ENSURING PERMEABLE REACTIVE BARRIER EFFICACY AND LONGEVITY

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Abstract: PRB technology is a technique of groundwater remediation where contaminants are removed from an aquifer by the flow through a permeable reactive barrier (PRB) filled with a special material called a "reactive material". In this paper problems connected with precipitate formation in zero-valent iron Fe^0 used as a reactive material were described – the precipitate may finally reduce the reactivity of this material and its hydraulic conductivity. Then, on the basis of the laboratory test changes of pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) concentration which accompany precipitate formation were demonstrated. Moreover, on the basis of hydrologic modeling the following rule was presented and proved: in order to increase PRB efficacy (in Funnel-and-Gate System) by increasing the hydraulic capture zone width, the ratio of the gate hydraulic conductivity ("gate" includes the reactive material in Funnel-and-Gate System of PRB Technology) to the aquifer hydraulic conductivity (k_{gate}/k_{aq}) should take the value of six. The precipitate formatted in zero-valent iron may reduce the hydraulic conductivity of the reactive gate. Therefore, it was assumed that the ratio of k_{gate}/k_{aq} should amount to 10. This value gives certainty that reduction in gate hydraulic conductivity due to precipitate formation will not impact the hydraulic capture zone width. The above mentioned solution can ensure effective and long-lasting treatment process in reactive barrier.

INTRODUCTION

Permeable reactive barrier (PRB) technology is a technique of groundwater remediation. Many toxic contaminants may be removed from groundwater by applying this technology. This technique is a passive one where contaminants are removed from an aquifer by the flow through a permeable barrier filled with a reactive material [2, 3, 5, 6, 9]. Many reactive materials may be used as a filler in PRB, but up to now zero-valent iron Fe^0 is the most common reactive material in the majority of field scale and commercial implementations [5, 8, 11]. The processes applied in it are [12]: chemical detoxification of halogenated hydrocarbons and precipitation of heavy metals.

Halogenated hydrocarbons, often present in groundwater, are very toxic whereas most hydrocarbons are non-toxic or slightly toxic. So, in the reactive material consisting of zero-valent iron Fe^0, a reaction which can change these chemicals into non-toxic hydrocarbons is created [12]. The zero-valent iron can act as reducing agent and generate a ferrous ion. The resulting electron activity is believed to reduce the halogenated

compounds to potentially non-toxic products. The overall reaction for detoxification of halogenated hydrocarbons (RCl) can be presented as [2]:

$$Fe^0 + H_2O + RCl \rightarrow RH + Fe^{2+} + OH^- + Cl^- \tag{1}$$
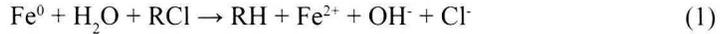
The reduction is primarily proceeded by the removal of the halogen atom and its replacement by hydrogen.

In the case of groundwater flowing through the industrial disposal sites it may bear positively charged inorganic cations such as Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}. All these cations are characterized by standard electrode potential higher than zero-valent iron. So it displaces hazard cations from groundwater, according to following reaction:

$$Fe^0 + CuSO_4 \rightarrow FeSO_4 + Cu^0 \tag{2}$$
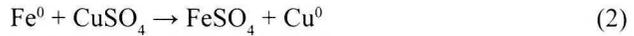
This reaction proceeds on condition that:

$$U_{Fe/Fe^{3+}} < U_{Cu/Cu^{2+}} \tag{3}$$

where:

$U_{Fe/Fe2+}$ – standard electrode potential (also known as standard redox potential, standard oxidation/reduction potential or ORP) [V].

The PRB is a technology that has the potential to effectively remediate subsurface contamination at many types of sites with significant cost savings compared to other ones. The economics of a PRB application depend largely on the useful life (longevity) of the reactive media.

PRB has several advantages over other methods of groundwater remediation. Reactive barrier can degrade or immobilize contaminants *in situ* without bringing them up to the surface. It also usually does not require continuous input of energy. PRB is currently built in two basic configurations: Continuous Reactive Barrier and Funnel-and-Gate System [5, 9] divided into: Funnel-and-Gate Open System and Funnel-and-Gate Closed System (Fig. 1) [7]. Both configurations require some degree of excavation and are limited to fairly shallow depths of aquitard, about 15 m [12]. The contaminant plume must not pass over, under or around the PRB and the reactive zone must reduce the contaminant to concentration goal without rapidly plugging with precipitates or becoming passivated. The Funnel-and-Gate System uses impermeable walls (sheet piles, slurry walls, etc.) to direct the contaminant plume to a "gate" containing the reactive material, whereas the Continuous Reactive Barrier is completely filled with the reactive material and is rather
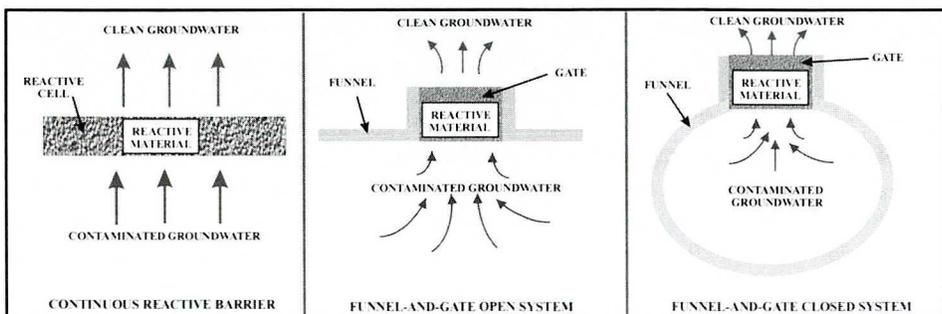
Fig. 1. Main types of PRB [7]

homogeneous. Due to the impermeable walls, the Funnel-and-Gate System has a greater impact on altering the groundwater flow than Continuous Reactive Barrier.

The two primary interdependent parameters of concern when designing a PRB are *hydraulic capture zone width* and *residence time*. Capture zone width refers to the width of the zone of groundwater that will pass through the reactive cell (in the case of Continuous Reactive Barrier) or gate (in the case of Funnel-and-Gate System) rather than pass around the ends of the barrier or beneath it. Capture zone width can be maximized by maximizing the discharge (groundwater flow volume) through the reactive cell or gate. Residence time refers to the amount of time during which contaminated groundwater is in contact with the reactive medium within the gate or reactive cell. Residence times can be maximized either by minimizing the discharge through the reactive barrier or by increasing the flow through thickness of the reactive barrier. Thus, the design of PRBs must often balance the need to maximize capture zone width (and discharge) against the desire to increase the residence time. Contamination occurring outside the capture zone will not pass through the reactive barrier. Similarly, if the residence time in the reactive barrier is too short, contaminant levels may not be reduced sufficiently to meet regulatory requirements [2].

The two primary goals of this study were:
– presenting (on the basis of laboratory measurement and literature survey) the precipitate formation possibility in zero-valent iron, which can coat the surface of it or occupy the available pore space and eventually reduce the reactivity and the hydraulic conductivity of this material. This effect could shorten the useful life of the reactive media causing necessity to replace it and thus make PRB more expensive. It was finally suggested to use some solution to prevent such a problem;
– presenting (on the basis of hydrologic modeling) the following rule: in order to increase PRB efficacy (in Funnel-and-Gate System) by increasing hydraulic capture zone width the gate hydraulic conductivity should be several times higher than aquifer hydraulic conductivity.

In the highly reducing environment produced by zero-valent iron, dissolved species, including oxygen, carbonate, sulphate, calcium, magnesium, iron, and silica can potentially interact to form precipitates that could deposit on the iron or within the pore spaces [3]. In this way the reactivity of this material and its hydraulic conductivity can be reduced which then leads to the failure of the whole system. The same effect may arise when in treated groundwater the pH is increasing as a result of reactions which occur in the reactive material.

In case when dissolved oxygen (DO) is present in groundwater as it enters the reactive iron material, iron is oxidized and hydroxyl ions are generated [2]:

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{4}$$
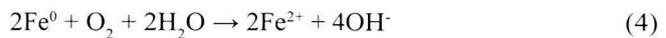
The importance of this reaction is that DO can quickly corrode the first few centimeters of iron layer in the reactive barrier [13].

Under oxygen conditions, Fe^{2+} (formed in reaction 4) oxidizes to Fe^{3+}, which can be written as:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{5}$$
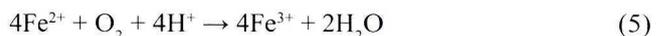
Fe^{3+} may then precipitate out as Fe(III) oxyhydroxide – FeO(OH) or Fe(III) hydrox-

ide – $Fe(OH)_3$ (reaction 6) at the elevated pH condition, in which case the permeability and reactivity as well could potentially become considerably lower in the first few centimeters of the reactive barrier at the influent end. So, the aerobic condition in groundwater is unfavorable to that material [13].

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)} \tag{6}$$

Fe(III) (oxy)hydroxides formed in the reactive material are converted over time to magnetite.

According to the reactions 1, 4 and 7 (reaction 7 proceeds slowly) the oxidation of Fe^0 to Fe^{2+} causes increase in pH (in weakly buffered system), which may next cause precipitation of Fe(III) hydroxide in aerobic condition (reaction 6) and Fe(II) hydroxide in anaerobic condition (reaction 8), and also precipitation of other compounds [13]. In accordance with Figure 2, $Fe(OH)_2$ is relatively insoluble and $Fe(OH)_3$ is extremely insoluble.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{7}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(s)} \tag{8}$$

In strongly buffered system the presence of bicarbonate (alkalinity) can limit pH increase, which can be written as:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{9}$$
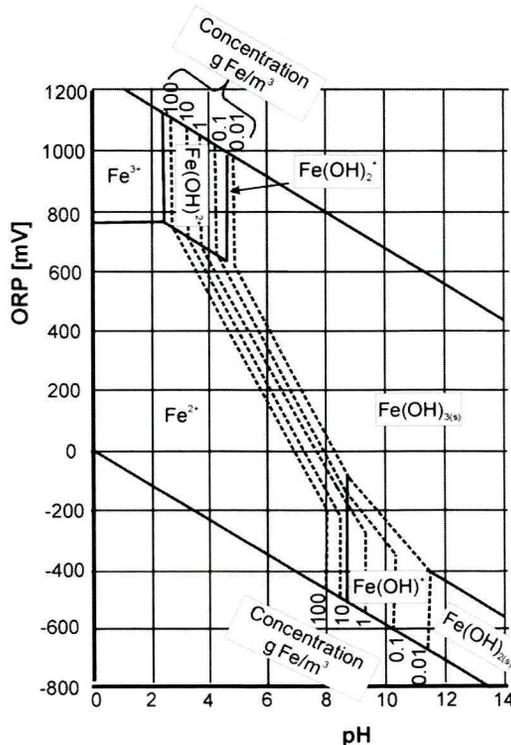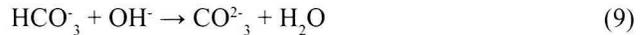
Fig. 2. The effect of pH and ORP on iron speciation (iron concentration: 0.01–100 g Fe/m³) [4]

The effect of pH on the mobility and precipitation of many inorganic hydroxides is shown in Figure 3 [15]. According to this Figure the increase in pH would be positive (for the condition when toxic cations are presented in the groundwater) if it was the main factor generating groundwater treatment process and if these cations did not precipitate out using reaction 2.
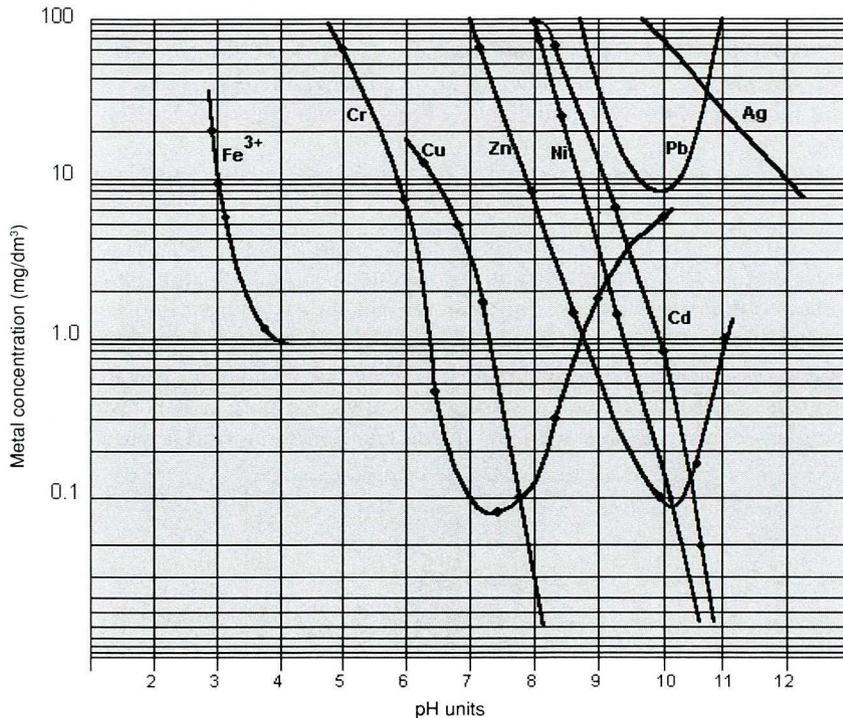
Fig. 3. Metals hydroxide solubility as a function of their concentration and pH [15]

The precipitate formation in zero-valent iron through pH increasing causes decrease in permeability of the reactive material and its reactivity. So it is unfavorable to the reactive material as well [13].

So, once contaminated groundwater passes through zero-valent iron the geochemical parameters like pH and oxidation-reduction potential (ORP) are changing radically. The pH is increasing while, at the same time, the ORP is decreasing. In that condition the bicarbonate (HCO_3^-) ions are converted to carbonate ions (CO_3^{2-}) (reaction 9). The CO_3^{2-} ion can then combine with the cations present in solution (Ca^{2+}, Fe^{2+}) to form carbonate mineral precipitates such as calcite ($CaCO_3$) and siderite ($FeCO_3$). At some sites, Mg^{2+} may precipitate in solid solution with $CaCO_3$. The potential for precipitation of calcite, magnesite and siderite minerals can be evaluated by monitoring the changes (losses) in alkalinity, ferrous ion, calcium and magnesium [3, 9].

Moreover, reducing conditions lead to reduction of sulphate to a lower oxidation state of sulphur, such as sulphide, which then can precipitate with inorganic constituents

like Fe, Cu, Zn, Pb, V, Mn. The "Green rust," a compound of ferrous or ferric ion containing hydroxide, chloride, and sulphate, is another precipitate that may be created in those conditions [2].

Dissolved silica is inorganic constituent present in groundwater that is of potential concern to the longevity of a barrier as well. Monomeric silicic acid, H_4SiO_4, is known to form polymers that may coat iron grains, producing a passivating film. It is unknown whether or to what extent dissolved silica acts as a corrosion inhibitor for granular iron [2].

Although, the effect of precipitate mass on reactivity is rather unclear, the amount of inorganic species lost as the groundwater moves through the reactive medium may be an important indicator of the type and degree of precipitation that is occurring [2, 3, 14].

METHODOLOGY OF THE RESEARCHES AND USED MATERIAL

The pH, oxidation-reduction potential (ORP) and dissolved oxygen (DO) are inorganic parameters that are easily monitored during column tests and are good indicators of conditions created in reactive barrier. For these reasons they were used in the laboratory test presented in the paper for determining whether conditions are favorable to formation of inorganic precipitates. The effect of pH, DO and ORP changing was observed in the laboratory test carried out in the measuring set shown in Figure 4. This test was conducted in the glass column packed with scrap iron taken from industrial waste lagoon "HK
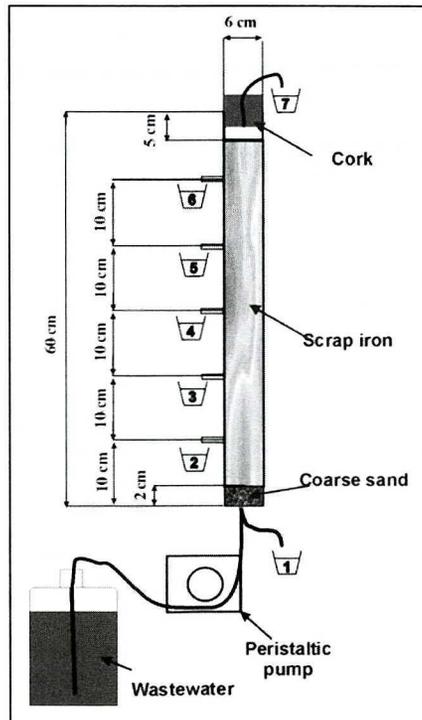
Fig. 4. Installation for simulation of flow and treatment processes of contaminated groundwater in reactive barrier; 1, 2, 3, 4, 5, 6, 7 – sampling points [13]

EKO GRYS" in Dąbrowa Górnicza, Poland and with fine sand [11]. Table 1 presents the grain-size distribution of iron used in the column test, whereas Table 2 presents its main hydraulic parameters.

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

Size grade [mm]	> 1.6	1.6–1.0	1.0–0.8	0.8–0.5	0.5–0.1	< 0.1
Mass fraction [%]	1.01	9.73	38.26	32.88	8.39	9.73

Table 2. Parameters of zero-valent iron Fe^0

Reactive material parameters	Value
Hydraulic conductivity [m/s]	$2.1 \cdot 10^{-2}$
Density [g/cm^3]	7.61
Bulk density [g/cm^3]	2.52
Effective porosity [-]	0.67

Both sand and iron were cleaned before filling column with them. Sand was cleaned with the use of distilled water whereas iron was first cleaned with spirit and then with distilled water. Both materials were next dried and carefully packed into column.

Wastewater was prepared by mixing distilled water (5 dm^3) and $CuSO_4 \cdot 5H_2O$ (71 mg). It was circulated in the column from bottom to the top (Fig. 4) and during that time redox processes were proceeded in it. The wastewater Darcian velocity amounted to 25.26 cm/h while the initial concentration of Cu^{2+} in wastewater amounted to 3.51 mg/dm^3. There were five sampling points along the column in order to draw wastewater out and to take measurements. The conditions in the column corresponded to the aquifer. The measurements were just begun after achieving steady state in the column i.e. after wastewater located in the column was changed five times.

As for any decontamination technology, it is important also to fully understand the factors that determine their efficiency. This section describes methodology for creation of theoretical models used to evaluate dependence between the gate hydraulic conductivity and aquifer hydraulic conductivity in a Funnel-and-Gate System of PRB Technology.

There are many kinds of programs for modeling groundwater and contaminants diluted in it, for example: FEFLOW, FLONET/TRANS, FLOWPATH II, FRAC3DVS, FRACTRAN, PRINCE, RBCA TIER 2 ANALYZER, VISUAL MODFLOW. The Visual MODFLOW program and its modules were chosen for PRB hydrologic designing because they allow [10]:
— to model the hydrodynamic field in the area of groundwater,
— to model the chemical distribution of contaminants,
— to calculate the quantity of water which flows through the specific area (Zone Budget module),
— to specify the direction of groundwater (Modpath module),
— to use in the model cut-off wall, which is characterized by different thickness and different hydraulic conductivity.

The theoretical model (Fig. 5) used for hydrologic modeling has the shape a of square (400/400 m). The surficial geology at the model consists of an upper sand aquifer and a clay aquitard which insulate the aquifer. The thickness of the aquifer is of depth up

to 12 m. Both the gate and cut-off wall were keyed into the underlying confining layer. The hydrologic modeling was carried out for:

–   Funnel-and-Gate System – total Funnel-and-Gate width in the model amounted to 220 m, whereas the thickness of the gate equaled to 5 m. The Funnel-and-Gate System was made of cut-off wall with a permeability of $1 \cdot 10^{-12}$ m/s and a thickness of 0.07 m. The system was orientated perpendicular to groundwater flow direction,
–   different site parameters, i.e.:
    –   aquifer hydraulic conductivity – the model was simulated with aquifer hydraulic conductivity from $1 \cdot 10^{-6}$ m/s to $5 \cdot 10^{-4}$ m/s. Moreover, the aquifer was set up as a homogeneous and hence the hydraulic capture zone in every model was symmetrical;
    –   hydraulic gradient – the model was simulated with an aquifer gradient from 0.01% to 0.5%;
–   different gate width – the model was simulated with gate width from 5 m to 30 m,
–   different gate hydraulic conductivity – the model was simulated with gate hydraulic conductivity from $1 \cdot 10^{-6}$ m/s to $5 \cdot 10^{-3}$ m/s,
–   different distance between the PRB and the source of contaminants – the model was simulated with distance between the PRB and the source of contaminants from 30 m to 120 m.
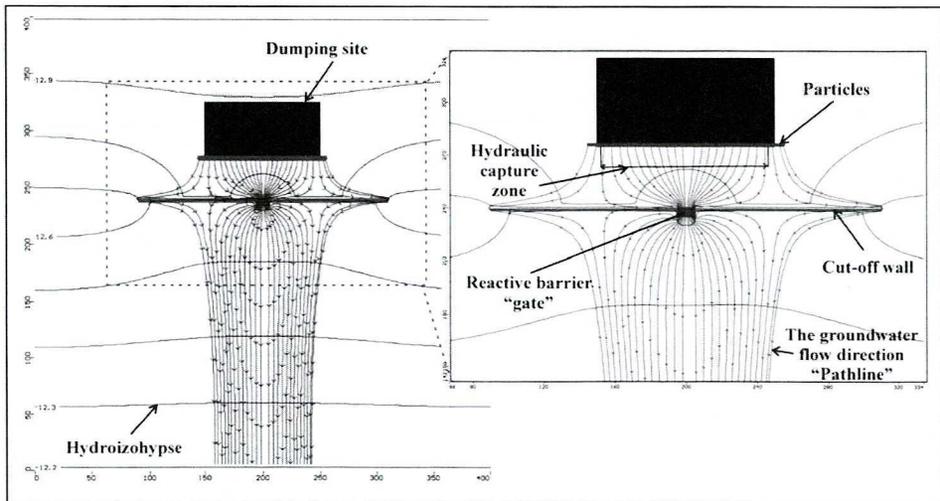
Fig. 5. The hydrodynamic field (theoretical) with the use of the Funnel-and-Gate System and the dumping site

By the use of such a model, the combined effect of several critical parameters can be incorporated simultaneously into one model.

In order to facilitate the analysis, it was assumed that the aquifer is isotropic and the source of contaminants (dumping site) has a shape of a rectangle (100/50 m). Specified head nodes were set along the first row (top row) and the last row (bottom row). Groundwater flew from top to bottom. The Modpath module and the Zone Budget module were used to delineate the capture zone width and to calculate sub-regional water budgets.

RESULTS AND DISCUSSION

The Figure 6 shows the results of the laboratory test, i.e. the value of pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO), measured in wastewater [11].
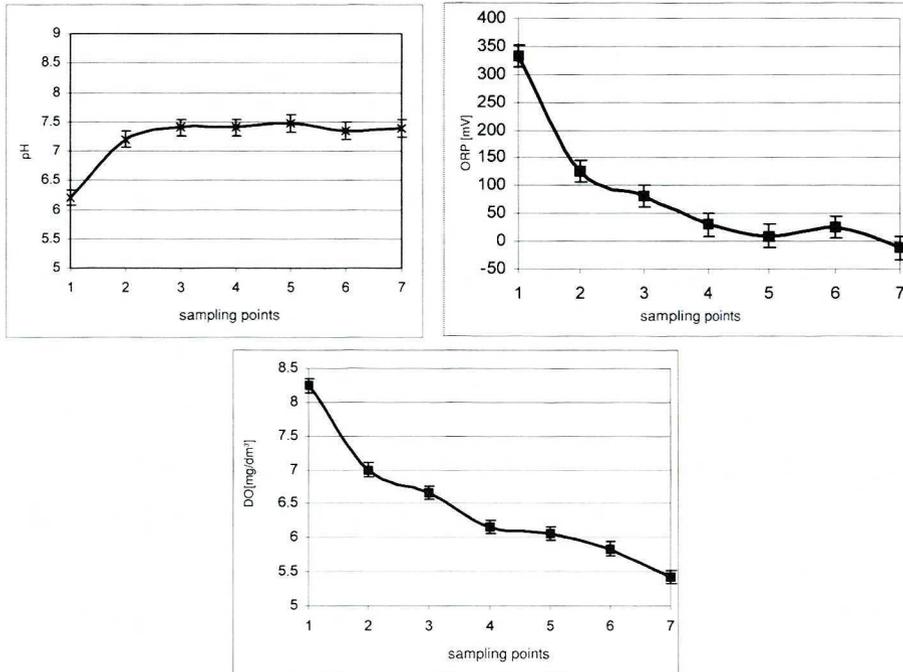
Fig. 6. pH, ORP and Do concentrations measured during laboratory tests (installation – see Fig. 4) [13]

In accordance with Figure 6, the reaction 4 proceeded quickly, evidenced by the fact that both the DO and the ORP dropped quickly as the wastewater entered the iron material. The value of ORP and DO for the first and the seventh sampling point amounted to $ORP_1 = 332$ mV; $DO_1 = 8.24$ mg/dm^3 and $ORP_7 = -12$ mV; $DO_7 = 5.42$ mg/dm^3, respectively. These parameters went down gradually.

In an iron medium, as conditions became more anaerobic in the column, pH increased (Fig. 6) as a result of reaction 4 and 7. This potential increased from 6.21 in the first sampling point and reached up to 7.20 in the second sampling point, and then it kept similar value in the remaining points.

As a consequence of pH, DO and ORP changes, it can be said that the oxidation of Fe^0 to Fe^{2+} (and maybe to Fe^{3+}) causes (with time) precipitate formation and decreasing reactivity and hydraulic conductivity of the iron used as a reactive material in column test.

In order to confirm the effect of precipitate formation more measurements need to be done. Either the column influent and effluent could be analyzed for inorganic, such as anions (carbonate – CO_3^{2-}, bicarbonate – HCO_3^- (alkalinity), nitrate – NO_3^-, nitrite – NO_2^-, sulphate – SO_4^{2-}, chloride – Cl^-, and silica – $SiO_2(OH)_2^{2-}$ or $SiO(OH)_3^-$), cations (Ca^{2+},

Mg^{2+}, Na^+, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+} and K^+) or the precipitate type formed in the column [3, 14].

The results of researches carried out at NAS Moffett Field and at Lowry AFB [3] show similar trends of pH and ORP changes. At NAS Moffett Field the groundwater pH rose from 7.0 to 10.9 and the ORP dropped from 134 to -821 mV in the iron, and at Lowry AFB the groundwater pH rose similarly from 6.9 to 11.5 and ORP dropped from -13 to -725 mV in the iron. DO concentration in groundwater at NAS Moffett Field dropped from 0.7 to 0.4 mg/dm^3. At both sites most of the dissolved calcium, iron, magnesium, manganese, sulphate, nitrate, and dissolved silica were removed from the groundwater flowing through the reactive barrier. Levels of alkalinity and dissolved solids were considerably reduced [3]. These constituents are likely to have precipitated out in the PRB, what confirms that problem connected with precipitate formation in zero-valent iron Fe^0 may arise.

To reduce PRB costs to a minimum, the zero-valent iron should be able to maintain its reactivity and hydraulic conductivity over time. So, in order to meet these conditions:

– the hydraulic conductivity of the reactive material should be a few times higher than hydraulic conductivity of aquifer. This solution may prevent blocking up of the reactive barrier and breakdown of the whole system,

– the pyrite (or other material) could be used as a pre-treatment zone with gravel before the contaminated groundwater goes to the zero-valent iron zone. This solution may remove DO from water and prevent pH increasing [13].

In this part of paper the main observations from the hydrologic modeling carried out for evaluating dependence between the gate hydraulic conductivity and aquifer hydraulic conductivity in Funnel-and-Gate System of PRB Technology are described. In order to present this dependence, their influence on Darcian velocity within the gate and on hydraulic capture zone width was characterized. In this section:

– Figure 7 shows the dependence between the Darcian velocity within the gate (v) and aquifer hydraulic conductivity (k_{aq}),
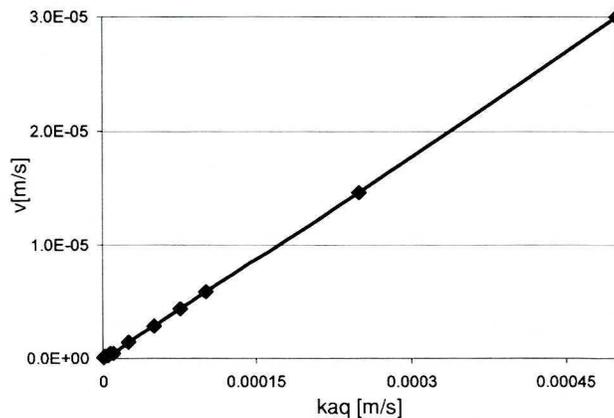
Fig. 7. The Darcian velocity within the gate as a function of different value of aquifer hydraulic conductivity

– Figure 8 shows the dependence between the Darcian velocity within the gate (v) and gate hydraulic conductivity (k_{gate}),

– Figure 9 shows the dependence between the hydraulic capture zone width (z) and hydraulic conductivity of the gate (k_{gate}), and hydraulic conductivity of the aquifer (k_{aq}).
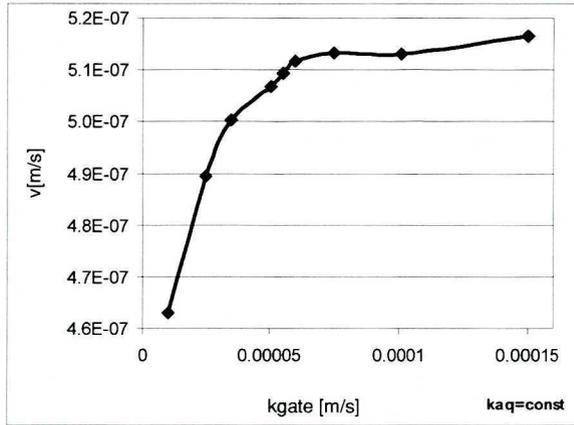
Fig. 8. The Darcian velocity within the gate as a function of different value of gate hydraulic conductivity
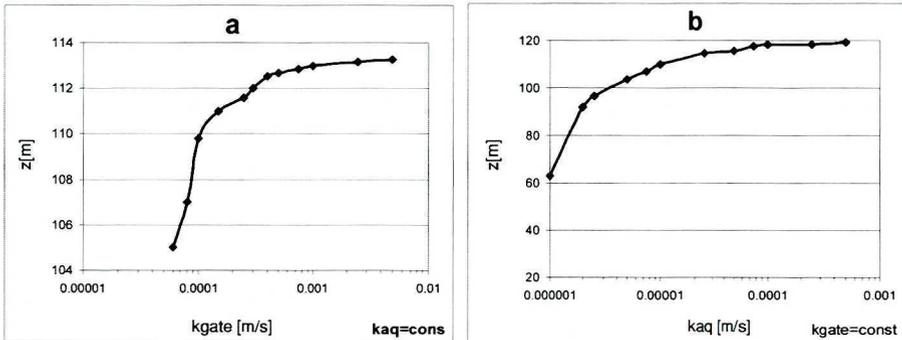
Fig. 9. The hydraulic capture zone width as a function of different value of: a) gate hydraulic conductivity, b) aquifer hydraulic conductivity

The graphs presented in Figures 7, 8, 9 came from some variant of the simulation on the model, because it was difficult to present all results in the paper. It was decided to do so because the results achieved from the rest of the simulations are similar i.e. the curves (the dependence) are the same but the values of the parameters are different.

In accordance with the equation 10 (Darcy's law) the groundwater velocity (Darcian) in aquifer is rising when hydraulic conductivity of aquifer is rising for the conditions that hydraulic gradient is constant.

$$v = -k\frac{\Delta H}{\Delta x} = -kI \qquad (10)$$

where:

v   – Darcian flux (velocity) [m/s],

ΔH   – head difference [m],

k   – hydraulic conductivity [m/s],

x   – length difference [m],

I   – hydraulic gradient.

In the model on which the simulations for assessing the dependence between Darcian velocity within the gate and aquifer hydraulic conductivity were carried out (Fig. 7) the following data were used:

–   the value of aquifer hydraulic conductivity amounted for each simulation to $1·10^{-6}$ m/s, $2.5·10^{-6}$ m/s, $5·10^{-6}$ m/s, $7.5·10^{-6}$ m/s, $1·10^{-5}$ m/s, $2.5·10^{-5}$ m/s, $5·10^{-5}$ m/s, $7.5·10^{-5}$ m/s, $1·10^{-4}$ m/s, $2.5·10^{-4}$ m/s, $5·10^{-4}$ m/s respectively,

–   the hydraulic gradient amounted to 0.2%,

–   the gate width amounted to 10 m,

–   the gate hydraulic conductivity had the same value as the aquifer hydraulic conductivity in particular simulation,

–   the distance between the PRB system and the source of contaminants amounted to 35 m.

Groundwater velocity within the gate was estimated using two tools:

–   Modpath module – by measuring distance that a particle covers during defined time,

–   Zone Budget module – by calculating the water discharge through the gate and measuring the lateral area of the gate.

In Figure 7 it can be noticed that the velocity within the gate is rising when aquifer hydraulic conductivity (k_{aq}) is rising for the conditions that hydraulic gradient is constant. That is why it may be said that the groundwater velocity within the gate is strictly correlated with aquifer hydraulic conductivity and thus with the velocity in the aquifer. Moreover, on the basis of hydrologic modeling, it was noticed that due to directing a large amount of water through the much smaller cross sectional area of the gate, groundwater velocity within the gate is higher then velocity in other places of the model (velocity in the aquifer).

The gate hydraulic conductivity (k_{gate}) influences the velocity within the gate as well. However, on the basis of Figure 8 it can be said that this influence was not as big as when the aquifer hydraulic conductivity was changing. Moreover, after reaching some value of gate hydraulic conductivity the velocity within the gate rose very slowly. This dependence was strictly connected with the value of aquifer hydraulic conductivity. In the model by means of which the results presented in Figure 8 were achieved the following data were used:

–   the aquifer hydraulic conductivity amounted to $1·10^{-5}$ m/s,

–   the hydraulic gradient amounted to 0.2%,

–   the gate width amounted to 14 m,

–   the value of gate hydraulic conductivity amounted for each simulation to $1·10^{-5}$ m/s, $2.5·10^{-5}$ m/s, $3.5·10^{-5}$ m/s, $5·10^{-5}$ m/s, $5.5·10^{-5}$ m/s, $6·10^{-5}$ m/s, $7.5·10^{-5}$ m/s, $1·10^{-4}$ m/s, $1.5·10^{-4}$ m/s respectively,

the distance between the PRB and the source of contaminants amounted to 35 m.

For Funnel-and-Gate System, the funnel part of the design is engineered to com-

pletely encompass the path of the contaminant plume and the overall design must prevent the contaminant plume from flowing around the treating zone in any direction [9]. For this configuration, hydraulic capture zone width appears to be most sensitive to funnel width [2], however, gate width and hydraulic conductivity of aquifer and gate have also some influence on hydraulic capture zone width. According to Figure 9, the hydraulic capture zone width (and the discharge through the gate) increased with the rise in hydraulic conductivity of aquifer and gate for constant value of funnel and gate width. So the change in groundwater velocity within the gate presented in Figures 7 and 8 due to changing in hydraulic conductivity of aquifer and gate had influenced hydraulic capture zone width as well.

In the model by means of which the results presented in Figure 9a were achieved the following data were used:
−   the aquifer hydraulic conductivity amounted to $6 \cdot 10^{-5}$ m/s,
−   the hydraulic gradient amounted to 0.08%,
−   the gate width amounted to 20 m,
−   the value of gate hydraulic conductivity amounted for each simulation to $6 \cdot 10^{-5}$ m/s, $8 \cdot 10^{-5}$ m/s, $1 \cdot 10^{-4}$ m/s, $1.5 \cdot 10^{-4}$ m/s, $2.5 \cdot 10^{-4}$ m/s, $3 \cdot 10^{-4}$ m/s, $4 \cdot 10^{-4}$ m/s, $5 \cdot 10^{-4}$ m/s, $7,5 \cdot 10^{-4}$ m/s, $1 \cdot 10^{-3}$ m/s, $2.5 \cdot 10^{-3}$ m/s, $5 \cdot 10^{-3}$ m/s respectively,
−   the distance between the PRB and the source of contaminants amounted to 35 m.

In the model by means of which the results presented in Figure 9b were achieved the following data were used:
−   the value of aquifer hydraulic conductivity amounted for each simulation to $1 \cdot 10^{-6}$ m/s, $2 \cdot 10^{-6}$ m/s, $3 \cdot 10^{-6}$ m/s, $5 \cdot 10^{-6}$ m/s, $7.5 \cdot 10^{-6}$ m/s, $1 \cdot 10^{-5}$ m/s, $2.5 \cdot 10^{-5}$ m/s, $5 \cdot 10^{-5}$ m/s, $7.5 \cdot 10^{-5}$ m/s, $1 \cdot 10^{-4}$ m/s, $2.5 \cdot 10^{-4}$ m/s, $5 \cdot 10^{-4}$ m/s respectively,
−   the hydraulic gradient amounted to 0.08%,
−   the gate width amounted to 20 m,
−   the gate hydraulic conductivity amounted to $5 \cdot 10^{-3}$ m/s,
−   the distance between the PRB and the source of contaminants amounted to 35 m.

Hydraulic capture zone width was estimated using Modpath module by measuring the width of all particles that would flow through the gate.

The simulations, whose results are presented in Figure 9, show that aquifer hydraulic conductivity had bigger impact on hydraulic capture zone width than gate hydraulic conductivity. In the case of gate hydraulic conductivity being constant, the higher value of aquifer hydraulic conductivity caused quick and continuous increase in hydraulic capture zone width, while increase in gate hydraulic conductivity caused limited increase in hydraulic capture zone width for constant aquifer hydraulic conductivity.

In accordance with Figure 9, it can be also claimed that when the value of gate hydraulic conductivity was six times higher than the aquifer hydraulic conductivity, the change in hydraulic capture zone width was very small. Hence, according to hydrologic modeling presented in the paper, when it is going to increase hydraulic capture zone width by increasing in gate hydraulic conductivity, this value should be only six times higher than aquifer hydraulic conductivity.

To sum up, hydraulic capture zone width can be controlled by changing the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity (k_{gate}/k_{aq}). While aquifer hydraulic conductivity is constant the gate hydraulic conductivity is the only parameter that may be changed. Moreover, according to the presented simulation, the ratio

of k_{gate}/k_{aq} should amount to six because the hydraulic capture zone width hardly changes at all above this value.

Unfortunately, due to different processes in zero-valent iron, the precipitate formation in it may reduce the reactivity of this material and the hydraulic conductivity of the reactive gate. So, incorporation of adequate safety factor (larger size of iron grain) into the PRB is one of the ways of achieving satisfactory hydraulic performance. Taking this factor into account, the gate hydraulic conductivity should be higher than followed from presented hydrologic modeling. In accordance with some of the designers of PRB, the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity should amount to 10 [1, 2]. This exact value was used by designers to achieve certainty that reduction in gate hydraulic conductivity would not impact the hydraulic capture zone width when the ratio of k_{gate}/k_{aq} drops below 6, at which point k_{gate} becomes an increasingly sensitive parameter. It should be explained here that using larger size of grain of iron (and in this way larger gate hydraulic conductivity) than needed it is not proper for PRB efficacy, because the reactivity of the used medium decreases as a result of lower surface contact of contaminants with the zero-valent iron.

CONCLUSIONS

1. The pH, ORP and DO are inorganic parameters that give important information about the potential of precipitate formation in reactive barrier filled with zero-valent iron and are easily monitored during column tests. As contaminated water moved through the column presented in the paper, it underwent radical geochemical changes, including a reduction in ORP and DO from 332 mV and 8.24 mg/dm³ to minus 12 mV and 5.42 mg O_2/dm³ respectively, and an increase in pH from 6.21 to 7.47. In order to confirm that precipitate arose and it might affect the reactivity and hydraulic performance of the PRB, the change in inorganic constituents could be noted between the influent and effluent end of the column.

2. One of the main parameters of concern when designing a PRB is hydraulic capture zone width. It increases or decreases as the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity increases or decreases, respectively. The aquifer hydraulic conductivity is constant, thus, when it is going to increase the hydraulic capture zone width for Funnel-and-Gate System, it is important to increase in the gate hydraulic conductivity up to the value six times higher than aquifer hydraulic conductivity (according to presented hydrologic modeling).

3. As a result of studies presented in the paper it may be said that incorporation of adequate safety factor (larger size of iron grain) into the PRB is one of the ways of ensuring its efficacy and longevity. This factor (the ratio of the gate hydraulic conductivity to the aquifer hydraulic conductivity) should amount to 10.

REFERENCES

[1]   Beitinger E., F. Tarnowski, M. Gehrke, H. Burneier: *Permeable treatment walls for in-situ groundwater remediation – how to avoid precipitation and bio-clogging*, Contaminated Soil '98, vol. 1, Edinburgh 1998.

[2]   Gavaskar A., N. Gupta, B. Sass, R. Janosy, J. Hicks: *Design guidance for application of permeable reactive barriers for groundwater remediation*, Battelle Columbus Operations Ohio, 2000.

[3]   Gavaskar A., B. Sass, N. Gupta, E. Drescher, W.S. Yoon, J. Sminchak , J. Hicks, and W. Condit: *Evaluating the longevity and hydraulic performance of Permeable Reactive Barriers at Department of Defense Sites*, Battelle Columbus Operations Ohio, 2003.
[4]   Hem J.D.: *Stability field diagrams as aids in iron chemistry studies*, JAWWA, **2**, 211 (1961).
[5]   Interstate Technology & Regulatory Council: *Permeable Reactive Barriers: Lessons learned/new directions*, Washington, http://www.itrcweb.org, 2005.
[6]   Lutyński A., T. Suponik: *Zastosowanie barier z węgla aktywnego do ochrony wód podziemnych przed odciekami ze składowisk odpadów przemysłowych*, Ochrona Środowiska, **4**, 37–40 (2004).
[7]   Lutyński A., T. Suponik: *Procedura projektowania bariery remediacyjnej*, Ekotechnika, **1**, 14–18 (2006).
[8]   Meggyes T., F.G. Simon, E. Debreczeni: *New developments in reactive barrier technology, The exploitation of natural resources and the consequences*, [in:] Green 3, International Symposium on Geotechnics Related to the European Environment, Berlin 2000.
[9]   Puls R.W., M.R. Powell, D.W. Blowes, R.W. Gillham, D. Schultz, T. Sivavec, J.L. Vogan, P.D. Powell: *Permeable reactive barrier technologies for contaminant remediation*, US EPA, RTDF, Washington 1998.
[10] Suponik T.: *Komputerowe projektowanie remediacji wód podziemnych*, [in:] Komputerowe projektowanie inżynierskie w zastosowaniach górniczych, S. Kowalik (ed.), Wydawnictwo Politechniki Śląskiej, Gliwice 2008, pp. 82–98.
[11] Suponik T.: *Wykorzystanie odpadów z obróbki powierzchni żelaza w oczyszczaniu wód gruntowych*, Górnictwo i Geologia, vol. 3, z. 3, Wydawnictwo Politechniki Śląskiej, Gliwice 2008, pp. 61–70.
[12] Suponik T., M. Lutyński: *Possibility of Using Permeable Reactive Barrier in Two Selected Dumping Sites*, Archives of Environmental Protection, **35**, 3, 109–122 (2009).
[13] Suponik T.: *Problems connected with the use of iron metal in reactive barrier*, (submitted to Geotechnique).
[14] Wilkin R.T., R.W. Puls: *Capstone report on the application, monitoring, and perofmance of permeable reactive barriers for ground-water remediation*, vol. 1, Office of Research and Development, US EPA, Cincinnati 2003.
[15] www.hoffland.net/src/tks/3.xml.

ZAPEWNIENIE SKUTECZNOŚCI I DŁUGOTRWAŁOŚCI DZIAŁANIA TECHNOLOGII PRB

Technologia przepuszczalnych reaktywnych barier (PRB) należy do metod remediacji wód gruntowych. W technologii tej zanieczyszczenia usuwane są bezpośrednio w warstwie wodonośnej poprzez przepływ skażonego strumienia wód gruntowych przez wypełnioną odpowiednim materiałem (aktywnym) barierę aktywną. W artykule przedstawiono problemy związane z tworzeniem się osadów w żelazie metalicznym stosowanym jako materiał aktywny technologii PRB. Osady te mogą zmniejszać aktywność materiału i jego zdolność filtracyjną. Tworzeniu się osadów mogą towarzyszyć zmiany pH, potencjału redox oraz stężenia tlenu. Zmiany te były obserwowane w badaniach laboratoryjnych przedstawionych w artykule. Ponadto w artykule przedstawiono i udowodniono następującą zasadę: aby zwiększyć skuteczność działania typu Funnel-and-Gate technologii PRB przez zwiększenie szerokości strefy oczyszczania, stosunek współczynnika filtracji materiału aktywnego do współczynnika filtracji warstwy wodonośnej (k_{gate}/k_{aq}) powinien przyjąć wartość 6. Ze względu na tworzenie się osadów w żelazie metalicznym, które mogą zmniejszyć jego zdolność filtracyjną, założono jednak, iż stosunek ten powinien wynosić 10. Wartość ta daje pewność, że zmniejszenie się wartości współczynnika filtracji materiału aktywnego na skutek tworzenia się osadów, nie wpłynie w znaczący sposób na szerokość strefy oczyszczania. Przedstawione rozwiązanie może zapewnić skuteczne i długotrwałe oczyszczanie wód gruntowych w typie Funnel-and-Gate technologii PRB.