



BAM

Bundesanstalt für
Materialforschung
und -prüfung

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Tamás Meggyes

**Permeable reactive barriers
for pollutant removal from
groundwater**

245

Forschungsbericht



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Safety and reliability in chemical and materials technologies

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Abstract

The removal of pollutants from the groundwater using permeable reactive barriers is a novel in-situ groundwater remediation technology. The most relevant decontamination processes used are chemical reduction, oxidation, precipitation and sorption, for which examples are given. Some common organic pollutants are halogenated hydrocarbons, aromatic and nitroaromatic compounds which can be treated in reactive barriers successfully. Lead, chromium and, in particular, uranium are dealt with in great detail among inorganic pollutants because of their occurrence in many European countries. Construction methods for cut-off walls and reactive barriers exhibit similar features. Apart from conventional methods, drilling, deep soil mixing, jet technology, arrays of wells, injected systems and biobarriers are applied to construct permeable reactive barriers. Permeable reactive barriers bear great potential for the future in remediation engineering.

Keywords:

groundwater remediation,
reactive barriers,
reduction,
oxidation,
precipitation,
sorption,
cut-off walls,
funnel-and-gate systems,
deep soil mixing,
jet technology,
arrays of wells,
injected systems,
biobarriers.

Zusammenfassung

Die Reduzierung von Schadstoffen im Grundwasser mit reaktiven Wänden ist eine neuartiges passives Sanierungsverfahren. Die am häufigsten angewandten Dekontaminierungsprozesse sind dabei chemische Reduktion, Oxidation, Ausfällung und Sorption, die im Bericht beispielhaft dargestellt sind. Kontaminationen mit halogenierten Kohlenwasserstoffen, aromatischen Verbindungen mit und ohne Nitrogruppen können mit reaktiven Wänden wirkungsvoll behandelt werden. Blei, Chrom und insbesondere Uran werden unter den anorganischen Schadstoffen detailliert behandelt, da solche Grundwasserverunreinigung in vielen europäischen Ländern auftreten. Baumethoden für Dichtwände und reaktive Wände weisen gemeinsame Merkmale auf. Neben den gewöhnlichen Methoden werden Bohrverfahren, deep-soil-mixing, Strahltechnologien, Brunnengalerien, Injektionssysteme und Biobarrieren angewendet, um reaktive Wände zu errichten. Die Technik der reaktiven Wände besitzt ein großes Potential für die Sanierungstechnik der Zukunft.

Stichwörter:

Grundwassersanierung,
reaktive Wände,
Reduktion,
Oxidation,
Ausfällung,
Sorption,
Dichtwände,
Trichter-und-Tor-Systeme,
deep-soil-mixing,
Strahltechnologie,
Brunnengalerie,
Injektionssysteme,
Biobarriere

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Part 1

Treatment processes for pollutants

Introduction

Soil and groundwater pollution became a major environmental issue for the developed world later than, for example, air pollution or waste treatment. Stringent regulations for emissions into the air were introduced in the European Union twelve years ago [Council of the European Community 1989]. The significance of drinking water quality has also been recognised. Directives for soil and groundwater conservation on a European level are nevertheless still lacking. The Soil Conservation Act and the corresponding directive were issued in Germany in 1998 and 1999. A number of techniques can be used for the remediation of contaminated soil as a source of groundwater pollution: excavation and soil washing, thermal treatment, solidification and stabilisation, etc. However, these technologies can be associated with high energy consumption and sometimes lead to new environmental problems. Efficient and economical techniques are therefore needed to remediate contaminated soil and groundwater. A review of long-term or extensive treatment technologies by *Bardos and van Veen* [1995] describes and compares the pump-and-treat method, soil vapour extraction, bioventing, phytoremediation, natural attenuation and permeable reactive barriers.

This article will focus on permeable reactive barriers (PRB) which provide a new and innovative method for groundwater remediation. The technology of permeable reactive barriers could potentially allow many more contaminated sites to be remediated effectively, thus greatly enhancing natural groundwater protection. The traditional "pump-and-treat" method or microbiological techniques have proved singularly unsuccessful for a number of potentially harmful chemicals, for example heavy metals leaching slowly from contamination sources, PAH with low bio-availability, etc. Groundwater remediation using permeable reactive barriers is an in-situ method with low energy demand and therefore more cost-effective than standard remediation techniques [Manz and Quinn 1997, Mitchell 1997]. The targeted chemicals to be removed from the groundwater by the reactive materials in permeable barriers are either decomposed to other, less dangerous compounds or efficiently fixed to the reactive material. Their mobility, availability and toxicity are significantly reduced in both cases.

In this article emphasis is laid on the explanation of the nature of the different decontamination processes. Experience gained and status of the application is described if available. The performance of PRBs in

field studies and commercial application was reviewed by *Vidic and Pohland* [1996] and by *Steimle* [1995]. One of the major outstanding issues in PRB technology is longevity of the reactive materials used. In order to clear their long-term performance the exact knowledge of the processes applied in reactive barriers is needed and this will help understand the mechanisms impairing their function.

Decontamination processes in PRBs

PRB technology is a novel groundwater remediation method which enables physical, chemical or biological in-situ treatment of contaminated groundwater by means of reactive materials. The most commonly used processes/reactions are: redox-reactions, precipitation, adsorption, ion exchange and biodegradation.

The reactive materials are placed in underground trenches downstream of the contamination plume forcing it to flow through them and by doing so, the contaminants are treated without soil or water excavation [Smyth et al. 1997]. Generally, this cost-effective clean-up technology impairs the environment much less than other methods do. The arrangement of a permeable reactive barrier is illustrated in *Fig. 1*.

Most PRBs are arranged in any of the following two configurations:

continuous reactive barriers enabling a flow through their full cross-section, and funnel-and-gate systems in which only special 'gates' are permeable for the contaminated groundwater.

Remediation costs using PRB systems are reported to be up to 50 % lower than those of the pump-and-treat method used so far [Schad and Gratwohl 1998].

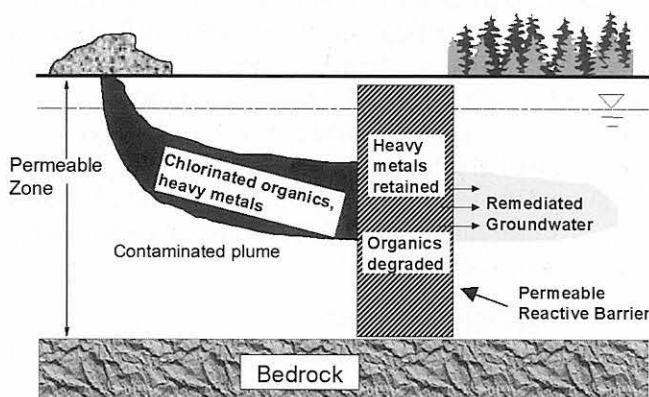


Fig. 1
Groundwater remediation using a permeable reactive barrier.

Operational life is expected to be 10 to 20 years, experience over such periods is however not yet available. For a compilation on PRB costs see Part 2 of this work.

This paper is organised with respect to the pollutants rather than the various remediation processes. The most extensively studied and applied reactive barrier type uses granulated iron particles. Here elemental iron acts as reducing agent and generates a ferrous ion by the redox reaction



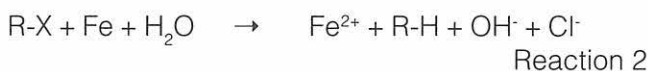
Even aqueous CO_2 can be reduced by elemental iron to hydrocarbons [Hardy and Gillham 1996] which remain sorbed to the iron surface. This reaction can lower the dechlorination rate of chlorinated organic compounds due to the slow desorption of the hydrocarbons.

Groundwater pollutants treated by permeable reactive barriers

Organic pollutants

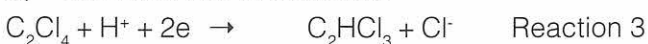
Halogenated hydrocarbons

A well studied application of iron-bearing permeable reactive barrier is the degradation of halogenated hydrocarbons (R-X) [Gillham and O'Hannessin 1994]. Numerous patents exist for this application [Gillham 1993, Cherry et al. 1996, Gillham et al. 1999]. The pollutants are removed from the groundwater by a redox reaction which can be written as follows:

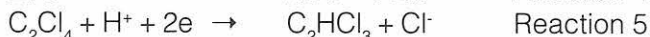
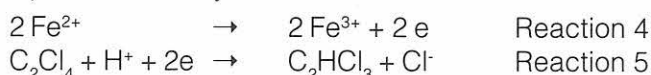


A redox reaction consists of two halfreactions, i. e. the oxidation of one partner and the reduction of another. In iron-bearing PRBs the elemental iron acts as reducing agent and it is oxidised to the ferrous ion Fe^{2+} , see Reaction 1. The potential of this half-reaction is independent of the pH and can be found in listings of the electrochemical series with 440 mV (in listings the reaction is displayed in the opposite direction, $\text{Fe}^{2+} + 2e \rightarrow \text{Fe}$ with a potential of -440 mV, because the oxidised form is written always on the left side). The reduction of chlorinated hydrocarbons can proceed via three different mechanisms [Matheson and Tratnyek 1994]. Tetrachloroethene is taken as an example for the following reactions.

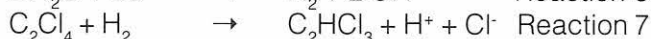
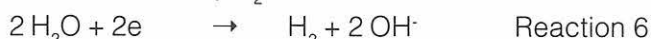
a.) Direct transfer of electrons:



b.) Reduction by Fe^{2+} :



c.) Reduction by H_2



In b.) the ferrous ion Fe^{2+} is the reducing agent. This reaction has a potential of -770 mV (in standard form $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$, $E^0 = 770$ mV) and is also independent of pH. In c.) water is reduced and elemental hydrogen is generated which acts as reducing agent in a catalytic reaction. It had be shown that the presence of elemental iron surfaces is necessary for the dehalogenation and that addition of hydrogen and Fe^{2+} had no influence on the degradation. Therefore it is most likely that the dehalogenation proceeds via sequence a.) More recent investigations postulate surface-bound Fe^{2+} to be involved in the reaction [Sivavec and Horney 1995]. In any case Reaction 6 occurs and the production of hydrogen in permeable reactive barriers is significant [Puls 1998]. In aerobic systems oxygen is a preferred oxidant for iron leading to rapid corrosion:



Dissolved oxygen is rapidly consumed at the entrance of an iron-bearing barrier (Reaction 8). The resulting precipitates could have influence on the hydraulic performance [Mackenzie et al. 1995]. The effect of other microbiological and geochemical processes on the long-term performance of barriers with zero-valent iron was studied by Gu et al. [1999]. According to the results the function of the walls could be impaired by the accumulation of iron hydroxides, carbonates and sulphides due to decreased permeability and reactivity.

In Reaction 6 and Reaction 8 OH^- is the product which also leads to an increase in pH in the PRBs [Puls 1998]. The rate of reaction is decreased at elevated pH values and a linear dependency of the observed rate and pH was measured [Matheson and Tratnyek 1994]. The reason for that behaviour is precipitation of slightly soluble iron carbonates and oxides on the reactive iron surface [Vogan et al. 1995, Sivavec 1996]. Other authors [Johnson and Tratnyek 1995] have mentioned the precipitation products siderite (FeCO_3), goethite (FeOOH) and "green rust" ($\text{Fe}_2(\text{OH})_4\text{Cl}_n\text{H}_2\text{O}$) depending on the composition of the groundwater. In column experiments in laboratory studies it was observed that the permeability was decreased by the precipitates [Sivavec 1996]. However, in pilot-scale and full scale installations the function was not impaired by precipitation reactions.

The reductive degradation of halogenated hydrocarbons is enhanced by the addition of sulphur species, e. g. FeS_2 . One reason for the increase of the rate is the rem-

oval of oxygen in Reaction 9 where hydronium ions are also generated resulting in lower pH values.



A detailed discussion on the influence of sulphur on the reaction of the degradation can be found elsewhere [Dahmke 1997].

Redox reactions occur spontaneously if the sum of the potentials of the two half-reactions is positive. The potential of half-reactions with organic compounds cannot be easily retrieved from handbooks. However, it can be calculated from the free energy ΔG^0_{R} of the reaction. The redox reaction takes place in aqueous solutions so that gas-phase values have to be transformed to aqueous-phase values using the following equation [Vogel *et al.* 1987]:

$$\Delta G^0_{\text{f}}(\text{aq}) = \Delta G^0_{\text{f}}(\text{g}) + RT \ln H$$

Equation 1

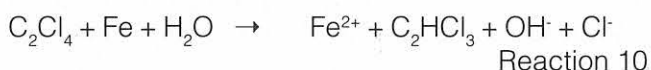
with the Henry's law constant H.

ΔG^0_{R} can be transformed to the potential E^0 by dividing by nF with n the number of exchanged electrons and F the Faraday constant.

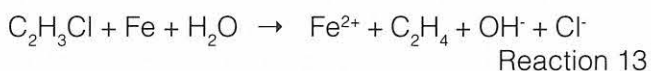
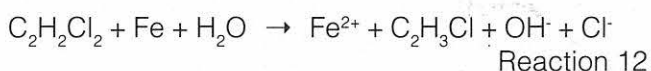
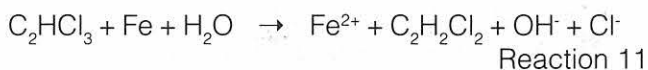
$$E^0 = -\Delta G^0_{\text{R}} / nF$$

Equation 2

Reaction 3 is dependent on pH because H^+ is involved and the potential for a pH of 7 is 580 mV [Vogel *et al.* 1987]. The potentials for various aliphatic hydrocarbons vary between 500 and 1500 mV [Matheson and Tratnyek 1994]. Combining Reaction 1 and Reaction 3 yields



Reaction 10 occurs spontaneously because the sum of the potential of the two half-reactions is positive ($E = 580 \text{ mV} + 440 \text{ mV} = 1020 \text{ mV}$). Trichloroethene as product of Reaction 10 is stepwise further degraded in hydrogenolysis reactions to ethene.



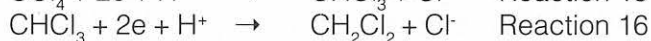
It has been shown that the degradation reactions are typically pseudo-first-order in substrate and that the reaction rate decreases with each dehalogenation step [Matheson and Tratnyek 1994]. The mechanism and the product mass balances are discussed in detail elsewhere [Orth and Gillham 1995, Orth and Gillham 1996]. For the design of a permeable reactive barrier for chloroethene removal it is important that the residence time of the pollutants in the wall (ratio of pore volume to flow rate) is long enough for a complete

degradation. Vinyl chloride, $\text{C}_2\text{H}_3\text{Cl}$, product in Reaction 12, is more hazardous and persistent than the higher chlorinated hydrocarbons. Vinyl chloride and 1,1-dichloroethene can also be degraded by oxidising agents (see chapter Aromatic compounds). An alternative pathway in which cis- and trans-dichloroethene is degraded by a reductive β -elimination induced by iron and zinc was studied by Roberts *et al.* [Roberts *et al.* 1996].

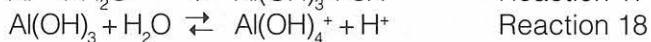
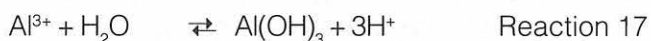


The potential of half-reaction 14 is 568 mV and 589 mV for the cis- and the trans-compound respectively. This is thermodynamically more favourable than the hydrogenolysis reactions (see Reaction 12) to vinyl chloride with potential of 407 and 428 mV respectively.

Investigations into reductive dehalogenation of chlorinated methanes by iron indicated that dichloromethane cannot be further reduced [Matheson and Tratnyek 1994]. 1,2-dichloroethane and chloroethane are not degradable by elemental iron either [Vogan *et al.* 1995].



The degradation rate can be enhanced by a factor of 100 with Fe/Pd bimetallic systems where even CH_2Cl_2 can be reduced [Grittini *et al.* 1995, Korte *et al.* 1995]. First laboratory results indicate that Al and Fe mixtures can increase the rate by a factor of 10 [Dahmke 1997]. In this application aluminium is acting as buffer according to Reaction 17 and Reaction 18. In addition, the formation of local cells increases reactivity.



Aromatic compounds

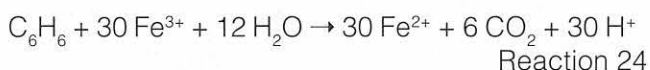
Aromatic compounds like benzene, toluene, ethylbenzene, xylene (i. e. BTEX) and PAHs etc. act as reducing agents and a degradation has to be performed oxidatively. When organic compounds are oxidised, the electrons released by the carbon transformation must be taken up by other substances, i. e. by electron acceptors. Possible half reactions are as follows:

	ΔE (mV) at pH 7	
$\text{O}_2 + 4 \text{H}^+ + 4 \text{e} \rightarrow 2 \text{H}_2\text{O}$	841	Reaction 19
$\text{Fe}^{3+} + \text{e} \rightarrow \text{Fe}^{2+}$	770	Reaction 20
$\text{NO}_3^- + 6 \text{H}^+ + 5 \text{e} \rightarrow \text{N}_2 + 3 \text{H}_2\text{O}$	676	Reaction 21
$\text{SO}_4^{2-} + 10 \text{H}^+ + 8 \text{e} \rightarrow \text{H}_2\text{S} + 4 \text{H}_2\text{O}$	-276	Reaction 22

Reaction 19 - Reaction 22 are known as oxidation reactions in natural systems and are sorted above by decreasing potential [Gallagher 1998]. Apart from Reaction 20 they are pH dependent and the values displayed are given for a pH of 7. The corresponding half-reaction for the oxidation of benzene, for example, is as follows:



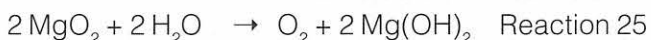
The potential for this half-reaction and also for BTEX compounds is in the range of 100 to 400 mV (i. e. -100 to -400 mV when the oxidised form is on the lefthand side) [Dahmke 1997]. Thus combining Reaction 23 with Reaction 20 yields the following reaction which occurs spontaneously (positive sum of potentials):



The oxidation of aromatic contaminants coupled with iron reduction (Reaction 24) and the role of microorganisms in such reactions was studied by Lovley *et al.* [Lovley *et al.* 1989]. Reaction 24 is the overall reaction and there are numerous single steps. The intermediate products were identified. A detailed discussion on this topic is given elsewhere [Grbic-Galic and Vogel 1987].

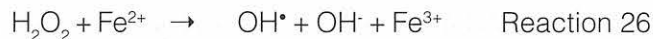
Removal of aromatic compounds by means of oxygen-releasing compounds

For the reactive barrier technology oxygen-releasing compounds (ORCs) are applied to enhance aerobic reactions [Bianchi-Mosquera *et al.* 1994]. In conjunction with biotreatment it provides a supplemental source of dissolved in-situ oxygen. Magnesium peroxide releases oxygen slowly in the presence of water.



Pollution arising from organic compounds like BTEX can be treated with ORCs (combination of Reaction 19 and Reaction 23). Also, compounds which cannot be easily degraded by reduction like vinyl chloride (see chapter Halogenated hydrocarbons) can be treated with ORCs because they are at least slightly reducing [Bell *et al.* 1997]. For certain applications it has been stated that the treatment by ORC barriers is less expensive than air sparging [Koenigsberg 1998]. Air sparging and ORC treatment are problematic in respect of the unwished oxidation of reduced compounds like sulphides or remobilization of heavy metals [Dahmke 1997]. Use of CaO_2 instead of MgO_2 to provide oxygen for contaminant degradation is described elsewhere [Cassidy and Irvine 1999].

Another oxidising agent is Fenton's reagent, which is H_2O_2 and FeSO_4 with iron as catalyst. The enhanced degradation of polycyclic aromatic hydrocarbons in soil with Fenton's reagent was studied by Martens and Frankenberger [1995]. The reaction of H_2O_2 with Fe^{2+} yields OH radicals which oxidise PAHs to more polar compounds resulting in an increased mineralisation.



Without catalysts the activation of hydrogen peroxide may be affected by adjusting pH or the reaction time.

Sorptive removal of organic pollutants

Sorptive removal is a good solution for the attenuation of non-halogenated organic compounds in groundwater. Organic contaminants are retarded by any natural material with high organic carbon content [Cohen 1991]. Even more efficient is the adsorption onto activated carbon which is already used for ex-situ cleaning of drinking water [Jekel 1979]. Sorption rates and permeability must be optimised for the application of sorption in PRBs and long regeneration cycles (in the order of several years) are required. Sorption is a function of temperature and it is favoured at low temperatures. At elevated temperatures desorption predominates. The behaviour can be described with isotherms which show the amount of sorbed material plotted against the concentration in the solution. In most cases there is no linear dependency. The Freundlich type adsorption isotherm gives a good approximation of the ability to remove pollutants:

$$K_d = C_s/C_w = K_{Fr} C_w^{1/n-1} \quad \text{Equation 3}$$

with K_d the distribution coefficient (l/kg), C_s the sorbed concentration (mg/kg), C_w the groundwater concentration (mg/l), K_{Fr} the Freundlich sorption coefficient, $1/n$ the Freundlich exponent which is between 0 and 1 ($1/n = 1$ yields a linear behaviour).

K_d decreases with increasing aqueous concentration of the solute. For hydrophobic compounds removed by natural adsorbents K_d is related to the organic carbon content of the solid. In addition, an empirical correlation exists with the water-octanol partition coefficient [Gratwohl and Peschik 1997]. The Freundlich sorption isotherm is widely applied, but has the fundamental problem that there is theoretically no upper sorption limit. Unlike Freundlich's isotherm, the Langmuir adsorption isotherm has a curved shape and asymptotically approaches a maximum [Fetter 1993].

The retardation R_d of contaminants which is the degree of reduction of velocity due to the sorption can be calculated from K_d according to the following equation [Fetter 1993]

$$R_d = 1 + K_d \rho / \Theta \quad \text{Equation 4}$$

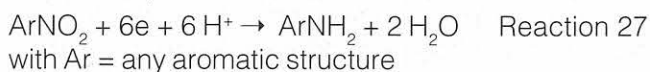
with ρ the bulk density and Θ the porosity.

ρ and Θ for activated carbon are around 0.5 so that the retardation factor R_d is approximately equal to K_d . For BTEX and PAHs the values of K_d on activated carbon (F300) are between 10^3 and 10^7 l/kg [Gratwohl 1997, Schad and Gratwohl 1998] at equilibrium. The K_d values obtained from kinetic experiments are lower because equilibrium conditions are reached only after 10^2 to 10^3 hours. Therefore, in spite of the high retardation factors, a residence time long enough to provide efficient contaminant removal from the groundwater flow has to be ensured by design, permeability etc. Aspects of the sorption kinetics are discussed elsewhere [Fetter 1993, Schad and Gratwohl 1998].

The removal of organic contaminants by sorption in funnel-and-gate systems is enhanced by biological degradation. However, this could lead to a decrease in the permeability of the barrier called bio-fouling [Gratwohl 1997]. This effect was also observed in iron PRBs [Powell *et al.* 1998] with iron-oxidising microbes. Reduction in permeability is undesired for the reaction zone, i. e. the gate in a funnel-and-gate system. This phenomenon exhibits however an interesting application for the construction of funnels. Flow rates were reduced by 99.9 % and more and it was possible to maintain them for four months without nutrient addition. The so-called biofilm processes are described in detail in Part 2 of this work.

Nitroaromatic Compounds

Nitroaromatic compounds (NACs) can be reduced via nitroso and hydroxylamine forms to the respective amino compounds.



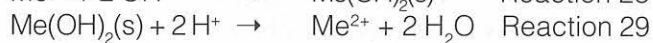
The potential of the half-reaction is 420 mV [Haderlein and Schwarzenbach 1995]. The authors found that Reaction 27 is abiotic and coupled with the oxidation of organic matter to CO_2 and water by iron reducing bacteria via the redox reaction of surface bound Fe^{2+} and Fe^{3+} . The results demonstrate that at pH values above 6.5 the ferrous ion Fe^{2+} is a powerful reducing agent for NACs and most likely also for other organic pollutants. The products of NAC reduction, the amines, exhibit considerable toxicity, so that the described treatment is not applicable for groundwater remediation polluted with NACs. However, NAC reduction with iron species displays a model system for laboratory investigations on reactive barrier technology.

Inorganic pollutants

Heavy metals

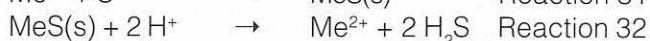
Cationic metals usually have limited mobility in soil and groundwater with high clay and organic content, high alkalinity and low permeability [Fetter 1993]. However, complexing agents like carbonates, hydroxides, sulphates, phosphates, fluorides and possibly silicates which are present in natural waters increase the solubility of metals [Langmuir 1978]. Precipitation is a possible reaction for heavy metal contamination to lower the concentrations in the groundwater. Other possibilities are sorption, precipitation subsequent to a chemical reduction or a combination of the different processes.

Precipitation of heavy metals is a commonly used process in waste water treatment plants. Precipitation is used in the same way in permeable reactive barriers to lower the heavy metal concentrations in groundwater. Chemical precipitation is a process by which a soluble substance is converted into an insoluble form by a reaction with the precipitant. Frequently used precipitants are hydroxides, sulphides, phosphates and carbonates. The solubility of heavy metal hydroxides, sulphides and carbonates is pH-dependent. Metal hydroxides exhibit amphoteric behaviour, i. e. solubility is high both at low pH (removal of hydroxide anions, see Reaction 29, with Me as a generic two-valent heavy metal) and high pH (formation of soluble hydroxo complexes, see Reaction 30). A minimum solubility for most heavy metals is observed between 9 and 11 [Chung 1989].



A cheap precipitant forming hydroxides is lime. Metal concentrations lower than 1 mg/l, sometimes less than 0.1 mg/l are achievable.

The solubility of metal sulphides is much lower than those of hydroxides and they are not amphoteric. However, at pH values above eight, hydrogen sulphide (H_2S) is emitted due to hydrolysis of the sulphides resulting in increasing metal concentrations in the solution.

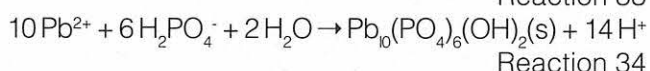
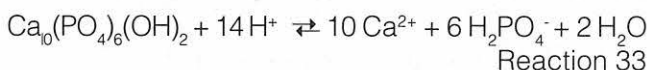


Permeable reactive barriers are systems with low energy consumption and it is therefore important that the precipitates are not changed back by any means to soluble forms. Unlike in waste water treatment plants, the precipitated material remains in the barrier for the whole period of operation. Spent barrier materials can be replaced by placing the reactive matrix in a double-walled structure with pre-fabricated elements [Beitinger and Fischer 1994]. Stability of the resulting precipitates

is therefore an important issue for the application of precipitation reactions in permeable reactive barriers.

Lead

Lead is a major contaminant in solid wastes and soils. Its concentration in drinking water is limited in most countries at very low levels (e. g. in Germany 0.04 mg/l). Lead forms various compounds with low solubility in water. A good example of the formation of very stable precipitates is the reaction of lead ions with hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. After dissolution of hydroxyapatite lead is precipitated as lead hydroxypyromorphite (solubility product $\log K_{\text{sp}} = -62.79$ [Allison *et al.* 1991]) [Ma *et al.* 1993].



Another reaction type which may control the immobilisation of lead with hydroxyapatite is surface adsorption but it was found not feasible by Ma *et al.* [1993]. In the presence of chloride, the precipitation of the even more insoluble chloropyromorphite $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ is possible (solubility product $\log K_{\text{sp}} = -62.79$ [Allison *et al.* 1991]) [Ma *et al.* 1994]. The reaction between heavy metals and apatite is rapid [Chen and Wright 1997] and the resulting precipitates are extremely insoluble. Apatite is therefore suitable as precipitant for permeable reactive barriers.

Chromium

Chromium exists in natural waters in the oxidation states +3 and +6. Hexavalent chromium occurs as an oxyanion in the form of CrO_4^{2-} or as $\text{Cr}_2\text{O}_7^{2-}$. Chromates are more soluble and mobile than Cr-III compounds. Due to their negative charge these anions are not attracted to negatively charged mineral surfaces [Powell *et al.* 1998]. Hexavalent chromium cannot be precipi-

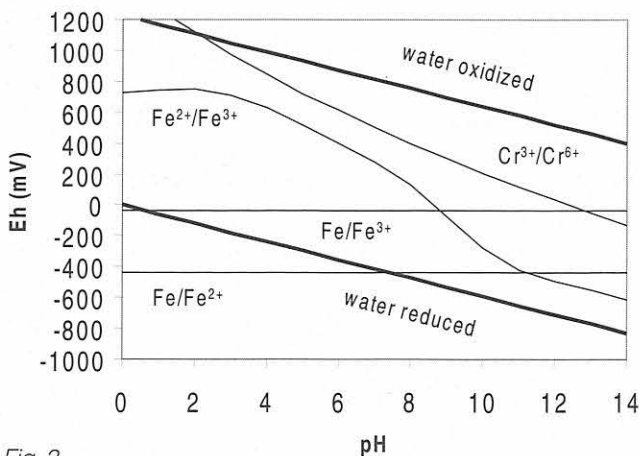
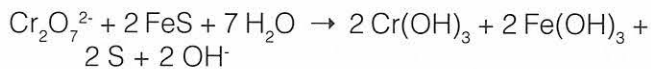


Fig. 2
pH-Eh diagram showing the stability fields for water and some iron and chromium species

tated as hydroxide. Prior to precipitation, chromium(VI) has to be reduced to chromium(III). The re-removal of chromium(VI) is performed with sulphide in a single step combining reduction and precipitation (Reaction 35) [Chung 1989].



Reaction 35

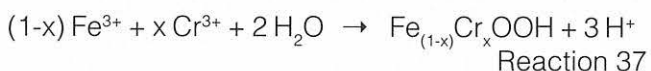
Reduction of chromate with elemental iron has been intensively studied [Blowes and Ptacek 1992, Powell *et al.* 1995, Powell *et al.* 1998]. The overall reaction can be written as:



Reaction 36

Reaction 36 occurs spontaneously as can be seen in Fig. 2. Couples with lower standard electrode potential reduce couples with higher potential. The stability lines as a function of pH were calculated by the computer programme Minteqa2 [Allison *et al.* 1991].

In a further step, iron and chromium are precipitated as oxyhydroxides [Powell *et al.* 1998].



Sorption on zeolites

A further possibility for chromate removal from groundwater is sorption on zeolites. Zeolites are naturally occurring aluminosilicates with open, cage-like structures. They exhibit high cation exchange capacity e. g. for transition metal cations such as Pb^{2+} . By modification of the surface with quaternary amines (for example hexadecyltrimethylammonium, HDTMA, $(\text{C}_{16}\text{H}_{33})(\text{CH}_3)_3\text{N}^+$) the zeolites are enabled to remove non-ionic organic compounds like benzene and chlorinated hydrocarbons due to the organic carbon content of the modified sorbent without lowering the sorption affinity for metal ions [Haggerty and Bowman 1994]. Negatively charged oxyanions like chromates are sorbed via ion exchange by the cationic surfactant [Bowman 1999]. The organo-zeolite is also applicable for the removal of other oxyanions like selenate and sulphate. The modified surface was found to be stable at pH values from 3 to 10, high ionic strength and exposure to organic solvents.

The removal of metal ions with different inorganic sorbent materials was studied in a comparative study by Lehmann *et al.* [1999]. They found that various modifications of ferric oxyhydroxide are strong sorbents for several heavy metals like chromium or zinc.

Uranium

Uranium is the heaviest naturally occurring element. All isotopes are radioactive, the half-lives of the two

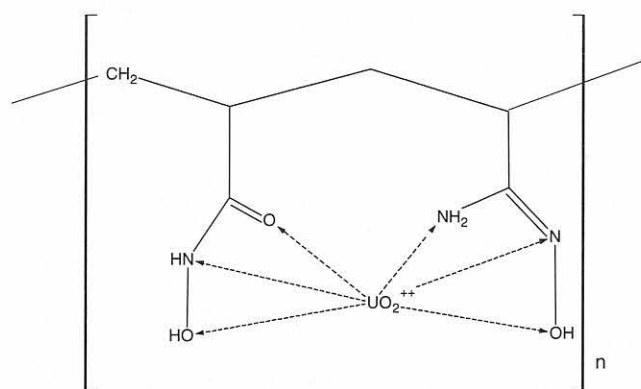


Fig. 3
Structure of Gopur 3000, a modified polyacrylonitrile for the removal of uranium.

relevant isotopes ^{238}U and ^{235}U are 4.5×10^9 and 7.0×10^8 years, respectively [Seilmann-Eggebert *et al.* 1981]. If uranium is present in groundwater, e.g. from mine tailings, it is dangerous not because of its radioactivity but because of its toxicity as a heavy metal. From the German Radiation Protection Act, 0.3 mg/l limit can be calculated for the radiation limit (7.0 Bq/l of the natural mixture of isotopes). Due to its toxicity a limit between 0.02 and 0.002 mg/l is under discussion [Merkel *et al.* 1998].

Uranium occurs mainly in the oxidation states +4 and +6. The hexavalent uranium, i. e. the uranyl ion UO_2^{2+} is more mobile than U(IV) compounds, similarly to Cr(VI) and Cr(III). Uranyl ions can be precipitated like lead ions with phosphate forming $(\text{UO}_2)_3(\text{PO}_4)_2$ ($\log K_{\text{sp}} = -49.09$, [Brown *et al.* 1981]). With hydroxyapatite or bone char which is hydroxyapatite with a small amount of carbon the precipitation of autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$ occurs ($\log K_{\text{sp}} = -47.28$, [Brown *et al.* 1981]). The reaction is similar to ion exchange processes. It is likely that ion exchange materials can also be applied in reactive barriers. Heavy metal removal using modified polyacrylonitrile was studied in the laboratory for the treatment of water percolating from mine tailings. Modified polyacrylonitrile, Gopur 3000, was tested at laboratory scale with copper, zinc, uranium, cadmium and nickel [Gohlke 1992]. Fig. 3 displays the structure with hydroxamic acid and amidoxime functional groups as modifications from the nitrile form.

Similar applications with modified polyacrylonitrile are described elsewhere [McComb and Gesser 1997, Miroshnik and Korovnikova 1998]. Other ion exchange processes for the adsorption of uranium (and other fission product solutions) use silicates, manganese dioxide, zirconium phosphate and titanium oxide. A detailed overview on inorganic ion exchangers for uranium is given in [Löwenschuss 1979].

Good removal results have been obtained by the reduction of U(VI) to U(IV) by elemental iron:

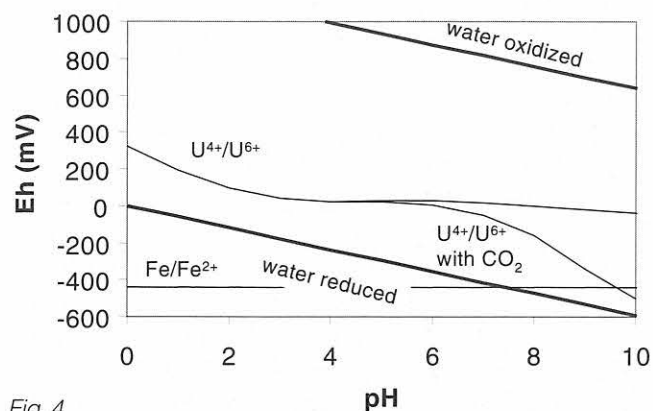


Fig. 4
pH-Eh Diagram showing the boundary line between U(IV) and U(VI) without and in the presence of 0.01 bar CO_2 .

The reduction of UO_2^{2+} occurs spontaneously as illustrated in Fig. 4. The solubility of uraninite UO_2 is in the range of 10^{-8} mol/l in a pH range between 4 and 14. Below 4 uranium becomes soluble. The behaviour of uraninite has been intensively studied because of its application as nuclear fuel and because it is a main constituent of uranium pitchblende [Bickel *et al.* 1996]. The measurement on the dissolution of spent fuel in deionized water under non-oxidising conditions gave results in the range of 10^{-9} to 10^{-5} mol/l. Under oxidising conditions where UO_2 can be transformed into the uranyl ion and if complexation reactions can occur, the solubility is enhanced. It is therefore important that Eh is below the boundary of the U(IV)/U(VI) curve in the U(IV) stability field. With CO_2 present the boundary line is shifted towards lower Eh at high pH. This behaviour is displayed in Fig. 4.

At elevated pH values in the presence of CO_2 (0.01 bar which is typical for groundwater conditions) it is more difficult to transform uranium to the oxidation state +4. An excellent review on the complex uranium solution equilibria is given by Langmuir [1978].

Adsorption of uranium onto surfaces

Uranium can also be removed by adsorption on surfaces. Morrison and Spangler [1992] have evaluated a range of uranium and molybdenum adsorption tests using a variety of materials. Good removal results have been obtained for lime, hematite, peat, ferric oxyhydroxide, phosphate and TiO_2 while clays exhibited low sorption potential. Precipitation and adsorption onto a surface are processes which can simultaneously occur in a chemical barrier. Sorption of uranium from groundwater was studied in a series of publications [Morrison and Spangler 1992, Morrison and Spangler 1993, Morrison *et al.* 1995]. Surface site complexation can be described with different models with or without electrostatic influence on charged surfaces [Allison *et al.* 1991]. With SOH as notation for a surface site the adsorption reaction of uranium onto ferric oxyhydroxide as sorbent can be written as follows:



Sorption, rather than precipitation, depends strongly on pH. If several contaminants are to be removed from the groundwater an optimum pH for operation of the barrier is needed. This is difficult to achieve for uranium in the presence of molybdenum because the latter is mobile at pH values above 8 while uranium exhibits low mobility [Morrison and Spangler 1993]. Sorption onto surfaces and reduction are both possible removal reactions in iron-bearing walls. To which amount and at what efficiency the distinct processes take place was studied in several articles [Fiedor *et al.* 1998, Gu *et al.* 1998]. It was found that Fe⁰ filings are much more efficient than adsorbents.

Geochemistry of the aqueous solution and sorbent properties that are most important in controlling adsorption/retardation behaviour of uranium and other environmentally relevant elements were reviewed in a technical report [Office of Radiation and Indoor Air and Office of Environmental Restoration 1999]. The distribution coefficient K_d (see section Aromatic compounds) of uranium at different pH values in various soils were retrieved from the literature and listed in a look-up table. The data exhibit large scattering but show a trend as a function of pH. The values of K_d listed in the report are displayed in Fig. 5. High K_d values were derived from adsorption experiments with ferric oxyhydroxide and kaolinite, low values from those with quartz which has low adsorptive properties. The pH dependence arises from surface charge properties of the soil and from the complex aqueous speciation of U(VI). The dissolved carbonate concentration has also great influence due to the formation of strong uranylcarbonato complexes. Retardation can then be calculated from K_d according to Equation 4.

Uranium removal from groundwater was studied using phosphate, zero-valent iron and amorphous ferric oxide barriers at Fry Canyon in Utah, USA [Naftz *et al.* 1996, Morrison 1998]. Precipitation as phosphate, reduction to immobile U(IV) compounds and adsorption onto sorbents were studied simultaneously in this field test.

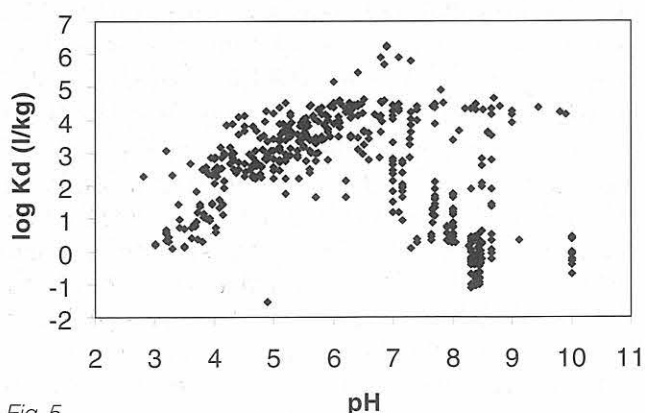


Fig. 5
Distribution coefficient K_d of uranium as a function of pH.

At least 90 % removal was found in each application and the Fe⁰ barrier was found to be most effective.

Biosorption of uranium was studied by Yang and Volesky [Yang and Volesky 1999]. The uptake of uranium was more than 500 mg/g. Biosorption is an ion exchange process between the uranium ions and the protons introduced to the binding sites of certain types of inactive, dead, microbial biomass [Volesky 1990]. The process is also suitable for other heavy metals (Pb, Cd, Cu, Zn, even Cr).

The possibility of the reduction of U(VI) using microorganisms seems to have some potential for field applications. First laboratory results on this method are presented elsewhere [Gorby and Lovley 1992].

Non-metallic inorganic contaminants

Nitrate

Nitrate, a non-metallic inorganic contaminant in drinking water, is a common problem in agriculture. Reduction to nitrogen is preferred because nitrate is then permanently removed from the soil and groundwater. However, reduction to ammonium or nitrite may also occur and latter is even worse than nitrate. As described above in connection with chromium and uranium, Fe(0) can also act as a reducing agent. Reaction 40 - Reaction 42 describe the possible pathways.



Reaction 40 is favoured thermodynamically due to the higher reduction potential (see Fig. 6). However, the formation of nitrite and ammonium was also observed in experiments [Till *et al.* 1998] and it was supposed that the reduction to ammonium goes via the nitrite-anion. Iron is not only the direct reducing agent of nitrate (see Reaction 40 - Reaction 42) but also a continuous source of hydrogen (combination of Reaction 1 and Reaction 6) to support biological denitrification. In addition, elemental iron enhances microbial transformation by removing inhibitory pollutants like Cr(VI). The biological pathway has the most desirable end product (N₂). Nitrate removal from the groundwater is improved by the combination of Fe(0) and microbial treatment. However, the effect of nitrate on iron-bearing walls applied for the removal of other pollutants has to be taken into account.

pH must remain in the tolerance range of common denitrifiers, i. e. below 10 [Till *et al.* 1998]. This may

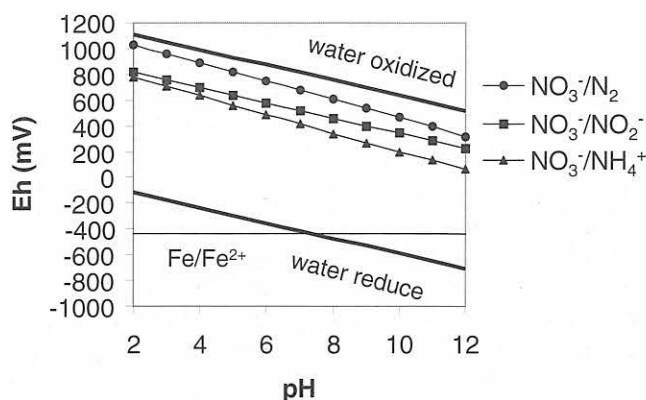
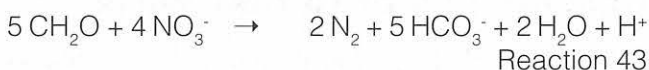


Fig. 6
Redox potential E_h of iron and nitrogen species as a function of pH.

necessitate the introduction of a buffer because hydroxyl anions are formed in Reaction 40 - Reaction 42.

In the heterotrophic reaction N_2 is the preferred product. The precise clarification of the mechanism is still lacking. Reaction 43 describes nitrate reduction in the presence of organic matter.



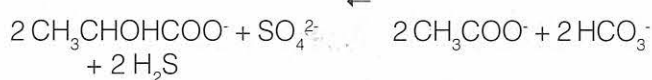
CH_2O represents the sum formula of carbohydrates. Experiments with good results have been performed using sawdust and wood waste as organic matter [Powell *et al.* 1998]. In the paper of Vogel [1998] it is described how micro-organisms enhance nitrate reduction to nitrogen gas by combining elemental iron and denitrifying organisms. The bacteria will use cathodic hydrogen from reduction of water as electron donor to generate N_2 instead of NH_4^+ .

Fig. 6 displays the stability lines of the different ions as a function of pH. The data were calculated using the geochemical simulation software PHREEQC [Parkhurst 1995].

Arsenate

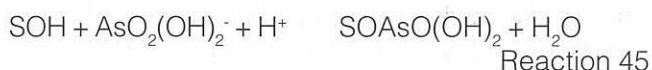
Arsenic has some industrial uses (paints, insecticides) so that there are numerous industrial sites with arsenic contamination. Arsenic occurs in the oxidation states +3 and +5. The prevalent As species in groundwater is As(III). This is relevant because it is more toxic than As(V) and more mobile because negatively charged As(V) oxyanions are better adsorbed onto mineral surfaces [Manning and Goldberg 1997]. The only compound with a solubility below 0.05 mg/l is As_2S_3 so that precipitation as sulphide is a possible pathway for a chemical barrier. However, at higher S^{2-} concentrations soluble sulpho complexes are formed [Jander and Blasius 1979]. Sulphide ions can be brought to

the subsurface by injection or directly be emitted by a barrier. This can be achieved by oxidation of organic matter by sulphate (see Reaction 22). The bacteria require an organic substrate which is usually a short-chain acid like lactic acid.



As sulphate is reduced to sulphide, this method is applicable for the treatment of acid mine drainage. Benner *et al.* describe a reactive barrier containing a mixture of municipal compost, leaf mulch, wood chip, gravel and limestone. Besides sulphate reduction the concentration of trace metals like nickel was also reduced by the changed geochemical conditions [Benner *et al.* 1999]. The removal of heavy metals from acid mine drainage using iron granules was described by Shokes and Möller [1999]: they observed the formation of arsenic co-precipitates with iron.

Another possibility to remove arsenic from groundwater is sorption onto ferric oxyhydroxide (S = surface site, see Reaction 39) [Driehaus *et al.* 1998].



The reaction is inhibited by phosphate. In order to shift the equilibrium towards the right hand side in Reaction 45 aerobic and weak acidic conditions are required. Sorption of arsenic onto clay minerals was studied by Manning and Goldberg [1997]. They found that As(III) is stable at a pH between 4 and 9. Heterogeneous oxidation above pH 9 results in more strongly adsorbed As(V). A detailed discussion on the pH and redox dependencies of arsenic is given elsewhere [Fetter 1993].

Phosphate

Phosphate is a nutrient which leads to extensive eutrophication. It can be removed from subsurface water by permeable reactive barriers using precipitation or adsorption before. Baker *et al.* studied different permeable reactive mixtures for phosphate removal [Baker *et al.* 1998]. The mixtures consist of a metal oxide for adsorption (e. g. iron oxides, alumina), a calcium source for precipitation (limestone, CaCO_3) and silica as permeable matrix. Calcium phosphates exhibit low solubilities (e. g. CaHPO_4 , $\log K_{sp} = -18.91$, [Baker *et al.* 1998]). The attenuation was in all experiments higher than 90 %. No breakthrough was observed when activated alumina was used in the column experiments. However, high adsorbent prices may be prohibitive for a field application.

Part 2

Engineering of permeable reactive barriers

Construction Methods

Reactive barriers were only introduced a few years ago and their construction methods have not yet been fully developed [Jefferis *et al.* 1997]. Though the operation of cut-off walls and reactive barriers is different – cut-off walls provide containment while reactive barriers treat the contaminants in situ – their geometry and some of the construction methods exhibit similar features [Debreczeni and Meggyes 1999]. The main configurations for systems with permeable reactive barriers are [Golder Associates Ltd. 1998]:

- continuous reactive barriers,
- funnel-and-gate systems,
- arrays of wells filled with reactive materials,
- injected systems.

Fig. 7 displays the most frequently used configurations i. e. the continuous reactive barrier and the funnel-and-gate system.

In the main, conventional cut-off wall construction methods have so far been used to build reactive barriers which is reasonable provided the impervious layer does not lie deeper than about 20m [Schad and Teutsch 1998]. This is especially true for funnel-and-gate systems as the funnel components are cut-off-walls anyway. Greater depths may result in increased technical problems and lead to prohibitive costs. With the development of the reactive barrier technology, deeper and more difficult installations will be undertaken for which more advanced methods will be needed. Systems using a high pressure jet technique

can help solve this problem and keep construction costs moderate.

In addition to their low operational costs, construction methods of reactive barriers exhibit further cost-saving features: the barriers are often installed in a semi-permanent fashion, built within the contaminated area only and they can start their operation immediately after installation [Day *et al.* 1999]. The two main types of reactive barriers, continuous permeable barriers and funnel-and-gate systems, allow the application of geotechnical construction methods which, as a rule, include slurry trenching, grouting and deep soil mixing. Interest in new methods is steadily increasing [Meiggs 1999] and a novel technique proposes using high-pressure jets and jet pumps [Debreczeni and Meggyes 1999].

Construction of Cut-off Walls

The most commonly used cut-off wall construction methods [Meggyes and Pye 1995] apply one of the following alternatives:

- excavating trenches using supporting fluids capable of solidifying and forming a diaphragm wall (single-phase diaphragm wall) or which – after excavation of the trench – are displaced by another material which, in turn, is capable of solidifying (twin-phase diaphragm wall);
- forming a thin slot by driving a beam into the ground, then consecutively retracting the beam and filling the space formed with a thick slurry (e. g. thin walls);

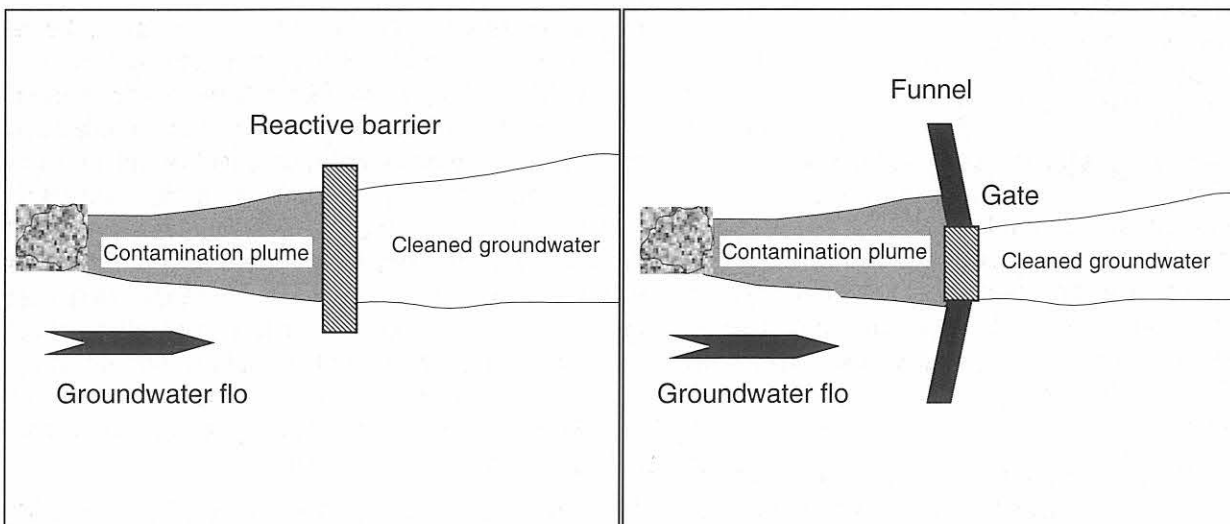


Fig. 7
Typical layout for systems with permeable reactive barriers

- driving strong elements into the ground (e. g. steel sheet-piles);
- constructing interlocking boreholes and using drill pipes or supporting slurries to stabilise the boreholes until they are backfilled with concrete to form a wall of interlocking columns.

Cut-off walls were first introduced around 1950 in reservoir and barrage construction, and since the early 1970s have also been used for containment of contaminated land [Arz 1988]. In order to meet the ever increasing requirements for high efficiency containment, especially in the field of landfill and remediation engineering, composite cut-off walls have been introduced using sheet piles, geomembranes or glass walls and tiles.

Single-phase Diaphragm Wall

Single-phase diaphragm walls consist of 0.4-1 m thick panels which are excavated from the soil using grab buckets, clamshells or vertical trench cutters. A self-hardening slurry is pumped in to stabilise the trench walls and form the final fill. Usually the 'pilgrim's pace' method is applied: primary panels 1, 3, 5 etc. are excavated and filled with slurry first. After a period of 36 - 48 hours, as soon as the slurry in the primary panels has hardened to a cuttable state, work begins on the secondary panels 2, 4, 6 etc. The cutter excavates the secondary panels with an overlap of 0.3-0.6 m cutting into the primary ones. Since the hardening process in the primary panels has not yet finished, an intimate contact is achieved between the primary and secondary panels. This feature has a positive advantage over the twin-phase method where gaps are created by removing the stop-end tubes. Also, using the single-phase method it is not necessary to dispose and replace the slurry, thus no typical fault lines are created. Verticality is usually a main issue [Ghezzi *et al.* 1999] to prevent gaps from being formed between adjacent panels, because even minor imperfections may drastically impair barrier performance: a 1 m² hole lets as much groundwater escape as a 100,000 m² high-quality cut-off wall does [Düllmann 1999].

Twin-phase Diaphragm Wall

Twin-phase diaphragm walls are constructed in two sequences. In the first phase, soil is excavated while a bentonite suspension stabilises the trench walls. In the second phase, the bentonite suspension is replaced by the cut-off slurry using tremie pipes (contractor method). The individual panels are confined by stop-end tubes.

Problems and deficiencies may arise when long stop-end tubes are retracted and the bentonite suspension is replaced by the cut-off slurry. In order to ensure an efficient replacement it is essential that the cut-off

slurry has a density exceeding that of the bentonite slurry by 500 kg/m³. If the bentonite suspension is not completely replaced, faults remain near the joints in an otherwise watertight wall.

Composite Cut-off Wall

In both single- and twin-phase systems, additional elements can be inserted into the cut-off wall to improve strength and/or watertightness. Sheet piles [Jessberger and Geil 1992], geomembranes [Boyes 1986] and glass walls/tiles are a few examples - with geomembranes applied most widely. These elements are inserted into the fresh bentonite cement mix immediately after placement. Because of their light weight, special construction apparatus is required to insert them into the cut-off wall and special locks provide watertight joints between the plastic geomembrane sheets [Meseck 1987, Stroh and Sasse 1987, Ghezzi *et al.* 1999]. The locks can be welded [Meseck 1987, Nussbaumer 1987] or filled with the slurry [Ghezzi *et al.* 1999] and checked after the cut-off slurry has hardened. Glass walls in composite cut-offs provide a high-degree of watertightness, however, their length is limited and the problem of forming a perfect watertight seal at the joints remains to be solved. Sheet pile walls can also be combined with bored piles around joints [Jessberger and Geil 1992, Düllmann *et al.* 1993].

Bored-pile Cut-off Walls and Jet Grouting

Bored-pile cut-off walls are constructed of contiguous or secant piles, with or without casing. The primary piles 1, 3, 5 etc. are sunk first, followed by the secondary ones 2, 4, 6 etc. By cutting into the primary piles while sinking the secondary ones and establishing an intimate contact between them, a high-degree of watertightness is achieved.

Cut-off walls can also be constructed of soilcrete columns, also called jet grouting, roddingjet and HPI (high pressure injection) [Tóth 1989, Kutzner 1991, Jessberger 1992]. A rotary drilling technique is used to construct the columns in conjunction with a high-density mud which serves both as a cutting and filling fluid. When the final depth is reached the drilling mud is diverted to the nozzles and the pump pressure simultaneously increased. The drill rod is retracted while being turned and in so doing the soil is cut and removed, the resulting void being filled with a cement or clay cement mix. In this way columns of soil-cement mix are constructed which, if suitably arranged, form a watertight cut-off wall.

A novel dual-phase jet grout system [Dwyer 1998] treats and contains contaminated underground bodies in such a way that contaminated spoils (drill cuttings)

remain in the subsurface. In Step 1, air and/or water is injected at high pressure to form a hollow underground storage cavern above the contaminated body, while clean soil from the cavern is removed to the surface. In Step 2, the contaminated body is treated and stabilised while contaminated drill cuttings are deposited in the hollow cavern formed in Step 1. By leaving pollutants and contaminated soil in the subsurface, the use of jet technology ensures containment and remediation without any health and environmental risk.

Thin Walls

Initially, groups of 4 - 8 sheet piles equipped with locks joining them together are vibrated into the ground. They are then simultaneously retracted while injecting a clay-cement and water mix into the void. Next, single, heavier steel beams, equipped with a special toe and fitted with injection nozzles, are inserted, enabling the use of stronger vibrators. The toe is also provided with a blade to guide the beam as it cuts into the previously constructed panel, so providing a given overlap which forms an extension of the pile rod [Arz 1988].

Feasible depths for thin walls are between 15 and 20 m. The thickness depends on the dimensions of the former toe which is usually 60-80 mm thick. Greater thickness increases the driving resistance and the retraction force, thus thicker formers are seldom used. Wall thickness is also influenced by the soil layers and injection pressure.

In coarse layers (sand, gravel) the vibration has the additional effect of compacting the surrounding medium thus achieving a reduction in permeability. Furthermore, the clay-cement mix usually penetrates into the pores of the soil thus the final wall thickness achieved can be twice the nominal thickness.

Driven thin walls are the most economical of all cut-off wall systems. This method enables up to 1000 m² of cut-off to be installed per shift. To achieve high-degree watertightness, very accurate pile guiding and control by precise instrumentation is required. The permitted misalignment is below 0.2 % for a thickness of 10 cm and a depth of 20 m.

For the containment of contaminated land double thin walls are frequently used providing a higher degree of safety. The cost benefit of thin walls is so great that a double thin wall is usually cheaper than any other construction. The cut-off wall chamber system can be regarded as an improvement to the double thin wall.

Sheet-pile Walls

Sheet pile walls are constructed using steel, precast concrete, aluminium or wood piles driven into the

ground individually or in groups and connected to each other by locks [Roth 1988, Weber et al. 1990, Jessberger and Geil 1992], [Rodatz 1994] with steel sheet piles being the most common application. The use of vibrators is not recommended since they can damage the locks. Sheet steel pile walls are easy to construct and can carry heavy loads, construction time is short and since no contaminated soil is excavated there is no disposal problem. However, the locks may still pose problems due to imperfect watertightness.

The range of application for the steel sheet-pile wall is small in comparison to diaphragm walls. Resistance to corrosion by leachates is to be cleared for future applications. Hein [1990] found that the rate of corrosion of steel sheet pile walls in water increases exponentially. The maximum corrosion can be estimated with sufficient accuracy for fresh and brackish water, while measurements indicate wide local variations for sea water. Jessberger and Geil [1992] investigated the corrosion of steel St Sp 37 in test fluids [Landesamt für Wasser und Abfall NRW 1985] and in leachates. The rate of corrosion was low in both inorganic mineral acids and municipal landfill leachates. Higher corrosion rates were found in organic acids and leachates from contaminated land. Corrosion protection can be improved by plastic coatings and cathodic protection [Wienberg 1992] using experience in maritime engineering [Rust 1992] and oil and gas pipelining and bitumen- and polyurethane-based seals.

Driven Cut-off Walls

In this method a caisson with a detachable and watertight sole plate is driven into the ground. Each cycle consists of 5 elements. After elements 3 and 4 have been driven, element 1 is filled with soilcrete and then retracted, causing the sole plate to detach under the load of soilcrete. A new sole plate is attached to the retracted element which is then driven into the ground in the next position. Meanwhile the soilcrete is compacted. There are always several elements already installed but not filled with soilcrete between the fresh soilcrete and the element being driven, this ensures that the sealing material is not mixed with the contaminated soil [Jessberger 1992, German Geotechnical Society 1993].

Injection and Frozen Walls

Injection of a solidifying liquid material into the ground fills the pores and fissures, thus reducing permeability. Cement suspensions, artificial resins or water glass-based materials whose compatibility with the groundwater is proven are used. Collar pipes are commonly used for injection purposes, consisting of plastic pipes provided with rubber collars around perforated pipe sections, and these are inserted into the casing of the

injection hole. As the casing is retracted, the annulus between the collar pipe and the hole will be filled with the cement suspension. After the suspension hardens, the rubber collar is lifted, forming perforations in the cement, and the actual sealing material is then injected into the surrounding rock. The distance between the injection holes is determined by the rock permeability, the viscosity of the injected material and the highest permissible injection pressure. At first, holes at greater distances are bored, between these further holes are then drilled [Kutzner 1991, Jessberger 1992, Schulze 1992, German Geotechnical Society 1993].

Frozen walls are constructed by inserting pipes into the ground in which a coolant or liquid nitrogen circulates. By freezing the soil, a closed, watertight body is produced which must be constantly cooled in order to be maintained. Frozen walls can be used as a temporary measure to close windows on cut-off walls, protect cut-off slurries from pollutants and remove highly toxic liquid or volatile materials from a contaminated body [Jessberger 1992, German Geotechnical Society 1993]. Recent developments [Dash et al. 1997, Mageau 1998] indicate that frozen soil permeability can be as low as 10^{-12} m/s and diffusivity is around 10^{-9} cm²/s. Installation of frozen walls requires little or no soil excavation and they can be removed by stopping the cooling (although they can last months without power) and there is no pollution to deal with and no wastes to dispose of. Feasible depths are a few hundred metres and frozen walls are effective in both clay and sand/gavel type soils. Advanced applications use extensive monitoring by thermistors, electro potential measurement, ground penetrating radar and dye injection. Applications include containment of contaminated groundwater plumes, protection of rivers, containment around and below leaking tanks. With US\$ 200-400 per m² installation cost and US\$ 20-25 per m² annual operational and maintenance costs [Mageau 1998], frozen walls may prove an efficient and environmentally sound application.

Construction of Reactive Barriers

The basic requirements the structure of a reactive barrier has to fulfil are [Beitinger and Bütow 1997, Smyth et al. 1997, Beitinger 1998]:

- replaceability of the reactive materials
- higher permeability than the surrounding reservoir
- stability against fines washed into barriers from the surrounding soil
- long life-span.

The selection of construction technique to be used depends mainly on site characteristics [Gavaskar 1999]:

- depth is probably the most important factor, greater depth involves more specialised equipment, longer construction time and higher cost
- geotechnical considerations: strength of the layers and presence of cobbles, subsurface utilities, buildings etc. influence construction technique selection
- soil excavation: handling and disposal of (contaminated) soil requires additional room on the site and increases costs
- health and safety is an important issue especially when entry of personnel into excavations is required.

The basic structure of reactive barriers consists of the part filled with reactive material preferably between (concrete) panels. The panels are separated from the surrounding soil by filter gravel which prevents fines from the soil from entering the reactive zone. To exclude any contact with oxygen from the air, the reactive barriers are covered with very low permeability materials (clay). The overall permeability of this multi-layered system must be higher than that of the surrounding soil to encourage groundwater to flow through the barrier instead of by-passing it.

Construction of Reactive Barriers Using Conventional Technology

The methods applied in cut-off wall excavation as described in the section "Construction of Cut-off Walls" can be used for reactive barrier trench excavation. Reactive materials can be filled into the trench using common earth moving machines. The funnel elements in funnel-and-gate systems are essentially cut-off walls and they are constructed using the cut-off wall construction methods. *Graveling* [1998] reports on the construction of a 400 m funnel-and-gate system in which sheet pile walls were used to construct the funnels and vibratory installation was applied. Four cells each 12 m wide served for the purpose of gates containing iron in view of the contaminant occurring. Residence time was determined from the influent chemistry, reaction rates and treatment goals. Residence time and flow velocity, in turn, yielded 0.6-1.8 m cell thickness resulting in 580 tons of iron. The gates were constructed as sheet piling boxes, the bottom lined with bentonite and geotextile, on which iron filings were placed surrounded with pea gravel to provide access for the groundwater. The gates were capped by geotextile and bentonite, and native soil was backfilled to grade. Barrier installation amounted to US\$ 200-250 per m², gate installation costs were US\$ 850-1000 per m².

Drilling and Deep Soil Mixing

Contiguous circular columns containing reactive material can be installed using drilling and deep soil

mixing [Day *et al.* 1999] which then form longer barriers. Caisson drills can be used to construct 0.5 to 2.5 m diameter columns. Usually a large circular casing is lowered into the ground, the soil is removed by augers and the hole filled with reactive material. Instead of casing, biodegradable polymer slurries [Hubble *et al.* 1997] or shear-thinning fluids [Cantrell *et al.* 1997] may be used as supporting fluids with significant cost benefits. Deep soil mixing mixes the soil with a slurry in situ without excavating the soil [Miller 1997]. A caisson is lowered into the ground, a set of multiple augers penetrates the ground and the reactive material is injected through the hollow kelly bar of the mixing tools. The reactive material must be injected in slurry form which then is mixed with the soil by the augers. The amount of reactive material is limited because the soil is not removed. Deep soil mixing is also used to construct containment walls in which case bentonite-cement mixture is injected and mixed with the soil in situ.

Construction of Reactive Barriers Using Jet Technology

This novel technique proposes using high-pressure jets and jet pumps [Debreczeni and Meggyes 1999]. The jet cutting head used in the trench excavation is joined to the drilling pipe by a hinged connector and a flexible pipe (see Fig. 8). This allows the drilling pipe to be swung from side to side within the trench by means of a hydraulic mechanism so as to achieve the appropriate length of excavation. Soil excavation in low-strength strata can be performed by slurry jets and in high-strength strata by a milling head which can be attached to the drilling pipe and operated by a hydraulic motor. The drillings can be transported to the surface through the drilling pipe by means of a jet pump. Where slurry jets are used in the trench excavation, both the jet cutting head and the jet pump can be operated by the same slurry pump. Depending on construction process and final barrier requirements, the slurry can either remain in the trench after excavation is complete and form the final barrier (single-phase technique) or will be replaced by the final barrier material (twin-phase technique).

After being pumped to the surface the drillings must be separated out from the slurry, which can then be re-circulated. Solid particles greater than 1 mm can be removed by arch or trommel screens, for finer materials a hydrocyclone must be used. The hydrocyclone can be operated by a second slurry pump. The cutting head and the drilling pipe can be carried by a drilling mast or supported by stop-end tubes or sheet piles which can be removed and re-used once the panels have been completed. Depending on local conditions, especially where mechanical cutting is used, air lift can be considered instead of jet pumping.

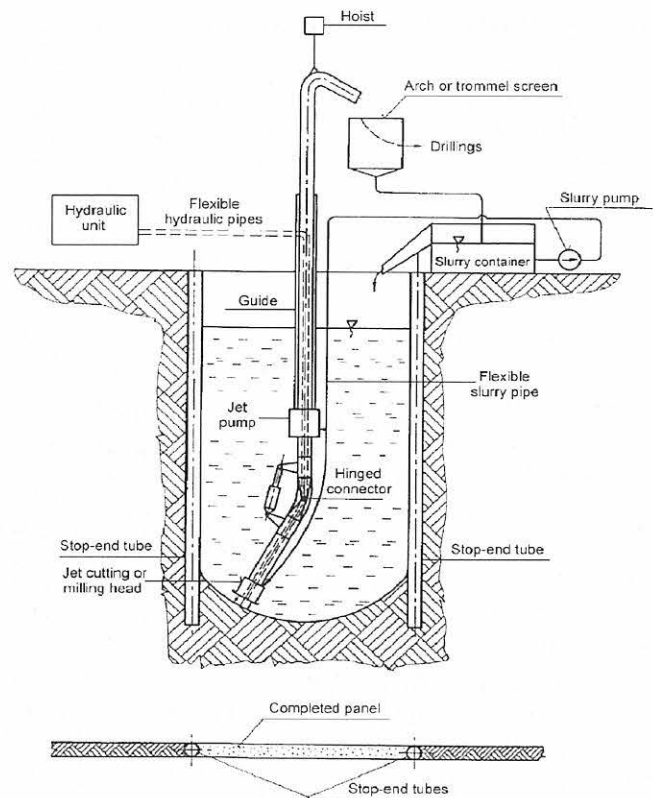


Fig. 8
Swinging-pipe jet equipment for cut-off wall or reactive barrier construction

The principal advantages of the jet method are:

- high flexibility at varying and greater depths
- light-weight equipment
- the method can easily be applied using commercially available shallow-depth drilling rigs
- low installation costs
- simple construction technique
- barrier thickness can be kept to a minimum
- easy way to place the reactive materials into the trench.

Applying Reactor Barrier Technology to Existing Containment Systems

Although cut-off technology is highly sophisticated and in most cases provides efficient containment, the groundwater reservoir separated by a cut-off wall from the surrounding reservoir very often requires treatment which results in additional costs. Applying reactive barrier technology to an existing containment system by opening up the cut-off wall at distinct points and filling the openings with reactive material [Bradl and Bartl 1999], thus transforming containment into a funnel-and-gate system, the groundwater can be suitably treated and it need not be pumped which helps reduce costs. The reactive material used must comply with the specific requirements by the pollutants in the groundwater.

Well-based Systems

An alternative to continuous barriers is to use arrays of wells [Wilson and Mackay 1997, Golder Associates Ltd. 1998]. This may be helpful at sites, where installation of permeable barriers may be impractical for technical or financial reasons. An array of wells can form the gate within a funnel-and-gate system or serve as a set of in situ reactors or can release substances that encourage biological or other processes. An array of wells is essentially a non-continuous reactive barrier with the advantage that drilling techniques can be used to construct them, allowing lower installation costs and greater depths. The wells filled with reactive materials have lower hydraulic resistance, thus the groundwater flow converges towards them. The amount of reactive material required for the wells is much less than for continuous reactive barriers. Residence time must provide for the reactions between the pollutant and the reactive material. The whole contaminant plume must flow through the array of wells in which respect an optimum well spacing is of great importance. If residence time is high, more than one array of wells may be required.

Well configurations used so far apply one of the following arrangements:

- The granular material (often zero-valent iron) is placed in baskets which in turn are placed in the wells. Permeability of these wells is two to five times greater than that of the surrounding aquifer.
- Impermeable devices placed in the wells can slowly release substances by diffusion through their walls due to concentration gradient [Wilson and Mackay 1995].
- Fine grained materials can slowly release substances, an example are oxygen-releasing compounds. The material is filled in tube-like filter sock with low hydraulic conductivity thus oxygen release to the flowing groundwater occurs mainly at the surface of the sock.

As a rule, well spacing should be twice of the well diameter, thus the effective length of an array of wells is about half of that of a reactive barrier. Wells with substance emitting filling may even have greater spacing.

Wells can also be arranged horizontally [HTI 1995] to deliver treatment agents such as vapour for air stripping, and oxygen and nutrients for bioremediation purposes. Technologies used include rotary rigs, "mole" systems and trenching methods [Flowmole 1995, Golder Associates Ltd. 1998].

Injected Systems

Injecting reactive materials into the ground at high pressure without strict geometrical boundaries in terms

of a "wall" is an attractive idea which provides high flexibility. Nevertheless, it has to be made sure that the contaminant plume is efficiently taken care of and no by-passing or fingering occurs which may impair the remediation effect. An injected system can control large and deep plumes even if their extension is irregular [Golder Associates Ltd. 1998]. Permeation grouting or ground fracturing are the most commonly used techniques so far, though it should be noted that the development of injected systems is at a fairly early stage. Researchers and end-users may benefit from adopting extensive knowledge and long-established methods in petroleum engineering, where techniques of strata fracturing, secondary recovery etc. have been developed over many decades at considerable expense by large oil companies on research and innovation. One of the disadvantages of injected systems is that recovery of the reactive material is practically impossible, therefore degradation principles should be preferred. If reactive/sorption processes are used, where the capacity of the reactive material is gradually exhausted, low costs should enable re-injection from time to time.

Two main types of injected systems seem to have been developed so far:

- injection into the existing pores of ground
- ground fracturing.

Using existing pores to inject reactive material is similar to geotechnical grouting. To establish the injection range, a spherical extension was assumed [Müller-Kirchenbauer 1969]:

$$R_s = \sqrt[3]{\frac{h k_o 3r}{n}} \sqrt[3]{t_e \left(1 - \frac{C}{m+1}\right)} \quad \text{Equation 5}$$

with R_s = range of injection for spherical extension

h = pressure head at the source of injection

k_o = permeability at the beginning of injection

r = radius of the bore hole

n = pore volume

t_e = time at the end of injection

C, m = specific constants of the injected material.

For cylindrical extension

$$R_c = \alpha R_s$$

holds with

R_c = range of injection for cylindrical extension

α = 2.3 - 2.6.

Range of injection largely depends on the pores available and injection wells may require a very close spacing in finely grained soils. Some authors suggest that 10^{-5} m/s is the permeability limit below which only pure liquids may be injected. Injecting bacteria, air microbubbles as oxygen supplier [Duba et al. 1996,

Koenigsberg 1998], cationic surfactants [Burris and Antworth 1990, Burris and Antworth 1992] have also been suggested.

Hydraulic Fracturing

Ground fracturing, as used in enhancing permeability around oil wells in petroleum engineering, aims at creating an improved zone by cracking the ground at high pressures and pumping sand or similar granular material into the cavity created. Using this method within the concept of barrier technology [Murdoch *et al.* 1997] [Gavaskar 1999], a part of the material filled in may be reactive material intended for pollutant treatment. As in petroleum engineering, the fractures are initiated from wells and are nearly horizontal structures so that they are capable of intercepting downward moving contaminant plumes. In addition to introducing reactive materials into the ground, a further advantage is that a high-permeability zone is formed which encourages groundwater flow. Fractured zones may also be applied to direct groundwater flow towards the gates in funnel-and-gate systems [Golder Associates Ltd. 1998]. Murdoch *et al.* found [1997] that the pressure required to fracture the ground increased with the depth but was surprisingly low: 500 kPa maximum was measured during a test at 2 m depth. The fractures usually have a preferred direction of propagation, they are therefore asymmetric with respect to the borehole and they climb in the preferred direction of propagation. Murdoch *et al.* [1997] report on 7-10 m fracture dimensions in silty clay, with 0.1-1.25 m³ filled-in material and 5-25 mm fracture thickness. The fracturing procedure can be monitored by recording both pressure and deformation of the ground surface which will lift to form a gentle dome. Applications include materials that alter redox conditions, adsorb contaminants or slowly release useful materials (e. g. oxygen, nutrients, porous ceramic granules, etc.). Using high-energy jets and adjustable outlets, directional fracturing feasible.

A new application of hydraulic fracturing aims at constructing vertical barriers [Gavaskar 1999] by creating controlled vertical fractures from a series of wells. The fractures are monitored through e.g. downhole resistivity sensors to ensure coalescence or overlap of the fractures. 8-10 cm barrier thickness can be achieved and some variability in thickness can be addressed by designing two parallel barriers.

Construction of Biobarriers

Subsurface biofilm barriers (i. e. biobarriers) consist of biofilm which in turn consists of deposited cells of micro-organisms and polymers, together with captured organic and inorganic particles [Cunningham *et al.* 1991, Cunningham *et al.* 1997, Sharp and Cunningham 1998]. Biobarriers may selectively plug permea-

ble strata with microbial biomass thus influencing the hydraulic conductivity. Investigations indicate that reducing the hydraulic conductivity by five orders of magnitude is possible, in column tests 92 to 98 % reduction in hydraulic conductivity was achieved. By reducing the overall permeability and mass transport properties of the aquifer matrix, biobarriers serve as an alternative technology for controlling the migration of contaminants from hazardous waste sites. Biobarrier technology may also be useful as a means of funneling contaminated groundwater through subsurface treatment systems (e. g. funnel-and-gate).

The first step in forming a biobarrier is the isolation and identification of potential barrier-forming bacteria from a field site. Once identified, these bacteria will be re-injected to serve as the inoculum for biobarrier formation. Extra cellular polymer (eps)-producing bacterial strains (i. e. mucoid phenotype) are desirable candidates for barrier formation. Several *Pseudomonas* and *Klebsiella* strains have been isolated from potential field sites. In addition to exhibiting high eps production, these bacteria also have the ability to biodegrade BTEX compounds – thereby raising the possibility that biobarriers can be constructed which actively biodegrade dissolved contaminants in addition to providing containment. These bacteria were found to grow well on either molasses or distillery waste which means that a low-cost nutrient source is potentially available for field scale biobarrier construction.

Once bacteria suitable for biobarrier construction have been isolated, the next step is to verify that biobarrier formation and hydraulic conductivity reduction can be achieved in laboratory scale packed bed reactors. Biobarrier experiments carried out by Cunningham in 0.9 m long, 15 cm diameter PVC and stainless steel columns under a hydraulic gradient of 1.0 m/m yielded a reduction in the hydraulic conductivity from an initial value of about 4 cm/min down to approximately 0.01 cm/min. Similar experiments were run in 0.3 x 0.9 x 0.15 m³ stainless steel lysimeters under a head of 0.03 m/m and reductions from 1 cm/min to approximately 10⁻⁵ cm/min were obtained. The reactors were packed with F-70 (60 % < 150 mm) and F-110 (60 % < 140 mm) sand and after inoculation were fed a medium of sodium citrate. The high-gradient column experiments required nutrient addition at about five day intervals to maintain biofilm barrier integrity while the lower-gradient lysimeter runs required nutrient addition at much larger (100 to 200 day) time intervals.

Biobarriers can be constructed by using an array of wells to introduce microorganisms, nutrients and oxygen into the ground. The activity of microorganisms leads to the development of contiguous columns of low permeability which in turn form the barrier (see Fig. 9).

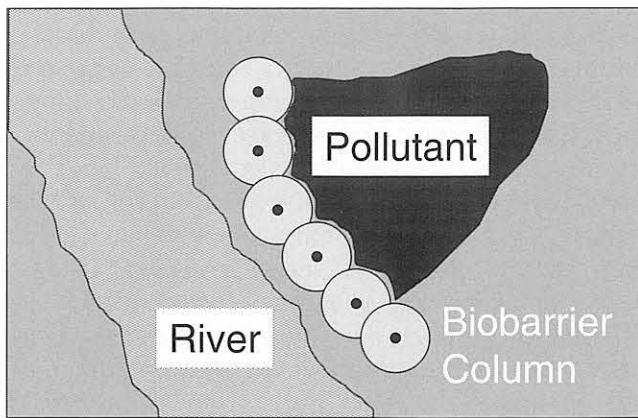


Fig. 9
Schematic Biobarrier Configuration [Hiebert 1998]

Biobarrier performance was found to be unaffected by exposure to heavy metal contaminants (strontium and caesium) at 1 ppm levels for periods up to 120 days. Similarly, biobarrier performance and formation was not influenced by the presence of carbon tetrachloride at concentrations of 100 mg/litre for extended periods and up to 300 mg/litre for short periods.

Biofilm barriers built under field-relevant hydraulic gradient conditions can achieve substantial (i. e. up to five orders of magnitude) reduction of hydraulic conductivity, and can be maintained indefinitely, without incurring significant costs for injecting additional nutrients. The findings also indicate the possibility of creating containment barriers in the field which extend above the background water table, thereby providing hydraulic containment of dissolved contaminants. These results suggest that biobarriers can be developed as an alternative technology for containing (and possibly biodegrading) dissolved organic contaminants. Preliminary economic estimates indicate that biobarrier technology would be cost-effective compared to existing containment alternatives such as grout curtains and slurry walls. Hiebert [Hiebert 1998] has found a cost range of US\$ 6.5 to 10.7 m for a biobarrier and US\$ 9.8 to 13.5 m for a grout curtain for a 30 m deep and 3200 m long barrier. A sheet pile wall of the same length but only 12 m depth costs US\$ 15 to 17 m. Vertical biobarriers can be constructed as contiguous cylinders [Hiebert 1998] by using an array of wells through which micro-organisms and nutrients are injected.

Possible fields of application are:

- stabilisation of mining spoil and problems caused by acid mine drainage
- selective plugging of high permeability water breakthrough zones in secondary oil recovery
- protection of rivers and lakes from pollutant plumes
- reinforcement to landfill liner systems
- plugging water “fingering” channels in earthen dams and berms

- introduction of pollutant degrading/reducing organisms into plumes of organic and metallic pollutants.

Costs of permeable reactive barriers

Remediation costs of chlorinated hydrocarbons in groundwater with permeable reactive barriers were compared with the pump-and-treat method in a report of the US Department of Defence. Cost saving is around 50-70 % for the example discussed in the report the on a longer time scale as can be seen in Fig. 10 [Reeter et al. 1999].

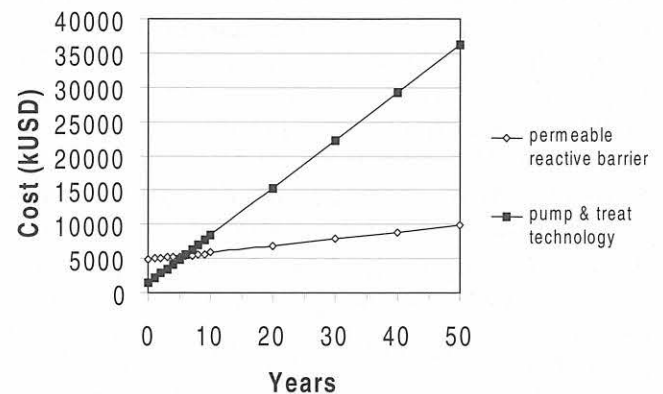


Fig. 10
Cost comparison of groundwater remediation with pump-and-treat technology and permeable reactive barriers [Reeter et al. 1999]

In this comparison, barrier maintenance costs of US\$ 268 k every ten years were inserted. This is equivalent to 25 % of the iron medium costs and is at the moment only a good guess because no long-term experience with PRBs exists. It is therefore not sure whether or not the above cost savings can be achieved. Further research on the long-term behaviour of permeable reactive barriers with time-accelerating experiments is therefore strongly needed. An integrated research programme on the application of reactive barriers for the remediation of contaminated sites supported by the German Federal Ministry for Education and Research will start in Germany in 2000 with several technical demonstration projects. The results of this programme will help extend our knowledge on the long-term behaviour and cost structure of permeable reactive barriers as a groundwater remediation technology.

Conclusions

Groundwater remediation using permeable reactive barriers is a promising new method for a variety of inorganic and organic pollutants. Well known chemical and physical processes are applied, sometimes in

combination of or enhanced by micro-organisms, in permeable reactive barriers:

Redox-reactions

Precipitation

Adsorption

Ion exchange

Biodegradation

Reactive material types used in the barriers are:

- those changing pH or redox potential, e. g. zero-valent iron: degradation of low chlorinated hydrocarbons,
- those causing precipitation,
- materials with high sorption capacity,
- those releasing nutrients/oxygen to enhance biological degradation.

Positive results achieved so far are:

- reaction mechanisms and influences are well studied (especially for zero valent iron)
- reaction kinetics of many processes are understood enabling informed design
- pilot test results suggest that large-scale application is feasible.

However, information on the long-term performance of PRBs is still required for a better understanding of the remediation processes.

Cost savings compared to traditional technologies such as the pump-and-treat method are expected. While extensive research and a large number of papers have dealt with the processes in permeable reactive barriers in the last few years, not so much attention has been paid to the development of construction methods. Construction methods used mainly rely on well-established techniques developed for cut-off walls (e. g. slurry trenching) due to similarities between cut-off walls and reactive barriers. With the development of the reactive barrier technology, deeper and more difficult installations will be undertaken for which more advanced methods will be needed. A number of novel technologies (high-pressure jet technology, biobarriers etc.) have recently broadened the range of techniques for engineering permeable reactive barriers.

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A Brief History of BAM

- 1870** The Prussian Ministry of Commerce, Trade and Public Works announces the establishment of a Mechanical and Technical Research Institute. Its task is to perform experiments of general scientific and public interest and to test the strength of components.
- 1904** The Royal Materials Testing Office is established in Berlin-Dahlem following the merger of the Royal Mechanical Testing Institute with the Royal Testing Station for Building Materials (founded in 1875) and the Royal Chemical Technical Testing Office (founded in 1877).
- 1919** Renamed the Public Materials Testing Office (MPA), the institute is responsible to the Prussian Ministry of Science, Fine Arts and Public Education; from 1936 the Public X-ray Investigation Office is included.
- 1920** The State Chemical Technical Institute (CTR) is established under the State Ministry of the Interior from the Military Testing Office, established in 1889 as the Central Research Office for Explosives.
- 1945** MPA and CTR are united and operate under the jurisdiction of Berlin City Council.
- 1954** The Federal Republic of Germany takes over responsibility for MPA/CTA as Federal Institute for Mechanical and Chemical Testing (BAM), renamed the Federal Institute for Materials Testing in 1956. In addition BAM takes over responsibility for public materials testing for the state of Berlin.
- 1969** Under the Statute on Explosive Substances BAM is granted the status of higher federal authority; an amendment to the law in 1986 adds the word "research" to BAM's title.
- 1975** Under the Statute on the Transport of Hazardous Goods BAM is given greater responsibility in the field of public technical safety.
- 1990** German reunification and a recommendation from the German Scientific Council strengthen BAM's function as a federal chemical technical institute. Its personnel is increased by staff gained from the defunct Office for Standardisation, Measurements and Product Testing (ASMW) and Academy of Sciences in the former GDR. Responsibility for public testing for Berlin is gradually ended.
- 1995** Following extensive reorganisation, under a decree from the Federal Ministry of Economics BAM is given a new statute, revised management structures and methods and a future-oriented profile as an essential element of the technical and scientific infrastructure of the Federal Republic of Germany.
- 1998** Under an amendment to the Statute on Explosive Substances, the European Directive on Explosives from 1993 is adopted into Federal German Law. It names BAM as the competent authority. Confirming BAM's position as higher authority, it links BAM as Notified Body to the European System of Conformity Assessment.
- 1999** Under the framework agreement between the Federal Institute of Physics and Metrology (PTB) and BAM covering metrology in analytical chemistry, BAM is included in the global cooperation of the Metre Convention and "Arrangement for mutual recognition of national standards and calibration certificates issued by national metrology institutes".

