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PROBLEMS CONNECTED WITH THE USE OF IRON METAL IN REACTIVE BARRIER

Summary. The redox reactions proceeded on an iron metal used as a reactive material in PRB Technology (Permeable Reactive Barriers Technology) were presented and described in the paper. These processes are: chemical detoxification of halogenated hydrocarbons and precipitation of heavy metals mainly. Moreover the problems connected with precipitate formation in that material and blocking up of the reactive barrier were described. On the basis of the laboratory test the changes of pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) concentration which accompany precipitate formation were demonstrated. At the end of the paper the pyrite was proposed to use as a material that could solve above mentioned problems. It can be easily available in large quantities from mine working.

PROBLEMY ZWIĄZANE Z ZASTOSOWANIEM ŻELAZA METALICZNEGO W TECHNOLOGII PRB

Streszczenie. W artykule przedstawiono i opisano procesy redox, przebiegające na powierzchni żelaza metalicznego użytego jako materiał aktywny w technologii PRB. Do procesów tych należą: chemiczna detoksykacja węglowodorów halogenowanych oraz wytrącanie jonów metali ciężkich. Ponadto, opisano problemy związane z wytrącaniem się różnych związków w barierze aktywnej i jej blokowaniem oraz przedstawiono, na podstawie badań laboratoryjnych, zmiany: pH, potencjału utleniająco-redukcyjnego, stężenia rozpuszczonego tlenu, które towarzyszą temu wytrącaniu. Na zakończenie wskazano piryt jako materiał, który mógłby rozwiązać przedstawione problemy. Jest on minerałem dostępnym w dużych ilościach podczas procesów wzbogacania węgla kamiennego.

1. Introduction

Different kinds of chemicals like dichloromethane, trichloromethane (chloroform), dichloroethane, trichloroethane, perchloroethylene, trichloroethylene, dichloroethene,

nitroaromatics, vinyl chloride, chlorophenols, carbon tetrachloride, trichloropropane, freon, inorganic anions or oxyanions (e.g. CrO_4^{2-}, $H_2AsO_4^-$, $HAsO_4^{2-}$, $H_2AsO_3^-$, $HSeO_4^-$, NO_3^-, PO_4^{3-}, SO_4^{2-}), positively charged inorganic cations, including the metals Cd, Co, Cu, Mn, Ni, Pb, Zn and complex cations such as UO_2^{2+} may occur in the groundwater as a contaminants. For treating them, PRB Technology was invented in the 1990's. This technique of groundwater remediation is the passive one, where contaminants are removed from an aquifer by the flow through a reactive barrier filled with a reactive material [1, 2, 3, 4]. The illustration of this process is shown in the Figure 1.
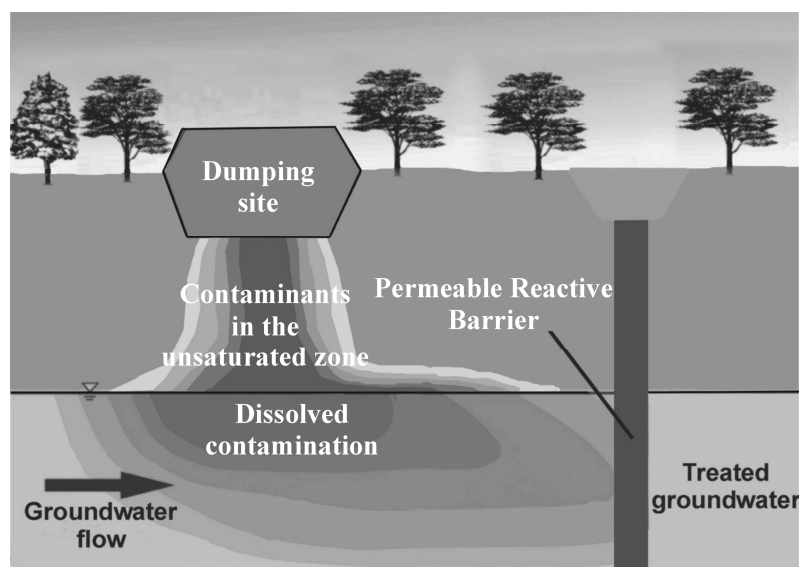

Fig. 1. The rule of groundwater treatment with the use of PRB Technology
Rys. 1. Zasada oczyszczania wód podziemnych za pomocą technologii PRB

As the contaminated groundwater moves through the reactive barrier, the contaminants are removed by physicochemical, chemical and/or biological processes [1, 3, 5]. Many reactive materials can be used as a filler in PRB. The processes applied in that materials are:

− redox reactions which lead to:
  − chemical detoxification,
  − precipitation of heavy metals,
− precipitation by pH control,
− adsorption,
− biodegradation of organic compound.

The essential issue that affects PRB efficiency and longevity is stability of reactive materials. It means that the candidate medium should be able to retain its reactivity and hydraulic conductivity over time. Unfortunately the stability of reactive materials can be upset

by precipitate formation in it – the precipitate may finally reduce the reactivity of reactive material and its hydraulic conductivity.

Up to now iron metal Fe(0) is the most common reactive material in the majority of field scale and commercial implementations. The Figure 2 shows places where iron metal were used as a reactive material in the USA, Europe and Japan. Scrap iron is relatively cheap and can be obtained in a granular form in the large quantities needed. With the use of this material PRB can degrade or immobilize contaminants *in situ* without a need to bring them up to the surface. In spite of the iron metal being so efficient, easy to use and cheap, during operation of permeable barrier filled with it some problems may appear. These problems connected with loss of stability of iron metal were discussed in the paper.

Fig. 2. Places where iron metal Fe(0) were used as a reactive material in PRB Technology [6]
Rys. 2. Miejsca zastosowania żelaza metalicznego Fe(0) jako materiału aktywnego w technologii PRB [6]

The three primary goals of this study were:

–   describing the groundwater treating processes (precipitation of ions and chemical detoxification of halogenated hydrocarbons) taken place in the reactive material in the form of iron metal,

–   presenting the problems appeared during treatment of contaminated water in the column filled with iron metal and thus in permeable barrier,

–   presenting the pyrite as a material which could solve above mentioned problems and can be produced from mine workings.

1.1. Chemical detoxification and precipitation of heavy metals

Toxicity is the degree to which a substance (toxin) is able to damage an exposed organism. Toxicity can refer to the effect on a whole organism, on a substructure of the organism or an organ [7]. The halogenated hydrocarbons presented often in the groundwater are very toxic whereas most hydrocarbons are atoxic or slightly toxic. So in case of using PRB Technology for removing halogenated hydrocarbons from groundwater, in the reactive material should be created reaction which can change these chemicals into atoxic hydrocarbons. Iron metal Fe(0) can be used as such a material. It can act as reducing agent and generates a ferrous ion according to reaction:

$$Fe^0 - 2e^- \rightarrow Fe^{2+}. \tag{1}$$

The resulting electron activity is believed to reduce the halogenated compounds to potentially atoxic products. The degradation of dichloroethene to ethene can be example of this reaction. It can be presented as:

$$2Fe^0 + C_2H_2Cl_2 + 2H^+ \rightarrow 2Fe^{2+} + C_2H_4 + 2Cl^-. \tag{2}$$
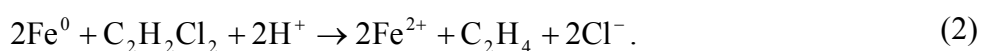
As a result it may be said that the reduction is primarily proceeded by the removal of the halogen atom and its replacement by hydrogen [1]:

$$Fe^0 + H_2O + RCl \rightarrow RH + Fe^{2+} + OH^- + Cl^-. \tag{3}$$

In case of groundwater flowing through the industrial disposal sites it may bearing positively charged inorganic cations like Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}. All these cations are characterized by higher standard electrode potential than zero-valent iron. In accordance with reaction 4 it displaces hazard cations from groundwater.

$$Fe^0 + CuSO_4 \rightarrow FeSO_4 + Cu^0. \tag{4}$$

This reaction proceeds on condition that:

$$U_{Fe/Fe^{2+}} < U_{Cu/Cu^{2+}}, \tag{5}$$

where:

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

1.2. Precipitate formation in iron metal

While using iron metal as a reactive material in PRB Technology some problems may appear. They are connected with the ability for precipitate formation, which could coat the surface of iron or occupy the available pore space and potentially reduce the reactivity of this material and the hydraulic flow ability of the reactive cell. So the stability of the reactive material is then upset. The reasons which can create this effect are:

− the present of dissolved oxygen (DO) in groundwater,

− increase in pH in a treated groundwater due to reactions which may occur in the reactive material.

In case of DO is presented in the groundwater as it enters the reactive iron cell, the iron is oxidized and hydroxyl ions are generated [1]:

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-. \tag{6}$$

The importance of this reaction is that DO can quickly corrode the first few centimetres of iron layer in the reactive cell.

Under oxygen conditions, the Fe^{2+} (formed in reaction 6) oxidizes to Fe^{3+}, what can be written as:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O. \tag{7}$$
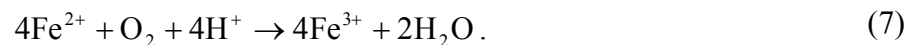
The Fe^{3+} may then precipitate out as Fe(III) oxyhydroxide – FeO(OH) or Fe(III) hydroxide – Fe(OH)$_3$ (reaction 8) at the elevated pH condition, in which case the permeability and reactivity as well could potentially become considerably lower in the first few centimetres of the reactive cell at the influent end. So, the aerobic condition in groundwater is unfavourable to that material [1].

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(s)}. \tag{8}$$

According to the reactions 3, 6 and 9 (the reaction 9 proceeds slowly) the oxidation of Fe^0 to Fe^{2+} causes increase in pH, which may next cause precipitation of Fe (III) hydroxide in aerobic condition (reaction 8) and Fe (II) hydroxide in anaerobic condition (reaction 10), and also precipitation of other compounds.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{9}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(s)}. \tag{10}$$
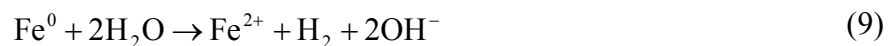
The effect of pH on the mobility and precipitation of many inorganic constituents is shown in the Figure 3 [8]. According to this Figure the increase in pH would be positive (for the condition when toxic cations are presented in the groundwater) if it was the main factor generating groundwater treatment process and if these cations did not precipitate out using reaction 4.
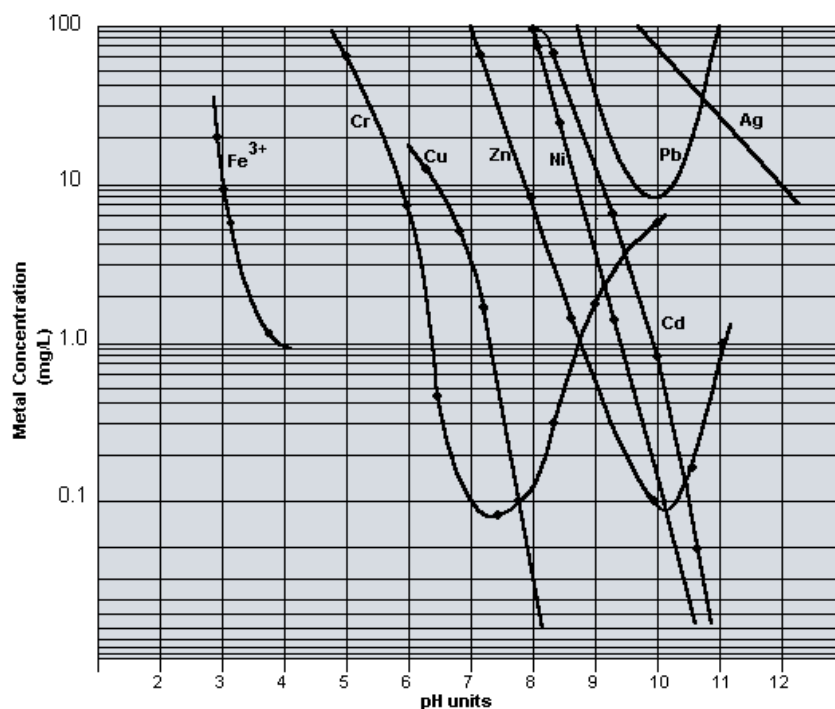

Fig. 3. Metals hydroxide solubility as a function of their concentration and pH [8]
Rys. 3. Rozpuszczalność wodorotlenków metali jako funkcja ich stężenia w wodzie i wartości pH [8]

The pH increasing through precipitation of mainly $Fe(OH)_2$, $FeO(OH)$, $Fe(OH)_3$, $FeCO_3$ and $CaCO_3$, causes decreasing in permeability of the reactive material and its reactivity. So it is unfavourable to the reactive material as well.

2. Methodology, results and discussion

The effect of pH increasing and DO decreasing, which reduces the reactivity of iron and probably hydraulic flow ability of reactive cell was observed in the laboratory test carried out in the installation shown in the Figure 4. This test was conducted in the glass column packed with scrap iron taken from industrial waste lagoon "HK EKO GRYS" in Dąbrowa Górnicza, Poland.
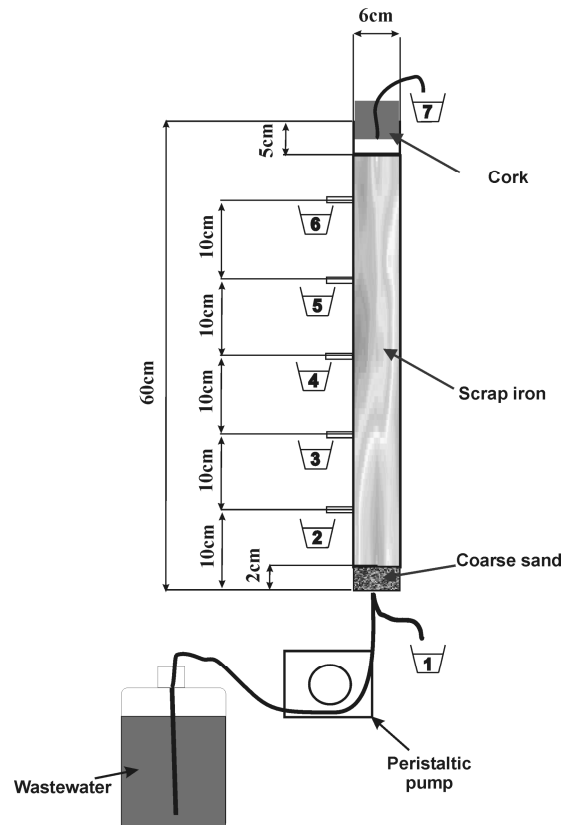
Fig. 4. Installation for simulation of flow and treatment processes of contaminated groundwater in reactive
barrier: 1, 2, 3, 4, 5, 6, 7 – sampling points
Rys. 4. Stanowisko badawcze do symulacji przepływu i oczyszczania zanieczyszczonych wód w barierze
aktywnej: 1, 2, 3, 4, 5, 6, 7 – punkty poboru wody

Wastewater was prepared by mixing distilled water (5 l) 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.
There were five sampling points along the column in order to draw wastewater out. The
conditions in the column corresponded to the aquifer. The Figure 5 shows the results of the
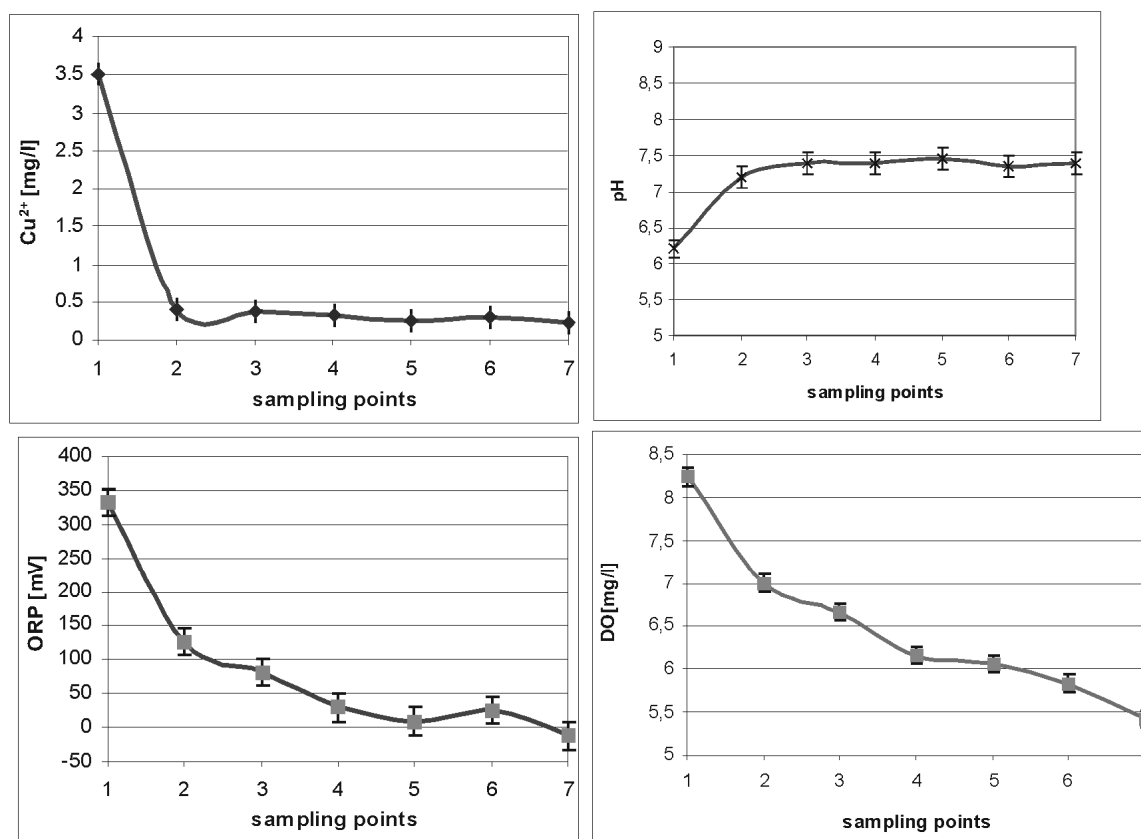test i.e. the value of pH, ORP, DO and Cu^{2+} concentration in wastewater.

Fig. 5. Changes of pH, ORP, DO and Cu^{2+} concentrations in contaminated water from the sampling points (installation – see Fig. 4)

Rys. 5. Zmiany pH, potencjału redox oraz stężeń tlenu i kationów miedzi Cu^{2+} w wodzie pobranej z punktów poboru (stanowisko badawcze – rys. 4)

According to the Figure 5, the reaction 6 proceeded quickly, evidenced by the fact that both the DO and the ORP dropped quickly as the wastewater entered the iron cell. 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/l and $ORP_7 = -12$ mV; $DO_7 = 5,42$ mg/l respectively. These parameters went down gradually.

The increase in pH value as a result of reaction 6 and 9 (when conditions are more anaerobic in the column) was confirmed as well. 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 rest points.

As a consequence of pH, DO and ORP changes, it can be claimed that the oxidation of Fe^0 to Fe^{2+} (and maybe to Fe^{3+}) causes precipitation of some other ions and decreasing reactivity and probably hydraulic flow ability of the iron used as a reactive material in PRB Technology. Inactivation of that material was confirmed by the fact that concentration of Cu^{2+} measured from the second sampling point was constant and amounts to ca. 0,3 mg/l (Fig. 5) –

the Cu^{2+} wasn't then removed from wastewater in the similar, efficient way as it was in the zone between the first and the second sampling point.

In order to confirm that observations the same test was carried out, however the value of pH for a raw wastewater was decreased to 4,97 (using sulfuric acid). The Figure 6 shows the results received in that test.
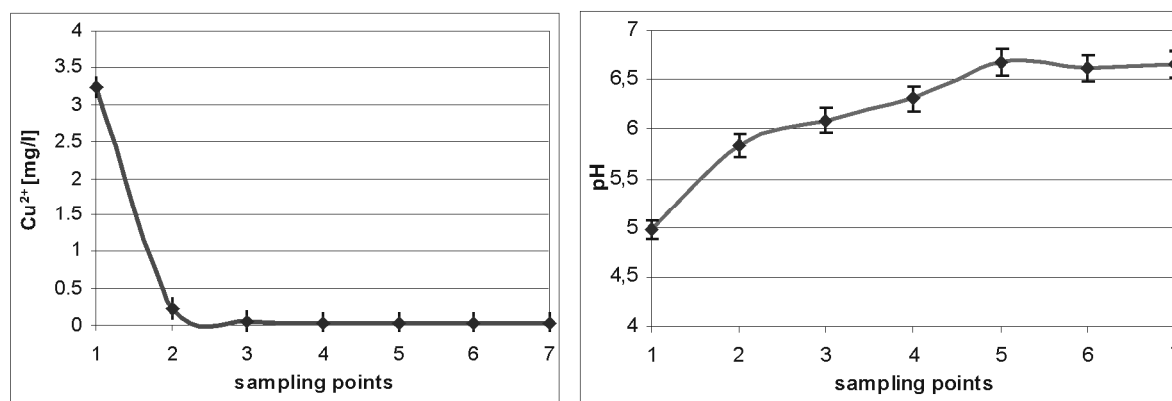

Fig. 6. Changes of pH and Cu^{2+} concentrations in contaminated water from the sampling points after reducing pH to 4.97

Rys. 6. Zmiany pH oraz stężeń kationów miedzi Cu^{2+} w wodzie z punktów poboru po obniżeniu pH do wartości 4,97

In accordance with the Figure 6 the value of pH once again increased along with the number of sampling point according to reactions 6 and 9 (in a lesser degree). With regard to Cu^{2+} concentration, it dropped from 3.24 mg/l at the influent end of the column to 0,04 mg/l in the third sampling point. In this way it was confirmed that iron used as a reactive material in PRB Technology is inactivated for removing Cu^{2+} from groundwater in a range of pH > ca. 7.3. The reason of iron inactivation may be connected with:

–   precipitate formation of inorganic constituents, which coats the surface of iron and causes a loss of contact of Cu^{2+} with iron,

–   pH value itself, i.e. once pH value is over 7.3 the reaction 4 does not proceed

In order to find out which reason is true the next measurement needs to be done.

According to the author, in order to solve problems connected with precipitate formation in an iron metal the pyrite could be used in PRB Technology as a mixture with iron metal or as a pre-treatment zone with sand before the wastewater goes to the iron metal zone.

In case of using pyrite as a pre-treatment zone in PRB Technology the DO could eliminated according to the reactions 11 and 12 (before the wastewater goes to the iron metal zone), and the Fe(III) hydroxides are precipitated. So one problem could be solved – there will not be DO in the iron metal zone. In order to avoid blocking up the pre-treatment zone

due to precipitation of Fe(III) hydroxides that zone could be build as a mixture of pyrite with gravel or coarse sand.

Moreover in accordance with the reactions 11 and 12, the pyrite generates hydrogen ions and in this way it could prevent inactivation of iron metal material due to pH increasing. In this case pyrite could be used in PRB Technology as a mixture with iron metal or also as a pre-treatment zone.

Additionally, the pyrite used as a reducing agent with iron metal is probably capable to remove halogenated hydrocarbons and heavy metals from groundwater of its own.

Unfortunately pyrite may contain metals such as nickel, cobalt, zinc, silver, gold and copper [7]. Their concentration in this mineral is rather low and finally they may be removed from groundwater (when there are in groundwater in the form of ions) by iron metal Fe(0) in further reactive cell of PRB Technology.

Pyrite is the most common of the sulphide minerals. It can be found in coal beds. Pyrite has a specific gravity of 4,95–5,10 and it is brittle, which means that it breaks or powders easily [7]. It all shows that pyrite is easily to separate by gravity processes and is easily to achieve in different kind of size.

The overall reaction of pyrite oxidation resulting in the release of Fe (II) ions, sulphuric acid and acidity generally is indicated as [4, 9]:

$$2FeS_{2(s)} \ + \ 2H_2O \ + \ 7O_2 \ \rightarrow 2Fe^{2+} + \ 4SO_4^{2-} \ + \ 4H^+. \tag{11}$$
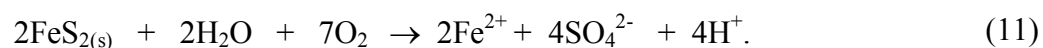
In the next step, oxidation of the Fe(II) ions leads to further acid production and the generation of Fe(III) hydroxides [4, 9]:

$$2Fe^{2+} \ + \ 5H_2O \ + \ 1/2O_2 \ \rightarrow \ 2Fe(OH)_{3(s)} \ + \ 4H^+. \tag{12}$$

These reactions continue until pyrite is depleted.

3. Conclusions

There are four types of processes which can be used in the reactive material in PRB Technology. These processes are: redox reaction, precipitation by pH control, adsorption and biodegradation. While using redox reactions the changing of toxic halogenated hydrocarbons into atoxic hydrocarbons follows or the precipitation of a toxic ions takes place. It can happen when in aquifer (in PRB) there is a reactive material that is characterized by reduction property (e.g. iron metal).

When iron metal is used as a reactive material in PRB Technology the precipitate formation occurs due to present of DO in groundwater and pH increasing in it. The precipitate may coat the surface of iron or occupy the available pore space and potentially reduce the reactivity of this material and the hydraulic flow ability of the reactive cell. It may cause (with time) blocking up of the reactive barrier and breakdown of the whole system.

The precipitation of the Cu^{2+} by redox reaction is a possible process in PRB Technology when the iron metal is used as a reactive material. However, as a result of this reaction the pH is rising quickly which causes inactivation of this material.

To keep PRB costs to a minimum level, the candidate medium should be able to retain its reactivity and hydraulic flow ability over time. So in order to meet this condition for iron metal as a reactive material the pyrite could be used as a mixture with iron or as a pre-treatment zone with sand or gravel.

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