierne obciążenie ładunkiem oczyszczalni ścieków. Podczas prowadzonych pomiarów terenowych zaobserwowano, iż wysokość złogów osadów przekraczała niekiedy wysokość czynnego przekroju strumienia ścieków. Zaprezentowano w pracy analizę wpływu zmian charakterystyk kanału wywołanych przez proces sedymentacji osadów na parametry przepływu ścieków. Osady zsedymentowane na dnie przewodów o średnicy 0,4, 0,5, 0,6 oraz 0,8 m powodować mogą zmniejszenie obwodu zwilżonego maksymalnie o 23,6 %; 22,9 %; 22,3 %; 21,6 % oraz promienia hydraulicznego o 39,6 %; 38,7 %; 38,3 % i 37,9 %. Należy przeprowadzić kolejne badania rozwojowe dotyczące innych średnic, kształtów oraz materiałów przewodów kanalizacyjnych.

Słowa kluczowe: kanalizacja grawitacyjna, parametry hydrodynamiczne przewodów kanalizacyjnych, kalibracja modelu hydraulicznego sieci kanalizacyjnej

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SYSTEMATIC AND SELECTION CRITERIA FOR ORC SYSTEM WORKING FLUID USED FOR A DETERMINED AMOUNT OF EXCESSIVE ENERGY

SYSTEMATYKA I KRYTERIA DOBORU CZYNNIKA ROBOCZEGO UKŁADU ORC DLA OKREŚLONYCH ZASOBÓW CIEPŁA ODPADOWEGO

Abstract: Increasing the efficiency of technological processes is considered as an important element of sustainable development concept in the decrease in greenhouse gas emissions and renewable energy utilization. The following paper reaches out against the market demands, showing ways of contributing into this trend. In technological processes, waste heat energy is often an unsolved problem. Attempts of utilizing that heat, especially in petrochemical industry, have come across many problems, such as low egzergy level, great dispersement, wide parameter range and the cost-efficiency of potential modernization. One of promising technologies of utilizing this heat is through *Organic Rankine Cycle* (ORC) system implementation. The following paper shows a global approach into the problem of achieving maximum efficiency of ORC. A complex review of thermodynamic fluids, available for use in ORC has been prepared, the fluids has been described in terms of temperature source range, safety of use, price and environmental impact. Guidelines in designing ORC, based on experience in introducing unconventional solutions in industry, are described. According to the results acquired, choosing these installations for excessive heat utilization enables not only an increase in efficiency of technological processes but also elevates the proecological image of the company.

Keywords: ORC system, working fluid, excessive heat utilization.

Because of the fact that the thermodynamic parameters of water, a common fluids used in basic power plants, are not satisfactory, especially with low parameters, already in 1960's a search for another fluid available for use in a binary cycle and for utilizing waste energy with the fluid temperature lower than 400 °C has been conducted [1].

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In [1] freon gas usefulness has been pointed out for use as a low-boiling fluid in the, so called, binary power plant, especially in supercritical parameter range, for which positive results of turbine work parameters may be expected.

The increase of interest in low-boiling working fluid occurred again with the development of ORC-based (*Organic Rankine Cycle*) technologies. Because of ORC's low energetic efficiency in comparison with piston and rotor engine based technology, the new developed technology was not put into any use for a long time. However, the possibilities of its implementation in utilizing low temperature unconventional energy sources, especially biomass combustion, have attracted yet another increase of interest in this technology.

This work is dedicated to solving the problem of choosing a proper working fluid for utilizing a given amount of energy.

Working fluid requirements

Working fluid requirements can be divided into general and specific requirements concerning thermodynamic efficiency of its implementation.

A thermodynamic fluid, being specifically an energy carrier taking part in heat conversion in an ORC system, should generally meet demands similar to those presented for refrigeration and heat pump fluids. The basic requirements for ORC fluids are:

– Chemical stability and durability in the whole heat range;
– High values of supercritical parameters;
– Chemical neutrality against the components of the installation;
– Safety of use – lowest possible toxicity, flammability and explosiveness;
– High volume heat efficiency (in order to apply a small working fluid stream and minimize the installation size);
– Environmental friendliness.

Aside these, ORC fluids should also meet specific thermodynamic requirements described below.

Obviously, fluids which are easiest to obtain are the best choice. These are substances easily produced in oil refining processes, such as propane and butane and its isomers. In order to increase the efficiency of cycle, more and more often synthetic fluids are used, such as one-, two- or multicomponent solutions of hydrocarbons and their derivatives.

Working fluid systematic

For systemizing a still increasing number of heat fluids (used also in refrigeration cycles), a uniformed system (being now an ISO standard) for classifying working fluids was introduced. The basic rule of this system is chemical structure of the substances as well as, interchangeable, their manufacture names are used.

It became a rule to mark the fluids with a few symbols, derived directly from their structure. This way, few substance groups have been introduced, most known of which are:

– HC – saturated hydrocarbons, substances with no halogenic content;

– FC – organic substances in which all hydrogen atoms in the particle have been replaced with fluorine;

– HFC – hydrofluorocarbons – carbon based compounds in which part of hydrogen atoms have been replaced with fluorine;

– CFC – chorofluorocarbons halogenic, very stable compounds, organic particle derivatives in which all hydrogen atoms have been replaced with fluorine and chlorine;

– HCFC – hydrochlorofluorocarbons, organic particles in which not all hydrogen atoms were replaced with fluorine or chlorine;

– HBFC – hydrobromofluorocarbons, organic compounds in which bromine atoms are present.

Aside from symbols mentioned above, a code number for each of the fluid may be marked by a single letter, as it is for typical refrigeration compounds (marked with 'R').

Second part of the code is commonly comprised of three of four digits. First number is the number of carbon atoms in a compound, decreased by one. Number 4 describes in this case a nonazeotropic solution, while number 5 – an azeotropic one. In particular cases, number 6 is used for organic compounds and 7 for inorganic. If the number is 0, it is omitted.

Second digit, given the first is in a range of 1–3, describes the number of hydrogen atoms in the particle, increased by one. If the first digit is 4 or 5, the second and third digit are used as a variable describing the solution composition. If the first number is 6, the second number becomes 0 for hydrocarbons, 1 for compounds containing oxygen, 2 for compounds containing sulfur and 3 for nitrogen. If the first number is 7, the second and third numbers are the particle mass indication.

The third digit, given the first ranges from 1 to 3, shows the number of fluorine atoms in a particle.

If there are isomers available, an additional a, b, c etc is placed behind the code number. For example, a working fluid marked as HFC-134a is a compound containing 2 carbon atoms, 2 hydrogen atoms, 4 fluorine atoms and no chlorine atoms. Therefore, its formula is $C_2H_2F_4$. This formula can be used for two different isomers: CHF_2-CHF_2 (HCF-134) and CH_2F-CF_3 (HCF-134a). Examples of other compound marking can be found in [2].

It is also important to notice that, especially in the refrigeration industry, an additional marking system is implemented – ie R134a instead of HCF-134a.

Ecological and safety indicators

In order to assess the impact of work fluids on the environment, two separate adverse phenomena possible to occur with the fluids's release to the atmosphere should be considered – depleting the ozone layer and contribution into the greenhouse effect.

Since 1970's it is known that some of the stable refrigeration agents, such as R11 or R12, permeating into the atmosphere are degraded by UV radiation, causing the depletion of ozone resources. A hazardous concentration of once released freons can sustain in the atmosphere for hundreds of years. Just the same important is the problem of freons absorbing the heat radiation of wavelength λ = 8–15 μm, the, so called, dispersed sun radiation.

The described above adverse effects of refrigeration fluid use were the reason for conducting research in order to assess the environmental impact of all contemporary and yet to be used work fluids. Three main environment impact indicators have been developed:

– *ODP* – Ozone Depletion Potential – characterizing the impact of a refrigeration fluid on the intensity of ozone decomposition, in relation to that of R11 working fluid: $\mathrm{ODP}_{\mathrm{R11}} = 1$;

– *GWP* – Global Warming Potential – characterizing the impact of a refrigeration on the greenhouse effect, in relation to the impact of CO_2 and an exposition time of 100 years;

– *TEWI* – Total Equivalent Warming Impact – used mainly in reference to refrigeration agents, in CO_2 equivalent tons.

The last of the mentioned parameters (*TEWI*) allows a full assessment on the agent's environmental impact. It takes into account the direct influence of the agent's release into the atmosphere, as well as the indirect result of CO_2 emission during electric energy production, ie heat pump compressors. It is possible to determine the value of this parameter based on the equation:

$$TEWI = GWP_n + GWP_s + E \ [\mathrm{kg\ CO_2}]$$

where: $GWP_n = GWP \cdot L \cdot n$, $GWP_s = GWP \cdot (1 - \alpha_0) \cdot m$, $E = E_a \cdot \beta \cdot n$;

$TEWI$ – total equivalent of global warning increase in CO_2/a;

GWP – potential of global warming in reference to CO_2;

L – annual loss of refrigeration agent caused by leaks, in kg/a;

n – device exploitation time, in years,

α_0 – measure of agent recycling (range from 0 to 1);

m – mass of agent in the installation, in kg;

E_a – annual energy consumption, in kWh/a,

β – CO_2 emission indicator for production of 1 kWh of energy, in kg CO_2/kWh.

It is important to notice that evaluating the *TEWI* parameter is available only for certain installments, not for specific agents.

Aside from the above indicators, it is worth mentioning the fluids toxicity indicators.

Two groups of toxicity level were created:

– Group A – work fluids which do not have a hazardous influence on employees in direct vicinity being exposed daily to an average concentration of 400 cm^3/m^3 or above;

– Group B – work fluids which do not have influence on employees in direct vicinity being exposed daily to an average concentration below 400 cm^3/m^3.

Table 1

Common thermodynamic working fluids in ORC systems and their comparison factors [3]

No.	Name	Chemical formula	Marking	Molar mass, M [g/mol]	Boiling point, $T_{s,n}$ [K]	Critical parameters				Freezing point, T_m [K]	Vaporization enthalpy, r [kJ/kg]	$T_{s,n}$ / $T_k = T_{km}$ [-]
						Temperature		Pressure, p_k [MPa]	Volume, v_k [m^3/kg]			
						t_k [^{o}C]	T_k [K]					
1	Ammonia	NH_3	R717	17.0	239.7	132.0	405.3	11.33	0.00427	195.4	1347.0	0.591
2	Water	H_2O	R718	18.0	373.0	373.8	647.0	22.06	0.00315	273.2	2256.0	0.577
3	*n*-Butane	C_4H_{10}	R600	58.1	272.6	150.8	425.2	3.80	0.00490	135.2	383.8	0.641
4	Isobutene	C_4H_{10}	R600a	58.1	261.3	134.9	408.1	3.65	0.00514	114.0	328.4	0.640
5	*n*-Pentane	C_5H_{12}	—	72.2	309.2	196.6	469.8	3.37		143.4	357.2	0.658
6	Benzene	C_6H_6	—	78.1	353.0	289.0	562.2	4.90		278.7	438.7	0.628
7	Toluene	C_7H_8	—	92.1	383.6	318.6	591.8	4.10		178.2	362.5	0.648
8	1,1,1,3,3-entafluorobutane	$CF_3CH_2CF_2CH_3$	R365mfc	148.1	314.5	186.9	460.1	3.25	0.00193	243.2	200.8	0.684
9	1,1,1,2-Tetrafluoroethane	CH_2F-CF_3	R134a	102.0	248.0	101.0	374.2	4.06	0.00195	172.2	215.5	0.663
10	Ethylbenzene	C_8H_{10}	—	106.1	411.0	343.0	616.2	3.50		178.2	339.9	0.667
11	Dichlorodifluoromethane	CCl_2F_2	R12	121.0	243.2	111.8	385.1	4.13	0.00179	115.5	166.1	0.632
12	1,1,1,3,3-Pentafluoropropane	$CHF_2CH_2CF_3$	HFC-245fa	134.1	288.4	157.5	430.7	3.64	0.00193	166.2	208.5	0.670
13	1,1,2,2,3-Pentafluoropropane	$CHF_2CF_2CH_2F$	HFC-245ca	134.1	298.2	178.4	451.6	3.86	0.00193	199.8	217.8	0.660
14	Trichlorofluoromethane	CCl_3F	R11	137.0	296.2	197.8	471.0	4.41	0.00182	162.0	178.8	0.629
15	—		HFE-245fa	150.0	—	170.8	444.0	3.73			—	—
16	1,1,1,3,3,3-Heksafluoropropane	CF_3CH2CF_3	HFC-236fa	152.0	272.0	130.6	403.8	3.18	0.00180	179.0	168.8	0.674
17	Dichlorotrifluoroethane	$CHCl_2CF_3$	R123	152.9	301.0	183.8	456.9	3.70	0.00182	166.2	171.5	0.659
18	2-Chloro-1,2,2,2-Tetrafluoroethane	CF_3CHClF	R124	136.5	261.2	122.3	395.5	3.62	0.00179	156.2	146.5	0.660
19	1,2-Dichlorotetrafluoroethane	$C_2Cl_2F_4$	R114	170.9	276.7	145.7	418.9	3.26	0.00172	179.2	136.2	0.661
20	1,1,2-Trichloro-1,2,2-Trifluoroethane	CCl_2FCClF_2	R113	187.0	320.4	214.1	487.3	3.41	0.00174	236.7	143.9	0.658
21	—	$CF_3CH_2CF_2CH_3$	SES 36	184.5	308.8	177.6	450.8	2.85	0.00186		129.3	0.685
22	*n*-Perfluoro-Pentane	C_5F_{12}	—	288.0	302.4	147.4	420.6	2.05			87.8	0.719

Table 1 shows a collection of selected working fluids, categorized according to the systematic mentioned above, with their basic physical properties mentioned. Selected fluids were also shown in Table 2, with their ecological factors.

Table 2

Working fluids and their impact on the environment

Marking	ODP	GWP_{100}	Safety group
R717	0.000	<1	B2
R718	0.000	<1	A1
R600	0.000	~20	A3
R600a	0.000	~20	A3
R601	0.000	11	b.d.
R365mfc	0.000	825	b.d.
R134a	0.000	1300	A1
R12	0.820	10600	A1
HFC-245fa	0.000	950	B1
R11	1.000	4600	A1
HFC-236fa	0.000	9400	A1
R123	0.012	120	B1
R124	0.026	620	A1
R114	0.850	9800	A1
R113	0.900	6000	A1
SES 36	0.000	3126	b.d.

The last criterion worth mentioning is the fluid flammability parameter. This category is divided into:

- Group A – fluids non-flammable in any concentration,
- Group B – fluids with a lower flammability limit of 3.5 % (or above) mixture with air,
- Group C – fluids with a lower flammability limit of below 3.5 %.

A comparison of fluids safety groups have been shown in Table 3.

Table 3

General characteristics of working fluids based on their toxicity and flammability

Criterion	Lower toxicity	Higher toxicity
Non-flammability	A1	B1
Lower flammability	A2	B2
Higher flammability	A3	B3

Division and practical use of working fluids

An increase of interest on low-boiling working fluids has been observed with the development of ORC-based technologies (organic Rankine cycle) [5, 10]. Because of its low energetic efficiency, the ORC systems have not received acclaim and recognition for a long time. But the possibility of selecting this technology for low-temperature unconventional energy reserve utilization, especially through dumped biomass combustion energy, has caused an increase of interest in this technology.

The Clausius-Rankine Cycle (C-R) is a cycle used in evaluating conventional, organic-fueled, water steam engines, as well as nuclear power plants [4, 11–15]. It can also be used for non-water fluid vapor engines evaluation – these fluids include low-boiling refrigerants (organic oils, freon, hydrocarbons etc). It is this kind of cycle, which is commonly known as Organic Rankine Cycle. Choosing the fluid's thermodynamic properties (like these shown on Belpaire's limit curves – Fig. 1) as a main criteria, three types of organic fluids can be distinguished – wet fluid, dry fluid and an isentropic fluid. This division is based on expansion process of a fluid in dry saturated vapor state in respect to the higher limit curve.

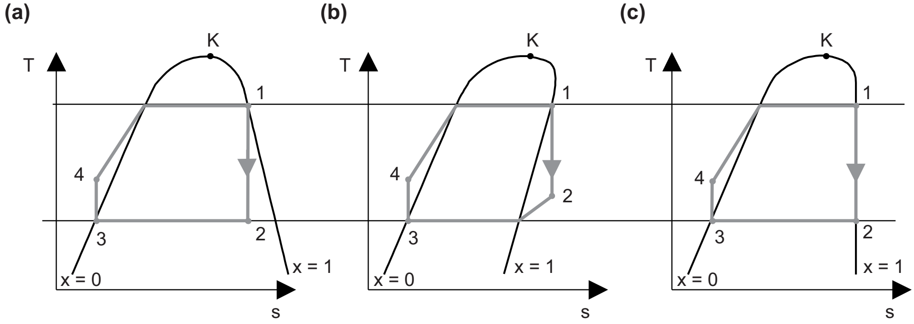

Fig. 1. ORC cycles for different work fluids: (a) wet, (b) dry, (c) isentropic

From a technological point of view, the most convenient type of fluid to use is the so called dry fluid, expansion of which unfolds in the overheated vapor area. This guarantees beneficial turbine work conditions, because the fluid flowing through it does not contain liquid drops.

Schematic diagram of the classical ORC cycle have been shown in Fig. 2 however internal regeneration is commonly introduced if such a fluid is utilized. The regenera-

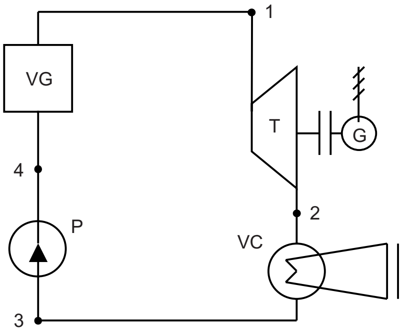

Fig. 2. Basic ORC cycle scheme, VG – vapor generator, T – turbine, G – electricity generator, VC – vapor condenser P – pomp

tion is based upon the fact, that the cooling fluid leaving the turbine (in a state of overheated vapor) empowers the heat exchanger (recuperator) before entering a condenser – the heat received in the recuperator is then transferred into the liquid being condensed from vapor in the condenser. Introduction of an internal regeneration causes preliminary heating of the liquid which enters the heat exchanger, in front of which the regeneration heat is utilized.

The ORC cycle in such an arrangement is accomplished through the following line of devices:

– A heat exchanger for heating the working fluid with the use of excessive heat;

– Dry saturated vapor generator, also empowered with excessive heat;

– Turbine, used for expanding the dry saturated vapor into the state of overheated vapor;

– A recuperator (overheated vapor cooler and liquid preheater also);

– A vapor condenser;

– A pump empowering the recuperator and any other further heat exchangers.

Selection criteria for orc system working fluids

When choosing a work fluid for ORC systems, special attention should be put on few basic criteria deciding whether the system will function properly:

– Jacob's phase shift number $Ja(T_1)$ for the upper source parameters and respectively, as an equal criteria $\Delta H\,(T_2)/h_{1,v}$ relation. According to [4], the ORC efficiency can be described with a following formula:

$$\eta = \frac{\Delta H\,(T_2)/\,h_{1,v}}{(c_p\,T_1\,/\,h_{1,v})\,\eta_c + 1} = \frac{\Delta H\,(T_2)/\,h_{1,v}}{Ja\,(T_1)\,\eta_c + 1}$$

where: T_1 – expansion start temperature within the turbine;
c_p – specific heat capacity;
$h_{1,v}$ – phase shift heat;
$\Delta H\ (T_2)$ = $h_2 - h_3$ (excess of enthalpy in respect to the condenser).

Because the Jacob number is directly proportional to the system's efficiency, It is important to choose a fluid which a possibly high Jacob number. The $\Delta H\ (T_2)/h_{1,v}$ relation should be possibly low [4].

– For under-critical cycles, the upper source temperature should be below the critical point.

– The relation of pressure in front of and behind the turbine should be moderate, because it is a factor determining the power of the pump.

– The saturation pressure of the lower source should be a bit higher than atmospheric pressure, enabling the easiness of keeping the installation airtight.

Having the above criteria in mind, it is possible to evaluate whether a work fluid is possible for implementation in a specific cycle. The final choice of a fluid is commonly based on one additional, often a critical parameter – the price of a given fluid. This factor verifies the cost-efficiency of the whole system.

Work range and efficiency comparison of working fluids

A number of possible fluids was tested for possible ORC system utilization. Six of the tested fluids were chosen further and their work characteristics under different work parameters have been evaluated. These fluids have been shown in Table 1 and Table 2. The crucial criteria were two work temperature limits, between which an ORC system was to be established. The upper temperature limit was consecutively set on 80, 100 and 120 ^{o}C, while the lower – approx. 35 ^{o}C. This is an average range of temperatures in an excessive refinery heat utilization process.

A basic Clausius-Rankine cycle (C-R cycle) was examined, with the use of different working fluids. Results of the analysis are shown in Table 4. One should notice the strong influence of temperature range on the basic C-R cycle, based on different fluids. Simultaneously, research on the possibility of using an ORC in lower temperature range has been conducted.

Table 4

C-R cycle efficiency comparison with different working fluids under different temperature limitation

Work fluid name	Mollar mass [kg/kmol]	C-R cycle efficiency (upper source temp.)			Saturation temp. (1 bar pressure) [^{o}C]	Critical point parameters	
		120 ^{o}C	100 ^{o}C	80 ^{o}C		[^{o}C]	[MPa]
SES 36	184.5	0.1681	0.1444	0.1124	35.26	177.55	2.85
R600 (*n*-Buthane)	58.1	0.1729	0.1451	0.1111	–0.84	150.80	3.72
R600a (isobuthane)	58.1	0.1691	0.1439	0.1187	–12.20	135.92	3.68
R365mfc*	148.1	0.1543	0.1277	0.1681	40.99	186.85	3.25
R123	152.9	0.1750	0.1462	0.1112	27.20	183.79	3.74
R124	136.5	—	0.1430	0.1103	–12.27	122.22	3.62

* – end temp. 42 ^{o}C because of the negative pressure area.

In this study, an ORC system, working in a temperature range of 73 ^{o}C to 32 ^{o}C has been examined – this range allows good cooperation of the system with an existing installation. Three different work fluids have been taken into consideration, for which the efficiency calculations in different configurations have been developed.

Firstly, a basic ORC system was examined, after that – a cycle with a heat regenerating exchanger implemented within. Based on the results, a working fluid providing the maximum efficiency within the given temperature range has been chosen. The efficiency of a Carnote cycle for this fluid was $\Delta\eta_c$ = 11.84 %.

Table 5 lists the calculations for ORC system efficiency. The Jacob number and $\Delta H\ (T_2)/h_{l,v}$ value, both also enlisted, were the reference factors. Analysis of the results shows that the use of SES 36 working fluid allows reaching the maximum efficiency of 11.58 %.

Table 5

Results of ORC efficiency calculations with different working fluids [16, 17]

No.	Marking	$Ja(T_1)$ [-]	$\Delta H\ (T_2)/h_{l,v}$ [-]	Basic ORC efficiency, η_{ORC}	ORC with RWC efficiency, η_{RWC}	Gain, $\delta\eta$
				[%]		
1	R123	2.331	1.143	10.63	10.64	0.09
2	R600a	3.387	1.256	10.57	10.72	1.42
3	SES 36	3.234	1.236	**10.87**	**11.58**	**6.53**

Other methods of increasing the efficiency, such as an overheated thermodynamic cycle, have also been taken into account In the study, but for the temperature range of interest, an increase in efficiency has not been achieved.

A different method of increasing the efficiency of a basic ORC cycle (with SES 36 working fluid) has also been examined – a concept to use a mixing heater powered at the outlet of the turbine. The results of this analysis showed an absolute increase of efficiency (in reference to a basic ORC) by $\delta\eta_t = 0.39$ % and a relative increase by $\Delta\eta = 3.59$ %, however, this increase is lower than in case of a heat regeneration exchanger utilization.

In general, one should notice that for the upper cycle temperature, utilizing a mixing heater does not provide higher efficiency in accordance to the exchanger. However, in a higher temperature range, one can expect that $\eta_{PM} > \eta_{RWC}$.

Conclusions

Results of analysis of different work variants of an ORC system with different working fluids showed validity of using an SES 36 fluid working in a low temperature range, in comparison with other commercial working fluids.

The highest work efficiency was achieved in a cycle with a heat regeneration exchanger coupled within, however it is important to point out that if the temperature of the upper source is higher, introducing a mixing heater might be a better idea.

The properties of criteria numbers ($Ja(T_1)$ and $\Delta H\ (T_2)/h_{l,v}$) are used in a different method of evaluating the cycle's efficiency.

Acknowledgement

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SYSTEMATYKA I KRYTERIA DOBORU CZYNNIKA ROBOCZEGO UKŁADU ORC DLA OKREŚLONYCH ZASOBÓW CIEPŁA ODPADOWEGO

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Abstrakt: Poprawa sprawności energetycznej procesów technologicznych stanowi obecnie – obok ograniczenia emisji gazów cieplarnianych i wykorzystania alternatywnych źródeł do produkcji energii – najważniejszy element idei zrównoważonego rozwoju. Niniejsza praca wychodzi naprzeciw rynkowym oczekiwaniom. wskazując możliwości wpisania się w ten trend. W procesach technologicznych ciepło odpadowe stanowi nie zawsze do końca rozwiązany problem. Zagospodarowanie tego ciepła. szczególnie w przemyśle rafineryjnym i petrochemicznym. napotyka na wiele trudności związanych z niską egzergią, znacznym rozproszeniem, dużym zróżnicowaniem parametrów i opłacalnością potencjalnej modernizacji. Jedną z obiecujących technologii utylizacji tego ciepła jest zastosowanie układu ORC. Niniejsza praca przedstawia globalne podejście do problemu uzyskania optymalnej sprawności układów ORC. z uwzględnieniem sprawności termodynamicznej. Przeprowadzono kompleksowy przegląd czynników termodynamicznych. możliwych do zastosowania w układzie ORC ze względu na zakres temperatury źródeł, bezpieczeństwo, cenę i ochronę środowiska. Stanowi ona zbiór ogólnych wytycznych przy wykorzystaniu literatury przedmiotu i doświadczenia badawczego zdobytego przy projektowaniu dla zakładów przemysłowych niekonwencjonalnych rozwiązań dotyczących zagospodarowania zasobów energii odpadowej. Jak się oczekuje. wykorzystanie instalacji do zagospodarowania energii odpadowej zapewni nie tylko poprawę wydajności procesów technologicznych. ale również poprawi proekologiczny wizerunek przedsiębiorstwa.

Słowa kluczowe: układ ORC, czynnik roboczy, zagospodarowanie ciepła odpadowego

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ANALYSIS OF WATER MANAGEMENT OF THE MICHALICE RESERVOIR IN RELATION TO ITS FUNCTIONS

ANALIZA GOSPODARKI WODNEJ ZBIORNIKA MICHALICE W ASPEKCIE JEGO ZAŁOŻONYCH FUNKCJI

Abstract: This paper focuses on the example of the Michalice reservoir located on the Widawa River. Its main functions are decreasing of flood danger beneath the reservoir, an availability of stored water in the basin for agriculture purposes and electric energy production, a creation of conditions for recreational use. Current water administration was analyzed. Special attention was paid to the proper use of the reservoir, and the benefits of its existence: the eutrophication rates, the classification of water, fish living and bathing purposes. It was affirmed that, the reservoir decreases the flood danger below the basin but it creates limited possibilities for recreation and pisciculture. Improper water management generates a danger of overflow onto the terrains around the reservoir. A small hydroelectric power station and fish ladder do not accomplish their tasks. Suggestions on how an improved water administration on the Michalice reservoir can occur are given.

Keywords: water reservoirs, water management, the exploitation of the reservoir, water quality

The Michalice reservoir on the Widawa River, is one of nine small water basins located in the Opole province, (southern Poland) it has a range of functions. These functions include, water storage in periods when water flow velocity is greater than the demand, or alternatively, if it is insufficient to need, flood protection, electric energy production, fishing (non-industrial pisciculture) and other recreational purposes [1–2] and agricultural irrigation [3].

The exploitation of the storage reservoir affects water management of the catchment basin both, in quantitative and qualitative ways [4–7]. Despite these varying functions,

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the reservoir maintains its condition without any difficulties [8]. However, fairly often, the reservoir's functions may be disturbed by the inflow of pollution into it, and this therefore causes a decrease in the quality of water in it. A substantial danger for the water basins is eutrophication [9–16]. Considering the significant role of small retention objects in the water management of regions, it is crucial that water management is led properly .

Proper administration of stored water requires work on a range of issues, including regulation of the frequency of the reservoir outflow discharge, leading on the reservoir's water administration while in regular use or in a situation of flood danger, selecting suitable reliable and controlling flows, measuring of sluice appliances. Furthermore, it is vital that the following is monitored: hydrology data in the catchment of the reservoir, issues concerned with the performance, safety, and stability of the ground barriers, the regulation method of water relations on the adjacent terrains, the water quality in the reservoir, spatial development around the reservoir together with, water-sewage management in the catchment, in order to preserve clear water in the water basin [5, 7, 17–19]. A significant factor in the optimum water basin utilization is the instruction of water administration, which is formulated by the Ordinance of the Polish Ministry of Environment, which oversee a range of water management duties [20]. This instruction ought be done, and lodged with the relevant department for each reservoir. Only then, can the reservoir be used.

The aim of this work is to analyze water management of the small Michalice dam against its prescribed functions.

Methods and materials

The research included stocktaking work on the Michalice reservoir and its devices and exploitation conditions. Current technical condition and the way water administration of the reservoir is deployed were rated. The analysis of the outflows from the Michalice reservoir and the water tract position in the reservoir were carried out from May 2005 to April 2006. [21]. In the study, the findings of the water quality research in the Michalice reservoir were gathered from two sampling stations: on the height of the Michalice village [Station 1] and above the reservoir's dam [Station 2] (Fig. 1), for the water samples collected during spring – autumn 2005 period [22]. The eutrophication state of the Michalice reservoir was gathered by the Ordinance of the Polish Ministry of Environment on the 23rd December 2002, it concerned determination of water susceptible to nitrates pollution from the agriculture settlements [23]. The quality of water in the reservoir was determined by a comparison of points that have been examined with the set limit on quality of water, being that required for fish live in [24] and for the safe bathing purposes [25]. The propositions of appropriate water management of the Michalice reservoir were given.

The Michalice reservoir is located at the 70.232th river-km of the Widawa River (Right bank of the Odra River tributary), about 1.5 km to the north from the town of Namyslow (Fig. 1). The reservoir was open for use from 2001, it is the second reservoir on this river, aside from the Stradomia reservoir situated on the upper watercourse of the river.

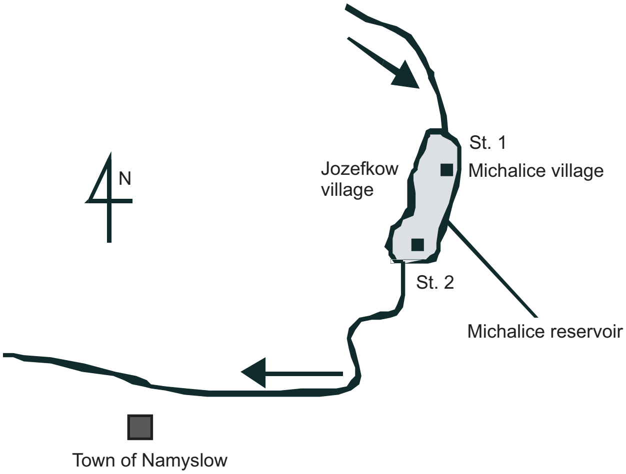

Fig. 1. The localization of the Michalice reservoir

At maximum crest backwater level (max crest width – 154, 20 m a.s.l.) the overall capacity of the reservoir is 1748195 mł with the total area – 95.7 ha. With regular backwater level (regular backwater level – 153, 50 m a.s.l.) the constant capacity of the reservoir accounts for 1191095 m^3 and the capacity available for flood control accounts for 557100 m^3, whereas its area amounts to – 92.98 ha. The average annual water outflow SSQ, in the Widawa River in a cross section of the reservoir is 2.04 $m^3 \cdot s^{-1}$, whereas the average mean water outflow is SNQ = 0.52 $m^3 \cdot s^{-1}$ [2, 26].

The dam on the Michalice reservoir is IV significance class. The overall length of the dam amounts to 455 m including discharging chutes. The cross-section of the dam has a trapezoidal shape (Fig. 2a). Located in the frontal dam of the reservoir are two constant surface spillways (Fig. 2b). These along with two bottom sluices, a small water power plant and fish channel constitute the main appliances in the dam body. Situated on the left side of the main part of the Michalice reservoir, there is the expansion tank,

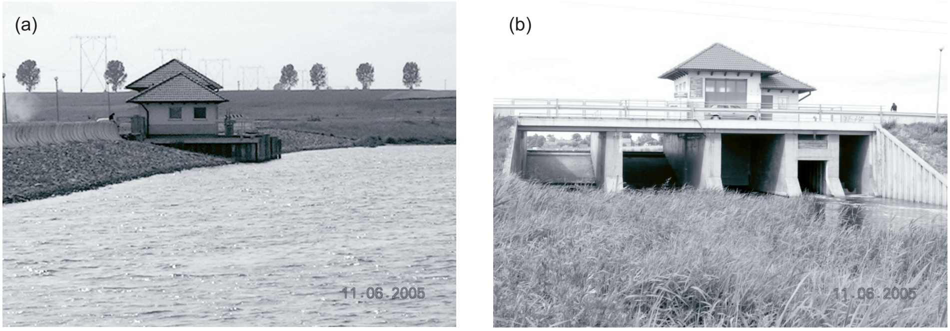

Fig. 2. The Michalice reservoir: (a) – The dam of the reservoir; (b) – The outflow from the reservoir together with the spillways, the exhaust from water power plant and fish ladder

which serves the purpose of collecting water for agriculture irrigation. The pumping stations for draining water are situated near the main part of the reservoir, in Jozefkow and Michalice

The reservoir's catchment area amounts to 509 km^2. Widawa is controlled in the reservoir area with the help of water gauges placed in the Michalice reservoir in the backwater zone, near the frontal dam and also, near the bridge in Namyslow. However, there is a lack of a water gauge patch directly under the reservoir. On the terrain of the reservoir, there is no meteorological station. The Michalice reservoir is under the administration of the Namyslow Community Office [1] and its main user is The Polish Angling Association.

The analysis of water management on the Michalice reservoir

Water management of the Michalice reservoir, can be divided into two operational states. The first is water administration in regular conditions of use and the second one, is flood danger state. The Regular conditions of water management on the reservoir occur when the following requirements are all met: the backwater level ordinate, does not exceed 153.50 m a.s.l., the inflow to the reservoir does not go beyond 3.0 $m^3 \cdot s^{-1}$, and a 'flood danger' emergency state is not announced. Additionally any damage to any part of the reservoir, has not threatened the reservoir's safety [2, 26]. During regular conditions of using the Michalice reservoir, controlled water management takes place, which means that the reservoirs fulfills agricultural and energy functions.

Water management in 'flood danger' state on the reservoir; occurs when at least one of the below conditions is met:

– the 'flood danger' emergency state was announced;

– the backwater level exceeds the normal backwater level ordinate, that is 153.60 m a.s.l.;

– the inflow to the reservoir went beyond 3.0 $m^3 \cdot s^{-1}$ [26].

The aim of the flood protection regulations are to effectively reduce flooding on the reservoir, this allows lightening spates in the valley of the Widawa River beneath the reservoir. Flood protection management is based on maintaining flood retention capacity which is filled up during an overflow.

The rules of water management can be established when the flood proceeding is divided into 3 stages:

a) the stage of filling the accidental or preparatory reserve;

b) the stage of filling the stable flood retention capacity;

c) the stage of recreating partially or entirely, filled flood reserve.

The period of the flood proceeding is carried out until the flood reserve is restored. Water administration on the Michalice reservoir in flood conditions is built on a fixed scheme of the outflow disposition [26]. According to Ciepielowski [27] this type of water management, while accumulating the wave crest, that is in the period when the inflows to the reservoir exceed allowed flow, the outflow equal to allowed flow is disposed. In the storage reservoir, the surplus of water over allowed Q is retained. Then, cutting of the wave crest is gained, however it happens only when the capacity of the wave crest fits entirely into the storage reservoir. In a case, where the capacity of the wave crest exceeds the scale of the storage reservoir, a situation occurs where, overall filling of the reservoir may happen before the crest inflow arrives, which precludes its reduction [27].

Hydrological monitoring

The information about the formation of the water tract position in the reservoir, is significant from the point of view of conduced water management on the reservoir. The Fig. 3 presents ordinate values of the Michalice reservoir's stored water tract from May 2005 to April 2006.

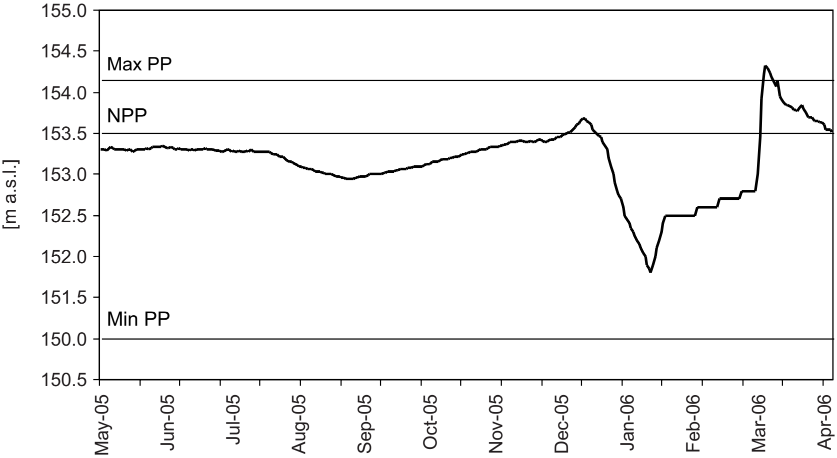

Fig. 3. The position of ordinate value of the water tract in the Michalice reservoir from May 2005 to April 2006

During the analyzed period the maximum level of backwater (Max. PP), which is specified in Water Management Instruction [26] on the level of 154.2 m a.s.l., was exceeded 13 cm. This situation occurred on the 28th March 2006 (Figs. 3, 4a). The described occurrence was due to the effect of melt water inflow to the reservoir. From the point of view of flood prevention, it is important to discharge prominently the reservoir, before the level of water in the Widawa River rises, this allows receiving and reducing of the spate wave. Otherwise, the inundation of the terrains beneath the reservoir's dam (town of Namyslow), Fig. 4a, as well as the undercut of terrains in the direct neighborhood of the reservoir will occur (Fig. 4b). In the analyzed period the minimum level of backwater (Min PP) which amounts to 151.00 m a.s.l. was not met. The ordinate value of regular backwater level (NPP) in the Michalice reservoir, which amounts to 153.50 m a.s.l., was exceeded only for 54 days during the research time (Fig. 3). During the remaining time, the water management was conduced under normal water level, accepted in Instruction [26].

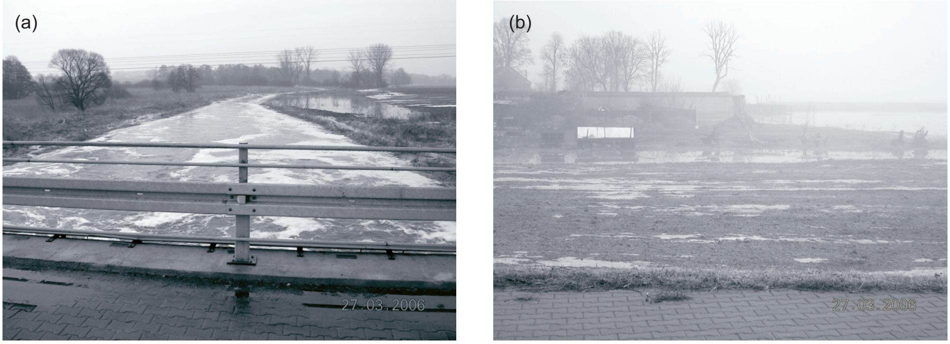

Fig. 4. (a) – The outflow from the Michalice reservoir on the Widawa River in March 2006; (b) – The undercut around the main part of the reservoir

The time of water retention in the reservoir

The time of water retention, which means the time it takes to exchange the reservoir's water overall, plays an important role in creating the reservoir's environment. It not only determines the hydrological system of the reservoir, but also together with intensity of water meddling, determines the matter circulation in the reservoir and what is more, it is a factor, which influences trophy state and water quality in the reservoirs [15, 28–29]. The retention time in the Michalice reservoir based on relation between water capacity outflowing from the reservoir to the capacity of the reservoir in the relevant period, was rated. In Fig. 5, the outflow from the reservoir from May 2005 to April 2006 and the water retention time are given.

The water outflow from the Michalice reservoir, in the period from May 2005 to April 2006, was quite stable. The average outflow amplification amounted to

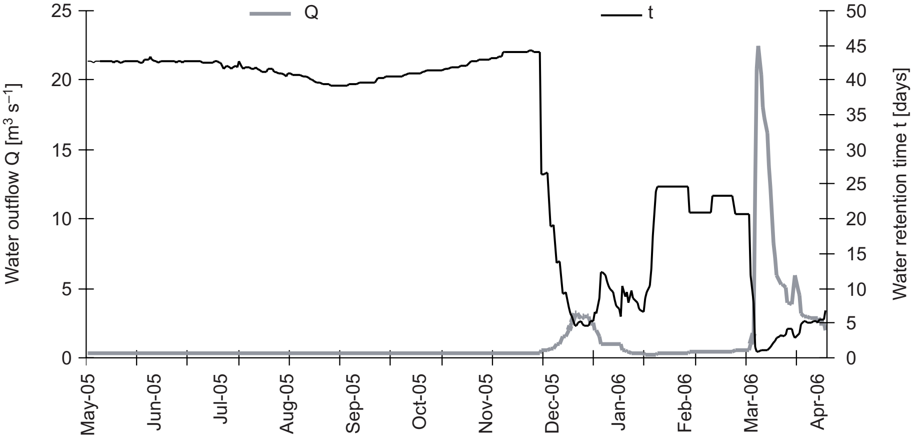

Fig. 5. Changeability of water outflow and water retention time in the Michalice reservoir during the period from May 2005 to April 2006

1.156 $m^3 \cdot s^{-1}$, and it was lower than water flow in the dam's cross – section of the Michalice reservoir [26], for the last 45 years, including 1997, when the flow amounted to 2.04 $m^3 \cdot s^{-1}$. The average time of water retention during this period amounted to 30.6 of day. During springtime of 2006 during March and April, the reservoir began to receive melt water. The effect of that, was a considerable decrease of the average twenty-four hours time of the retention, which amounted to about one day, an increase of an average daily outflow to 22.5 $m^3 \cdot s^{-1}$ on March 28, 2006,which exceeded the allowable flow value Q = 18.69 $m^3 \cdot s^{-1}$ given in Instruction [2, 26]. During summertime 2005, the lowest rate of outflows from the reservoir were registered (0.3 $m^3 \cdot s^{-1}$), and at the same time, vastly higher values of the average water retention time – 43.4 of day were noticed. During the reservoir's exploitation, the cast from the reservoir should be at least equal to unassailable flow Q = 0.26 $m^3 \cdot s^{-1}$. The average value of water capacity in the reservoir in the analyzed period amounted to 1.041 mln m^3 and the amplitude of water table variations in the reservoir was about 2.53 m.

Small water power plant

The small water power plant located in the frontal dam of the Michalice reservoir (Fig. 2b) is characterized by the following technical parameters: power output – N = 62.4 kW, the parameter of Q = 2.04 $m^3 \cdot s^{-1}$, the light of the upper channel B = 4.0 m. An assumed annual average production of electric energy 464809 kWh, the turbine type: Francis turbine with a vertical axis, rotor diameter D = 1230 mm [2], is currently out of order due to the turbine's failure.

Fish ladder

A properly working fish ladder plays an important role, it enables fish migration, so fish can live in a mixed environment. It enables migration of fish up the river across the reservoir's dam. The existing fish ladder on the Michalice reservoir which is a chamber type (Fig. 2b) with light b = 2.0 m, flow velocity 0.19 $m^3 \cdot s^{-1}$ and eight, 2 meters long chambers with ferroconcentrate baffles does not function properly. The filed investigations on the Michalice fish ladder, carried out on it in the years 2006–2008, show that it is inefficient. The main reasons for this are too little water depth on the entrance to the fish ladder from the lower water and in the chambers. Secondly, too low feeding or even perhaps the feeding deficit. It is very important matter, during fish migrations and spawning time [30]. Water management on the Michalice reservoir should provide for the vital requirement of a properly functioning fish ladder in the water, especially as shown in similar periods as those mentioned above.

The water quality in the reservoir

Table 1 presents the outcomes of chosen physico-chemical indicators of the Michalice reservoir water from 2005 [22].

The pH-value of water sampled in summer time from the reservoir, indicated the process of water alkalization – values within the confines of 8.8–8.9 (Table 1).

Table 1

The quality of stored water in Michalice reservoir in the year 2005

Sampling sites	Research periods	pH	Chlorophyll *a* [μg · dm^{-3}]	Concentration					
				NO_3^- [mg · dm^{-3}] Nitrates(V)	NO_2^- [mg · dm^{-3}] Nitrites(III)	NH_4^+ [mg · dm^{-3}] Ammonia	Total N [mg · dm^{-3}]	PO_4^{3-} [mg · dm^{-3}] Phosphates	Total P [mg · dm^{-3}]
Station 1 Waters of the Michalice reservoir	spring	—	87.4	7.75	0.144	0.588	3.49	< 0.050	0.162
	summer	8.8	48.1	< 0.50	< 0.046	0.66	—	< 0.050	0.260
	autumn	—	18.3	< 0.50	< 0.046	0.575	—	< 0.057	0.158
Station 2 Waters of the Michalice reservoir	spring	—	61.5	5.54	0.135	0.541	3.13	0.068	0.141
	summer	8.9	37.8	< 0.50	< 0.046	0.66	—	0.081	0.245
	autumn	—	20.2	< 0.50	< 0.046	0.66	—	< 0.074	0.212

The analysis shows that, in summer water temperature in the Michalice reservoir was 20.8–23.0 ^{o}C. In autumn water temperature in the reservoir was 12.9–14.2 ^{o}C. The dissolved oxygen contents in all analyzed periods in the reservoir's water were oxygenated properly (7.13–12.2 mg $O_2 \cdot dm^{-3}$). The highest level of nitrates(V) and nitrates(III) were observed in spring, while, in summer and autumn minute quantities of these elements were registered in the reservoir's waters. Higher ammonia concentration in the water was registered in summer [22].

The analyses carried out, in the year 2005, indicated high chlorophyll *a* concentration in the waters of the reservoir, in spring and summer time (87.4 $\mu g \cdot dm^{-3}$), Table 1. The extortionate presence of phytoplankton in algae form, which causes water bloom, is objectionable.

The analyses presented in Table 1 shows that, among other eutrophication indicators, the chlorophyll *a* concentration in waters of the reservoir in the spring and summer period helps indicate the eutrophical character of these waters. Either, a higher phosphorus or nitrogen concentration (Table 1) implies the eutrophication of water samplings taken from the reservoir body [23].

The analysis of water in the reservoir in terms of requirements for inland waters, that being a liveable environment for salmon and carp species living in normal conditions [regulation 2002a] showed that, the water temperature (for carp species) and ammonia nitrogen $N\text{-}NH_4^+$, which does not exceed a value of 0.78 mg $N\text{-}NH_4^+ \cdot dm^{-3}$, comply with these requirements. The most adverse conditions for fish living were nitrates(III), which exceeded the required [24] value of 0.01 mg $NO_2^{Ż} \cdot dm^{-3}$ for salmon species, and 0.03 mg $NO_2^{Ż} \cdot dm^{-3}$ for carp species, phosphorus (summer) and water temperature (Table 1) for salmon species.

The reservoir should also be used for recreation purposes [2, 26]. However, it can be noted the quality of water in the reservoir at the height of Michalice village (Fig. 1, Station 1), on account of a slightly raised phosphorus concentration, does not comply with the requirements on water, which is used in lidos in inland waters [25]. The too excessive contamination of the reservoir may have been contributed also by too large loads of anglers' baits. Equally important is proper water and sewage management led in the catchment of the reservoir, as well as, on agricultural holdings and lodges that are located around the reservoir.

The study carried out on the Michalice reservoir shows, that during the analyzed period, the reservoir was in the second stage of the utilization development. This stage usually lasts 2–10 years from the moment of tankage. The overall rise of the reservoir's fertility takes place, because the sediments are not fully formed and are from flooded soils along with decomposed greenery, which gives the water biogenic substances. During this period a mass expansion of some phytoplankton forms may occur [31].

Conclusions

As Mioduszewski and Los state [4] a large constriction in the use of the small retention reservoirs is that, these objects do not have a guaranteed constant availability of use by the professional services, which are able to operate the sluice devices in a proper way. The Michalice reservoir, administrated by the Community Office in Namyslow, has been in use since year 2001 thus, it is relatively new reservoir. The devices condition does not arouse any objections. The observations confirm a periodical renovation of the devices (Fig. 2). Only the small water power plant and the fish ladder do not work as they were intended to [2]. The Small water power plant should be redesigned once more, to fulfill its purpose, as presented in the reservoir's project plan. Furthermore, the fish ladder should be converted because at present it does not accomplish its role.

The water management of the reservoir in regular backwater level periods, as well as, during flood water level periods should follow a set procedure in order to provide proper functioning and exploitation on the reservoir's devices and to prevent danger for people and the surrounding estate. So that the reservoir cannot negatively affect the adjacent terrains, as it had in March 2006 (Fig. 4).

The main danger for the Michalice reservoir is the quality of water condition. In the analyzed period large quantities of chlorophyll *a*, nitrogen and phosphorus were noticed. This shows the eutrophic character of water in the Michalice reservoir, it means the use of the reservoir for recreation is limited. The water bloom occurrence confirms this. In turn, the nitrates(III) concentration exceeded an acceptable limit for salmon and carp species, and phosphorus along with temperature levels for salmon species.

In order to lead optimum water management on the Michalice Reservoir, it is necessary to continue a hydrologic monitoring of water quality. An automatic hydro-met station should be installed in the catchment of the reservoir. A water gauge should be placed under the reservoir. The analysis of water quality should be carried out at least 3 times a year – at the beginning of the growing season (April/May), during the growing season (July, August), and after the end of growing season (October/November).

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ANALIZA GOSPODARKI WODNEJ ZBIORNIKA MICHALICE W ASPEKCIE JEGO ZAŁOŻONYCH FUNKCJI

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Abstrakt: Na przykładzie zbiornika Michalice na rzece Widawie, którego założonymi funkcjami są zmniejszenie zagrożenia powodziowego poniżej zbiornika, wykorzystanie zgromadzonej w zbiorniku wody dla rolnictwa i do produkcji energii elektrycznej, stworzenie warunków do wypoczynku i rekreacji, przeanalizowano aktualną gospodarkę wodną. W pracy wykonano analizę odpływów wody ze zbiornika do rzeki Widawy, poziomów wody w zbiorniku i jakości wody retencjonowanej w zbiorniku. Szczególną uwagę zwrócono na ważne, z punktu widzenia prawidłowego użytkowania zbiornika walory użytkowe wody: ocenę eutrofizacji wód zbiornika, klasyfikację wód do bytowania ryb i do kąpieli. Stwierdzono, że zbiornik zmniejsza zagrożenie powodziowe poniżej zbiornika i stwarza ograniczone możliwości dla rekreacji i hodowli ryb. Niewłaściwa gospodarka wodna na zbiorniku stwarza jednak zagrożenie podtopień terenów wokół czaszy zbiornika. Mała elektrownia wodna i przepławka dla ryb nie spełniają stawianych im zadań. W pracy podano propozycje prawidłowych zasad gospodarki wodnej na zbiorniku Michalice.

Słowa kluczowe: zbiorniki wodne, gospodarka wodna, eksploatacja zbiornika, jakość wody

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IDENTIFICATION OF ODOUR-GENERATING SUBSTANCES IN PHOSPHATE ROCK PROCESSING OPERATIONS

IDENTYFIKACJA ZWIĄZKÓW ODOROTWÓRCZYCH W PROCESACH PRZETWARZANIA SUROWCÓW FOSFOROWYCH

Abstract: There is no kind of odour control law in Polish legislation. Therefore, Polish citizens and many branches of industry have got problems which are connected with the influence of volatile chemical substances which affect the drop of air quality. Couples of government attempts of solving this situation by proposing suitable projects were rejected by industry and scientist. The phosphate ores manufacturing especially superphosphate production was chosen as an example of a branch of industry which is a source of odours. In due to characterize odour problem in the light of superphosphate production the exhaust gases were analyzed and the results were compared with reference to professional literature. The gas samples were taken in FOSFAN S.A Company during superphosphate manufacturing and analyzed using TD-GC/MS method. There were identified over 80 volatile organic compounds like alkanes, cycloalkanes and aromatic compounds. Probably the most significant influence for odour perception is connected with presence of sulphur volatile organic compounds. In addition to lack of professional data connected with smell of gas mixture consisted with different particles there is no possible to exclude the influence of other particles for human smell perception. Finally the new method of further research was suggested. This research includes not only analysis of organic matter in waste gases but also in phosphate rocks and superphosphate fertilizer. To obtain comparable results the whole research should be provided during the same day of production. This sort of research could give a solution for deodorization and preventing the drop of air quality. It could be also helpful in course to develop new law projects. It is predicted that in future the production of superphosphate fertilizer will increase. Thereby the greater amount of odours will be released into the atmosphere. That is why further research combined with creating well functioning odour control law is so important to be established.

Keywords: odours, super phosphate, volatile organic compounds

The notion of odour-generating substances is very wide as malodorous compounds are very complex group of chemical particles. Mostly these chemicals differ as for the

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odour and their mixtures can have very diversified and often unpredictable odours. This is why the presence of malodorous compounds in the air possess many problems starting from their identification and determining their concentration and finishing with selecting the method of their neutralization. As manufacturing companies are developing, more and more people complain to various bureaus about too much drop in air quality. This issue has become a ranging problem and the lack of projects which could solve it is making things worse. There is a noticeable gap in Polish legislation as there is no law which would regulate in comprehensive way the problems of odour-generating compounds presence in the air. The suggested solutions concerning the possible concentration of odour-generating compound in the air and the resulting norms and rules creation are based on the odour analysis carried out by panel of qualified people who are sensitive to odours. The test is done several times but still it depends on subjective judgment of panel members. Such judgment, according to latest assumptions of "odour bill" draft, is to be a foundation to carry penalty on the manufacturers, or even either stopping the production or closing the factories by local authorities. It has not been mentioned how one can check and control the decisions of authorities. According to the assumptions of bill draft local authorities will not need to consult the specialist in the field of odour nuissance before imposing restrictions on given company. Polish Confederation of Employers does object to this form of bill as it might cause more problems than solutions. Next projects or assumptions suggested by Ministry of Environment should include some alternative solution to such stalemate which will derive ideas from ready made and running "odour bills" that are effective in for example Holland or Japan. However, the way of specifying permissible concentration of odour in the air is not the only barrier that obstructs the accomplishment. Next problem is the cost of pilot analysis, laboratory equipment and modernization of manufacturing systems that are the source of odour-generating substances. Literature data says that Poland cannot afford introducing reformation in this field [1–3].

In the majority of countries legal protection of air quality is based on setting reference unit which specifies the amount of odour-generating substances in the air. In EU the European odour unit $\mathrm{ou_E}$ is used which is described in norm EN 13725:2003. Moreover, the grade of odour nuissance is generally connected to pointing permissible amount of emission caused by different kinds of odour-generating sources and modelling dispersion of odour-generating substances in the air. The standards of odour quality of the air specify permissible level of odour-generating substance concentration in the air – adequately for the specified concentrations the frequency of their yearly outpass which is often given as percentile of average concentration as the subject to one hour [4, 5].

The works on standardization of test methods used in olfactometry are being performed all the time, however, they have different objectives that is why the regulations differ from one another even within EU. The law in this field will not be systemized unless there is a quick possibility of odour assessment which would free the legislator from subjective results obtained by the panel members who specify the concentration of odour-generating compounds using their smell. Maybe the solution lies in creating electronic sensor, colloquially called "electronic nose", that would specify the odour concentration. The works on such device are in progress in many countries, however, the universal sensor that would specify odour concentration in any conditions have not been created. It is connected to a very complicated mechanism of sensing, identification and memorizing the smells by a human who has not been well-known yet. As we can see, the creation of law that is fully adequate to the nature of the problem is really hard and it might take a few or many years of intensive scientific and specialized work.

In this elaboration the emphasis was put on the problems of odour nuissance that goes with production of simple superphosphate. Reaction of the degradation of phosphoric raw material containing fluorapatite, as the most essential compound can be introduced as follows:

$$2Ca_5F(PO_4) + 7H_2SO_4 + 3H_2O = 7CaSO_4 + Ca(H_2PO_4) \cdot H_2O + HF$$

This reaction is conducted in two successive stages. In the first stage a fluorapatite available on the surface of granules of milled raw material is subjected to degradation. In this stage phosphoric acid is obtained according to an undermentioned chemical reaction [6, 7]

$$Ca_5F(PO_4) + 5H_2SO_4 + 2.5H_2O = 5(CaSO_4 \cdot 0.5H_2O) + 3H_3PO_4 + HF$$

When the sulphuric acid delivered as the substrate ends, the process limits only to the other stage of the fluorapatite acidulation reaction of the following chemical equation:

$$Ca_2F(PO_4)_3 + 7H_2SO_4 + 5H_2O = 5[Ca(H_2PO_4)_2 \cdot H_2O] + HF$$

Reactions of the phosphoric raw materials acidulation with sulphuric and phosphoric acid are exothermic [6]. The superphosphate continues to cure in the store for about 6–8 weeks. Even in the ready product the reaction mentioned above can not achieve the equilibrium, however its rate is very slow.

Phosphate rocks used for the production of simple superphosphate include some amount of organic matter. Exactly these organic compounds, during reaction between sulphuric acid and phosphate rock gives origin for volatile odour-generating substances causing drop of air quality in the surrounding of fertilizer manufacturing plants based on superphosphates.

The concentration of organic compounds in phosphate rocks oscillates in a range of 0.3 % to over 1.7 %. Approximately one fifth of organic compounds is soluble, the insoluble phase is based on kerogenic-type compounds. The kerogenic substances are geopolymers ie heterogeneous organic phase consisting of components of aliphatic, aromatic, ester and lipid character. Part of them contains large amount of sulphur, nitrogen and oxygen, and due to their properties the creation of metal-organic complexes is allowed [8].

Westerlich et al carried out an analysis of organic compounds contained in Tunisian phosphate rocks. The organic compounds were extracted from the phosphate rock samples to methyl chloride and ethyl acetate solutions. The mixtures obtained according to the following procedure were analyzed using GC/MS methods. Approximately 80 various chemical compounds were detected including aliphatic, aromatic hydrocarbons, parafinnes, hydrocarbons containing branched carbon chains, cyclic hydrocarbons, esters, thiols, heterocyclic compounds, lipid acids, amines, carboxylic acids, large amount of sulphur containing compounds as well as steroids and other. The samples of sulphuric acid solution were also analyzed by the same chromatography analysis. Sulphuric acid found to be carrier of organic compounds such as paraffins and esters. However these compounds are not potentially odour-generating [9].

Taking into consideration keeping good relationships with the local community the Chemical Manufacturing Plants producing phosphorus fertilizers are deciding to carry the modernization of production installations out and to establish cooperation with external companies, in order to determine the efficient method of the odour nuisance reduction. One of methods consists in using technical antiodorous preparations for vapouring interior of the chimney-shaped emitter. As a result of specific physico-chemical processes, occurring between malodorous molecules and neutralizing particles, being included in composition of antiodorous preparation, the osmic properties of odorous molecules present in waste gases from chimney-shaped emitter are blocked [10].

Many methods of the deodorisation also exist, using various properties of odour generating substances and technical-exploitation conditions in industrial plants. The part of them was presented in the undermentioned table (Table 1).

Table 1

List of selected methods of the deodorisation [4]

Deodorisation technique	Application	Advantages	Disadvantages
Method invented by Kurmeier, in which an oxidant (chlorine) is introduced to waste gases before entering into the absorber filled up with calcareous stone sprinkled with water	Deodorisation of waste gases from manufacturing plants using animal wastes and from objects of public utilities	Significant effectiveness and low costs of conducting the process	Obtaining large amounts of troublesome sewages
Ozonization	Deodorisation of waste gases from manufacturing plants processing fish, fats, rubber and in chemical as well as pharmaceutical industry	Low costs, waste-free, the possibility of joining with different methods in order to enhance the effectiveness of the process and the easiness of cleaning the installation	A requirement of removing ozone from gasses after deodorisation is a disadvantage of this process
Thermal oxidation	Burning gasses is being used for the deodorisation in coffee incinerators and bitumen manufacturing plants	Simple handling and waste-free	Expensiveness of the exploitation and problems at conducting processes at the change of the temperature of introduced gasses

Table 1 contd.

Deodorisation technique	Application	Advantages	Disadvantages
Sorption-oxidation method consist in joining absorption and thermal oxidation	Deodorisation of gasses containing solvents	Low costs and the unattended handling	High investment costs and the narrow range of applications
Condensation method	Deodorisation of gasses coming from objects of public utilities, animal and agricultural waste-processing plants, the foundry or the paint shop	Low costs	Obtaining unusually troublesome sewages
Masking	The deodorisation of gasses from animal farms, dumps, restaurants or toilets	Low costs, the simple handling, using the chemical compounds safe for the external environment	The high capacity of the ventilation system is required, strong dependence on weather conditions

Compounds being included in antiodorous preparations composition are not toxic for animals, plants and people and are readily biodegradable. Nowadays it is recommended to abandon traditional antiodorous preparations (eg containing aldehydes), which react with functional groups of odour generating substances, as in of such reactions environmental pollutions of the different type can occur. Modern preparations act on the basis of physicochemical processes, rather than of only chemical reactions [10].

Materials and methods

The gas samples were collected from simple superphosphate based fertilizer manufacturing plant. The samples were collected during ordinary working day applying the built in place system of the scheme presented in Fig. 1.

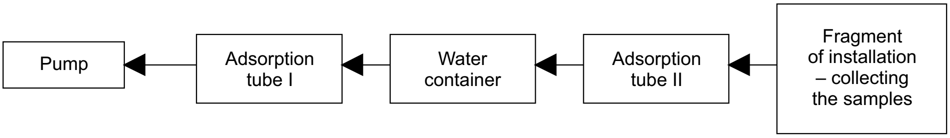

Fig. 1. Scheme of sample collection system

The first tube was filled with Carbosieve SIII adsorbent intended for adsorption of highly volatile compounds nC_2-nC_5 whereas second tube was filled with Tenax TA/Carbograph1TD adsorbent intended for collecting nC_2-nC_{26} compounds. The samples were being collected under constant flow rate = 100 cm^3/min for 60 minutes. The gas samples were subsequently collected to two plastic containers. Two repetitions of sample collection were carried out. The containers and the tubes with the adsorbed gas were secured and placed for TD-GC/MS method analysis. The TD-GC/MS method is the gas chromatography using thermal conductivity detector coupled with mass spectroscopy. This method allows for both quantitative and qualitative analysis of volatile compounds in gas samples. For conducting the analysis of collected samples the apparatus with HP-VOC 60 m; 0.2 mm; 1.1 μm) chromatographic column built-in with cold trap U-T6SUL Inert Sulphur Trap (C_2-C_{12}) was applied. The experiments were made with the initial temperature of 40 ^oC increasing by 5 ^oC per minute obtaining 200 ^oC at the inert gas (He) flow through the column with the flow rate 0.9 cm^3/min and *mz* = 15–200 applying so-called “cold trap” [11, 12].

Results

The alkanes with the total concentration of 3.970 mg/m^3 found to be the most abundant group of chemical compounds in exhaust gases from manufacturing of simple superphosphate. Another large group of chemicals was cycloalkanes with a total concentration of 1.189 mg/m^3. Additional two groups of compounds: aromatic hydrocarbons and sulphur chemicals were found to be present at the same concentration range as cycloalkanes, however the aromatic hydrocarbons concentration – 0.657 mg/m^3 – is higher than sulphur chemicals – 0.529 mg/m^3 (Table 2).

Table 2

The sulphur chemicals identified in analyzed samples

No.	Retention time [min]	Name of compound	Concentration [mg/m^3]
1	6.99	dimethyl sulfide	0.019
2	9.50	methylthioethane	0.064
3	11.48	2-methylthiopropane	0.096
4	12.97	1-methylthiopropane	0.052
5	14.54	dimethyldisulfide	0.042
6	15.46	2-methylthiobutane	0.083
7	18.72	2-methyltetrahydrothiophene	0.033
8	19.05	2-methyl-3-methylthiobutane	0.020
9	19.92	2,5-dimethyltetrahydrothiophene	0.045
10	20.08	2-methyltetrahydrothiophene	0.028
11	24.20	methyl-2-buthyldisulfide	0.057
Total concentration			0.529

The sulphur chemicals are thought to be the odour-generating compounds. The noteworthy fact is that among them only two types of disulfides can be distinguished. Kosmider et al performing their research based on the phosphoric acid manufacturing plant demonstrated that the most significant group of compounds containing sulphur was exactly disulfides [4]. These differences can result from distinct profile of phosphoric acid and superphosphate manufacturing processes, where only the reaction between sulphuric acid and phosphate rock is common. It is possible that odours can be generated during further stages of phosphoric acid manufacturing. The discrepancies in composition of exhaust gases can result also from using different types of phosphate rocks. The particular phosphate rock is composed from wide spectrum of organic compounds, which quantity and concentration depends on place and period of rock formation [1].

Westerilch et al and Blazy et al did not reveal the presence of the compounds listed above in the organic phase during analysis of the phosphate rocks. It gives evidence that the thesis advanced by Westerilch et al concerning the generation of odours during reaction between sulphuric acid and phosphate rock is right. Therefore, apparatuses or even entire installations absorbing or neutralizing odour generating substances should be located on the outlet of the gas pipeline carrying gasses from the reactor [8, 9].

Finally on account of data deficiency in available references the comprehensive research regarding organic compounds in simple superphosphate manufacturing was suggested. The analysis of organic phase in phosphate rock and the subsequent analysis of exhaust gases during fertilizer manufacturing from previously investigated phosphate rock should be carried out. Determination of organic compounds concentration in ready product should constitute the successive step. The comprehensive investigations mentioned above could be very helpful with assessing the influence of phosphate rock organic phase components on odours formation in distinct stages of fertilizer manufacturing process. The results were also interesting for the people occupying with methods for deodorization of odours in phosphate industry, giving the opportunity for raising new approach to related problems. It could be chance for developing new solutions for improvement of odours neutralizing techniques in the phosphate rock-applied industry.

From the phosphate rocks yield and use forecast, results that on account of increasing demand for food in next several decades we can expect increased production of phosphate fertilizers. The renewable methods of gaining phosphates are not cost-effective yet in comparison with extracting. Due to this fact, in near future the emission of odour-generating substances will increase together with superphosphate manufacturing. It demonstrates how relevant works on law regulations and deodorization in this range are. In this elaboration the common discrepancies concerning comprehensive approach to identification of odour-generating compounds in phosphate rock-applied industry as well as neutralization of their presence in atmosphere were presented. The possible solutions for this problem were also suggested. Taking into consideration all factors mentioned above it can be stated that range of odour nuissance problems are essential for every developing society and require fast and efficient regulations.

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IDENTYFIKACJA ZWIĄZKÓW ODOROTWÓRCZYCH W PROCESACH PRZETWARZANIA SUROWCÓW FOSFOROWYCH

Instytut Technologii Nieorganicznej i Nawozów Mineralnych
Politechnika Wrocławska

Abstrakt: W polskim ustawodawstwie istnieje bardzo dotkliwa dla obywateli i przedsiębiorców luka dotycząca regulacji prawnych związanych z uciążliwością zapachową. Po przeprowadzeniu analizy publikowanych projektów aktów prawnych i literatury z tego zakresu stwierdzono, że „ustawa odorowa" w proponowanym przez administrację państwową kształcie nie może wejść w życie. Jako przykład gałęzi przemysłu będącej przyczyną powstawania uciążliwości zapachowej wybrano procesy produkcyjne wykorzystujące surowce fosforanowe ze szczególnym uwzględnieniem produkcji superfosfatu prostego. W celu scharakteryzowania problemu dokonano analizy doniesień literaturowych dotyczących diagnozy i składu fosforytów pod kątem obecnej w nich fazy organicznej, z której w czasie produkcji nawozu powstają odoranty. W celu określenia obecności konkretnych związków odorotwórczych pobrano próbki gazów wylotowych z instalacji produkującej superfosfat prosty. Próbki te zanalizowano metodą TD-GC/MS pod kątem identyfikacji lotnych związków organicznych. Zidentyfikowano ponad 80 różnych związków a wśród nich: dużo alkanów, cykloalkanów, aromatów i organicznych związków siarki. Najprawdopodobniej za złowonność gazów wylotowych w największym stopniu odpowiedzialne są właśnie związki siarki. Ze względu na znikome informacje dotyczące właściwości złowonnych mieszanin różnych związków nie można wykluczyć wpływu innych składników na zapach analizowanych gazów wylotowych. Ostatecznie ze względu na brak danych w dostępnej literaturze zaproponowano przeprowadzenie kompleksowych badań dotyczących związków organicznych w produkcji superfosfatu prostego. Z prognoz dotyczących wykorzystywania surowców fosforowych wynika, że w ciągu następnych kilku dekad czeka nas wzrost produkcji m.in. nawozów fosforowych. Dlatego należy jak najszybciej uporać się z problematyka uciążliwości zapachowej.

Słowa kluczowe: odory, superfosfat, lotne związki organiczne

Varia

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Literaturę prosimy zamieszczać wg poniższych przykładów:

[1] Kowalski J. and Malinowski A.: Polish J. Chem. 1990, **40**, 2080–2085.

[2] Nowak S.: Chemia nieorganiczna, WNT, Warszawa 1990.

[3] Bruns I., Sutter K., Neumann D. and Krauss G.-J.: *Glutathione accumulation – a specific response of mosses to heavy metal stress*, [in:] Sulfur Nutrition and Sulfur Assimilation in Higher Plants, P. Haupt (ed.), Bern, Switzerland 2000, 389–391.

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