Physicochem. Probl. Miner. Process. 49(1), 2013, 13−23

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received May 1, 2012; reviewed; accepted May 12, 2012

GROUNDWATER TREATMENT WITH THE USE OF ZERO-VALENT IRON IN THE PERMEABLE REACTIVE BARRIER TECHNOLOGY

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Abstract: The industrial dumping sites located in the southern provinces of Poland pollute groundwaters with metals. In the article, the possibility of groundwater (polluted by metals) treatment with the use of Permeable Reactive Barrier Technology has been presented. In this technology, the contaminants are removed from the aquifer by a flow of the groundwater through a PRB filled with a special reactive material. The wastewater (which simulated groundwater) circulated through the column filled with zero-valent iron in the laboratory tests. During the tests, the treatment processes proceeded. Chromium, copper, nickel, cobalt, lead, cadmium and zinc, occurring in the water as cations and anions, have been removed in the iron bed. The rapid metal removal has likely occurred due to the reduction and precipitation/co-precipitation and/or due to adsorption onto the iron metal surface or/and onto the iron corrosion products. Barium Ba^{2+} was the only metal, which has not been removed from the wastewater in the column. A rapid decrease of the redox potential and oxygen concentration as well as an increases of the pH value and stabilizations have also been observed during the flow of water through the column. Due to the Fe/Fe^{2+} half reaction during the treatment processes, the iron concentration has increased as well.

Key words: *remediation, dumping site, groundwater, PRB Technology, metals*

Introduction

In the southern provinces of Poland, there are plenty of industrial dumping sites for the hard coal and non-ferrous metal ores mining as well as dumps resulting from the manufacture of non-ferrous metals. They affect the quality of ground and surface water. The leachate from these dumping sites may contain following elements: As, Ba, B, Cd, Cu, Cr, Pb, Li, Mo, Ni, Rb, Sr, Tl, U, Zn (Twardowska et al., 2004; Pasieczna et al., 2008; 2010a; 2010b; Pasieczna and Kowalska, 2010; Nowak, 2008; Jarosiński et al., 2006, Suponik, 2012). An efficient removal of heavy metals as well as radionu-

http://dx.doi.org/10.5277/ppmp130102

clides and arsenic was achieved by the multibarrier presented in the study of Groudev et al. (2007).

In the article the possibility of the removal of Ni, Ba, Zn, Co, Cr, Cd, Pb and Cu from the groundwater with the use of zero-valent iron (ZVI, Fe^0) using Permeable Reactive Barrier (PRB) Technology has been presented. The application of ZVI for cationic and anionic metals removal has been investigated (Wilkin and McNeil, 2003; Rangsivek and Jekel 2005; Li and Zhang 2007; Fiore and Zanetti 2009; Puls et al., 1998; Meggyes et al., 1998). The main mechanisms suggested in these papers are reduction and precipitation/co-precipitation, and adsorption.

The results of the research on the copper removal from wastewater has also been presented elsewhere (Suponik, 2009). Cu^{2+} is characterized by a higher standard electrode potential than Fe^0, hence iron displaces this hazardous cation from groundwater:

$$Fe^0 + CuSO_4 \rightarrow FeSO_4 + Cu^0 . \tag{1}$$

This reaction (called cementation) is a well known in hydrometallurgy (Ekmekyapar et al., 2012). The reaction proceeds under condition that:

$$U_{Fe/Fe^{2+}} < U_{Cu/Cu^{2+}} \tag{2}$$

where $U_{Fe/Fe2+}$ is the standard electrode potential (ORP), V.

It was assumed in the paper that, cationic and anionic metals such as Ni^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+} and $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, may probably be removed from groundwater when the zero-valent iron is used as a reactive material in a permeable reactive barrier, as all these ions are characterized by a higher standard electrode potential than iron (Fe^0). Finally, these metals may be precipitated out by a reactive material as Ni^0, Cd^0, Pb^0, Co^0 and $Cr_xFe_{(1-x)}OOH$ (see reaction 4) (Puls et al., 1998), $Cr(OH)_3$ and Cr_2O_3 (ITRC, 2011).

Chromium(VI) is very toxic, whereas chromium(III) is slightly toxic and is easy to precipitate. Hence, the reduction of chromium(VI) into chromium(III) is the reaction which allows to remove it from groundwater (Suponik, 2011). The overall reaction for the hexavalent chromium, which occurs in water (under typical ground water pH and ORP conditions) as an oxyanion in the form of CrO_4^{2-} or as $Cr_2O_7^{2-}$ can be presented as (Meggyes et al., 1998):

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O. \tag{3}$$

In a further step, iron and chromium are precipitated as chromium(III) hydroxides or chromium-iron hydroxide solid solutions (Puls et al., 1998):

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH + 3H^+. \tag{4}$$

In accordance with Wilkin and McNeil (2003), when the value of pH is lower than 7, the process which causes the cationic metals removal is the adsorption onto the iron surface or onto the iron corrosion products, whereas if a neutral or an alkaline pH condition occurs in the groundwater, the precipitation of carbonate species will provide different types of sorption surfaces and a potential for metals coprecipitation.

According to the study of Li and Zhang (2007), the sorption/surface complex formation is the removal mechanism for metal ions with a standard potential very close to, or more negative, than that of iron. The predominant removal mechanism, for metals with a greatly more positive and slightly more positive ORP than that of iron, is respectively the reductive precipitation, and the sorption and/or reductive precipitation. In the research presented in the paper of Li and Zhang (2007), the nanoscale zero-valent iron has been used as a reactive material for the removal of metal cations in water. The article also includes a claim that as the pH of the groundwater passing through zero-valent iron substantially increases (e.g. reactions 5 and 6), the precipitation of metal hydroxides may play an important role in the immobilization of metals – the following hydroxides are characterized by low solubility product: $Cu(OH)_2$, $Pb(OH)_2$, $Cd(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$, $Zn(OH)_2$, $Ba(OH)_2$.

The primary goal of this study was to assess the possibility of the treatment of the groundwater, contaminated by dumping sites located in the provinces of southern Poland. The zero-valent iron used as a reactive material in PRB Technology has been applied for that purpose.

Materials and methods

The laboratory tests carried out to determine the possibility of groundwater treatment were conducted in a glass column (Fig. 1) packed with scrap iron taken from a machining plant and with coarse sand located at the bottom of the column. The wastewater has been made to circulate through the column from bottom to 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 the iron, on the bottom of the column and on the top of the iron bed (between iron and cork). The wastewater Darcian velocity used in the tests amounted to 0.02 m/day, 0.19 m/day and 0.50 m/day. These values corresponded to the groundwater velocity under industrial dumping sites located in southern Poland (the information has been obtained from the technical documentations of several dumping sites). This way, the conditions in column corresponded to the aquifer under the dumping sites in southern Poland.

Since the results of the tests for each velocity were similar the values for the Darcian velocity amounting to 0.50 m/day, were presented in the article.

There were seven sampling points in the installation in order to draw wastewater out and to take measurements. The wastewater (synthetic) was prepared by mixing distilled water (20 dm^3) with 108 mg $CuSO_4 \cdot 5H_2O$, 82 mg $CoCl_2$, 84 mg $NiSO_4 \cdot 7H_2O$, 140 mg $BaCl_2 \cdot 2H_2O$, 228 mg $ZnSO_4 \cdot 7H_2O$, 20 mg K_2CrO_4, 36 mg $CdSO_4 \cdot 8/3H_2O$ and

28 mg $PbCl_2$. This way, the allowable concentration of chemicals in the simulated groundwater has been exceeded within the meaning of legal regulations (Journal of Laws of 2009 No. 27 item 169). Since the pH of the groundwater under the dumping sites for the hard coal mining and non-ferrous metal ores mining, and for the manufacture of non-ferrous metals is respectively slightly acidic and rather neutral or alkaline (in southern Poland), it has not been purposely changed in the laboratory tests. The quantitative analysis of chemicals were carried out for:

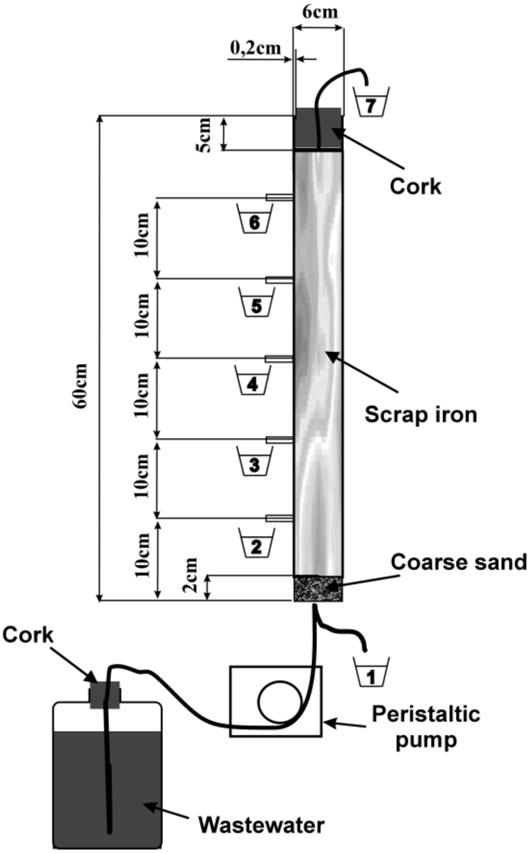

Fig. 1. Installation for simulation of flow and treatment processes of contaminated groundwater in reactive barrier; 1, 2, 3, 4, 5, 6, 7 – sampling points

- Cr^{6+}, UV-Vis Spectrophotometer DR5000 HachLange – 1,5-diphenylcarbohydrazide method; method 8023 of Hach Co.; test results are measured at 540 nm;
- Cu_{total}, UV-Vis Spectrophotometer DR5000 HachLange – bicinchoninate method; method 8506 of Hach Co.; test results are measured at 560 nm;

- Co_{total}, UV-Vis Spectrophotometer DR5000 HachLange – 1-(2-pyridolozo)-2-naphthol (PAN) method; method 8078 of Hach Co.; test results are measured at 620 nm;
- Ni_{total}, UV-Vis Spectrophotometer DR5000 HachLange – 1-(2-pyridolozo)-2-naphthol (PAN) method; method 8150 of Hach Co.; test results are measured at 560 nm;
- Ba^{2+}, UV-Vis Spectrophotometer DR5000 HachLange – turbidimetric method; method 8014 of Hach Co.; test results are measured at 450 nm;
- Zn_{total}, UV-Vis Spectrophotometer DR5000 HachLange – zincon method; method 8009 of Hach Co.; test results are measured at 620 nm;
- Cd_{total}, JY 2000 Spectrometer – Inductively Coupled Plasma Atomic Emission Spectroscopy method (ICP-AES);
- Pb_{total}, 2000 Spectrometer – Inductively Coupled Plasma Atomic Emission Spectroscopy method (ICP-AES);
- Fe_{total}, UV-Vis Spectrophotometer DR5000 HachLange – FerroVer method; method 8008 of Hach Co.; test results are measured at 510 nm;
- SO_4^{2-}, UV-Vis Spectrophotometer DR5000 HachLange – SulfaVer 4 method; method 8051 of Hach Co.; test results are measured at 450 nm;
- Cl^-, UV-Vis Spectrophotometer DR5000 HachLange – Mercuric Thiocyanate method; method 8113 of Hach Co.; test results are measured at 455 nm.

Concentrations of the Ni, Co, Cu, Zn, Cd, Pb metals in the wastewater, which was prepared by adding metal compounds to distilled water, were measured in a spectrophotometer and a spectrometer as a total value: Ni_{total}, Co_{total}, Cu_{total}, Zn_{total}, Cd_{total}, Pb_{total}. Since there were no metals speciation (at the beginning) in the wastewater other than the Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} cations, the removal of the metals in the second oxidation state has been assessed in the article.

The pH, ORP, dissolved oxygen (DO), conductivity and temperature are important parameters that are easily monitored during column tests and are good indicators of conditions created by ZVI. They were measured for: a) pH, PORTAMESS 913 pH with SenTix 4 electrode1; b) ORP, PORTAMESS 913 pH with POLYPLAST ORP electrode; c) conductivity and temperature, PORTAMESS 913 Cound, d) concentration of DO, PORTAMESS 913Oxy with oxygen SE 302 probe.

The scrap iron is easily available in large quantities at a reasonable price. It should have a high content of iron metal (>90%), low carbon content (<3%), and nonhazardous levels of leachable trace metal impurities (ITRC, 2011). It must be free of any surface coating (oils or grease) that inhibit its reactivity.

Both sand and iron (in the form chips and swarf, Fig. 2) were cleaned before using them to fill the column. The sand was cleaned with the use of distilled water, whereas iron was first cleaned with a thinner (painter's naphtha), dried in the moisture teller, and then, just before the application, cleaned with distilled water. Both materials were then carefully packed into the column.

The measurements have begun just after the achievement of a steady state in the column, i.e. after the wastewater in the column had been changed ten times.

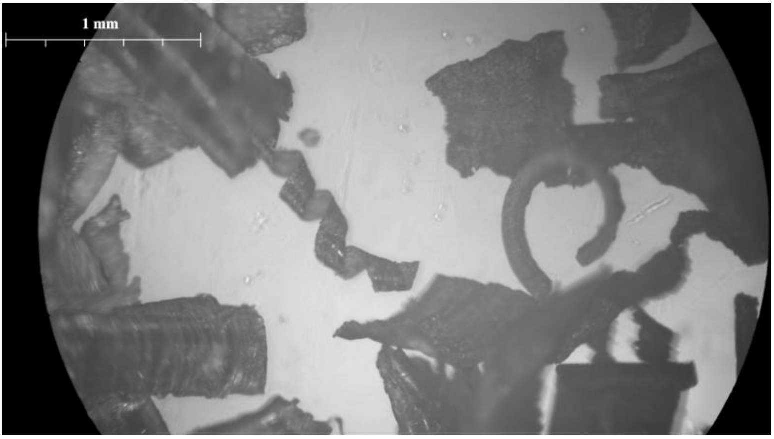

Fig. 2. Zero-valent iron Fe(0) used in laboratory tests

Table 1 presents the grain-size distribution of scrap iron used in the column test. The maximum size of the iron grain amounted to 4 mm. The material used in the size determination and in the measurements of the hydraulic parameters (Table 2) has also been cleaned with thinner (painter's naphtha) and dried in a moisture teller.

For a correct measurement of iron density (according to Polish Standard PN-88/B-04481), benzene (analytically pure) was applied in the test and a pycnometer with a sample was heated in a water bath (distilled water did not penetrate the measured material and lumps of iron were created in the pycnometer). The hydraulic conductivity of the reactive material was measured with the use of Kaminski's pipe method, while the bulk density and the effective porosity were determined in accordance with the Polish PN-88/B-04481 standard and King's method respectively (Pazdro et al., 1990; Wieczysty, 1982).

Table 1. Particle size distribution of zero-valent iron used in column test

Particle size, mm	4.0–2.0	2.0–1.6	1.6–1.0	1.0–0.71	0.71–0.5	<0.5
Mass fraction, %	1.77	1.28	7.26	38.79	36.57	14.33

Table 2. Parameters of zero-valent iron

Reactive material parameters, unit	Value
Hydraulic conductivity, m/s	$4.47 \cdot 10^{-4}$
Density, g/cm^3	7.85
Bulk density, g/cm^3	1.96
Effective porosity, –	0.46

Results and discussion

The scrap iron used in the tests shows an ability to create reductive conditions in a glass column and as a result, to remove cationic and anionic metals present in wastewaters in the following oxidation states: Cr^{6+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} (Table 3). In the present of iron, between the 1st and 2nd sampling point, the pH increased quickly as a result of the reactions 5 and 6 (reaction 6 proceeds slowly):

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{5}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{6}$$

This potential increased from 6.44 in the first sampling point to reach 7.98 in the second point. Following that, it slowly decreased at the remaining points.

Similar values of sulphates (SO_4^{2-} decreased very slowly in the iron bed, Table 3) and a small increase of pH in the column showed that the metals did not precipitate (or they precipitated to a small degree) in the form of sulphides or hydroxides. Therefore, the reductive precipitation and/or the adsorption on iron surface or on the iron corrosion products were probably the groundwater (contaminated with metals) treatment mechanisms.

In accordance with Table 3, reaction 5 proceeded quickly, evidenced by the fact that both DO and the ORP dropped quickly as the wastewater entered the iron material. The value of ORP and DO for the 1st and the 7th sampling points amounted to ORP_1 = 186 mV; DO_1 = 7.25 mg/l and ORP_7 = –70 mV; DO_7 = 4.59 mg/dm^3 respectively. These parameters decreased gradually.

The significant decrease of metals occurred already at the lower part of the iron bed – between the 1st and the 2nd sampling points. Low concentrations of the metals were still observed at the second point, while there was no evidence of any of the observed metals – except barium – at the 3rd sampling point. Its concentration kept a similar value at all points of the installation presented in Fig. 1. The half reaction of barium Ba/Ba^{2+} is characterized by a lower standard electrode potential than Fe/Fe^{2+}, which explains the treatment difficulty of water contaminated with barium in the 2nd oxidation state. Zinc, at the same time, is also characterized with a lower standard electrode potential than Fe^0 and was completely removed in the lower part of the iron bed. It might have been precipitated out in the form of hydroxide – $Zn(OH)_2$ (pH increased slightly, Table 3) or, more probably, adsorbed on the iron surface, what was suggested by Li and Zhang (2007):

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O\ . \tag{7}$$

According to reactions 1 taking place in the system, and also reaction 7, the wastewater should be richer in Fe^{2+} and Fe^{3+} respectively, at the next sampling points.

Table 3. The results of the research carried out in the installation presented in Fig. 1

Parameter, unit	Values for the following sampling points						
	1	2	3	4	5	6	7
pH	6.44	7.98	7.83	7.90	7.80	7.66	7.74
ORP, mV	186	121	95	64	–3	–38	–70
Conductivity, mS/cm	0.1507	0.1621	0.1999	0.381	0.720	0.904	1.040
DO, mg/dm^3	7.25	6.13	5.26	5.09	4.54	4.77	4.59
Temp., ^{o}C	17.8	18.2	18.3	17.7	17.8	17.8	17.6
Cr^{6+}, mg/dm^3	0.202	0.005	<0.001	<0.001	<0.001	<0.001	<0.001
Cu^{2+}, mg/dm^3	1.27	0.05	<0.04	<0.04	<0.04	<0.04	<0.04
Ni^{2+}, mg/dm^3	0.841	0.013	<0.006	<0.006	<0.006	<0.006	<0.006
Co^{2+}, mg/dm^3	1.772	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Ba^{2+}, mg/dm^3	5.0	5.5	4.5	5.0	6.0	5.5	5.0
Pb^{2+}, mg/dm^3	0.985	0.122	<0.005	<0.005	<0.005	<0.005	<0.005
Cd^{2+}, mg/dm^3	0.695	0.005	<0.001	<0.001	<0.001	<0.001	<0.001
Zn^{2+}, mg/dm^3	2.79	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe_{total}, mg/dm^3	<0.02	5.05	6.89	7.60	10.80	14.51	15.84
SO_4^{2-}, mg/dm^3	14	13	12	13	12	11	12
Cl^-, mg/dm^3	8.8	8.2	9.5	8.2	9.1	9.9	8.2

The total concentration of iron increased from <0.02 mg/dm^3 (detection limit in the spectrophotometer) in the untreated water, to 15.84 mg/dm^3 at the 7th sampling point. A higher value of conductivity at successive points has also confirmed the increase of the iron concentration. The conductivity increased from 0.1507 mS/cm in the raw wastewater to 1.040 mS/cm at last measuring point (Table 3). The above means that reactions 1, 5, 6 and probably others, proceeded quickly while the wastewater has been flowing through the column.

To some degree, the temperature increase in the wastewater flowing through ZVI has also confirmed the occurrence of the 1, 3, 5, 7, and probably 8, 9, 10, 11 reactions:

$$Fe^0 + NiSO_4 \rightarrow FeSO_4 + Ni^0 \tag{8}$$

$$Fe^0 + CoCl_2 \rightarrow FeCl_2 + Co^0 \tag{9}$$

$$Fe^0 + PbCl_2 \rightarrow FeCl_2 + Pb^0 \tag{10}$$

$$Fe^0 + CdSO_4 \rightarrow FeSO_4 + Cd^0 . \tag{11}$$

The temperature of the wastewater in the column increased from 17.8^{o}C at the 1st sampling point to 18.3^{o}C at the 3rd point, and then dropped to the value of 17.8^{o}C ± 0.1^{o}C at the remaining points (4, 5, 6, 7). The increase of the temperature in the lower part of the column probably occurred due to the negative enthalpy of reactions 1, 3, 5, 7 as well as 8, 9, 10 and 11, which could have caused (among others) the removal of cationic and anionic metals (Ni, Co, Cr, Cd, Pb, Cu) from the water and the increase of the iron concentration (Fe^{2+}, Fe^{3+}) in it. The decrease of temperature at remaining sampling points (4, 5, 6, 7) occurred due to the air temperature in the laboratory which was $17.6^{o}C \pm 0.2^{o}C$.

Conclusions

The industrial dumping sites in the southern provinces of Poland pollute groundwater with metals. Most of them may be removed with the use of zero-valent iron in the PRB Technology. In accordance with the results presented in the article, the cationic and anionic forms of Cr^{6+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} have been removed. Barium (Ba^{2+}) was the only assessed metal which remained in the wastewater after the treatment processes in the column. Rapid metals removal occurs most likely due to the reductive precipitation/coprecipitation and/or due to the adsorption onto the iron metal surface or/and onto the iron corrosion products.

As a result of the treatment processes in the column, a significant decrease of ORP (from 186 mV to –70 mV) and DO (from 7.25 mg/dm^3 to 4.59 mg/dm^3) and an increase of pH from ca. 6.5 up to ca. 7.8 occurred in the wastewater. At the same time, due to the Fe/Fe^{2+} and Fe/Fe^{3+} half reactions, the iron concentration (and the conductivity) increased. These reactions to a some degree, have confirmed the reduction and precipitation/coprecipitation of metals (reactions 1, 3, 8, 9, 10, 11), while also confirming the reduction of O_2 and H_2O (reactions 5, 6). Moreover, a significant increase of conductivity between the 1st and 7th sampling point showed that when iron was oxidized, the reductions of substances other than metals occurred (e.g. O_2).

Since the temperature of wastewater increased (from $17.8^{o}C$ to $18.3^{o}C$) in the lower part of the iron bed, the exothermic processes in the wastewater can be assumed to occurred. The reactions of cationic and anionic forms of metals (Ni, Co, Cr, Cd, Pb, Cu) removal and the reactions of oxygen reduction have a negative enthalpy.

In order to check the mechanisms of the groundwater treatment with zero valent-iron and to assess the type of the treatment processes (reductive precipitation/coprecipitation or adsorption), the changes in the oxidation states of metals in the wastewater flowing through the column should be analysed.

References

EKMEKYAPAR A., TANAYDIN M., DEMIRKIRAN N., 2012, *Investigation of copper cementation kinetics by rotating aluminum disc from the leach solutions containing copper ions,* Physicochemical Problems of Mineral Processing, vol. 48, issue 2, 355–367.

FIORE, S., ZANETTI M. C., 2009, *Preliminary Tests Concerning Zero-Valent Iron Efficiency in Inorganic Pollutants Remediation,* American Journal of Environmental Sciences 5(4), 556–561.

GROUDEV S., SPASOVA I., NICOLOVA M., GEORGIEV P., 2007, *Acid mine drainage cleanup in a uranium deposit by means of a passive treatment system*, Physicochemical Problems of Mineral Processing, vol. 41, 265–274.

ITRC (Interstate Technology & Regulatory Council), 2011, *Permeable Reactive Barrier:Technology Update*, PRB-5. Washington, D.C.: Interstate Technology & Regulatory Council, PRB: Technology Update Team. Washington: http://www.itrcweb.org.

JAROSIŃSKI A., NOWAK A. K., WŁODARCZYK B., 2006, *Charakterystyka odpadów i ścieków z ZG „Trzebionka" SA,* Ekotechnika nr 1/37, 43–45.

JOURNAL OF LAWS OF 2009, NO. 27, ITEM 169; Rozporządzenie Ministra Środowiska z dnia 28 stycznia 2009 r. zmieniające rozporządzenie w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego.

LI, X.-Q., ZHANG W. X., 2007, *Sequestration of Metal Cations with Zerovalent Iron Nanoparticles: A Study with High Resolution X-Ray Photoelectron Spectroscopy (HRXPS)*, Journal of Physical Chemistry 111(19), 6939–6946.

MEGGYES T., HOLZLOHNER U., AUGUST H., 1998, *A multidisciplinary approach to improving the safety and durability of landfill barriers,* in: *Contaminated and derelict land,* Sarsby R.W. (ed), Kraków. Thomas Telford, London, 413–420.

NOWAK A. K., 2008, *Ekologiczno-techniczne aspekty pozyskiwania koncentratów cynku i ołowiu,* Praca doktorska. Wydział Inżynierii i Technologii Chemicznej Politechnika Krakowska. Kraków.

PASIECZNA A., DUSZA-DOBEK A., KOWALSKA Z., 2010a, *Szczegółowa mapa geochemiczna Górnego Śląska 1:25000. Arkusz Katowice.* Państwowy Instytut Geologiczny, Warszawa. www.mapgeochem.pgi.gov.pl (dostęp: 24.02.2012).

PASIECZNA A., KOWALSKA Z., 2010, *Szczegółowa mapa geochemiczna Górnego Śląska 1:25000. Arkusz Mysłowice.* Państwowy Instytut Geologiczny, Warszawa. www.mapgeochem.pgi.gov.pl (dostęp: 24.02.2012).

PASIECZNA A., BIEL A., PAULO A., 2010b, *Szczegółowa mapa geochemiczna Górnego Śląska 1:25 000. Arkusz Imielin,* Państwowy Instytut Geologiczny, Warszawa. www.mapgeochem.pgi.gov.pl (dostęp: 24.02.2012).

PASIECZNA A., LIS J., SZUWARZYŃSKI M., DUSZA-DOBEK A., WITKOWSKA A., 2008, *Szczegółowa mapa geochemiczna Górnego Śląska 1:25 000, Arkusz Chrzanów,* Państwowy Instytut Geologiczny, Warszawa.

POLISH STANDARD PN-88/B-04481, 1988, Grunty budowlane – Badania próbek gruntu. Polski Komitet Normalizacji, Miar i Jakości.

PULS R.W., POWELL M.R., BLOWES D.W., GILLHAM R.W., SCHULTZ D., SIVAVEC T., VOGAN J.L., POWELL P.D., 1998, *Permeable reactive barrier technologies for contaminant remediation,* Washington: United States Environmental Protection Agency.

PAZDRO Z., KOZERSKI B., 1990, *Hydrogeologia ogólna*, wyd. Geologiczne, Warszawa.

RANGSIVEK, R., JEKEL M. R., 2005, *Removal of Dissolved Metals by Zero-Valent Iron (ZVI): Kinetics, Equilibria, Processes and Implications for Stormwater Runoff Treatment,* Water Research 39, 4153–4163.

SUPONIK T., 2009, *Zastosowanie żelaza metalicznego w technologii PRB,* rozdział w monografii *Rekultywacja i rewitalizacja terenów zdegradowanych*, ed. Grzegorz Malina. Wydawnictwo Polskiego Zrzeszenia Inżynierów i Techników Sanitarnych, Odział Wielkopolski (Inżynieria na rzecz ochrony środowiska, red. Jan F. Lemański, Sergiusz Zabawa, nr 866), Poznań, 161–172.

SUPONIK T., 2011, *Optimization of the PRB (Permeable Reactive Barriers) parameters for selected area of dumping site*, The Publishing House of the Silesian University of Technology (monographs no 328), Gliwice.

SUPONIK T., 2012, *Removing contaminants from groundwater polluted by the Trzebionka Mine Settling Pond located in Upper Silesia (Poland)*, Physicochemical Problems of Mineral Processing, vol. 48, issue 1, 169–180.

TWARDOWSKA I., ALLEN H.E., KETTRUP A.A.F., LACY W.J. (eds.), 2004, *Solid waste: assessment, monitoring and remediation,* Waste Management Series 4; Elsevier.

WILKIN R. T., MCNEIL M. S., 2003, *Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage*, Chemosphere 53, 715–725.

WIECZYSTY A., 1982, *Hydrogeologia inżynierska*, PWN, Warszawa.