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**IN-SITU TREATMENT OF GROUNDWATER CONTAMINATED WITH UNDERGROUND
COAL GASIFICATION PRODUCTS****OCZYSZCZANIE IN-SITU WÓD PODZIEMNYCH ZANIECZYSZCZONYCH PRZEZ PRODUKTY
PODZIEMNEGO ZGAZOWANIA WĘGLA**

In the paper the contaminants that may be generated in Underground Coal Gasification (UCG) process were listed and include mainly mono- and polycyclic aromatic hydrocarbons, phenols, heavy metals, cyanides, ammonium, chloride and sulphate. As a method of UCG contaminated groundwater treatment a Permeable Reactive Barrier technology was proposed. To assess the effectiveness of this technology two tests were carried out. Granulated activated carbon (GAC) and zeolite, and granulated activated carbon and scrap iron were applied in the first and second test respectively. For these materials the hydro geological parameters called reactive material parameters were determined and discussed. The results of the experiments showed that GAC seems to be the most effective material for phenols, BTX, PAH, cyanides and slightly lowers ammonia removal, while zeolites and scrap iron removed free cyanide, ammonia and heavy metals respectively.

Keywords: Underground Coal Gasification, underground water, contaminants treatment, reactive barrier

Podziemne Zgazowanie Węgla (PZW) jest alternatywną metodą pozyskiwania energii z węgla. Jest to zespół przemian termicznych i chemicznych przebiegających bezpośrednio w złożu węgla, zachodzących pomiędzy substancją organiczną a czynnikiem zgazowującym, jakim może być powietrze, tlen, para wodna, dwutlenek węgla. Poza wieloma zaletami metoda ta niesie za sobą także wiele zagrożeń, które były rozważane w ramach projektu HUGE 2 (nr RFCR-CT-2011-00002). Jednym z nich jest zagrożenie środowiska wód podziemnych produktami PZW, do których należą wielopierścieniowe węglowodory aromatyczne, BTX, fenole, metale ciężkie, cyjanki, jony amonowe, chlorki i siarczany. W celu zminimalizowania tego zagrożenia w pracy rozważono zastosowanie w obszarze reaktora PZW technologii Przepuszczalnej Bariery Reaktywnej (PRB). W technologii tej zanieczyszczenia usuwane są in-situ poprzez przepływ wód przez odpowiednio dobrany materiał reaktywny. W tablicy 1 przedstawiono podstawowe parametry bariery, które należy określić, aby skutecznie i długotrwale chronić środowisko wodne przed zanieczyszczeniami. Jako materiał reaktywny w pracy wybrano, na podstawie zdolności oczyszczania, granulowany węgiel aktywny (do usuwania związków organicznych) oraz żelazo metaliczne i alternatywnie zeolity (do usuwania

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związków nieorganicznych i pozostałych związków organicznych po złożu węgla aktywnego). Badania prowadzone były w dwóch instalacjach badawczych składających się z pompy perystaltycznej oraz dwóch szeregowo połączonych szklanych kolumn filtracyjnych (rys. 1). W obu instalacjach pierwsza kolumna wypełniona była granulowanym węglem aktywnym, zaś druga odpowiednio w pierwszej i drugiej instalacji, żelazem metalicznym i zeolitami. Materiał reaktywny poza zdolnościami do usuwania zanieczyszczeń, musi również charakteryzować się długotrwałą i stabilną przepuszczalnością dla wód. Dlatego też jego skład ziarnowy dobrano w taki sposób, aby współczynnik filtracji materiału reaktywnego zawierał się między 2×10^{-4} i 6×10^{-3} m/s (co oznacza że powinien charakteryzować się maksymalnymi wartościami współczynnika filtracji dla piasku drobnoziarnistego i gruboziarnistego). Tabele 3 i 4 przedstawiają odpowiednio skład ziarnowy materiału reaktywnego zastosowanego w badaniach laboratoryjnych oraz jego główne parametry hydrogeologiczne. Zastosowany w badaniach roztwór przygotowany został poprzez zmieszanie wody destylowanej z odpowiednimi masami odczynników chemicznych, uzyskując w ten sposób stężenia zanieczyszczeń podobne do wartości przedstawionych w pracach (Kapusta & Stańczyk, 2011; Liu & in., 2006). W tabelach 5 i 6 oraz na rysunkach 2-8 przedstawiono wartości parametrów fizykochemicznych oraz stężeń substancji chemicznych zmierzonych w wodach pobranych z instalacji badawczych 1 i 2. We wnioskach pracy stwierdzono, iż granulowany węgiel aktywny jest odpowiednim materiałem do usuwania z wód fenoli, BTX, wielopierścieniowych węglowodorów aromatycznych, wolnych cyjanków oraz w mniejszym stopniu również jonów amonowych. Węgłe nie wpływały na temperaturę wód oraz na potencjał redox i przewodność elektrolityczną. Zeolity z kolei skutecznie usuwały wolne cyjanki, jony amonowe oraz w pewnym stopniu fenole. W zależności od składu chemicznego wód oraz powinowactwa metali do zeolitów mogły one również usuwać metale ciężkie. Zeolity nie wpływały natomiast na temperaturę i powodowały znaczące obniżenie się wartości pH oraz przewodności elektrolitycznej wody. Przepływająca przez złożę zeolitu woda wzbogacała się z kolei (z całą pewnością w początkowym etapie pracy złoża) w rozpuszczony tlen, co miało odzwierciedlenie w wyższych wartościach potencjału redox w kolejnych punktach poboru wody. Ostatnim analizowanym w pracy materiałem było żelazo metaliczne. Chociaż nie wpływało ono w żaden sposób na stężenie związków organicznych w wodach, przyczyniło się do usunięcia z nich wszystkich metali ciężkich. Żelazo spowodowało ponadto wzrost temperatury i wartości pH oraz zdecydowane obniżenie się potencjału redox i stężenia tlenu rozpuszczonego. Rozważając zastosowanie wymienionych materiałów reaktywnych w technologii PRB do usuwania produktów PZW trzeba pamiętać o ograniczonej pojemności sorpcyjnej węgla aktywnego oraz zeolitów oraz o konieczności poddawania ich reaktywacji. Fakt ten oraz duże trudności technologiczne związane z zainstalowaniem materiału oraz jego wymianą stanowią wyzwanie do dalszych analiz i prac w tym obszarze.

Słowa kluczowe: Podziemne Zgazowanie Węgla, wody podziemne, usuwanie zanieczyszczeń, bariera reaktywna

1. Introduction

Underground Coal Gasification (UCG) is an alternative technology of energy extraction from coal (Vasyuchkov, 2008) which was invented over one century ago. UCG is a thermo-chemical process (taking place underground), during which follows the conversion of solid fuel into gaseous fuel being a mixture of combustible components and quantity of inert gases (Wachowicz et al., 2010). One of the drawbacks of this technology is the environmental risk associated with water pollution in surrounding aquifers. The substances leached from the gasification zone are mainly mono- and polycyclic aromatic hydrocarbons, phenols, heavy metals, cyanides, ammonium, chloride and sulphate (Kapusta & Stańczyk, 2011; Kapusta et al., 2010; Humenick et al., 1980; Humenick, 1984; Sturner et al., 1982; Liu et al., 2006).

In order to decrease the risk of groundwater contamination by UCG, the PRB (Permeable Reactive Barrier) Technology was considered to be used. This technique of groundwater remediation is a passive one where contaminants are removed from an aquifer by flowing through a reactive barrier filled with a special material called a "reactive material" (Gavaskar et al., 2000; Gavaskar et al., 2003; Puls et al., 1998; ITRC, 2005; Suponik, 2011).

In accordance with Table 1, to design properly the PRB a reactive material parameters and a groundwater treatment parameters (which describe treatment processes) need to be determined. For tested (in the paper) materials, the treatment processes in a column tests were assessed and the reactive material parameters according to methodology/engineering standard were determined. Since, the evaluation of the effectiveness of contaminants removal from groundwater was the main aim of the experiments the groundwater treatment parameters were not calculated in detail, i.e. the decay kinetic parameters were not calculated.

2. Materials and wastewater used in laboratory tests

A number of research papers have been written on the removal of organic and inorganic compounds (presented in the article) from aqueous solutions (e.g. Blanco-Martinez et al., 2009; Kiran & Chandrajit, 2011; Massol-Deya & Ning-His Tang, 1996; Zh. Liang, 2009; McLaren & Farguhar, 1973; Gala & Sanak-Rydlowska, 2011). Based on these articles and others the following reactive materials were used in the column tests:

- granulated activated carbon (GAC) – most of organic compounds are mainly sorbed by hydrophobic bonding to organic material, therefore, a large amounts of organic material (less polar and more aromatic) is required for high sorption degree of organic compounds at slightly basic conditions. So, for removing organic compounds from wastewater an activated carbon was used,
- zero-valent iron (ZVI, Fe(0)) and zeolite (optional) – used mainly for removing inorganic compounds by redox processes and precipitation, and by adsorption and/or ion exchange processes.

TABLE 1

Main parameters of Reactive Barrier (Suponik, 2011)

Optimization of the Reactive Barrier parameters	Determination of reactive material parameters and groundwater treatment parameters	Reactive material parameters	Groundwater treatment parameters		
		<ul style="list-style-type: none"> • Hydraulic conductivity, • Effective porosity, • Bulk density, • Dispersion parameters. 	Adsorption parameters and/or decay kinetic parameters		
	Optimization of the geometrical Reactive Barrier parameters	Types of Reactive Barrier technology			
		Continuous Reactive Barrier	Funnel-and-Gate System		
			Funnel-and-Gate Open System	Funnel-and-Gate Closed System	
		Location of Continuous Reactive Barrier	Location of Funnel-and-Gate Open System	-	
		Orientation of Continuous Reactive Barrier	Orientation of Funnel-and-Gate Open System	-	
		-	Gate location	Gate location	
		Width of Continuous Reactive Barrier	Width of Funnel-and-Gate Open System	-	
		-	Gate width	Gate width	
		-	Gate orientation	Gate orientation	
Thickness of Continuous Reactive Barrier		Gate thickness	Gate thickness		
Geometrical Reactive Barrier parameters					

The granular activated carbon (WACC 8X30 type) was taken from Carbon – Elbar Katowice Ltd (<http://www.carbon.arg.pl>). It was manufactured from shells of coconut by steam-gas method. The main properties of activated carbon used in the tests is presented in Table 2.

Zeolites – next material assessed in laboratory tests, are micro porous crystalline solids with well-defined structures. Natural zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, with high internal and external surface areas, and high cation exchange capacities (Gottardi, 1985). Due to their micro porous structure they are commonly used as adsorbents. These minerals are particularly useful for removing cationic species such as ammonium and some toxic metals from water. The zeolite used for the experiments was a natural zeolite of 0.5-1.0 mm fraction manufactured by ZEOCEM Slovakia (www.subiopolaska.com). So, it exhibit superior hydraulic characteristics and are suitable for use in filtration systems. This zeolite has a porosity of 24-32% and is composed mainly of SiO₂ (65-70%), Al₂O₃ (11-13%) and other alkaline metals oxides.

TABLE 2

Properties of granular activated carbon (GAC) used in the laboratory tests (<http://www.carbon.arg.pl>)

Properties, unit	Value
grain-size distribution, mm	0.6-2.4
Specific surface, m ² /g	min. 1000
Iodine number, mg/g	min. 1000
moisture, %	max. 5
ash, %	max. 12
pH	ca. 8
Hardness, %	min. 98
Bulk density, g/dm ³	480 +/- 30

Another material used in the study was a ZVI – scrap iron. It was taken from the machining plant where it was treated as waste. The scrap iron is easily available in large quantities at a reasonable price. It should have a high fraction of iron metal (>90%), low carbon content (<3%), and nonhazardous levels of leachable trace metal impurities (ITRC 2011). The material must be free of any surface coating (oils or grease) that inhibit its reactivity, so it has been cleaned before using them in laboratory tests – first with a thinner (painter’s naphtha), dried in the moisture teller, and then, just before the application, cleaned with distilled water.

To reduce Reactive Barrier costs, the reactive material should be able to maintain its hydraulic conductivity over time. Due to different processes in reactive barrier (e.g. precipitate formation, inflow of small particles, growth of biomass), hydraulic conductivity of reactive material could be changed with time, and treatment zone can clogged finally. Therefore, a proper selection of hydraulic conductivity of reactive material is one of the main requirements for effective and long lasting reactive barrier performance (Suponik, 2011).

In order to ensure longevity and efficacy of reactive material, its hydraulic conductivity should be a few times higher than hydraulic conductivity of aquifer. This solution may prevent the blocking up of the reactive barrier and breakdown of the whole system. Therefore, incorporating an adequate safety factor (larger size of reactive material grain) into the PRB is one of the way of achieving satisfactory hydraulic performance and thus ensuring its efficacy and longevity. In accordance with some of the designers of PRB, (Beitinger et al., 1998; Gavaskar

et al., 2000) this factor (the ratio of the hydraulic conductivity of reactive material to the aquifer hydraulic conductivity) should amount to 10 (Suponik, 2010). To achieve certainty that reduction in hydraulic conductivity of reactive materials used in the tests would not impact on their long lasting performance this safety factor was also taken into consideration in the research presented in the paper. It should be explained here that using a larger size of grains of reactive material (and in this way larger hydraulic conductivity of reactive material) than needed is not proper for Reactive Barrier efficacy, because the reactivity of the used medium decreases as a result of lower surface contact of contaminants with used materials (Suponik, 2011).

Since, the experiments were carried out to solve general problems and there are not (at the moment) a specific area in which reactive barrier would be used, it was assumed in the paper that hydraulic conductivity of reactive material should be sufficient large to be used in most of the underground permeable areas. Therefore, it was assumed that hydraulic conductivity of reactive material should have a value in the range from 2×10^{-4} to 6×10^{-3} m/s, meaning that should be characterized by the maximum value of hydraulic conductivity for fine and coarse sand (Domenico & Schwartz, 1990). This values were achieved after removing some size grades or after changing their mass fraction. In order to facilitate this adjustment the Hazen's equation was applied:

$$k = 0,0116 \cdot d_{10}^2 \text{ [m/s]} \quad (1)$$

where: d_{10} — effective grain size, mm.

The reactive material parameters were determined on the basis of the following methodology/engineering standard:

- PN-88/B-04481 – grain-size distribution, density and bulk density,
- Kaminski's pipe method – hydraulic conductivity (Marciniak et al., 1998),
- King method – effective porosity (Pazdro & Kozerski, 1990).

Table 3 presents the grain-size distribution of reactive materials used in the tests, so after adjusting the value of hydraulic conductivity, while Table 4 shows the reactive material parameters.

The wastewater (synthetic solution which simulated groundwater contaminated with UCG (Underground Coal Gasification)) was prepared by mixing distilled water with desired amounts of the following pure substance: phenols, benzene, toluene, xylene, naphthalene, fluorene, phenanthrene, pyrene, anthracene, $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{NiSO}_4 \times 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$, NaCl, K_2CrO_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KCN. The concentrations of contaminants in this solution were similar to the values reported in literature (Kapusta & Stańczyk, 2011; Liu et al., 2006). The initial conductivity and pH of the solution amounted to 22 mS/cm and 7.9 respectively. Since pH after adding the substances amounted to 5.5, it was adjusted to the intentional value by slow titration with ultra-pure sodium hydroxide.

This way, the initial concentration of chemicals and the initial values of physicochemical parameters (presented in Table 5 and 6) were achieved. The quantitative analysis of chemicals were carried out for:

- Cr^{6+} , NH_4^+ , CN^- , Phenols, Fe_{tot} , SO_4^{2-} , Cl^- ; UV-Vis Spectrophotometer DR5000 HaachLange,
- Cu, Ni, Zn; JY 2000 Spectrometer (Inductively Coupled Plasma Atomic Emission Spectroscopy Method (ICP-AES),
- Total Organic Carbon (TOC), Shimadzu Analyzer TOC-V_{CSH} with ASI-V sampler,

BTX (benzene, toluene, p-xylene) and PAH (fluoranthene, phenanthrene, anthracene, pyrene, naphthalene, fluorene); HPLC – UVD 340u Gynkotek; column RP-18 Hypersil Gold, flow 1 cm³/min in gradient analysis Me/H₂O, before HPLC analysis the PAH were extracted in cyclohexane, cyclohexane was evaporated and PAH were dissolved in Me (Me to methanol).

TABLE 3

Grain-size distribution of reactive materials used in the tests

Size grade [mm]	Mass fraction [%]		
	GAC	zeolite	ZVI
3,2-2,0	2.15	-	1.67
2,0-1,5	3.02	-	1.62
1,5-1,02	71.89	17.78	8.45
1,02-0,75	19.55	39.03	42.78
0,75-0,5	3.41	40.13	38.32
0,5-0,3	-	3.06	5.71
0,3-0,1	-	-	1.45

TABLE 4

Parameters of reactive materials used in the column tests

Reactive material parameters, unit	Value for:		
	GAC	zeolite	ZVI
Hydraulic conductivity, m/s	7.18×10^{-4}	2.94×10^{-4}	4.85×10^{-4}
Density, g/cm ³	1.55	1.99	7.85
Bulk density, kg/m ³	482.9	974.3	1962,8
Effective porosity, -	0.23	0.20	0.42

The pH, redox potential (ORP), dissolved oxygen (DO), conductivity and temperature are important parameters that are easily monitored during column tests and are convenient indicators of conditions created in columns. They were measured with Knick PORTAMESS meters.

3. Methodology

In order to determine the possibility of UCG-products contaminated groundwater treatment the tests were carried out in the following installations:

- two glass columns packed (carefully; batchwise) with granulated activated carbon (in first column) and with ZVI – scrap iron (in second column), and with coarse sand located at the bottom of the columns – installation 1 (Fig. 1),
- two glass columns packed (carefully; batchwise) with granulated activated carbon (in first column) and with zeolite (in second column), and with coarse sand located at the bottom of the columns – installation 2 (Fig. 1).

Surface coatings may decrease the sorption capacity and the sorption kinetics resulting in earlier breakthrough of the contaminants (Roehl et al. 2005). Therefore, the coarse sand (as a filter) was applied before the main bed.

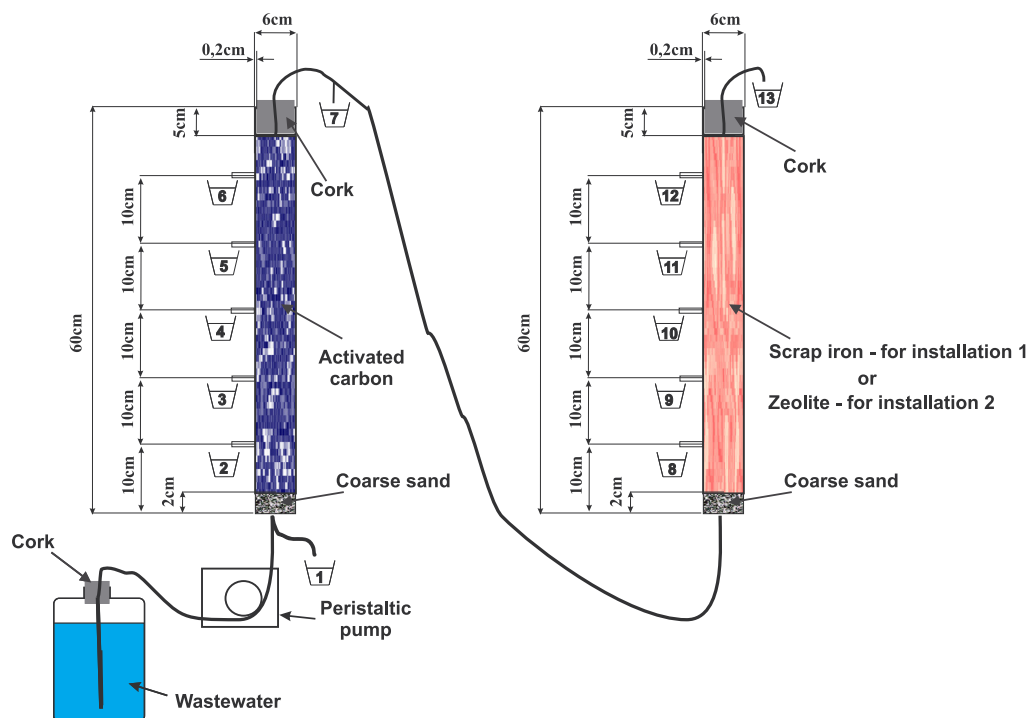


Fig. 1. Installations for simulation of flow and treatment processes of contaminated groundwater in reactive barrier consisted of activated carbon and scrap iron (in installation 1), and activated carbon and zeolite (in installation 2); numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 – indicate sampling points

The wastewater has been made to circulate through the columns of the installations from bottom to the top with the use of a peristaltic pump (type ZALIMP PP1B-05A) and during that time the treatment processes occurred. Fabric filters made by TAMFELT Co., were placed between the sand and reactive materials used in the columns (granulated activated carbon, scrap iron and zeolite), on the bottom of the each column and on the top of the reactive material beds (between reactive materials and cork).

As it was mentioned above, the experiments were carried out to solve general problem with no relation to specific site, so, it was assumed that the groundwater Darcian velocity would be 0.50 m/day, which corresponds to the average seepage velocity as a fast and very fast (in accordance with Kleczkowski et al., 1990). This high value was used because it is unfavourable for kinetics of the most treatment processes proceeded in the reactive materials. Therefore, the conditions in the columns corresponded to the aquifer in the region of UCG (except the temperature) and they are the most unfavourable for most of the processes which are used for removing contaminants from groundwater.

There were thirteen sampling points in the each installation for drawing out the wastewater and to take measurements. The measurements have begun just after the achievement of a steady state in the column, i.e. after the solution in the column had been changed ten times.

4. Results and discussion

The detailed values of physicochemical parameters and concentration of chemicals measured in solution taken from sampling points (see Fig. 1) are presented in Tables 5 and 6 below. The results of column tests are also shown in Figures 2-8.

The TOC content decreased more significantly in the GAC bed while the zeolites removed slightly less of TOC (Fig. 2). In case of phenols similar situation was observed (Fig. 3a), zeolite and especially GAC removed phenols while the ZVI did not contribute to the removal of these contaminants. These results were expected since phenols are characterized with a high dissociation constant ($pK_a = ca. 10$) which indicates that they are not dissociated at neutral pH and are mainly sorbed by hydrophobic bonding to organic material.

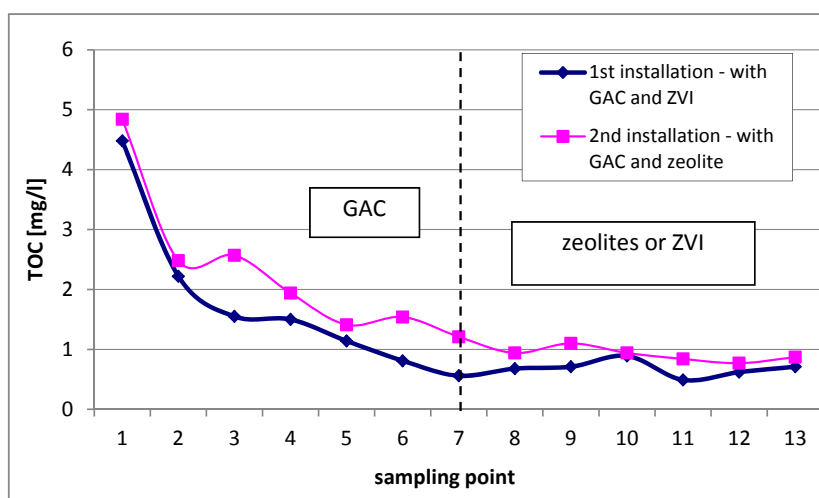


Fig. 2. The value of TOC measured in water sampled during column tests in 1st installation - with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

In the research presented by Blanco-Martinez et al. (2009) it was shown that at pH less than 9.8 the surface of carbon is positively loaded and at pH near 7 phenol molecules are more protonated than at higher values. Thus, they are attracted to the positive charged surface of activated carbon. At pH of 11 the surface of GAC is negatively loaded and therefore repulses the phenol molecules. Kiran and Chandrajit (2011) studied also the adsorption of phenols (and cyanide) on GAC and showed that maximum adsorption (for them) occurred in the pH 8 to 9, thus similar to the pH measured in the installations presented in Fig. 1 (see Fig. 5a).

The monoaromatic hydrocarbons, abbreviated BTX, which stands for benzene, toluene and three xylene isomers, are aromatic hydrocarbons containing one unsubstituted benzene ring. So, they are mainly sorbed by hydrophobic bonding to organic material, what was confirmed by the results presented in Fig. 3b. To sum up, GAC adsorbed BTX while ZVI did not remove it and the same case was observed in case of zeolite for which the concentration did not decrease. In accordance with Massol-Deya and Ning-His Tang (1996) the amount of p-xylene adsorbed per

TABLE 5

The physicochemical parameters and the concentration of chemicals measured in water sampled during column tests (columns were filled with GAC and ZVI – see Fig. 1)

No of samp. point	React. mater.	pH	ORP mV	cond. mS/cm	DO, mg/l	temp °C	TOC mg/l	phenols, mg/l	NH ⁴⁺ mg/l	CN ⁻ mg/l	benzene, mg/l
1	Initial sample	8,01	177	21,7	7,5	16,1	4,48	4,04	3280	1,84	0,540
2	GAC	7,94	154	21,5	6,5	16,2	2,22	3,04	2830	1,67	0,418
3		8,05	86	22,0	4,4	16,1	1,55	2,97	3250	1,47	0,421
4		8,14	91	21,8	6,1	16,0	1,50	1,48	3020	1,11	0,348
5		8,29	72	21,9	5,7	16,0	1,14	1,09	2990	0,97	0,308
6		8,14	84	21,4	5,8	16,1	0,81	0,84	2870	1,24	0,294
7	Outflow from GAC	8,21	116	21,5	5,0	15,9	0,56	0,64	2910	0,88	0,211
8	ZVI	8,49	14	21,8	2,4	16,9	0,68	0,74	2840	0,71	0,197
9		8,61	-299	21,6	0,5	17,8	0,71	0,59	2730	0,82	0,147
10		8,71	-257	21,6	0,8	17,6	0,89	0,57	2700	0,74	0,214
11		8,79	-280	21,3	0,9	17,7	0,49	0,49	2920	0,94	0,221
12		8,80	-319	21,7	0,4	17,4	0,62	0,74	2940	0,78	0,184
13	Outflow from ZVI	8,79	-356	21,3	0,2	17,5	0,71	0,81	2750	0,80	0,194
No of samp. point	React. mater.	toluene, mg/l	xylene (sum) mg/l	PAH, mg/l	Cr ⁶⁺ , mg/l	Cu, mg/l	Fe _{total} mg/l	Zn, mg/l	Ni, mg/l	SO ₄ ²⁻ , mg/l	Cl ⁻ , mg/l
1	Initial sample	0,141	0,121	3,288	0,091	0,55	BDL	0,16	1,24	550	784,1
2	GAC	0,091	0,099	2,015	0,104	0,54	BDL	0,15	1,19	526	808,5
3		0,087	0,087	1,974	0,087	0,64	BDL	0,15	1,31	610	784,5
4		0,009	0,089	1,547	0,091	0,64	BDL	0,13	1,16	564	809,0
5		BDL	0,047	1,015	0,110	0,59	BDL	0,14	1,24	640	810,2
6		BDL	0,067	0,879	0,090	0,48	BDL	0,12	1,39	517	798,4
7	Outflow from GAC	BDL	0,054	0,378	0,094	0,67	BDL	0,14	1,21	530	788,1
8	ZVI	BDL	0,041	0,415	0,014	0,21	3,2	0,09	0,21	620	791,4
9		BDL	0,069	0,397	BDL	BDL	13,1	0,01	0,01	665	804,8
10		BDL	0,014	0,579	BDL	BDL	14,8	BDL	BDL	550	794,1
11		BDL	0,034	0,486	BDL	BDL	14,1	BDL	BDL	458	781,4
12		BDL	0,028	0,407	BDL	BDL	16,7	BDL	BDL	541	794,0
13	Outflow from ZVI	0,009	0,041	0,378	BDL	BDL	21,1	BDL	BDL	647	781,5

BDL – below detection limit

The physicochemical parameters and the concentration of chemicals measured in water sampled during column tests (columns were filled with GAC and zeolite – see Fig. 1)

No of samp. point	React. mater.	pH	ORP mV	cond. mS/cm	DO, mg/l	temp °C	TOC mg/l	phenols, mg/l	NH ⁴⁺ mg/l	CN ⁻ mg/l	benzene, mg/l
1	Initial sample	7,96	182	22,2	7,8	18,4	4,84	3,84	3040	1,48	0,527
2	GAC	8,08	150	22,0	4,4	18,6	2,48	3,14	3180	1,16	0,448
3		8,1	160	22,1	5,1	18,5	2,57	2,64	2840	1,22	0,371
4		8,14	155	22,1	4,8	18,5	1,94	2,31	2760	1,07	0,387
5		8,25	179	22,1	5,1	18,8	1,41	1,94	2640	0,89	0,289
6		8,45	183	22,0	5,3	18,6	1,54	2,01	2740	0,57	0,274
7	Outflow from GAC	8,49	193	21,8	5,8	18,4	1,21	1,42	2740	0,61	0,204
8	zeolite	8,21	194	20,4	6,2	18,3	0,94	1,14	2410	0,71	0,214
9		7,89	201	19,1	6,8	18,3	1,10	1,21	2560	0,49	0,190
10		7,81	248	19,8	7,4	18,6	0,94	0,97	2210	0,48	0,208
11		7,91	265	19,1	7,8	18,4	0,84	1,01	2040	0,58	0,154
12		7,66	248	18,6	7,1	18,5	0,77	0,87	2720	0,27	0,189
13	Outflow from zeolite	7,55	276	18,4	7,4	18,6	0,87	1,02	1840	0,32	0,148

No of samp. point	React. mater.	toluene, mg/l	Xylene (sum) mg/l	PAH, mg/l	Cr ⁶⁺ , mg/l	Cu, mg/l	Fe _{total} mg/l	Zn, mg/l	Ni, mg/l	SO ₄ ²⁻ , mg/l	Cl ⁻ , mg/l
1	Initial sample	0,161	0,104	3,101	0,082	0,67	BDL	0,15	1,02	625	775,5
2	GAC	0,097	0,084	1,789	0,100	0,51	BDL	0,12	1,15	460	759,9
3		0,054	0,062	1,897	0,094	0,48	BDL	0,14	1,11	554	789,1
4		0,094	0,074	1,547	0,084	0,74	BDL	0,16	1,04	495	771,5
5		0,018	0,069	1,249	0,079	0,69	BDL	0,14	1,24	487	789,6
6		BDL	0,051	0,948	0,084	0,61	BDL	0,14	1,11	497	782,4
7	Outflow from GAC	BDL	0,064	0,448	0,074	0,59	BDL	0,12	1,01	630	772,5
8	zeolite	BDL	0,067	0,314	0,064	0,67	0,1	0,13	0,94	625	770,4
9		BDL	0,041	0,248	0,091	0,87	0,5	0,15	0,67	674	794,5
10		BDL	0,074	0,297	0,088	0,81	0,4	0,16	0,84	587	804,5
11		BDL	0,034	0,374	0,072	0,91	0,4	0,15	0,64	629	801,2
12		0,004	0,027	0,227	0,087	0,94	1,1	0,17	0,55	649	794,5
13	Outflow from zeolite	BDL	0,064	0,246	0,074	0,84	0,4	0,14	0,61	624	796,8

BDL – below detection limit

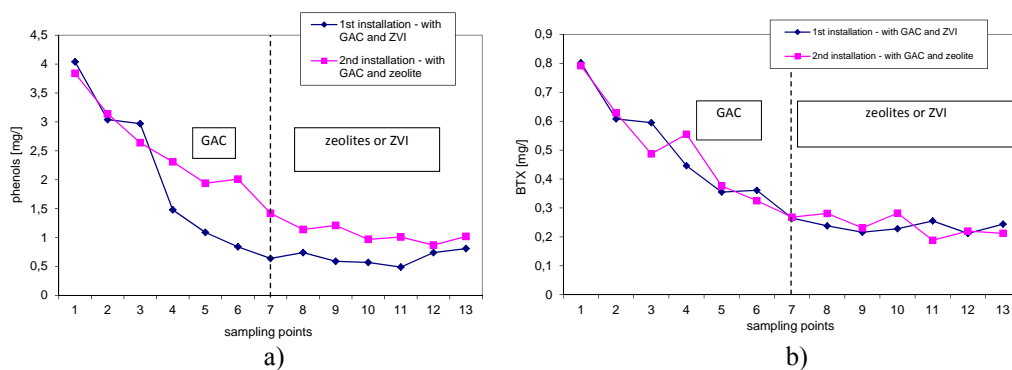


Fig. 3. The value of a) phenols and b) BTX, measured in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

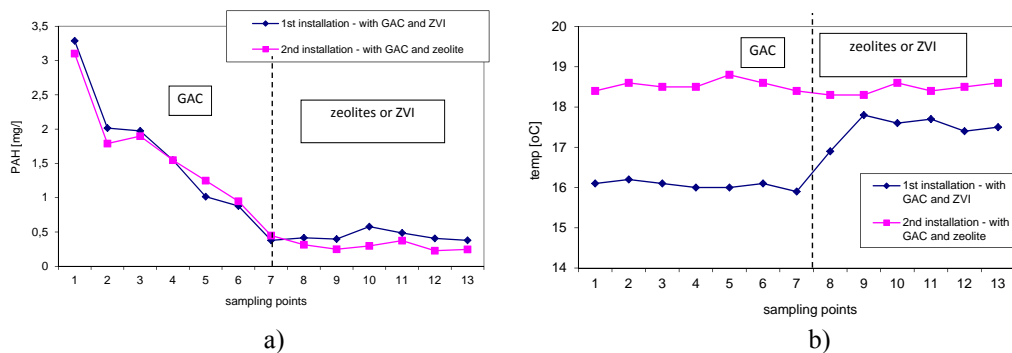


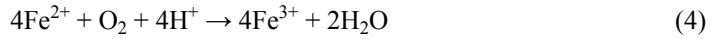
Fig. 4. The value of a) PAH and b) temperature, measured in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

unit mass of activated carbon is greater than that of toluene which in turn is greater than that of benzene.

In both presented installations the same level of PAH removal was observed (Fig. 4a). More detailed measurements revealed that naphthalene was also removed by zeolite which is confirmed in literature (see Chang 2004). ZVI did not contribute to the removal of PAH. Thus, as it was expected, an activated carbon is an indispensable tool in groundwater purification, especially for the removal of mono- and polycyclic aromatic hydrocarbons and phenols.

ZVI caused increase in temperature of the solution while GAC and zeolite maintained constant temperature (Fig. 4b). It happened due to the value of adsorption enthalpy is lower than the value of chemical reaction enthalpy (Suponik, 2012). The temperature of air in the laboratory amounted to $16.3^{\circ}\text{C} \pm 0,2^{\circ}\text{C}$ and $18.5^{\circ}\text{C} \pm 0,2^{\circ}\text{C}$ respectively for 1st and 2nd installation.

During the contaminants removal in ZVI the pH increased quickly mainly as a result of the reactions 2, 3 and 4 (reaction 3 proceeds slowly) (Fig. 5a).



At the same time in the 2nd installation the zeolite stabilized pH value because it creates a natural buffer in the system by establishing an optimal pH level. In case of GAC a slight increase in pH was observed (Fig. 5a).

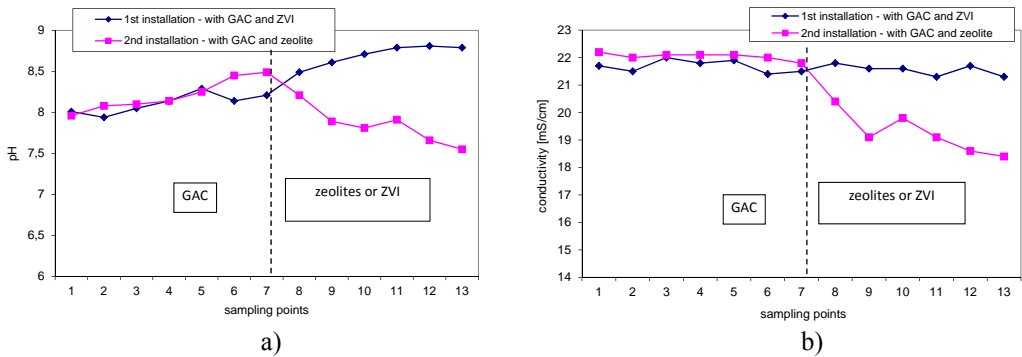


Fig. 5. The value of a) pH and b) conductivity, measured in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

In accordance with Figure 5b zeolite significantly lower the conductivity because it probably removed some of the cationic metals. The GAC bed did not have any impact on the conductivity and the same situation was observed with ZVI. In case of second one, it happened, due to scrap iron removes cationic and anionic metals as a result of reduction (ferric and ferrous iron appears in solution in exchange for heavy metals) and precipitation/co-precipitation, and adsorption (Suponik, 2012, 2013). Thus, as a result the conductivity in the second column of 1st installation did not changed.

In accordance with Matsis and Grigoropoulou (2007) and Chul Choi et al. (2008) fresh activated carbon might lower dissolved oxygen (DO) for a short period of time, and might, as a result, decrease ORP. Figures 6a and 6b confirm this to some extent.

In accordance with Table 5, reaction 2 (and later reaction 4) proceeded quickly, evidenced by the fact that both the DO and the ORP dropped quickly as the solution entered the iron material – reduction of heavy metals contributes the ORP decreases probably as well.

A slow increase of ORP and DO was observed while the solution flowing through zeolites (Figures 6a and 6b).

Generally, cyanide compounds are present in the environmental matrices as simple and complex cyanides. The stability of these compounds is pH dependant and therefore their potential environmental impacts and interactions can vary depending on the system. Of these compounds, simple cyanides such as KCN and NaCN are most dangerous forms of cyanide (Desai and Ramakrishna 1998). In the alkaline conditions free cyanide is present predominantly in neutral HCN

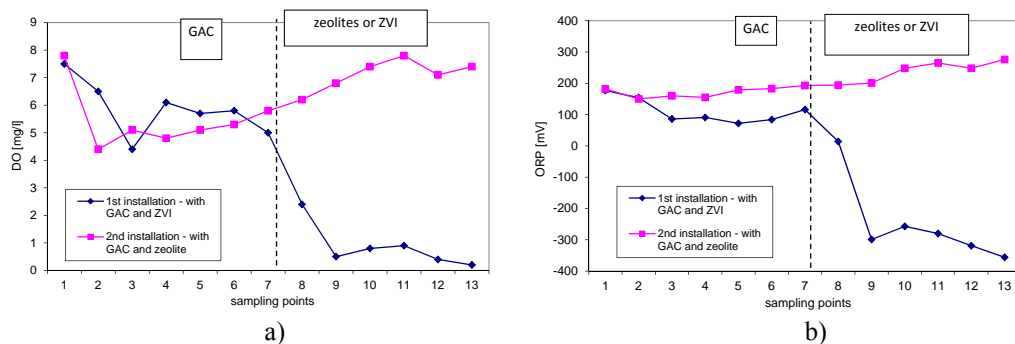


Fig. 6. The value of a) DO and b) ORP, measured in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

form. In the installations presented in Figure 1 GAC removed free cyanides (CN^-) well while zeolite removed them in less efficient manner. According to the measurements the ZVI did not remove CN^- (Fig. 7a). Kiran and Chandrajit (2011) studied the adsorption of cyanide on GAC and showed that extent of adsorption is not dependent on pH in ranges of 7-10. So, in tests presented in this paper the sorption strength did not changed.

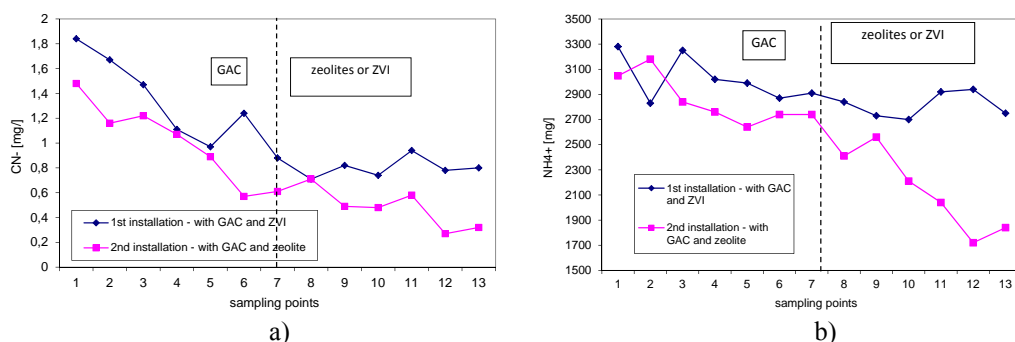


Fig. 7. The value of a) free cyanides (CN^-) and b) ammonia (NH_4^+), measured in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

Zeolite removed ammonia while GAC removed it as well but the reduction follows a slower rate. So, removal of the ammonium ions from groundwater through adsorption with natural zeolites is found to be very promising what was also investigated and confirmed by Ivanowa et al. (2010). The fact that natural zeolites can be modified thermally or chemically to improve its adsorption capacity, causes that it is interesting material for applying it in reactive barrier. Zh. Liang (2009) and McLaren and Farguhar (1973) also studied zeolites and showed that removal of the ammonium ions with zeolites is a result of ion exchange and/or adsorption. To sum up, the natural zeolite from Slovakia is suitable as an adsorbent for ammonia ions removal from groundwater contaminated by UCG.

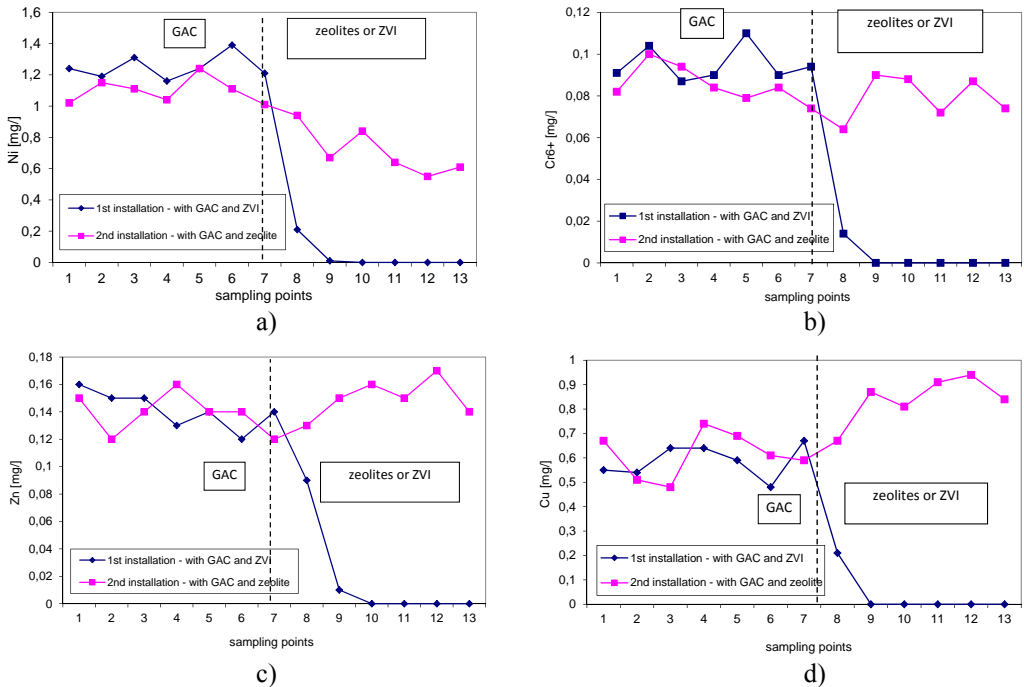


Fig. 8. Nickel, Chrome, Zinc and Copper ions concentration in water sampled during column tests in 1st installation – with GAC and ZVI (see Fig. 1) and in 2nd installation – with GAC and zeolite (see Fig. 1)

In accordance with Fig. 8 GAC did not removed metals while the iron removed them very efficiently. The rapid metal removal in ZVI bed has likely occurred due to the reduction and the precipitation/co-precipitation, and/or due to the adsorption onto the iron metal surface or/and onto the iron corrosion products (Suponik 2013). Removal of nickel by zeolite was much lower than that of iron. Unfortunately zeolite released a significant amount of zinc, copper and also chromium (Cr^{6+}) from their body.

5. Conclusions

The possibility of using GAC, ZVI and zeolite as a reactive material for removing contaminants from groundwater polluted by UCG was confirmed in the presented column tests. The following conclusions can be drawn with reference to each material used:

- GAC seems to be the most effective adsorbent. It removes most efficiently phenols, BTX, PAHs and cyanides (slightly lowers ammonia) at the same time it causes pH increase. It does not affect conductivity, temperature and redox potential. The drawback of this material is that it almost does not remove metals. Under in situ conditions, the sorption capacity of the GAC is strongly influenced by the hydrochemistry of the groundwater,
- zeolite: this adsorbent removes free cyanide and ammonia and removes phenols slightly. Zeolite may either release metals to water or remove them from it which depends on the

content of metals in water and the affinity of metals to the zeolite. It does not affect temperature but at the same DO is increasing which confirms why the value of ORP is also higher in the consecutive sampling points. Nevertheless, it causes significant decrease of pH and conductivity,

- scrap iron: this material effectively removes metals nevertheless it does not have any significant impact on organic compounds. It causes pH and temperature increase while the DO and redox potential is decreasing.

Taking into account obtained results GAC seems to be the most promising PRB filling material for organic contaminants removal appeared in groundwater as a result of UCG. A major advantage of zeolite is its ability to remove ammonia and free cyanides while scrap iron is very effective in removing metals.

The drawback of GAC and zeolite is their limited capacity and the fact that they must be replaced periodically, while ZVI may work without replacement.

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