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## PROCESSES AND REACTIVE MATERIALS USED IN PRB TECHNOLOGY

**Summary.** The processes used the most often in PRB technology are presented and described in the paper. These processes are: redox reactions, precipitation by pH control, adsorption and biochemical reactions. They proceed in the reactive materials listed in the paper. The list of these materials were obtained on the basis of laboratory and field research made by authors of different kind of papers.

While proper reactive material is selected, it should pay attention the type of contaminants presented in the groundwater. Reactivity, hydraulic performance, stability, environmentally compatible by-products, availability and price are the factors that decide which reactive material ought to be used in the specific condition.

## PROCESY I MATERIAŁY AKTYWNE STOSOWANE W TECHNOLOGII PRB

**Streszczenie.** W artykule przedstawiono i opisano najczęściej stosowane procesy w barierze reaktywnej technologii PRB. Do procesów tych należą: reakcje redox, wytrącanie przez regulację pH, adsorpcja oraz reakcje biochemiczne. Procesy te przebiegają w materiałach aktywnych przedstawionych w pracy. Listę materiałów otrzymano na podstawie badań laboratoryjnych i polowych wykonanych przez wymienionych w artykule autorów różnych prac.

Podczas wyboru odpowiedniego materiału aktywnego powinno zwracać się uwagę na rodzaj zanieczyszczeń znajdujących się w wodach gruntowych. Czynniki decydującymi o wyborze najlepszego dla określonych warunków rodzaju materiału aktywnego są jego aktywność, zdolność filtracyjna, stabilność, zgodność ze środowiskiem (materiał aktywny nie powinien ujemnie wpływać na środowisko przyrodnicze) oraz dostępność i cena.

### 1. Introduction

Contaminated groundwater is a significant problem for the environment. Chlorinated hydrocarbons, aromatic hydrocarbons and contaminants such as anions or oxyanions (e.g.

$\text{CrO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_3^-$ ), positively charged inorganic cations, including the metals Cd, Cu, Ni, Pb, Zn, can pollute groundwater. For treating them, PRB technology (*Permeable Reactive Barrier*) was invented in the nineteen nineties. 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 [5, 6, 7].

**The two primary goals of this study were:**

- presenting the processes used in PRB technology,
- presenting the reactive materials used the most often in PRB technology.

## 2. Treatment processes

As the contaminated groundwater moves through the reactive barrier, the contaminants are removed by physicochemical, chemical and/or biological processes [3, 6]. Many reactive materials can be used as a filler in PRB. The processes applied in these materials are:

- redox reactions which lead to:
  - chemical detoxification,
  - precipitation of heavy metals,
- pH control (precipitation),
- adsorption,
- biochemical reactions which lead to:
  - degradation of organic compound
  - precipitation of heavy metals by sulphate-reducing bacteria.

### Redox reactions

Up to now zero-valent iron Fe(0) is the most common reactive material in the majority of field scale and commercial implementations. First of all it is used for treatment of plumes contaminated with chlorinated hydrocarbons, chromium and arsenic [3, 6]. Scrap iron is not expensive and can be obtained in a granular form in the large quantities needed.

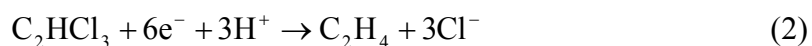
## Chemical detoxification

Halogenated hydrocarbons, often present in the groundwater, are very toxic, whereas most hydrocarbons are non-toxic or slightly toxic. So, in the reactive material should be created reaction which can change these chemicals into non-toxic hydrocarbons.

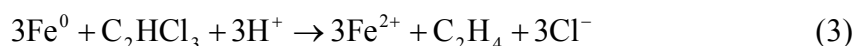
In the reactive material consisted of zero-valent iron Fe(0), it can act as reducing agent and generates a ferrous ion by the redox reaction:



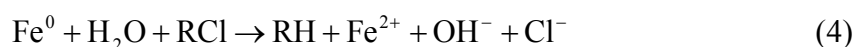
As the zero-valent metal in the reactive cell corrodes, the resulting electron activity is believed to reduce the halogenated compounds to potentially non-toxic products, e.g. the degradation of trichloroethylene to ethene can be written as:



The overall reaction for trichloroethylene detoxification can be presented as:

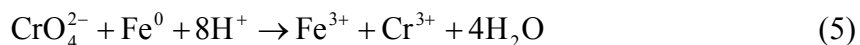


Hence, it may be said that the reduction proceeds primarily by the removal of the halogen atom and its replacement by hydrogen [3].



### *Precipitation of heavy metals*

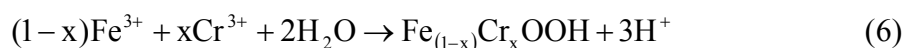
Chromium (VI) can be also removed from groundwater by chemical reduction with iron (iron promotes reduction). Chromium in the oxidation states (VI) is very toxic, whereas chromium (III) is slightly toxic and easy to precipitate. Hence, reduction of chromium (VI) into chromium (III) is the reaction which allows to remove it from groundwater. The overall reaction for the hexavalent chromium can be written as [6]:



Such reaction is important due to negative charge of these anions which are not attracted by negatively charged mineral surfaces. That is why other anions and oxyanions containing Se(VI), As(III), As(V), Tc(VII) are also important groundwater contaminants.

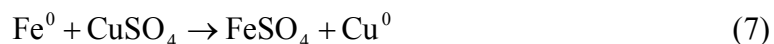
Reaction 5 occurs spontaneously. Couples with a lower standard electrode potential reduce couples with a higher potential [6].

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



Both reduction of chromium(VI) into chromium(III) and precipitation of chromium(III) hydroxides or chromium-iron hydroxide are sensitive to pH.

In the case of groundwater flowing through the industrial, mine and nuclear disposal sites it may bear positively charged inorganic cations such as  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and complex cations such as  $\text{UO}_2^{2+}$ . All these cations are characterized by higher standard electrode potential than zero-valent iron. In accordance with reaction, it displaces hazard cations from groundwater [10]:



The reaction 7 proceeds on condition that:  $U_{\text{Fe}/\text{Fe}^{2+}} < U_{\text{Cu}/\text{Cu}^{2+}}$

where:

$U_{\text{Fe}/\text{Fe}^{2+}}$  - standard electrode potential, **V, Precipitation by pH control**

Contaminant precipitation with the use of PRB technology can also be conducted without changing redox conditions. The solubility of metals is dependent on (apart from reduction potential) pH conditions, aqueous concentrations of reacting species, and reaction kinetics. Hence, it was found that contaminants precipitation can be performed in reactive material by changing pH conditions. The effect of pH on the mobility of many inorganic constituents is shown in Figure 1 [16].

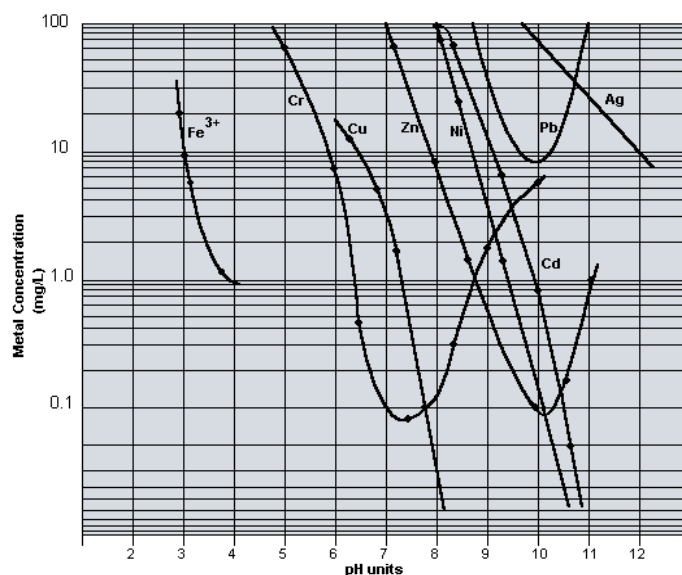


Fig. 1. Metals hydroxide solubility as a function of their concentration and pH [16]

Rys. 1. Rozpuszczalność wodorotlenków metali w zależności od stężenia i pH roztworu [16]

As one can see, the solubility, and thus mobility, of many inorganic compounds is reduced in a range of neutral to slightly basic pH (in this case sparingly soluble metal hydroxides arise),

while the solubility and mobility of them can increase in either very acidic or, in the case of amphoteric hydroxides, very basic pH solutions (then dangerous metal anions e.g. chromate, arise). Neutral or slightly basic pH conditions can be achieved by using such materials as limestone [2].

The pH control used in PRB may be applied for groundwater affected by acid mine drainage (AMD). AMD refers to the outflow of acidic water from e.g. coal mines. The water may contain elevated levels of potentially toxic metals and non-metals such as nickel, copper, lead, arsenic, aluminium, and manganese. The AMD effect arises as a result of exposure of sulphide minerals like pyrites, to atmospheric oxygen and water [2].

### **Adsorption**

Contaminants adsorption (including ion exchange) on a different kind of materials is well known process used in sewage and water treatment technology. Adsorption is a process that occurs when a liquid solute accumulates on the surface of a solid adsorbent, forming a molecular or atomic film (the adsorbate). With regard to strength of fixation between adsorbent and adsorbate, the adsorption process can be divided on:

- physical adsorption - the adsorbate adheres to the surface only through Van der Waals interactions (weak fixation of molecules or atoms);
- chemisorption – the adsorbate adheres to the surface through the formation of a chemical bond (higher strength of fixation than physical adsorption).

The manner and strength of fixation is of great importance in relation to the possibility of remobilisation, and is strongly influenced by parameters like the concentration, solubility, and speciation of the contaminants and co-solvents, and the prevalent pH, Eh and temperature conditions [8].

There are a large number of materials that are able to immobilize contaminants by sorption, including granulated activated carbon [5], coal, charcoal, zeolite, activated aluminium oxide, silica gel, montmorillonite, kaolinite, peat, compost, sawdust, ion-exchange resins. Hence, it was found that they may be used as a reactive material in PRB technology, especially for contaminants which are not susceptible to Eh or pH changing processes. To select proper and effective sorption material for PRB, it must meet the following conditions: high sorption capacity, high selectivity for the target contaminants, fast reaction kinetics, high hydraulic permeability, long-term effectiveness, it needs to be non-harmful to the environment, available at reasonable costs [8], insoluble, not biodegraded, and easy to apply. Unfortu-

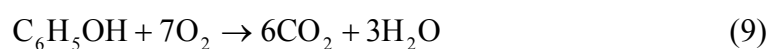
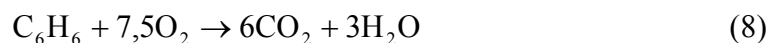
nately, sorption material should be replaced and regenerated frequently due to effects of potential desorption or reversed ion-exchange [5]. This aspect makes adsorption barrier rather expensive and not attractive comparing to other types.

### Biochemical reactions

Many contaminants, including hydrocarbons, volatile organic compound, inorganic constituents, and radioactive constituents, can be addressed through biological reactions in PRB [7].

#### *Biodegradation of organic compound*

In the groundwater there are micro organisms which can decay hazardous hydrocarbons using them as a source of carbon and/or energy. Biodegradation of organic compound is a molecule alteration of hydrocarbons due to enzymes, leading to a formation of less or non-toxic compounds such as CO<sub>2</sub>, H<sub>2</sub>O, inorganic compounds and biomass. Benzene and phenols can be biodegraded according to the following reactions:



Sustained conditioning of the aquifer system generally is important for biological processes in PRB. Biodegradation process runs slowly, and in order to accelerate it a favourable condition should be created in reactive barrier. The most important factors that the biodegradation is dependent on are [12]:

- concentration of oxygen in water (>0.2gO<sub>2</sub>/m<sup>3</sup>),
- concentration of nutrients in water (C:N:P = 100:10:1),
- temperature (15-45°C),
- redox potential (Eh >50mV),
- pH (acceptable 5.5-8.5 pH).

Therefore, such bio-barriers can be optimized by adding: nutrients, air, oxygen and an electron donor.

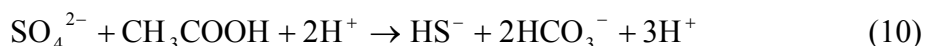
Bio-barriers can consist of a zone containing barrier material, or may simply be a zone in the native soil where degradation is stimulated. Examples of materials that can be applied in PRB to promote bioremediation enhancement include the following [11]:

- solid oxygen-releasing (e.g. ORC® - Oxygen Releasing Compound) – material which is able to supply enough O<sub>2</sub> over a period of 6 to 12 months to support aerobic biodegradation [15];
- solid carbon (e.g. sawdust, compost, peat and granular activated carbon – used as bio-filters) – organic compounds are first adsorbed on the surface of an adsorbent, and after increasing the number of micro organisms, they can be desorbed and oxidized by them.

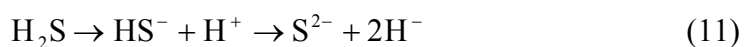
Groundwater contains low concentrations of oxygen. Apart from the use of solid oxygen-releasing the oxygen might be supply to groundwater by the use of biosparging technology (air is pumped into aquifer) or by pumping of water into saturation zone, in which O<sub>2</sub> or pure substance like H<sub>2</sub>O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> are dissolved.

#### *Precipitation of heavy metals by sulphate-reducing bacteria*

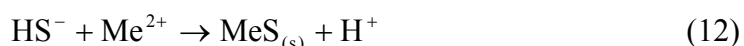
In accordance with many studies [e.g. 1] the primary removal mechanisms for the metals are sulphate-reducing bacteria (SRB). SRB are those bacteria that obtain their energy by oxidizing organic compounds or molecular hydrogen H<sub>2</sub> while reducing sulphates SO<sub>4</sub><sup>2-</sup> to sulphides, especially to hydrogen sulphide H<sub>2</sub>S [9]. The SRB are obligate anaerobes which prefer conditions between pH 5 and 8. Moreover, they need to have some organic material in their surroundings. A typical overall conversion equation is (neglecting the small amount of organic material required to produce biomass):



The reduction product of reaction 10, hydrogen sulphide, is a volatile gas. The form in which sulphide occurs depends on the pH. HS<sup>-</sup> and S<sup>2-</sup> which occur at neutral and high pH respectively are both water soluble. H<sub>2</sub>S is the predominant form at low pH <6 [2].



The sulphides react with metals to precipitate them as metal sulphides, many of which are stable in the anaerobic conditions of the treatment system [2]. The heavy metals react with dissolved sulphide according to the following reaction:



The example of biomaterial that encourages growth of sulphate-reducing bacteria in PRB are coastal hay, wood chips, saw dust, livestock manure [1], and sludge and compost. In order to buffer initial pore water solutions against pH drops associated with fermentation, the limestone may be used to provide bicarbonate alkalinity.

Bio-barriers are considered a unique type of PRB. Although most bio-barriers are designed to deliver amendments into the subsurface using relatively passive techniques (e.g. slow injection or diffusion of oxygen or air, correction of pH), some bio-barriers require substantial energy input to deliver amendments to the proper aquifer depth and then circulate and mix the amendments within the subsurface. PRB then works less passively than traditional and may incur greater operation and maintenance costs [7].

### 3. Reactive materials

The essential issue that affects PRB efficacy is proper selection of reactive material and its quality. The reactive materials used in PRB and shown in Table 1 ought to fulfil some condition. The factors affecting their selection are [3]:

- reactivity** - the candidate medium should be able to degrade the target contaminants within an acceptable residence time,
- hydraulic performance** - selection of the particle size of the reactive medium should take into account the trade-off between reactivity and hydraulic conductivity. Generally, higher reactivity requires lower particle size (higher total surface area), whereas higher hydraulic conductivity requires larger particle size,
- stability** - the candidate medium should be able to retain its reactivity and hydraulic conductivity over time,
- environmentally compatible by-products** - the by-products generated during degradation should not have harmful effects of their own on the environment,
- availability and price** - the candidate medium should be easily available in large quantities at a reasonable price.

Type of contaminants is the most important factor during reactive material selection. A compilation of laboratory and field research into chemicals treated with reactive material is provided in the Table 1 [3, 4, 7, 13, 14]. It is divided in the contaminant group (inorganic and organic), in the reactive material type, and finally in the type of the principal reaction which allows to remove contaminants from groundwater.



Table 1

The reactive materials used in laboratory or field test  
for different kind of contaminants [3, 4, 7, 13, 14]

	CONTAMINANTS	REACTIVE MATERIAL	TYPE OF REACTION
Inorganic chemicals	Aluminum (Al), antimony (Sb), barium (Ba), cadmium (Cd), chromium (CrVI), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), silver (Ag), strontium-90 (Sr), Thallium (Tl), technetium (Tc), uranium (U), arsenic (As), selenium (Se), Nitrate (NO <sub>3</sub> <sup>-</sup> ), sulphate (SO <sub>4</sub> <sup>2-</sup> ),	Zero-Valent Metals	Precipitation barriers - redox reactions
	chromium (Cr), Molybdenum (Mo), technetium (Tc), uranium (U), arsenic (As)	Ferrous hydroxide, ferrous carbonate, ferrous sulphide	
	cadmium (Cd), Molybdenum (Mo), uranium (U), arsenic (As), selenium (Se), Sulphate (SO <sub>4</sub> <sup>2-</sup> ),	Limestone	Precipitation barriers - pH control
	Arsenic (As), selenium (Se),	Activated alumina	Adsorption barriers
	antimony (Sb), bismuth (Bi), cesium (Cs), chromium (Cr), cobalt (Co), mercury (Hg), Molybdenum (Mo), silver (Ag), technetium (Tc), tin (Sn), uranium (U), zirconium (Zr), arsenic (As),	Activated carbon	
	technetium (Tc), Uranium (U),	Exchange resins	
	chromium (Cr), lead (Pb), Molybdenum (Mo), uranium (U), copper (Cu), Cadmium (Cd), zinc (Zn), nickel (Ni), arsenic (As), Sulphate (SO <sub>4</sub> <sup>2-</sup> ),	Peat, lignite, brown coal	
	Aluminum (Al), Barium (Ba), cadmium (Cd), cobalt (Co), cesium (Cs) chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), strontium-90 (Sr), uranium (U), zinc (Zn), arsenic (As), selenium (Se),	zeolite	
Cadmium (Cd), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), tin (Sn), zinc (Zn), Sulphate (SO <sub>4</sub> <sup>2-</sup> ),	coastal hay, wood chips, saw dust, livestock manure, sludge, compost	Precipitation barriers – biochemical reactions	
Organic chemicals	Fuel hydrocarbons	solid carbon, ORC <sup>®</sup> compound,	biodegradation barriers
	TCE	Ultramicrobacteria	
	TCE, DCE, cVOC, PCB, nitroaromatics, VC, PCE, TCA, chlorophenols, CT, TCM, DCM, TCP, feron, DCA, CHCl <sub>3</sub> , AOX	Zero-Valent Metals	Chemical detoxification – redox reactions
	cVOC	Ferrous minerals	
	TCE	Zeolite Activated carbon Clays	Adsorption barriers
BTX, phenols, VOC, PAH	Activated carbon		

## 4. Conclusions

1. There are four types of processes which can be used in the reactive material. The processes are:
  - redox reaction – by the use of that reaction 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 there is a reactive material that is characterized by reduction property (e.g. zero-valent iron Fe(0)),
- precipitation by pH control – by changing pH conditions into neutral or slightly basic the precipitation of the toxic ion can appear,
  - adsorption – by the use of adsorbent material in aquifer the contaminants accumulate on the surface of it and are retarded with reference to groundwater flow,
  - biochemical reaction which is divided in:
    - degradation of organic compound – molecule alteration of hydrocarbons due to enzymes, leading to formation less or non toxic compounds like CO<sub>2</sub>, H<sub>2</sub>O, inorganic compounds and biomass,
    - precipitation of heavy metals by sulphate-reducing bacteria (SRB) – the heavy metals precipitation (as metal sulphides) in the company of SRB and in proper pH and Eh conditions.
2. Above-mentioned processes proceed in the reactive materials presented in Table 1. PRB efficacy depends on proper selection of this material. Reactivity, hydraulic performance, stability, environmentally compatible by-products, availability and price are the factors that decide which reactive material ought to be used in the specific condition.

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### List of Abbreviations

AMD	– acid mine drainage
AOX	– adsorbable organic halides
BTX	– benzene, toluene, xylene
CT	– carbon tetrachloride
DCA	– dichloroethane
DCE	– dichloroethene
DCM	– dichloromethane
ORC <sup>®</sup>	- oxygen release compound
PCB	- polychlorinated biphenyl
PCE	– perchloroethylene
PAH	– polycyclic aromatic hydrocarbon
PRB	- permeable reactive barriers
SRB	– sulphate-reducing bacteria
TCA	– trichloroethane
TCE	- trichloroethylene
TCM	– trichloromethane
TCP	– trichloropropane

VC	– vinyl chloride
VOC	– volatile organic compound
cVOC	– chlorinated volatile organic compound

Recenzent: Dr hab. inż. Barbara Tora

## Omówienie

Znanych jest wiele metod powstrzymywania bądź likwidacji zanieczyszczeń ze środowiska gruntowo-wodnego. Każda z nich jest skuteczna i efektywna, jeżeli jest stosowana w ściśle określonych, specyficznych warunkach. W technologii PRB zanieczyszczenia są usuwane bezpośrednio w warstwie wodonośnej przez przepływ skażonego strumienia wód gruntowych przez wypełnioną odpowiednim materiałem barierę reaktywną.

W pracy przedstawiono i opisano główne procesy fizykochemiczne, chemiczne i biochemiczne, które mogą przyczynić się do wyeliminowania zanieczyszczeń z wód gruntowych z zastosowaniem technologii PRB. Do procesów tych należą: reakcje redox, wytrącanie przez regulację pH, adsorpcja oraz reakcje biochemiczne. Wybór i skuteczność stosowania wymienionych procesów zależą głównie od rodzaju i stężenia zanieczyszczeń oraz warunków panujących w określonym obszarze. Stosując się do powyższego, dla różnych zanieczyszczeń organicznych i nieorganicznych, przedstawiono w pracy materiały aktywne, za pomocą których można oczyszczać wody gruntowe. Dane te otrzymano na podstawie przeglądu literatury fachowej oraz badań własnych.

Przy doborze materiału aktywnego do określonych warunków, poza rodzajem i stężeniem zanieczyszczeń oraz zdolnością ich usunięcia w założonym czasie za pomocą określonych procesów, należy wziąć pod uwagę również inne czynniki. Należą do nich:

- zdolność filtracyjna – selekcja wielkości ziaren materiału aktywnego powinna być rozpatrywana jako kompromis pomiędzy jego aktywnością i przepuszczalnością hydrauliczną. Dzieje się tak, ponieważ im wyższa przepuszczalność materiału aktywnego, tym niższa jego aktywność i odwrotnie, im wyższa aktywność, tym niższa przepuszczalność materiału aktywnego,
- stabilność – materiał aktywny powinien zachować założoną aktywność (tj. zdolność do usunięcia zanieczyszczeń) i przepuszczalność hydrauliczną przez określony długi czas,
- zgodność ze środowiskiem – jest rozumiana jako brak ujemnego oddziaływania materiału i powstających produktów na środowisko,
- dostępność i cena.