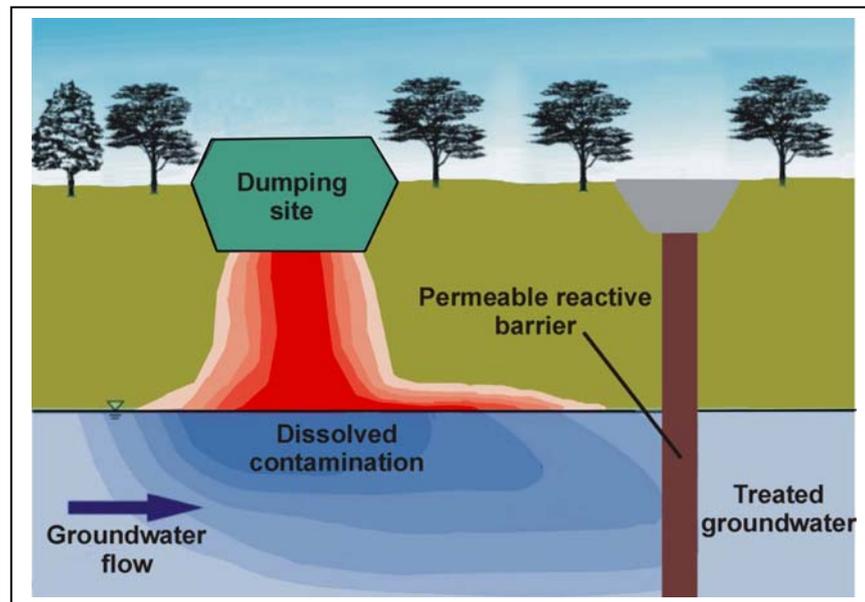


Groundwater remediation with the use of PRB Technology

PRB TECHNOLOGY – how does it work and when to use it

Contaminated groundwater is a significant problem for the environment. Halogenated hydrocarbons, mineral oils, aromatic hydrocarbons, and contaminants such as chromium and uranium and a lot more can pollute groundwater. For treating them, **PRB technology** (*Permeable Reactive Barrier*) was invented in the nineteen nineties. This novel 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. The illustration of this process is shown in the Figure.



PRB has several advantages over other methods of groundwater remediation. Reactive barrier can degrade or immobilize contaminants *in situ* without need to bring them up to the surface. It also usually does not require continuous input of energy. PRB technology can be use in order to:

- prevent deterioration of groundwater quality in existing improperly situated or improperly protected dumping sites,
- prevent deterioration of groundwater quality for dumping sites which protection was damaged,
- protect groundwater when new dumping site is created,
- remove contaminants presented in the groundwater due to leakage of pipelines and tanks, or breakdown of machines and appliances.

Treatment processes in PRB TECHNOLOGY

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

1. Redox reactions,
 - Chemical detoxification,
 - Precipitation,
2. pH control,
3. Adsorption,
4. Biodegradation.

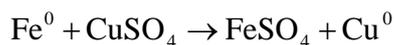
Chemical detoxification

Halogenated hydrocarbons often presented in the groundwater are very toxic whereas most hydrocarbons are atoxic or slightly toxic. So in the reactive material should be created reaction which can change these chemicals into atoxic hydrocarbons. For example in the reactive material consisted of reducing agent like iron metal Fe(0), it can generate a ferrous ion Fe²⁺. As the zero-valent metal in the reactive cell corrodes, the resulting electron activity is believed to reduce the halogenated compounds to potentially nontoxic products. The overall reaction for degradation of chlorinated hydrocarbons can be written as:



Precipitation

Using redox reaction the precipitation of toxic ions may take place. It can happen when in aquifer there is reducing agent. For instance in case of groundwater flowing through the industrial areas it may bearing positively charged inorganic cations like Cd, Co, Cu, Ni, Pb, Hg, Tc, and complex cations such as UO₂²⁺. All these cations are characterized by higher standard electrode potential than reducing agent such as zero-valent iron. So it displaces hazardous cations from groundwater:



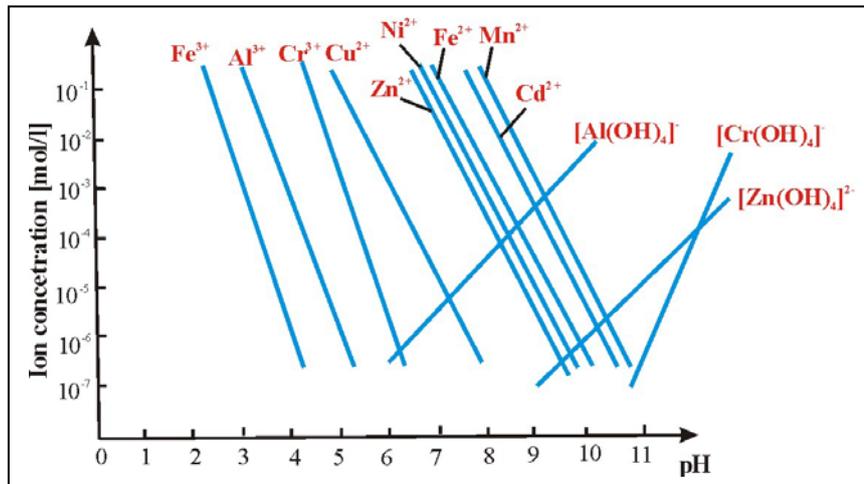
$$U_{\text{Fe}/\text{Fe}^{2+}} < U_{\text{Cu}/\text{Cu}^{2+}}$$

where:

$U_{\text{Fe}/\text{Fe}^{2+}}$ - standard electrode potential [V]

pH control

Contaminant precipitation can also proceed in reactive material by changing pH conditions. The effect of pH on the mobility of many inorganic constituents is shown in the Figure (Anielak).



As one can see, the solubility, and thus mobility, of many inorganic compounds are reduced in a range of neutral to slightly basic pH, while the solubility and mobility of them can increase in either very acidic or in some cases very basic pH solutions. Neutral or slightly basic pH condition can be achieved by using material such as limestone, hydrated lime, compost.

Adsorption

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).

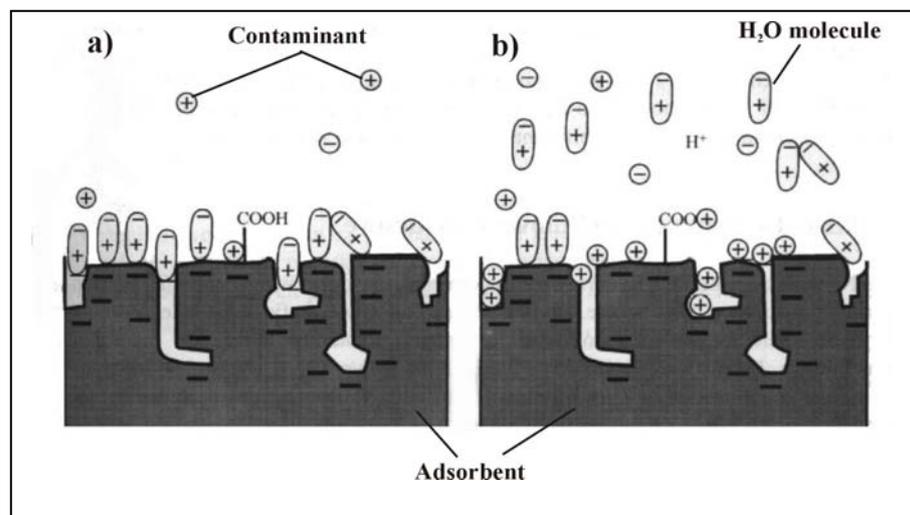


Fig. Adsorbent surface a) before, b) after adsorption process of contaminants [Anielak]

There are a large number of material that are able to immobilize contaminants by sorption, including granulated active carbon, zeolite, montmorillonite, peat, compost, sawdust, etc. The proper material for PRB must meet the following conditions: high sorption capacity, high selectivity for the target contaminants, fast reaction kinetics, high hydraulic permeability, long-term effectiveness, non-harmful to the environment, available at reasonable costs, and it ought to be: insoluble, not biodegraded, and easy to apply. Unfortunately sorption material frequently should be replaced and regenerated due to effects of potential desorption or reversed ion-exchange. This aspect causes that adsorption barrier is rather expensive and not attracted compare to other type.

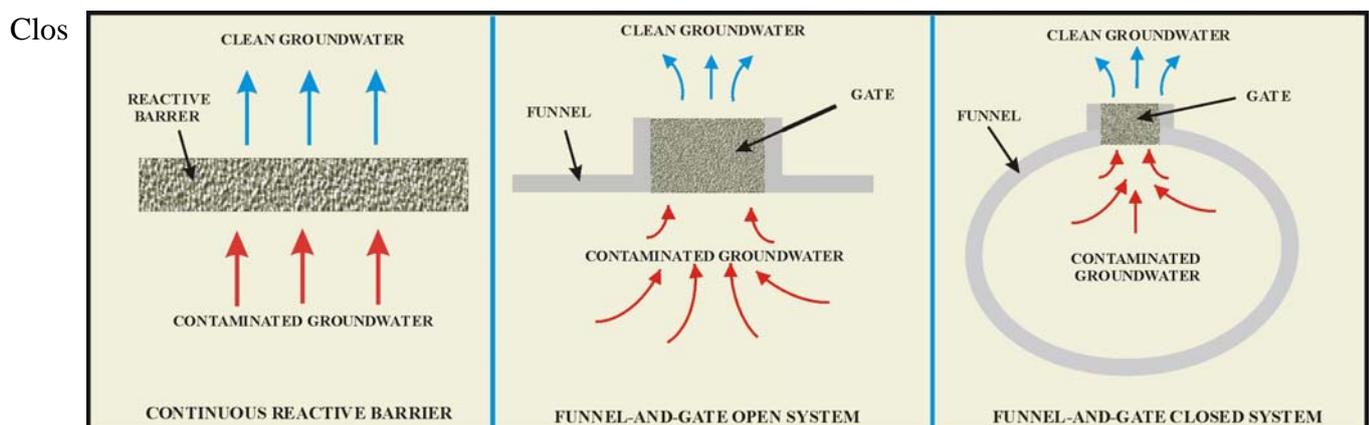
Biodegradation

In the groundwater there are a 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 formation less or non toxic compounds like CO₂, H₂O, inorganic compound and biomass. Biodegradation process runs slowly. In order to accelerate it in the reactive barrier the favourable condition should be created. The most important factors that the biodegradation is dependent on, are:

- concentration of oxygen in water (>0,2gO₂/m³),
- concentration of nutrients in water (C:N:P = 120:10:1),
- temperature (optimal 28-33°C),
- redox potential (Eh >50mV),
- pH potential (acceptable 5,5-8,5 pH).

Main configurations of PRB TECHNOLOGY

PRB is currently built in two basic configurations: Continuous Reactive Barrier and Funnel-and-Gate System divided into: Funnel-and-Gate Open System and Funnel-and-Gate



THE REACTIVE MATERIAL

Abovementioned processes should proceed in the condition that permit effectiveness and long-lasting performance of reactive materials. Overall factors affecting the best selection of the reactive material are:

- 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,
- 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 (Gavaskar, U.S. Department of Defense: Evaluating the longevity, Wilkin)

CONTAMINANTS		REACTIVE MATERIAL	TYPE OF REACTION
Inorganic chemicals	Molybdenum (Mo), uranium (U), technetium (Tc), cesium (Cs)	Activated carbon	Sorption or substitution barriers
	Molybdenum (Mo), mercury (Hg), uranium (U), arsenic (As), phosphorus (P), selenium (Se), copper (Cu)	Ferric oxides	
	Molybdenum (Mo), uranium (U), aluminum (Al), barium (Ba), cadmium (Cd), manganese (Mn), mercury (Hg), nickel (Ni), uranium (U),	Magnetite	
	Molybdenum (Mo), uranium (U), chromium (Cr), arsenic (As), lead (Pb), sulfate	Peat, lignite, coal	
	Aluminum (Al), barium (Ba), cadmium (Cd), manganese (Mn), mercury (Hg), nickel (Ni), uranium (U), strontium-90 (Sr), Arsenic (As), chromium (Cr), lead (Pb), selenium (Se)	zeolite	Precipitation barriers
	Molybdenum (Mo), uranium (U),	Lime, flyash	
	Molybdenum (Mo), uranium (U), arsenic (As), cadmium (Cd), selenium (Se), sulfate	Limestone	
	arsenic (As), manganese (Mn), molybdenum (Mo), selenium (Se), uranium (U), technetium (Tc), aluminum (Al), barium (Ba), cadmium (Cd), lead (Pb), nickel (Ni), technetium (Tc), chromium (Cr), strontium-90 (Sr), sulfate, nitrate, chromium (CrVI),	Zero-Valent Metals	
Organic chemicals	cVOC	Ferrous minerals	Degradation barriers
	Fuel hydrocarbons	ORC [®] compound	
	TCE, DCE, cVOC, PCB, VC, PCE, TCA, chlorophenols, CT, TCM, DCM, TCP, DCA, CHCl ₃ ,	Zero-Valent Metals	
	TCE	Zeolite Activated carbon Clays	Sorption barriers
	BTEX, phenols, VOC, PAH	Activated carbon	

List of Abbreviations

BTEX	- benzene, toluene, ethylbenzene, xylene
CT	- carbon tetrachloride
DCA	- dichloroethane
DCE	- dichloroethene
DCM	- dichloromethane
ORC [®]	- oxygen release compound
PCB	- polychlorinated biphenyl
PCE	- perchloroethylene
PAH	- polycyclic aromatic hydrocarbon
PRB	- permeable reactive barriers
TCA	- trichloroethane
TCE	- trichloroethylene
TCM	- trichloromethane
TCP	- trichloropropane
VC	- vinyl chloride
cVOC	- chlorinated volatile organic compound

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