Permeable Reactive zerovalent iron barriers (ZVI-barrier)

Generic guideline

Target audience: Scientists, Consultancies, contractors, authorities, feasibility test labs

AQUAREHAB is co-funded by the European Commission within the Seventh Framework Programme

Project website address: aquarehab.vito.be

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1 INTRODUCTION

Permeable reactive zerovalent iron barriers (ZVI-barriers) are an innovative in-situ remediation technology for contaminated groundwater. This document intends to provide information about this technology and its application area and boundary conditions for consultants, authorities, contractors and feasibility testing labs. The aim is to offer support when evaluating the feasibility and the impact of the ZVI-barrier technology to rehabilitate degraded waters, as well as when designing, implementing and monitoring ZVI-barriers.

This document was composed in the frame of the FP7 project AQUAREHAB (GA 226565), and comprises outcomes and lessons learned during this project.

2 BACKGROUND INFORMATION ON THE ZVI-BARRIER TECHNOLOGY

2.1 GENERAL EXPLANATION OF THE TECHNOLOGY PRINCIPLE

Permeable reactive barriers (PRBs) are installed in the subsurface downstream of a contamination source. In the barrier, pollutant removal processes are activated, which degrade the pollutants in the groundwater while it flows through the barrier. Generally, no pumping is involved and the naturally present hydraulic gradient is the driving force to move the groundwater through the barrier. Therefore, the PRB technology is a semi-passive to passive technology.

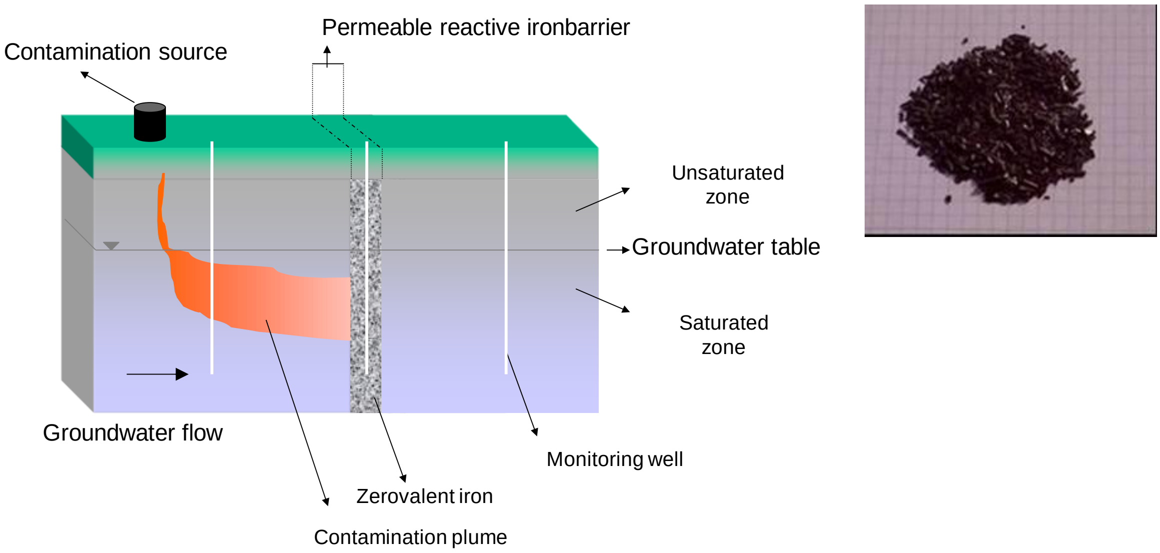


Figure 1 Schematic representation of the ZVI-barrier technology.

Permeable reactive zerovalent iron barriers (ZVI-barriers), are a kind of PRBs where part of the soil in the saturated zone is replaced, after excavation, by zerovalent iron (ZVI) containing filling, resulting in a physical permeable barrier as shown in Figure 1. ZVI is a reactive material that is able to remove a number of pollutant types from the passing groundwater. After installation, the system can remain reactive for years to a few decades.

Alternatively, the ZVI can be injected into the subsurface, creating **a reactive zone**. This technology, requiring finer sized ZVI (micro & nano), is not considered here but is subject of DL5.5.

The use of **granular** (mm-size) zero-valent iron for in-situ remediation of groundwater contaminated with chlorinated solvents via ZVI-barriers is a proven technology (Matheson & Tratnyek; 1994; Gillham, 1996; Gavaskar, 2000). Chlorinated solvents like tetrachloroethylene (PCE) and trichloroethylene (TCE) can be degraded abiotically by reductive dehalogenation in the presence of zerovalent metals like iron. Although the use of metals for treating chlorinated organic compounds has been reported in the early seventies (Sweeny and Fischer, 1972), it took more than 20 years to install the first field-scale Fe^0 PRB. Since then, the technology has been evolving from an innovative to an accepted standard technique with more than 120 applications worldwide. Scrap iron filings, which are by-products of mechanically processed cast iron, are typically used as reactive media.

2.2 TARGETED SUBSTANCES

An overview of the substances that can be targeted by the ZVI-barrier technology are summarized in Table 1 along with potential emission sources of the different substances.

Table 1 Overview of substances that can be tackled by ZVI-barrier technology.

Targeted substances		References
Class	Specific substance	
Chlorinated ethenes & ethanes *Emission source: Drycleaner activities, degreasing activities, ...*	Tetrachloroethylene (PCE) Trichloroethylene (TCE) Cis-dichloroethylene (cDCE) Trans-dichloroehtylene (tDCE) 1,1-dichloroethylene (1,1DCE) Vinylchloride (VC) Hexachloroethane 1,1,2,2-tetrachloroethane 1,1,1,2-tetrachloroethane 1,1,1-trichloroethane (111TCA) 1,1,2-trichloroethane (112TCA) 1,1-Dichloroethane (11DCA)	Gillham & O'Hannesin, 1994 Gillham, 1996 Fennelly & Roberts, 1998 Lookman et al., 2004 Dries et al., 2004 Miehr et al., 2004 Dries et al., 2005 Velimirovic et al., 2013
Chlorinated methanes & propanes *Emission source: Chemical industry, Agricultural activities*	Tetrachloromethane (PCM) Trichloromethane (TCM) 1,2,3-trichloropropane 1,2-dichloropropane	*Matheson & Tratneyk, 1994* *Gillham, 1996* *Johnson et al., 1998* *Wan et al., 1999*
Other chlorinated aliphatics *Emission source: chemical*	Hexachlorobutadiene	*Gillham, 1996*

Targeted substances		References
Class	Specific substance	
industry		
Pesticides & herbicides *Emission source: Agricultural activities, gardening*	Hexaclorocyclohexanes (HCHs) Dichlorodiphenyltrichloroethane (DDT) …	*Conq et al., 2010.*
Nitrobenzenes *Emission source:*	nitrobenzene	*Gillham, 1996* *Scherer et al., 2001*
Nutrients *Emission source: agriculture & feedstock*	Nitrates	*Westerhoff & James, 2003* *Miehr et al., 2004* *Liu et al., 2005.*
Dyes *Emission source: textile industry*	Azo dyes (Orange I, Orange II, Orange IV, Acid Blue 113, Allure Red, Amaranth, Crocein Orange G, Napthol Blue Black, Sunset Yellow FCF, Tartrazine, acid Red 3B, …)	*Cao et al., 1999* *Sangkil & Tratneyk, 2000*
Explosives *Emission source: military activities*	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) 1,4,6-tronitrotoluene (TNT) Octahydro-1,3,5,7-tetranitor-1.3.5.7-tetrazocine (HMX)	*Miehr et al., 2005* *Park et al., 2005* *Wanaratna et al. , 2006*
Metals (via immobilisation) *Emission source: mining, industrial activities*	Cathionic metals (Cu, Ni, Zn) Selenium Uranium Chromium Arsenic	*Melita et al., 2001* *Su & Puls, 2003* *Wilken & McNeil, 2003* *Miehr et al., 2004* *Dries et al., 2005* *Noucbactep et al. 2005*
Brominated & fluorinated compounds *Emission source: chemical industry*	Tribromomethane (TBrM) 1,2 dibromomethane 1,2-dibromo-3-chloropropane Trichlorotrifluoroethane (Freon 113) Trichlorofluoromethane (Freon 11)	*Gillham, 1996*
Chemicals misc	Carbon disulfide	*Claire.co.uk TDP20*

2.3 REACTION PATHWAYS FOR CHLORINATED ETHENES

The reduction of contaminants into less toxic or less mobile compounds is mainly driven by the oxidation (corrosion) of Fe^0 (reaction 1) or surface-bound Fe^{2+} (reaction 2), and to a lesser extent by dissolved or surface hydrogen generated as a product of anaerobic corrosion as given in reaction 3 & 4 (Scherer *et al.*, 1999). Another important reaction causing anaerobic corrosion of iron is the reaction of zerovalent iron with water (reaction 4). Especially this reaction is responsible for the pH-increase that is often associated with zerovalent iron application, and the generation of hydrogen.

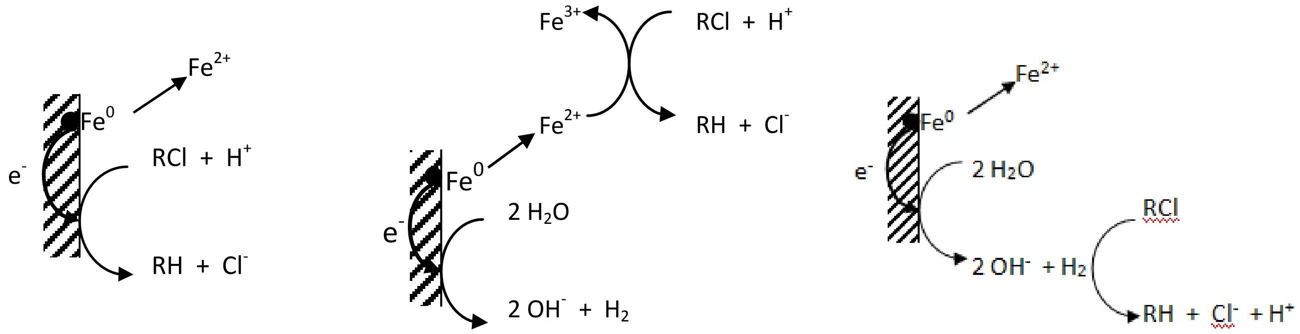
$$Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \qquad \text{(Reaction 1)}$$

$$2\ Fe^{2+} + RX + H^+ \rightarrow 2\ Fe^{3+} + RH + X^- \qquad \text{(Reaction 2)}$$

$$H_2 + RX \rightarrow RH + H^+ + X^- \qquad \text{(Reaction 3)}$$

$$Fe^0 + 2\ H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^- \qquad \text{(Reaction 4)}$$

These three possible reactions are also schematically given in Figure 2. The relative importance of the different reactions is function of the Fe^0 material and potentially also the composition of the groundwater.



1.Direct reduction on de Fe^0 surface

2. Reduction by Fe^{2+}

3. Reduction by hydrogen gas

Figure 2. Possible reaction mechanisms for reductive dechlorination of CAHs by zerovalent iron (based on Matherson & Tratnyek, 1994).

Reduction of chlorinated ethenes is believed to proceed through different pathways in which different reactions are involved, including hydrogenolysis (replacement of chlorine by hydrogen), reductive elimination (dichloro-elimination) and hydrogenation (reduction of multiple bonds) (Arnold and Roberts, 2000). A schematic diagram showing the hypothesized reaction pathways is provided in Figure 3.

The relative importance of the different pathways is expressed by the molar conversion model (Figure 4) which is strongly dependent in the iron type and possibly the composition of the groundwater. Indications have been collected within AQUAREHAB that the molar conversion model can change over time (Bastiaens et al., in preparation).

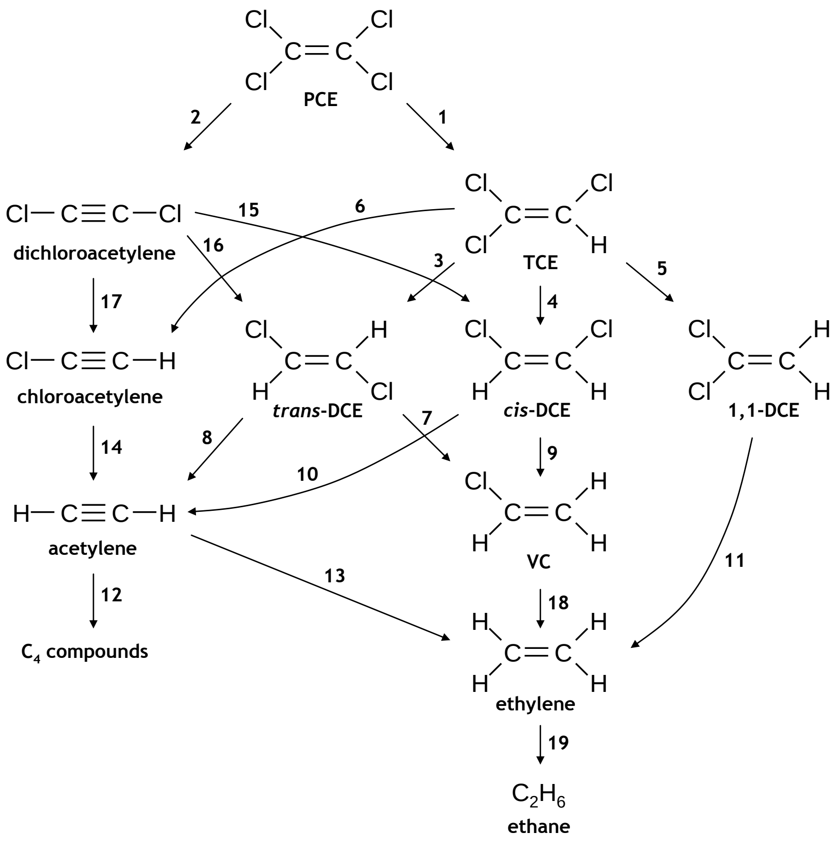
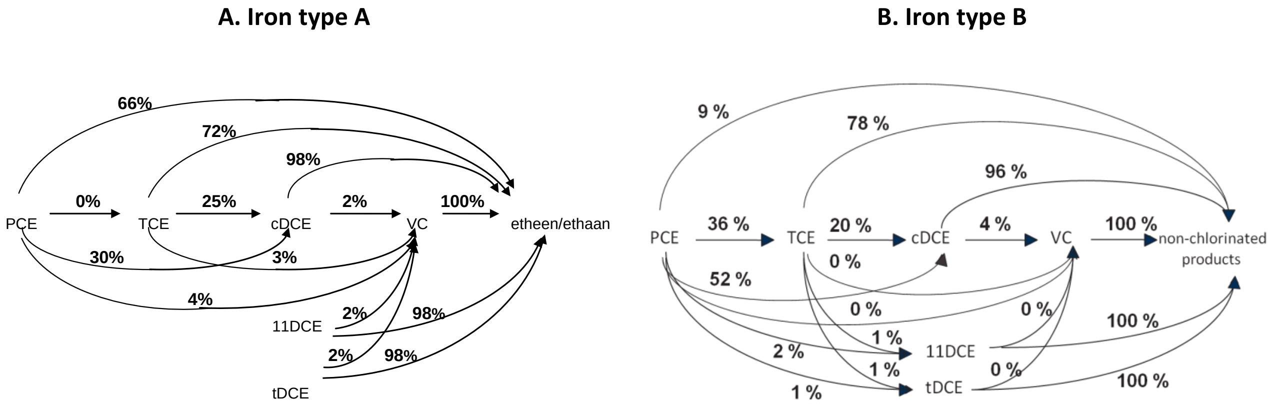


Figure 3. Hypothesized reaction pathways for the degradation of chlorinated ethylenes during reduction by Fe^0. Reactions 1, 3, 4, 5, 7, 9, 14, 17 and 18 correspond to hydrogenolysis reactions, while reactions 2, 6, 8 and 10 are reductive *β*-elimination reactions. Reaction 11 proceeds via reductive *α*-elimination and reactions 13, 15, 16 and 19 are hydrogenation reactions (Arnold and Roberts, 2000).


A. Iron type A

B. Iron type B

Figure 4 Example of a molar conversion model (iron dependent; Source: VITO)

Figure 4.A displays a molar conversion for a type of ZVI for which the primary degradation pathway occurs via reductive *β*-elimination accounting for 66% of tetrachloroethylene (PCE) removal and 72% for trichloroethylene (TCE) removal. This pathway involves a two-electron transfer in which chlorine atoms on adjacent carbons are released as chloride ions, with the concomitant formation of a triple bond (Farrel *et al*., 2000). PCE and TCE are transformed directly to ethane via the production of short-lived intermediates such as chloroacetylene and acetylene (Arnold and Roberts, 2000). Hydrogenolysis of PCE and TCE results into the formation of the

partially dechlorinated products including dichloroethylene (DCE) and the more toxic vinyl chloride (VC), accounting in the example for a low percentage of the total degradation products. An advantage of ZVI types that follow predominantly the β-elimation pathway is that only limited amounts of lower chlorinated (and toxic) ethenes are formed. A disadvantage that has been observed is that some of these ZVI-types only slowly degrade the lower chlorinated compounds that are already presented in the contaminated groundwater. Figure 4.B illustrates a significantly different reaction pathway for another iron type.

2.4 REACTION RATES

Reported dechlorination rates, however, can vary widely among different studies, due to differences in the used iron, solution chemistries and iron pretreatments (Farrel *et al.*, 2000).

Redutive dechlorination of pollutants by the ZVI is often described by a pseudo-first-order model (Johnson et al., 1996):

$$C = C_0 e^{-kt} \qquad \text{(equation 1)}$$

where C is the concentration at any time and C_0 is the initial concentration of parent compound (mg L^{-1}), k is the pseudo-first-order rate constant (h^{-1}) and t (h) is the reaction time. The natural logarithmic transformation of eq. (7) yields a linear equation with the first-order rate constant k_{obs} as slope:

$$\ln (C / C_0) = - k * t \qquad \text{(equation 2)}$$

Half lives (times needed to reduce the pollutant concentration by a factor 2) can be calculated as:

$$t_{1/2} = \ln (2)/k = 0.693/k \qquad \text{(equation 3)}$$

Mass normalized rate constants (k_M, L g^{-1} h^{-1}) and specific surface area normalized rate constants (k_{SA}, L m^{-2} h^{-1}) can be calculated using the following relationship (Johnson et al., 1996; Nurmi et al., 2005):

$$k = k_M \rho_M = k_{SA} a_s \rho_M = k_{SA} \rho_a \qquad \text{(equation 4)}$$

with a_s as the specific surface area of iron based particles (m^2 g^{-1}), ρ_M as the mass concentration of the iron based particles (g L^{-1}) and ρ_a as the surface area concentration of iron based particles (m^2 L^{-1} of solution).

An overview of half live and degradation rates from literature and AQUAREHAB data is given in Table 2.

Table 2 Overview of half-lives for degradation of CAHs by granular ZVI.

Component	*Half lives $t_{1/2}$ (h)*
Methanes:	
CarbonTetrachloride (PCM)	*0.31 – 0.85 (a)*
Trichloromethane (TCM)	*4.8 (a)*
Ethanes:	
1,1,1-Trichloroethane (111TCA)	*1.7 – 4.1(a)*
Ethenes:	
Tetrachloroethene	*2.1 – 10.8 (a); 3.2 (c); 1.9 (e)*
Trichloroethene	*1.1 – 4.6 (a); 2.4 (c); 2.8 (d); 2.0 – 4.1 (e); 6.8 – 11.6 (f)*
1,1-dichloroethene	*3.74[l]; 15.2 (d)*
trans 1,2-dichloroethene	*4.9 (a); 6.9 (c); 7.6 (d)*
cis 1,2-dichloroethene	*10.8 – 33.9 (a); 47.6 (c); 54 (e)*
Vinylchloride	*10.8 – 12.3 (a); 4.7 (c)*
Others:	
1,2,3-Trichloropropane	*24.0 (b)*
1,2 dichloropropane	*4.5 (b)*
1,3-dichloropropane	

(a) Not published data Univ. Waterloo (Canada);(Gillham, 1996). (b) Focht (1994); (c) Sivavec and Horney (1995); (d) Mackenzie et al. (1995); (e) AQUAREHAB-Vito, 20°C; (f) Vito, 12°C.

2.5 DEVELOPMENT STAGE OF THE TECHNOLOGY

The ZVI-barrier technology is an **available and proven technology** with more than 100 application in the field. Some details for a number of ZVI-barriers is given in Table 3.

The acceptability is good in a number of European countries like UK, Belgium, The Netherlands, Denmark, Germany, ...), but not yet applied and approved in other countries and areas where soil & groundwater remediation is starting or focussed on the classical dig&dump and pump&treat approaches.

Table 3: Examples of ZVI-barriers implemented in the field

Site	*Canacian FB Bordon Canada*	*Industrial facility new Jersey USA*	*Industrial site (Intersil) Sunnyvale, Californie, USA*	*Industrial facility Upstate New York USA*	*Industrial site Moutain view, Californie USA*
Scale & Barrier type	*Pilot Continuous barrier*	*Pilot in-situ vessel (downward flow)*	*Full scale 2 Funnels & 1 gate*	*Pilot 2 Funnels& 1 gate*	*Full scale Continuous barrier*
Installation date	*6/1991*	*11/1994*	*12/94-1/1995*	*5/1995*	*9/1995*
Composition filling material	*iron (22 w%)+ sand (78 w%)*	*100% iron*	*220 ton iron*	*iron*	*90 ton iron*
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	*D: 10 m L: 5.5 m T: 1.6 m*	*diam. fiberglass tank: 2.44m H tank: 2.44 m*	*D: 6 m (3.4-6.1 m-mv) H: 3.4 m L funnels: 67 m + 76 m L gate: 11 m T: 1.2 m*	*D: 4.6 m L funnels: 4.6 m + 4.6 m*	*D: 4.6-3.1m-mv H: 1.5 m L: 13.4 m T: 1.4 m*
Pollutants	*TCE: 250 mg/l PCE 43 mg/l*	*PCE: 1200-4000 µg/l TCE: 425-450 µg/L*	*TCE: 200 µg/l CDCE: 1400 µg/l 500 µg/l VC freon-113*	*TCE: 30-380 µg/l VC: 4.9-7.1 µg/l CDCE: 98-550 µg/l 111TCA: 3.2-13 µg/l*	*TCE: tot 1 mg/l CDCE: 5-10 mg/l VC: 5-50 µg/l*
Installation method	*'Clamshell excavated trench'*		*Gate: trench box Funnel: soil-bentonite slurry*	*Gate: trench box Funnel: 'sealable sheet pile'*	*Excavation and backfilling using a Backhoe*
Location monitoring wells	*2 wells upstream 6 wells in the barrier 3 wells downstream*	*Side ports along the reactor*	*In downstream 10cm part of ZVI barrier*	*Downstream ZVI, in gravel zone*	*In downstream section of ZVI barrier*
Costs of filling material	*NA*	*NA*	*170 000 US$ (650 US$/ton)*	*30 000 US$ (650 US$/ton)*	*60 000 US$ (650 US$/ton)*
Installation costs	*NA*	*NA*	*600 000 US$*	*200 000 US$*	
Total costs	*NA*	*NA*	*770 000 US$*	*NA*	*100 000 US$*
Information source	*Gavaskar et al., 1998*	*Gavaskar et al., 1998*	*Gavaskar et al., 1998*	*Gavaskar et al., 1998*	*Gavaskar et al., 1998*

NA = Not available

Table 3: Examples of ZVI-barriers implemented in the field (cont. 1)

Site	Electronic company Belfast Northern-Ireland	Industrial site Coffeyville, Kansas USA	Lowry AFB Denver, Colorado USA	Moffett Federal Airfield, Californie USA	USCG Elizabeth City, N-Carolina USA
Scale & Barrier type	Full scale funnel & 1 gate	Large scale 2 funnels & 1 gate	Pilot 1 Funnel & 1 gate	Pilot 1 Funnel & 1 gate	Large scale Continuous barrier
Installation date	12/1995	1/1996	11-12/1995	4/1996	6/1996
Composition filling material	15 ton iron	70 ton iron	Iron	Iron	450 ton iron
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	D: 12.2 m L funnels: 30 m + 30 m H in vessel: 5 m T: 5 m in vessel	D: 5.2-8.5 m-mv H: 3.3 m L funnels: 149 m + 149 m L gate: 6.1 m T: 1 m	D: 5.5 m	D: 7.6 m L gate: 3.4 m T gate: 1.8 m	D: 7.6 m (0.9 – 7.9 m-mv) H: +/- 7 m L: 45.6 m T: 0.6 m
Pollutants	TCE: 300 mg/l 112TCA: 200 µg/l cDCE: 2 mg/l Traces other CAHs	TCE: 400 µg/l	TCE: 1000 µg/l VC: 251 µg/l CDCE: 250 µg/l	TCE: > 20 mg/l PCE: 500 µg/l	TCE: up to 16 mg/l Cr: 6-10 mg/l
Installation method	Cylindrical ’ vessel’ Funnels: slurry barriers	Funnel: soil bentonite slurry	Gate: trenched Funnels: ‘sealable-joint sheet pile’	Gate: trenched Funnels: ‘sealable-joint sheet pile’	Continuous trencher
Location monitoring Wells	Different heights in ‘vessel’	At different locations in the ZVI-barrier	At different locations in the ZVI-barrier	At different locations in the ZVI-barrier	Upstream and downstream of the ZVI-barrier
Costs of filling material	20 000 US$ (450 US$/ton)	50 000 US$ (650 US$/ton)	32 500 US$ (650 US$/ton)		171 000 US$ (380 US$/ton)
Installation costs	315 000 US$	350 000 US$	NA	NA	NA
Total costs	375 000 US$	400 000 US$	137 500 US$	380 000 US$	500 000 US$
Information source	Gavaskar et al., 1998	Gavaskar et al., 1998	Gavaskar et al., 1998	Gavaskar et al., 1998	Gavaskar et al., 1998
	Long term monitoring data ITRC 2011				Long term monitoring data ITRC 2011

NA = Not available

Table 3: Examples of ZVI-barriers implemented in the field (cont. 2)

Site	Denver Federal Center Lakewood, Colorado USA	Somersworth sanitary Landfill, New Hampshire USA	Military reservation Massachusetts USA	Alameda Naval Air Station, California USA	Edenkoben Germany
Scale & Barrier type	Large scale 1 funnel & 4 gates	Pilot Funnel & 1 gate	Pilot 2 parallel continuous barrier	Pilot 1 Funnel & 1 serial gate	Pilot: Funnel + 1 gate large scale: funnel + 6 gates
Installation date	10/1996	10-11/1996	11/1996	11-12/1996	1/1998 2/2001
Composition filling material	iron	Iron	Ni-plated iron	Iron + aerobic O_2-sparging zone	Granular iron
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	D: 6.1 m (3.4 - 4.6 tot 6.1-7.6 m-mv) H: 3.4 – 4.6 m L funnels total: 316 m L gates: 4 x 12.2 m T: 0.6 – 1.8 m	D: 12.2-13.7 m L funnels total: 3.4 m Gate: 2.4 m diam.	L: 7.6 m D: 24-34mt bgs distance between barrier: 7.6 m T: 5 cm	D: 4.6 m	Pilot: L 30m; D: 15 m Large scale: L 440 m, D: 15 m
Pollutants	TCE: 700 µg/l DCE: 700 µg/l VC: 15 µg/l	TCE: 310 µg/l PCE: 3.7 µg/l VC: 387 µg/l CDCE: 565 µg/l	PCE: 5-150 µg/l TCE: 5-150 µg/L	cDCE VC BTEX 1-5 mg/l	cDCE; 111TCA, TCE, PCE
Installation method	Funnel: 'sealable joint sheet pilings'	Gate: Caisson Funnels: 'slurry wand	Hydraulic fracturing technique (overlapping vertical planes)	Gate: trench box Funnels: 'sheet pile'	Gate: 2 vertical flowthrough chambers
Location monitoring Wells	NA	At different locations in the ZVI-barrier	23 monitoring wells	At different locations in the ZVI-barrier	NA
Costs of filling material	NA	100 000 US$	NA	375 US$/ton	NA
Installation costs	NA	175 000 US$	NA	NA	NA
Total costs	1000 000 US$	275 000 US$	500 000 US$ (for 2 years)	NA	350 000 euro/ 1 750 000 euro
Information source		Gavaskar et al., 1998	Gavaskar et al., 1998	ITRC. 2005	Birke et al., 2003

NA = Not available

Table 3: Examples of ZVI-barriers implemented in the field (cont. 3)

Site	*Rheine Germany*	*Tübingen Germany*	*Copenhagen Freight Yard Copenhagen, Denmark*	*Rocky Flats Environmental Technology Site (RFETS) in Golden, CO*	*F.E. Warren Air Force Base Spill Site 7 in Cheyenne, WY*
Scale & Barrier type	*Pilot: continuous barrier*	*Large scale funnel & 3 gates*	*Continuous Trench*	*Funnel & gate with In-situ vessels*	*Continuous trenches (3)*
Installation date	*6/1998*	*10/1998*	*1998*	*1998*	*1999*
Composition filling material	*Granular and 'sponge' iron*	*Iron*	*ZVI granular (83 tons)*	*ZVI granular (300 ft³ per vessel)*	*ZVI pure and ZVI mixed with sand*
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	*L: 22.5 m; D: 6 m*	*L: 200 m; D: 10 m*	*L = 50 ft, T = 3 ft, D = 20 ft*	*Funnel 230 ft long with collection trench Gate with 2 vessels*	*L = 568 ft, T = 4 ft, D = 15 ft*
Pollutants	*PCE, TCE, cDCE*	*TCE, cDCE, VC*	*PCE, TCE, DCE, VC*	*PCE, TCE, DCE, VC, CCL4, CHCL3, U*	*TCE, DCE, VC*
Installation method	*Soil borings with overlap*	*NA*	*Excavated with sheet piles*	*Funnel & Gate with 2 reactive vessels*	*Excavated trench box*
Location monitoring Wells	*NA*	*NA*	*3 upgradient, 3 downgradient, 4 within barrier, 1 further downgradient, 1 further upgradient, 2 sentinels aside PRB*	*NA*	NA
Costs of filling material	*NA*	*NA*		*NA*	NA
Installation costs	*NA*	*NA*		*NA*	NA
Total costs	*170 000 euro*	*350 000 euro*	235 000 $	*590 000 $*	2 400 000 $
Information source	*Birke et al., 2003*	*Birke et al., 2003*	*Rtdf.org*	*Rtdf.org*	*Rtdf.org*

NA = Not available

Table 3: Examples of ZVI-barriers implemented in the field (cont. 4)

Site	*Katwijk* *Netherlands*	*Travis Air Force Base* *Fairfield, California* *USA*	*Pease Air Force Base, Site 73* *Porthsmount, New Hampshire* *USA*	*Pease Air Force base, site 49* *New Hamphire* *USA*	*Berbau* *Germany*
Scale & Barrier type	*Continuous trench*	*Pilot scale* *Continuous barrier*	*Full-scale* *Continuous barrier*	*Full scale* *2 continuous barriers*	*Pilot* *Funnel & 3 gates*
Installation date		*6/1999*	*8/1999*	*8/2000*	*9/2001*
Composition filling material	*ZVI granular (125 tons)* *Mix of 20% ZVI and 80% sand over 90 meter and mix of 40% ZVI and 60% sand over 30 meter*	*Iron (303 tons)*	*Iron*	*Iron and Iron/sand*	*Iron*
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	*L = 120 m, T = 30 cm; D = 5,5 m*	*L 10.7 m* *D: 6-12 m bgs* *T: 1.5 m*	*L: 46 m* *D: 0.6 - 10 m bgs* *T: 0.76 m*	*barrier 1: L: 46 m; D: 4.6 m; T: 0.76 m* *barrier 2: L: 11.6 m; D: 4.6 m; T: 1.8 m*	*NA*
Pollutants	*TCE, DCE, VC*	*TCE, cDCE*	*TCE, DCE, VC*	*TCE, DCE, VC*	*TCE (high concentrations)*
Installation method	*Continuous trencher*	*Jetting (using guar gum)*	*Biodegradable slurry*	*Biodegradable slurry*	*Hydro-installation*
Location monitoring Wells	2 in source, 3 in plume, 4 behind PRB, 2 lateral, 1 upgradient, 6 in PRB	NA	NA	NA	*NA*
Costs of filling material		*NA*	*NA*	*NA*	*NA*
Installation costs		*NA*	*NA*	*NA*	*NA*
Total costs	183 000 €	*NA*	*NA*	*NA*	*120 000 euro*
Information source	*SKB Bodembreed 3 symposium*	*IRTC, 2005*	*IRTC, 2005*	*IRTC, 2005*	*Birke et al., 2003*

NA = Not available

Table 3: Examples of ZVI-barriers implemented in the field (cont. 5)

Site	*Case #26* *Vermont* *USA*	*Oberursel* *Germany*	*Amersfoort* *Netherlands*	*West-Flanders* *Belgium*	*Mohawk* *Sunnyvale, Czalifornia* *USA*
Scale & Barrier type	*Ful scale* *Continuous barrier*	*Large scale* *Funnel & 1 gate*	*large scale* *Funnel & disconnected gate (270 m downstream of funnel)*	*Large scale* *Funnel & 3 gates*	*Full scale* *Continuous barrier*
Installation date	*9/2001*	*1/2002*	*5/2002*	*9/2002*	*2003*
Composition filling material	*Iron-sand mixture*	*Iron*	*Granular iron*	*Bimetallic iron Pd/Fe^0*	*Iron*
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	*L: 76 m* *D: 4.6 m* *T:1m*	*L:175 m; D: 4-17 m*	*L: 170 m* *D: 13-15 m* *Gate: 200 m^3*	*L: 345 m* *D: 13 m*	*L: 2013 m* *D: 6-10 m*
Pollutants	*TCE, PCE, cDCE*	*VOCls*	*PCE: 953 µg/l* *TCE: 1262 µg/l* *cDCE: 928 µg/l*	*PCE: 198 µg/l* *TCE: 99 mg/l* *111TCA: 164 µg/l* *cDCE: 1623 µg/l* *tDCE: 65 µg/l*	*CAHs*
Installation method	*Excavation and backfill*	*NA*	*Gate: In situ reactor with different compartments*	*Gate: in situ reactors*	*Biopolymer slurry wall*
Location monitoring wells	NA	*NA*	*NA*	*NA*	NA
Costs of filling material	*NA*	*NA*	*NA*	*NA*	NA
Installation costs	*NA*	*NA*	*NA*	*NA*	NA
Totale costs	*NA*	*NA*	*NA*	*NA*	NA
Information source	*IRTC, 2005*	*Birke et al., 2003*	*Weythingh et al., 2003* *Bastiaens et al., 2002* *personal communication*	*Geeraert et al., 2003*	*ITRC, 2005*
					Long term monitoring data ITRC 2011

NA = Not available;

Table 3: Examples of ZVI-barriers implemented in the field (cont. 6)

Site	Site CC Antwerpen Belgium	Offutt Air Force Base, Hardfill#2 Nebraska USA	Offutt Air Force Base Nebraska USA	Site A Antwerp Belgium	Vandenberg AFB site 15 California US
Scale & Barrier type	Large scale 3 Funnel & 2 gates	Full scle Continuous barrier	Full scale	large scale continuous barrier (with 1 impermeable part)	PRB 2x 50 m long by injection
Installation date	10/2003	11/2003	3/2004	8/2005	2009
Composition filling material	Iron & sand	Iron & sand	Iron	Iron & sand mixture	BOS 100 (ZVI coated with activated carbon) amended with guar gum slurry
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	Funnel: L: 95m+8m+35 m D: 5 m Gate: L: 25m +25 m D: 5 m	L:106 m D: up to 10.6 m bgs T: 0.46 m	L: 76 m D: up to 1.6 m bgs T: 0.45 m	L:220 m D: 4.5-6 m T: 30 cm	PRB1: L 50 ft, T 5 ft, D 71 ft PRB2: L 50 ft, T 5 ft, D 50 ft
Pollutants	TCE: 250 µg/l cDCE: 6000 µg/l VC: 180 µg/l	TCE	TCE	TCE cDCE	TCE, DCE, VC
Installation method	Gate: Continuous trenching Funnel: slurry wall	Continuous trencher equipment	Continuous trencher equipment	Continuous trenching	Deep soil mixing
Location monitoring wells	NA	NA	NA	at different distances upstream and downstream of ZVI-barrier	NA
Costs of filling material	NA	NA	NA	NA	NA
Installation costs	317 000 euro	NA	NA	290 000 euro	NA
Totale costs	515 000 euro *	NA	NA	470 000 euro*	NA
Information source	personal communication	ITRC, 2005	ITRC, 2005	personal communication	ITRC 2011

NA = Not available; * comprising 30 year monitoring costs (no renewal of the ZVI)

Table 3: Examples of ZVI-barriers implemented in the field (cont. 7)

Site	*Soil mixing barrier Belgium*
Scale & Barrier type	*Pilot scale – source zone treatment*
Installation date	*2013*
Composition filling material	*ZVI (3 ton)*
Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)	*2 pilots*
Pollutants	*chlorinated ethenes*
Installation method	*Soil mixing*
Location monitoring wells	NA
Costs of filling material	NA
Installation costs	NA
Totale costs	NA
Information source	*Personal communication*

NA = Not available

2.6 APPLICABILITY AND BOUNDARY CONDITIONS OF THE TECHNOLOGY

The ZVI-barrier technology is recommended under the following conditions:

- The pollutants present in the groundwater are degradable by ZVI, and their degradation does not result in accumulation of harmful metabolites.
- Pollutants are present in the dissolved phase.
- The depth of the groundwater contaminant plume is preferably not located deeper than 8 - 12 m bgs. For deeper plumes (12-30 m bgs), the installation cost will increase significantly, and the technical possibilities for installing a barrier need to be evaluated.
- With respect to the hydrogeological characteristics of the site:
  - The groundwater flow direction needs to be known and relatively stable during the year.
  - The presence of a shallow impermeable layer sealing the bottom of the contamination plume is an advantage for the ZVI-barrier technology as it prevents contaminants passing underneath the ZVI-barrier. Also when no low permeability layer is present, ZVI-barriers can be applicable when this aspect is taken into account during the feasibility and design phase.
  - In principle, the ZVI-barrier technology is applicable for a wide range of groundwater flow velocities. For higher flow velocity, larger dimensions of the ZVI-barrier are generally needed (to ensure sufficient contact time) and the longevity of the system will be lower, all resulting in higher costs.
  - The hydraulic conductivity of the barrier needs to be equal or higher than the permeability of the surrounding aquifer.
- The site is accessible for the installation of the barrier, which implies the excavation of aquifer trench of soil and refilling it with ZVI. After the installation, there are no above ground remainings of the ZVI-barrier. The area needs to stay accessible for monitoring and potentially for renewal of the ZVI-filling. ZVI-barriers are often installed along routes and under parking areas.
- The geochemical characteristics of the groundwater are a point of attention towards formation of precipitates in the ZVI-barrier, and consequently clogging of the system over time. Therefore, for ZVI-barrier application the concentration of calcium, magnesium, silicon, manganese and (bi)carbonate are preferably not high (see DL4.3 part A.2). Generally, the lower the concentration of these elements, the longer the ZVI-barrier is expected to be functioning. Note that the groundwater velocity is determining how much water is passing through the barrier during a certain period, and how much precipitates can be formed in the barrier.

The use of ZVI-barriers is not recommended and or possible:

- For pollutants that have not been shown to be degradable, or that are transformed in harmful reaction products that are not degraded adequately by the ZVI.
- For sites where free product is expected to migrate into the barrier.
- For sites with groundwater contaminations situated in deep subsurface (> 30 m bgs), due to technical and budget issues.
- High oxygen concentrations in the groundwater will lead to aerobic corrosion of the ZVI-barrier, and potentially clogging of the ZVI-barrier at longer term. The life-time of the ZVI-barrier system is expected to decrease when oxygen is present in elevated concentrations.
- For site with high nitrate concentration in the groundwater

2.7 SECONDARY EFFECTS

2.7.1 Positive effects

During anaerobic corrosion of ZVI, **hydrogen** is generated as shown in Figure 5. This hydrogen can stimulate micro-organisms, like anaerobic CAH-degrading and sulphate reducing species. Within the AQUAREHAB project it was proven that hydrogen can serve as sole electron donor for anaerobic biodegradation of chlorinated compounds (Figure 5).

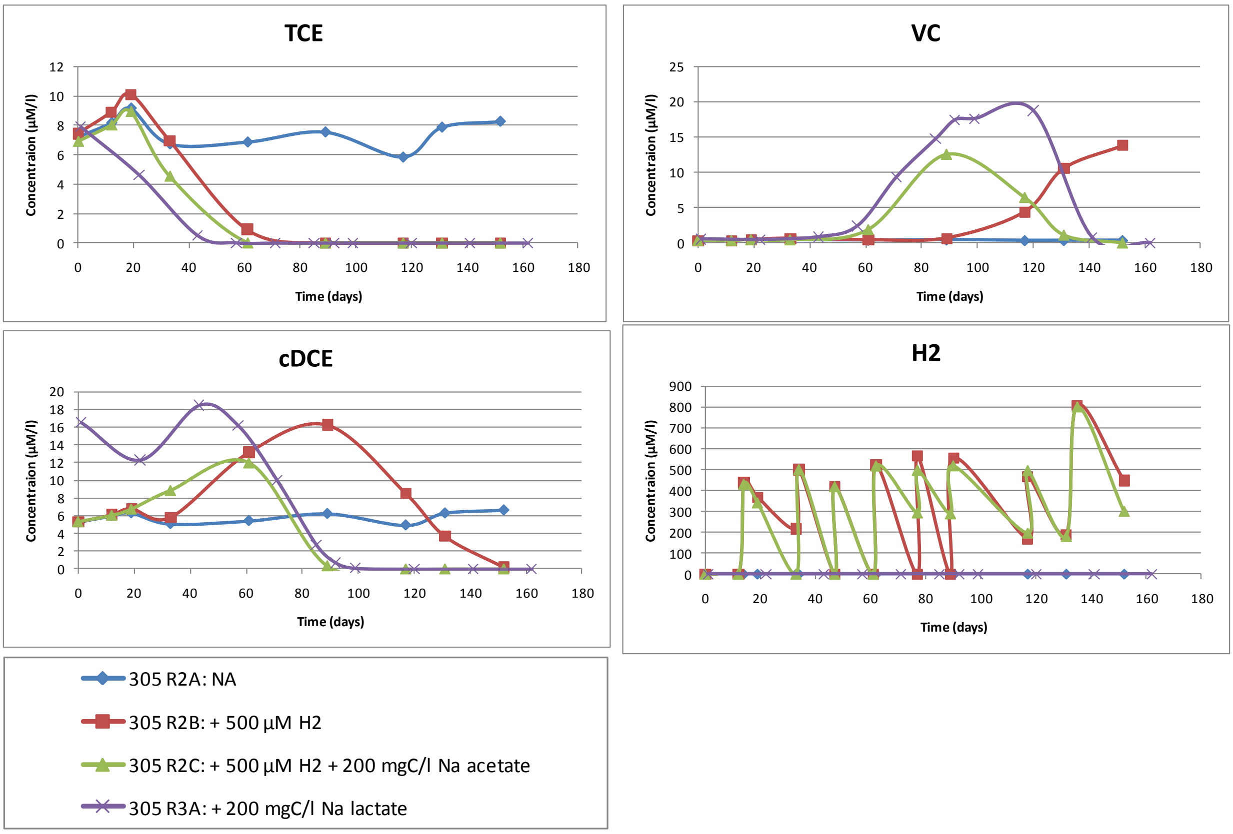


Figure 5: Use of hydrogen as sole electron donor for CAH-biodegradation (red curve) in lab scale batch degradation tests (Source: VITO) – NA, natural attenuation (no electron donor addition).

In addition, the **reduced redox potential** (ORP) that is created by the ZVI, also stimulates anaerobic bacteria like CAH-degrading and sulphate reducing species.

The reduced ORP and stimulation by hydrogen of sulphate reducing bacteria, creates conditions where pollutants like **metals can be removed** from the groundwater by in-situ bioprecipitation as insoluble metal sulfides, besides via direct immobilisation on the ZVI surface. It has been shown that the presence of ZVI does not only improve in-situ bioprecipitation processes, but it is also necessary to initiate these processes under some conditions (Diels et al., 2002; Kumar et al, 201x). In addition, indications were provided that the metal precipitates were more stable when ZVI was present (Kumar et al., submitted).

2.7.2 Negative secondary effects

Oxidation of ZVI by oxygen in the groundwater or mineral precipitates or buildup of hydrogen gas can decrease the hydraulic permeability of the ZVI-system, and alter the groundwater flow.

2.8 COST OF THE TECHNOLOGY

Cost drivers for ZVI-barriers comprise (1) the dimensions of the barrier (depth, length and thickness), (2) the price of the ZVI, (3) the local situation on the site (accessibility, surroundings buildings, underground constructions, type of subsurface ...), and (4) the local contractor costs (country dependent).

The investment cost of ZVI-barriers are relatively high, while the maintenance costs is nearly non-existing with exception of regeneration of the barrier system and monitoring. Total costs (site investigation, design, implementation, maintenance & monitoring) for ZVI-barriers, considering a 30 years operational time, have been calculated to range between 642 and 2397 keuro (EPA 2002 and calculation made within AQUAREHAB). This comprises costs for 1 renewal of the ZVI-material after 15 years of operation, which may not be needed for each site. The associated relative cost structure is given in Figure 6

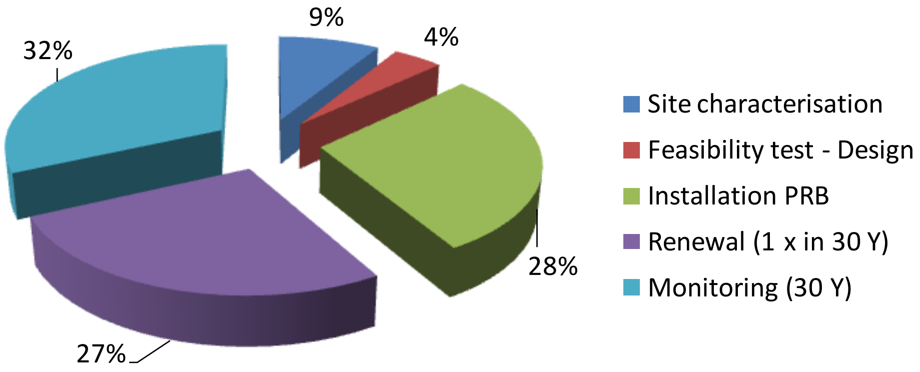


Figure 6 Relative cost structure (%) of ZVI-barriers comprising on operational time period of 30 years. Note, except renewal of the ZVI-material after 15 years and monitoring, no maintenance costs are involved.

Pump and treat technologies do have a lower initial investment cost, but are associated with higher maintenance costs (maintenance of equipment, electricity, discharge of iron sludge, activated carbon, ...). When the operational time is more than 8-10 years, ZVI-barriers are believed to be economically favourable (ITRC report, 2005). Similar conclusions have been reached in other studies on permeable reactive barriers (PRBs). The ITRC report (2005) concludes that, compared with P&T, installations costs of PRBs are higher (driven mainly by length and depth of the barrier), but O&M costs are lower resulting in overall cost savings over the project life if the useful life of the reactive media approaches 10 years. In a USEPA economic analysis of the implementation of PRBs (Powell et al., 2002) implementation costs of 22 PRBs were analyzed and compared, where possible, to P&T systems for similar situations. The cost comparisons indicated that, depending upon the situation, implementing a PRB can either be more or less expensive than a P&T in terms of capital expenditures, but routine operation and maintenance costs favour the PRBs. They state, however, that a major unknown with regard to implementing PRBs is the potential need for replacement or rejuvenation of the reactive media.

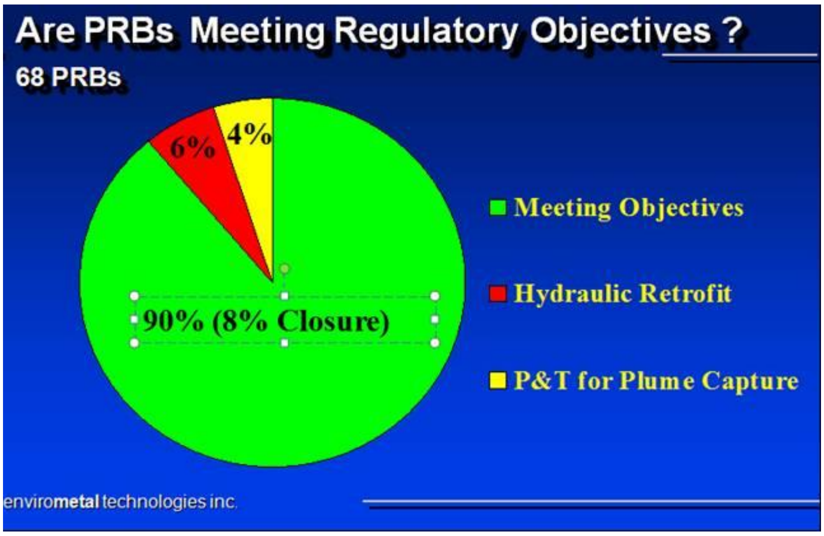
More information on the costs for specific PRB projects can be found in table 3.

2.9 PERFORMANCE OF THE TECHNOLOGY

The **abatement rate** can be defined as the substance concentration after the technology implementation divided by the substance concentration before implementation of the technology. The ZVI-technology aims at an abatement rate close to 100%, which means that flux reduction rate in the ZVI-barrier for the pollutants is almost 100%. The local regulatory limits are determining for the exact targeted abatement rates that need to be taken into account during the barrier design. Note that in general, the ZVI-barrier does not affect the pollution concentration upstream and does not deal with the pollution that is already downstream of the barrier. The barrier does prevent spreading of the upstream pollutants to the area which is located downstream .

Efficiency drivers are (1) the degradation rates of the different pollutants and their breakdown products, which are function of the component and the type of ZVI used, (2) the groundwater flow velocity, (3) the thickness of the barrier (flow through path and contact time) and (4) the inactivation of the ZVI-barrier over time (permeability & reactivity).

Performance. In 2005, ETI (Canada) evaluated the performance of 68 ZVI-barriers and reported that 90% of the systems performed well and did meet with the regulatory objectives. Hydraulic issues seemed to be the major reason for underperforming ZVI-barriers.



2.10 LONGEVITY OF THE TECHNOLOGY

The long-term performance of ZVI-barriers is influenced by (1) the composition of the groundwater, (2) the groundwater velocity through the barrier and (3) the mass, type and grain size of the ZVI used. Generally, the time period during which the technology can be operational without making significant additional investments is at least 10 to 30 years depending on the rate of the flow through the system and the levels of total dissolved solids (ITRC, 2005).

The need for regeneration of the ZVI-barrier is advised to be taken into account for every 15 to 20 years (O'Hannesin, 2003). This regeneration process, may for instance imply the replacement of a part of the ZVI. Regeneration of the reactive material is easier to achieve for funnel & gate barriers than for continuous trench barriers. For F&G-barriers the gates are typically made with in-situ vessels from which the reactive material can be removed in a relatively simple manner.

Case studies ITRC 2011 with respect to longevity issues

> **Elisabeth City (US)**: This PRB is approximately 140 feet long, 2 feet thick, and 22 feet deep and was constructed by continuously trenching (dry) and backfilling with 100% ZVI. Installed in 1996, this PRB site started showing a noticeable decline in down gradient chromium concentrations 2–3 years after installation (Puls 2007). TCE also started to show a noticeable decline 6–7 years after installation. Down gradient concentrations of both chromium and TCE declined below target cleanup levels (100 and 5 µg/L, respectively). There was no evidence of a decline in PRB performance in groundwater sampling conducted 13 years after installation, and down gradient TCE and chromium concentrations continue to remain low compared to pre-installation and up gradient levels.
>
> **The PRB at Monkstown (Ireland)** was installed in 1995 and was monitored consistently for the first 10 years. It is a funnel-and-gate type PRB with an innovative design. The PRB experienced a loss in hydraulic performance and a decrease in plume capture within the first 5 years of operation. The loss in hydraulic performance was due to precipitation build-up within the first several inches of the PRB. This cemented iron material was removed, and again the PRB was put into service; however, within 5 years there was additional loss in hydraulic performance and reactivity due to precipitation. The loss of reactivity and hydraulic conductivity was confirmed by high TCE concentrations down gradient of the PRB during the 10 years of operation.
>
> Another PRB where longevity appeared to be limited is in **Canon City, Colorado**. It is a funnel & gate system designed to remove molybdenum and uranium. Within the first 2 years after installation in 2000, the PRB suffered sharp permeability losses due to precipitate build-up in the first few inches of ZVI near the inlet, as evidenced by groundwater mounding along the up gradient ZVI interface. A decrease in pH inside the PRB indicated that ZVI reactivity had declined. In the third year, mounding grew sharper, and by the fourth year, groundwater was relatively stagnant in the ZVI and was mostly bypassing the PRB.
>
> **At the CAAP, Nebraska**, a continuous reactive barrier (no funnel walls) was installed in 2003 by trenching under a head of guar gum slurry. In approximately 1 year, the permeability and reactivity of the ZVI PRB appeared to be considerably reduced. Two possible causes for the early loss of performance were suggested: (1) heightened microbial activity at the influent end that led to excessive sulfide precipitation or (2) uneven degradation of guar gum slurry that may have penetrated the upgradient aquifer during construction and that promoted excessive microbial activity and sulfide precipitation. This is an example of a construction artefact affecting performance, rather than a gradual decline in reactivity or hydraulics.

A PRB installed at **OU-12, Hill AFB, Utah**, in 2005 for removal of TCE demonstrates the deleterious effects of relatively higher nitrate flux in the groundwater. Nitrate levels in the influent groundwater have fluctuated between 2–13 mg/L. Performance started to decline in less than 1 year after installation. A geochemical study indicated that nitrate may have rapidly passivated the ZVI (see also 2.6).

The field experience at these various sites indicates that PRBs are capable of sustained longer term performance but can be affected by construction artefacts and site-specific geochemistry. It is not always exactly clear which site-related and/or PRB construction-related factors determine the difference between sustained and limited longevity.

3 OVERVIEW OF A GENERIC APPROACH TO DETERMINE APPLICABILITY OF A ZVI-BARRIER FOR A SPECIFIC SITE OR AREA

For a successful application of the ZVI-barrier technologies, the following stepped approach is recommended:

Step 1: site characterisation

A site characterisation is required for checking the application and boundary conditions associated with the technology (see section 2.6). The site characterisation comprises:

- Identification of the type and concentration of pollution that is present
- Determination of the location of the pollution (soil, groundwater, depth, etc.)
- Collection of information on the geology (type of layer, permeability, etc.)
- Collection of hydrological data (groundwater flow direction, groundwater flow velocity, etc.)
- Evaluation of the accessibility of the site

A detailed list of relevant parameters is given in annex 1.A

Step 2: Feasibility test at lab scale

As the implementation of a ZVI-barrier is associated with a significant investment cost, feasibility tests at lab scale are considered to be valuable prior to the installation of the system in the subsurface. Different types of feasibility tests exist.

In case a new type of iron is envisioned or a ZVI-application is considered for non-regular pollutant /groundwater chemistries, it is advised to perform batch degradation experiments in a first step. It needs to be emphasised that not all ZVI-materials do have sufficient degradation capacities towards pollutants such as chlorinated compounds (Velimirovic et al., 2013).

For each ZVI-barrier implementation, lab scale column tests are required to deduce degradation rates of the pollutants and other parameters needed as input parameters for the design of the ZVI-barrier. Groundwater from the site, and the selected ZVI type are used in these tests. Minimal required contact times of the groundwater and the ZVI to meet the regulatory limits are calculated. A time period of 3 to 6 months is generally needed for these tests.

Within the AQUAREHAB project, an improved test procedure has been elaborated which allows to deduce parameters related to the de-activation of the ZVI over time, enabling to estimate the life-time of the barrier for specific sites.

Step 3: Design & dimensioning of pilot/full scale

PRB-barriers can be installed as continuous barriers or funnel-and-gate systems. For the latter, permeable barrier parts (gates) are altered with impermeable barrier parts (funnels) that have the function to funnel the groundwater through the gate.

For an envisioned installation location at the site and the selected barrier type, the required length and depth of the barrier to catch the groundwater contamination plume are determine based on the collected field information. Based on the expected concentration in the influent of the barrier, the groundwater flow velocity, the design parameters deduced from the feasibility test and the regulatory limits, a minimal thickness (contact time) of the ZVI-barrier is deduced. At that time, also the mass of ZVI in the barrier is determined. Often a sand/ZVI mixture is used as barrier filling material, where at least 30-40% of ZVI is recommended.

Step 4: Implementation of the ZVI-barrier

This step comprises the installation of the ZVI-barrier conform to the design parameters. Barriers are installed by excavating the soil, and refilling of the trench with the ZVI-containing barrier material. Different implementation methods have been described and used, comprising continuous trenching and refilling of a stabilised (sheet piles, or guar gum) trench.

Step 5: Monitoring of the ZVI-barrier

A post installation monitoring aims at following the performance of the barrier, where reduced pollutant concentrations downstream of the ZVI-barrier are envisioned. Generally, permanent groundwater monitoring wells are installed upstream and downstream of the ZVI-barrier and are sampled during the whole operation time. Besides chemical parameters, other parameters like the groundwater level are to be followed.

Step 6: Closing the site

Generally, ZVI-barriers are expected to remain in the subsurface once the site is closed. The removal of a ZVI-barrier needs to be considered when (Smith et al., 2003):

- Release of pollutants can be expected at the long term (in case of immobilisation).
- The hydraulic permeability of the barrier has been reduced to an extent that an unacceptable increase in groundwater or redirection of the groundwater flow is created.
- The reactive material itself release hazardous components.

Steps 2 to 5 are elaborated in more detail in the next sections.

Interesting overview documents:

- ITRC, 2011
- **Burmeier, H., Birke, V., Ebert, M., Finkel, M., Rosenau, D., Schad, H. (2006):** Anwendung von Reinigungswänden zur Sanierung von Altlasten. Handlungs-Leitfaden, BMBF Nr. 0271241, 471 S.
- ITRC, 2005
- Carey et al., 2002
- Vidic, 2001
- EPA/540/R-98/501
- EPA/600/R-98/125
- Sutherson, 1997

4 GENERIC APPROACH FOR FEASIBILITY TESTING (STEP 2)

4.1 INTRODUCTION

As the implementation of a ZVI-barrier is associated with a significant investment cost, feasibility tests at lab scale are considered to be valuable prior to the installation of the system in the subsurface. Different types of feasibility tests exist.

- In case a new type of iron is envisioned, it is advised to test its reactivity via batch degradation experiments. It needs to be emphasised that not all ZVI-materials do have degradation capacities towards pollutants such as chlorinated compounds (Velimirovic et al., 2013).
- Also when a ZVI-application is considered for non-regular pollutant types or groundwater chemistries, lab scale feasibility tests are recommended.
- For each ZVI-barrier implementation, a lab scale column feasibility test is needed for deriving design parameters (degradation rates, minimal required retention times, ...). Within the AQUAREHAB project, the test procedure has been further elaborated to derive also parameters for estimating the longevity of the ZVI-systems via numerical modelling.

4.2 EVALUATION OF THE REACTIVITY OF ZVI VIA STANDARDISED BATCH TESTS

Within AQUAREHAB, a standardised test procedure has been elaborated to evaluate and compare the reactivity of ZVI-materials (Velimirovic et al., 2013) which is also applicable for granular ZVIs which are needed for ZVI-barrier applications. Briefly, the standardised test consists of a batch experiment in which ZVI-mediated degradation of a mixture of CAHs (PCE, TCE, cDCE and 1,1,1-TCA, 5 mg L^{-1} each) is followed in time. Glass vials (160 ml) are filled anaerobically with 50 g L-1 of granular ZVI and 100 ml of CAH-containing anaerobic artificially contaminated groundwater. The bottles are capped with butyl/PFTE grey septa and incubated on a shaker at groundwater temperature (12°C in Belgium). A control set without ZVI particles is to be included to reveal non ZVI-mediated losses of the chlorinated compounds (e.g. photodegradation, adsorption, leakage, samplings). In function of time (after 0, 14, 28, 49 and 105 days), the CAH-concentrations are followed as well as pH and ORP. Mass recoveries are made on molar basis (PCE + TCE + cDCE + VC + 1,1,1-TCA + 1,1-dichloroethane (1,1-DCA) + chloroethane (CA) + acetylene + ethene + ethane) to determine if sorption has occurred.

A similar test procedure can be used for evaluating the degradability of other pollutant types, in different types of groundwaters.

First order degradation rate constants and half-lives can be deduced as explained in section 2.4. More details are described in DL5.5. It needs to be emphasised that accumulation of reaction products (like OH^-) result in a degradation rate that is different under in-situ continuous conditions. Therefore, degradation rates determined via batch degradation experiments can be used for reactivity screenings of ZVI-materials, but are not suitable for designing ZVI-systems. For the latter purpose, column tests as described below are commended.

4.3 DETERMINATION OF ZVI-BARRIER DESIGN PARAMETERS FROM LAB SCALE COLUMN TESTS

The aims of the column feasibility test are (1) determination of pollutant degradation rates for the compounds present in the groundwater and their breakdown products, (2) estimation of the required minimal hydraulic retention time to reduce the concentration of all pollutants (and their breakdown products) below the regulatory limits, and (3) obtaining a first indication of the impact of mineral precipitates on the ZVI-process, i.e. on the longer term performance of the ZVI-barrier.

The test procedure consists of the following consecutive phases:

- Phase A: Sampling of representative groundwater from the site where a ZVI-barrier application is considered (see section 4.3.1)
- Phase B: Set-up of a lab scale experiment & monitoring (see section 4.3.2)
- Phase C: Data processing (see section 4.4)

The different phases are described briefly below and more details are given in Annex A.3.

4.3.1 Sampling of groundwater from the site (Phase A)

For the feasibility test, groundwater is used from the site where application of a ZVI-barrier is considered. The groundwater should be representative for the water that is expected to enter the envisioned iron barrier. Groundwater is to be sampled with minimal volatilisation of the pollutants present, which implies use of glass bottles that are completely filled without headspace (detailed guidelines are given in Annex A.2). Exposure of groundwater samples to atmospheric oxygen during sampling and sample transport should be avoided. The glass bottles are stored at 4°C until use.

Required volumes of water: 20-40L for short-term evaluation; 40-80L for long-term evaluation. Preferably, groundwater for the column test is to be collected from a single field visit to minimise fluctuation of the pollutant concentrations.

The following parameters are recommended to be analysed: Ca^{2+}, Mg^{2+}, Fe^{2+}/Fe^{3+}, $Mn^{2+,}$ (bi)carbonate, sulphate, nitrate, pH, ORP, CAHs.

Figure 7 Sampling of groundwater at the field.

4.3.2 Experimental set-up of a lab scale column test (Phase B)

The experiments are typically performed in at least 0.5 m long columns. These have intermediate sampling points for instance at 5 cm, 10 cm, 15 cm, 20 cm, 30 cm, 40 cm from the inlet) for sampling of groundwater. The columns are homogeneously filled with ZVI or a ZVI/sand mixture. From a Teflon bag, groundwater is slowly pumped through the column (from bottom to top) to saturate the pores (see Figure 8).

Once saturated, the desired groundwater flow velocity can be set. This velocity is based on the flow velocity in the field. In case of very slow field flows, increased flow velocities can be used to perform the test within a reasonable time frame, taken into account the assumption explained in annex A.3.

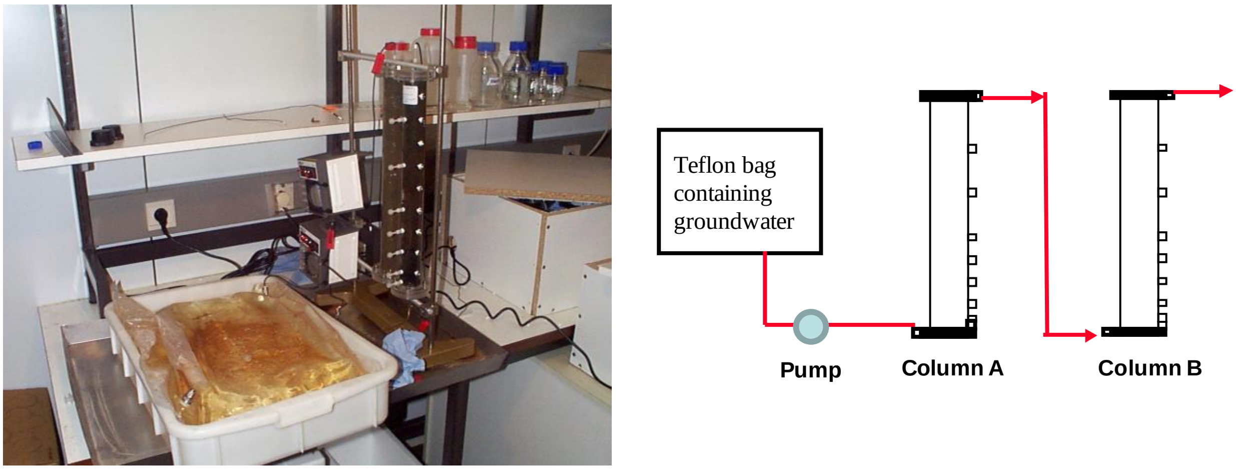


Figure 8: Experimental set-up

The following parameters need to be determined before the start of the experiment:

Characteristics of the ZVI—material:	
Specific surface area of the iron	X m^2/g
Experimental parameters:	
Flow velocity of the groundwater	X cm/day
Hydraulic retention time	X hours
Pore volume	X ml
Porosity	X
Bulk density	X g/cm^3
Iron/liquid-ratio	X g: 1 ml
Surface area of iron per volume of liquid	X m^2 : 1 ml
Temperature	X °C

The column experiment is being performed at field groundwater temperature (for instance typically 12°C in Belgium).

Two operational phases can be distinguished.

- **Phase 1 of the test (first 40-50 pore volumes for 0,5 m of column length)** is considered the short-term test. Here the rate at which groundwater is pumped through the column is to be set as close as possible to groundwater flow velocity in the field. During the last 10-20 pore volumes of this test phase the column is considered closest to steady state, and most sampling campaigns are to be scheduled in this period. At least the following samplings and analyses are recommended during this period:
    - 3 pH-profiles & ORP profile
    - 2 geochemical concentration profiles (Ca^{2+}, Mg^{2+}, Fe^{2+}/Fe^{3+}, Mn, (bi)carbonate, and sulphate) – established between 30 & 50 PV, with at least 10 PV difference
    - 4-5 steady state concentration profiles for CAHs
    - Hydrogen production at the effluent (in function of time)
    - (Li tracer test)
- **In phase 2 of the test (> 40-50 pore volumes for 0,5 m column length)** a larger flow velocity is applied to study the longer-term iron deactivation of the ZVI in a shorter experimental time. The following samplings and analyses are recommended minimally:
    - 3 pH-profiles & ORP profile
    - 5 concentration profiles of CAHs
    - 0-1 geochemical concentration profile
    - Hydrogen production at the effluent (in function of time)
    - (Li tracer test)

4.4 DATA PROCESSING (PHASE C)

Based on the chemical analyses mentioned above, concentration profiles can be prepared for each of the pollutants (and breakdown products). The concentration profiles at 'steady state' (=equilibrium between transport and degradation of the pollutants) are used to calculate degradation rates. These calculations can be performed in different ways:

Method 1: Determination of pollutant degradation rates by linear regression of LN-transformed data based on a pseudo first order degradation kinetic as illustrated in Figure 9.

Eq. 1 can be transformed into the equation $C = C_0 e^{-kt}$ (eq. 2) and $\ln (C/C_0) = -kt$ (eq. 3)

With C_0 = pollutant concentration at start ($t = t_0$)
C = pollutant concentration at time t
k = First order degradation rate constants (h^{-1})

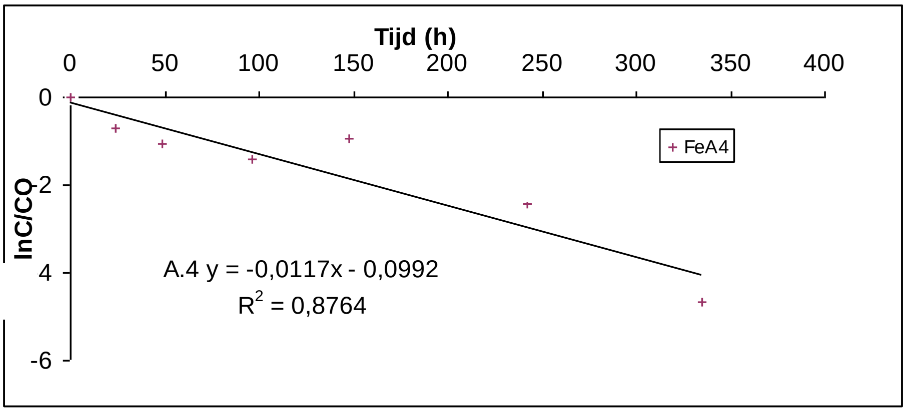


Figure 9: Determination of K-value (k = 0.0117 h^{-1}) via linear regression of LN-transformed data (pollutant concentration in function of contact time in the column = concentration profile at 1 time point)

Method 2: Degradation rate constants can also be determined via fitting of the concentration profiles based on a pseudo first order degradation kinetic. During this fitting process, also molar conversion factors (f-values) need to be estimated. These factors are related with the degradation pathways (mostly a combination of degradation pathways) followed, which differ significantly between particles and the geochemical conditions as described in section 2.3. Figure 4 displays an example of a molar conversion model.
More details on the formulas behind the fitting are given in annex A.3.

Method 3 & 4: Within AQUAREHAB methodological protocols were elaborated for estimating different model parameters (iron corrosion rates, Mineral precipitation rates, pollutant degradation rates and iron deactivation parameters) from the results of the column study. These are described below in section 5.2.

5 GENERIC APPROACH TO DESIGN A ZVI-BARRIER (STEP 3)

5.1 INTRODUCTION

Based on site information collected in step 1 (see section 3) a conceptual model of the pollution at the site needs to be prepared and used as a basis for the ZVI-barrier design.

- At first, it is advised to check the conceptual model with the application area and boundary conditions of ZVI-barrier technology (see section 2.6).
- If the site conditions are still within the application area, a next action is to list potential locations for implementing the ZVI-barrier to control further migration of the contamination.

Before each ZVI-barrier implementation, a column feasibility test is needed for deriving design parameters (degradation rates, minimal required retention times, ...) as described in 4.3.2 and 4.4. Based on results from the column test and the site information, a PRB-concept can be selected and it's dimensions can be elaborated.

5.2 PARAMETER ESTIMATION

5.2.1 Methodology

As explained before, within AQUAREHAB methodological protocols were elaborated for estimating model parameters (iron corrosion rates, mineral precipitation rates, pollutant degradation rates and iron deactivation parameters) from the column feasibility tests. To estimate these additional parameters, the feasibility test procedure was extended with some measurements. The methodology described below is more complex in comparison with method 1 & 2 (see 4.4) but generated additional and more reliable results.

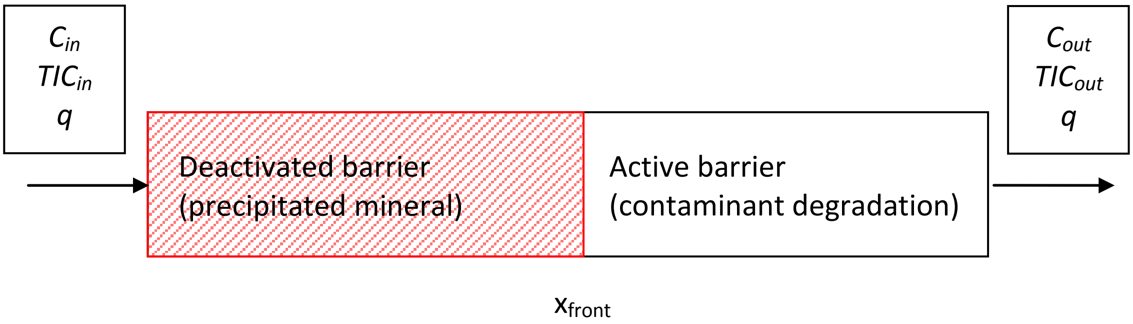
Method 3: The protocol relies on an automatic parameter estimation tool, such as PEST (Doherty, 2007) to perform model calibration. During this process parameter values are automatically adjusted to obtain a good fit between simulated and measured concentration profiles. The "fit" between simulated and measured concentrations is typically quantified by the total sum of the squared deviations between all laboratory measurements and their corresponding model-predicted values; these deviations should be as small as possible.

The methodology consists of three consecutive steps:

- Step 1: (manual) estimation of initial parameter values.
- Step 2: (automatic) estimation of geochemical parameters.
- Step 3: (automatic) estimation of pollutant degradation and iron deactivation parameters.

The steps are elaborated in detail in Annex A.3.

Method 4: The estimation procedure described above is quite elaborate and may require significant technical input. A simpler approach, based on a simplified model to estimate the PRB longevity under field conditions was explored within WP7 (DL7.4). The input parameters required by the simplified model are estimated on a short-term column experiment (phase 1 only) using the methodology proposed above. This simplified model assumes that a mineral front develops in the PRB under low flow velocities (field conditions) and that before the front all the reactive surface area is depleted. Hence, only behind the deactivation front contaminants are actively degraded. The mineral front advances with the aging of the barrier according to the formula reported in Figure 10.



$$\frac{dx_{front}}{dt} = \frac{(TIC_{in} - TIC_{out}) \cdot \phi \cdot 1000 \cdot mv \cdot q}{S_0 \cdot T_c}$$

Figure 10. Simplified model conceptualization. *C* is the contaminant concentration (mol L^{-1}), *TIC* is the total inorganic carbon concentration (mol L^{-1}), *q* is the darcy velocity (m_{bulk} s^{-1}), ϕ is the porosity (-), *mv* is the average mineral volume of carbonate minerals ($m^3_{mineral}$ mol^{-1}), S_0 is the reactive surface ($m^2_{reactive\ surface}$ m^{-3}_{bulk}) and *Tc* is the thickness parameter ($m^3_{mineral}$ $m^{-2}_{reactive\ surface}$).

The main advantage of using the simplified model instead of the full numerical model is that the barrier longevity under different conditions (e.g. groundwater velocities, carbonate concentrations) and design parameters (e.g. barrier thickness) can be much more rapidly assessed. Hence, it may provide a useful screening and design tool. However, the required input parameters need to be available. In case input from more complex ‘estimation procedure (method 3) is required as input, the added value of the simplified model can be questioned.

5.2.2 Example model output (method 3, phase C)

Figure 11 shows examples of simulated and measured concentration profiles for an iron barrier column test, after automatic calibration of the model (Table 4). to fit observed concentrations using the method 3 outlined above. The methodology was applied to two different deactivation models (see DL7.2). In table 2 the calibrated parameters are reported together with the estimated confidence interval.

Table 4: Technology model for ZVI-barriers elaborated within AQAUREHAB

Technology Model	Costs
Codes used	Column scale: PHAST/MIN3P/FREEQC Field scale: RT3D
Model input	Topography information and soil information, groundwater flow field, contaminant and inorganic concentrations, degradation rates, corrosion rates,
Model output	Evolution of contaminant plume and predictions of the remediation efficiency of the reactive barrier.
Links to technology models	Will become available via the AQUAREHAB website (www.vito.aquarehab)

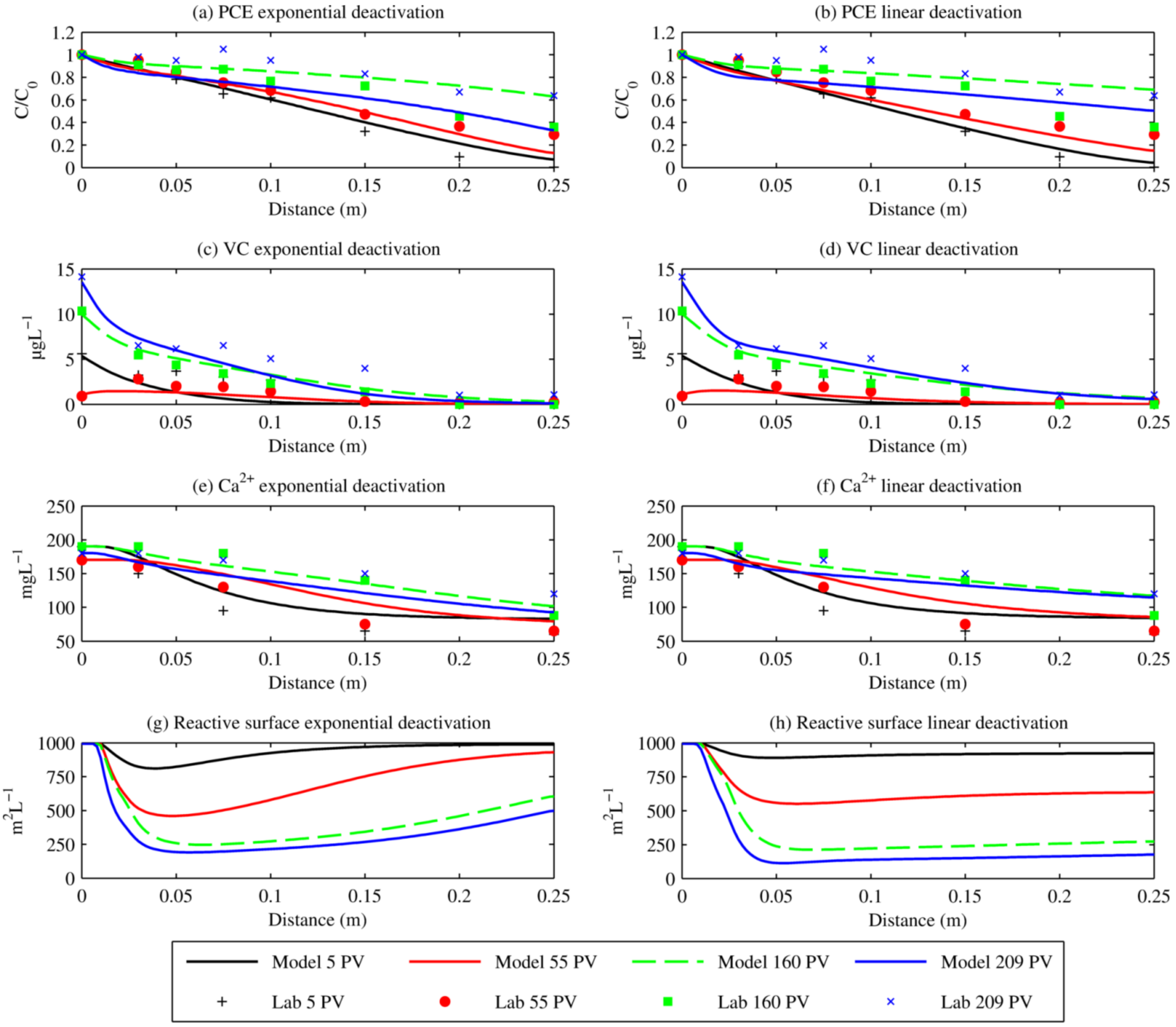


Figure 11 Measured and simulated profiles for the calibration step. (a, c, e, g) PCE, VC, dissolved calcium and reactive surface profiles with the exponential deactivation model and (b, d, f, h) PCE, VC, dissolved calcium and reactive surface profiles with the linear deactivation model.

Table 5 Calibrated model parameters for the column test reported in DL7.2

Parameter	Literature range	Initial value[b]	Exponential deactivation		Linear deactivation	
			Optimal value	95 % confidence limit	Optimal value	95 % confidence limit
log k_{PCE} (mol m^{-2} s^{-1})	NA[a]	-13.07	-13.01	-13.13 to -12.89	-12.97	-13.13 to -12.82
log k_{TCE} (mol m^{-2} s^{-1})	-12.72[c] to -10.89[d]	-12.69	-12.47	-12.56 to -12.38	-12.46	-12.54 to -12.38
log $k_{trans\text{-}DCE}$ (mol m^{-2} s^{-1})	NA	-14.18	-13.66	-13.82 to -13.51	-13.69	-13.80 to -13.59
log $k_{cis\text{-}DCE}$ (mol m^{-2} s^{-1})	-10.60[d]	-12.66	-12.22	-12.36 to -12.09	-12.21	-12.30 to -12.12
log k_{VC} (mol m^{-2} s^{-1})	NA	-14.24	-13.31	-13.50 to -13.11	-13.32	-13.46 to -13.17
log k_{IrC} (mol m^{-2} s^{-1})	-12.46[e] to -7.20[e]	-10.23	-9.88	-10.04 to -9.72	-9.90	-10.05 to -9.74
log $k_{eff,,IC}$ (mol L^{-1} s^{-1})	-10.89[f] to -8.51[e]	-10.89	-9.38	-10.50 to -8.26	-9.38	-10.48 to -8.27
α_{IC} (-)	2.0[f] to 5.0[f]	5.0	2.1	-85.1 to 89.4	-	-
α_{CC} (-)	5.5[f] to 90.0[g]	85.0	175.0	101.9 to 248.0	-	-
T_c (m)	1E-8[h] to 4E-4[i]	1.0E-5	-	-	3.1E-8	2.5E-8 to 3.7E-8

[a] Not applicable. [b] k_{PCE}, k_{TCE}, $k_{trans\text{-}DCE}$, $k_{cis\text{-}DCE}$, k_{VC} were estimated from the concentrations at 5 PV, k_{IrC} was estimated from the rate of gas generation, $k_{eff,,IC}$, α_{IC} and α_{CC} were taken from column C of Jeen et al. (Jeen et al., 2007), T_c from the visual inspection of the SEM images. [c] From Prommer et al. (Prommer et al., 2008). [d] From Wrust et al. (Wüst et al., 1999). [e] From Li et al. (Li et al., 2006). [f] From Jeen et al. (Jeen et al., 2007). [g] From Jin et al. (Jin suk et al., 2009). [h] From Zhang et al. (Zhang and Gillham, 2005). [i] From Kamolpornwijit et al. (Kamolpornwijit et al., 2004).

5.2.3 Conclusions

The additional testing and modelling required to assess iron barrier longevity pose several challenges:

- More time is needed to perform the column test, as ideally gradual deactivation is reproduced in the column test.
- Costs will be higher, not only because of longer test times but also due to additional (geochemical) measurements.

- Significant technical input is needed when using the model, especially for estimating the parameters in the model from the column data.

Within AQAUREHAB some trails have been made to run the model by technology developers (not deeply skilled in modelling), leading to the following conclusions:

- ✓ Without a user interface and a description on how to use the model, it was not possible to run the simplified model, also not for modellers that did not developed the model. With an interphase, integration of input data and creating output is possible.
- ✓ For each site, the model needs to be calibrated. The calibration procedure requires knowledge of the model and the code. Therefore it was concluded that a modeller needs to be involved.

5.3 DETERMINATION OF MINIMAL REQUIRED HYDRAULIC RETENTION TIME

The minimal required hydraulic retention time of the groundwater in a ZVI-barrier is determined by performing a number of simulations (Figure 12). The input parameters for these simulations are:

- Expected concentrations of the pollutants at the entrance of the ZVI-barrier
- The degradation rates determined via the measured concentration profiles
- The molar conversion model that has been determined for the specific iron & groundwater
- The groundwater flow velocity at the site

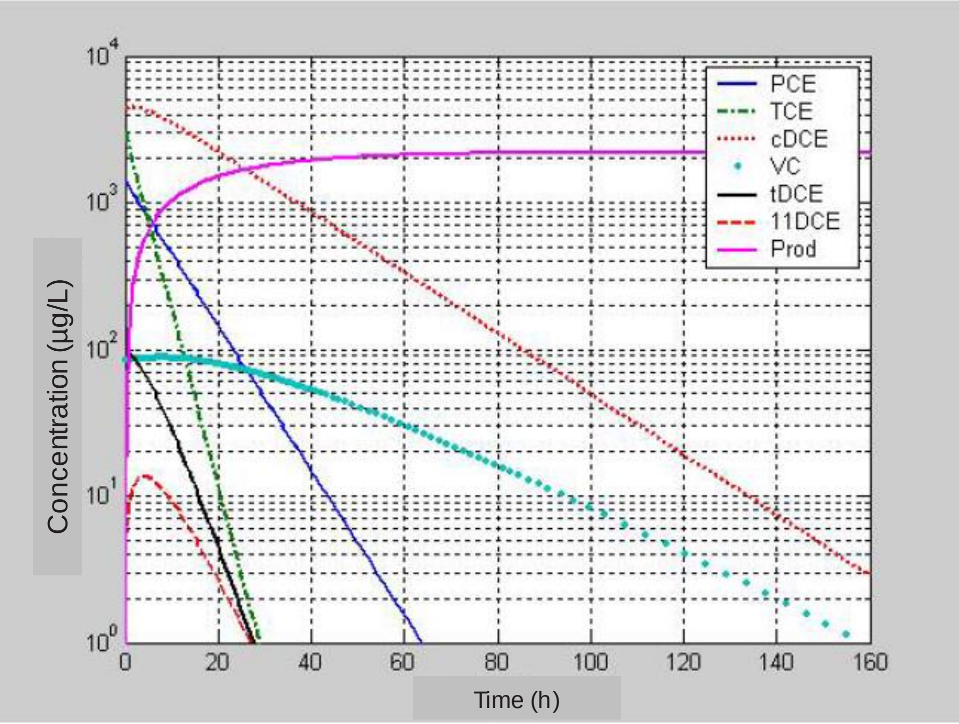


Figure 12: Example of simulated concentration profiles in a ZVI-barrier.

Further the desired effluent concentrations, mostly based on regulatory limits for the pollutants (and breakdown products), are used to determine for each compounds the desired minimal hydraulic retention time. An example of such evaluation is given in Table 6 with data from Figure

12, where vinyl chloride was the compound determining the overall minimal required hydraulic retention time. Mostly, VC or cDCE are the determining the minimal HRT (Source: VITO).

Table 6 Example of minimal required hydraulic retention times for CAHs to be reduced below the desired limits.

CAH-compound	Max. expected concentration (µg/l)	Target value after the barrier (µg/l)	Half live time (h)	Required minimal contact time (h)
PCE	1400	32	6.1	120 h (VC is determining)
TCE	3000	56	2.5	
cDCE	4400	40 (cDCE + tDCE)	14.6	
11DCE	5		4.8	
tDCE	98	40 (cDCE + tDCE)	3.3	
VC	84	4	17.3	

It is up to the consultant to take a decision about the safety factor for the design of the ZVI-barrier in the field. A safety factor of 2 is often used on the minimal required hydraulic retention time.

5.4 LONGEVITY ASPECT

Classical approach

Classically, after about 40 pore volumes of water have been pumped through the column, a sample is taken from the influent and effluent of the column for inorganic analyses. The parameters considered are listed in Table 7. Based on the difference in concentrations measured in the influent and effluent of the column, and the amount of water that was passed through the column, the amount of precipitates in the column can be estimated. Generally, no calculations are performed. The data are compared with the data from sites where a ZVI-barrier has been installed. Based on the performance of these real barriers, a rough indication is given, such as the barrier is expected to work at least x years'.

Table 7 Overview of inorganics parameters measured (once, influent & effluent after 40 PVs)

Class of compounds/ measurement	Specific compounds
Cations	Barium, Calcium, Iron, Magnesium, Manganese, Potassium, Silica, Sodium, ammonium
Anions	Chloride, sulphate, nitrate, nitrite, ortho-phosphate, sulfides (bromide)
Group parameters	Alkalinity (as mg HCO_3/L); DOC (mg/L C), Total dissolved solids (mg/L)

The procedures elaborated within AQUAREHAB

An alternative is to model. Within AQUAREHAB, after parameter calibration (Table 5), the developed technology model (Table 4) can be run to estimate barrier longevity in the field. Parameter values in the model are set equal to values determined during calibration, and using a flow velocity representative for field conditions (which is typically lower than flow velocity used in the column experiment). The model then predicts gradual deactivation of the barrier due to mineral precipitation, yielding simulated breakthrough curves for the different pollutants at the downstream end of the barrier. An example is shown in Figure 13. Breakthrough occurs due to partial or complete deactivation of the iron in the barrier, which occurs at a rate determined by the rate of inflow of geochemical components in groundwater, among other things. These processes are accounted for in the model. Figure 13 includes example calculations with the full numerical model (blue line), and also the simplified model (red line) as discussed above. As can be seen, the two models provide a similar estimation of PRB longevity, indicating that the simplified model may be useful as a screening tool. Table 8 reports the PRB longevity estimated with the simplified model and the full numerical model under different flow and geochemical conditions.

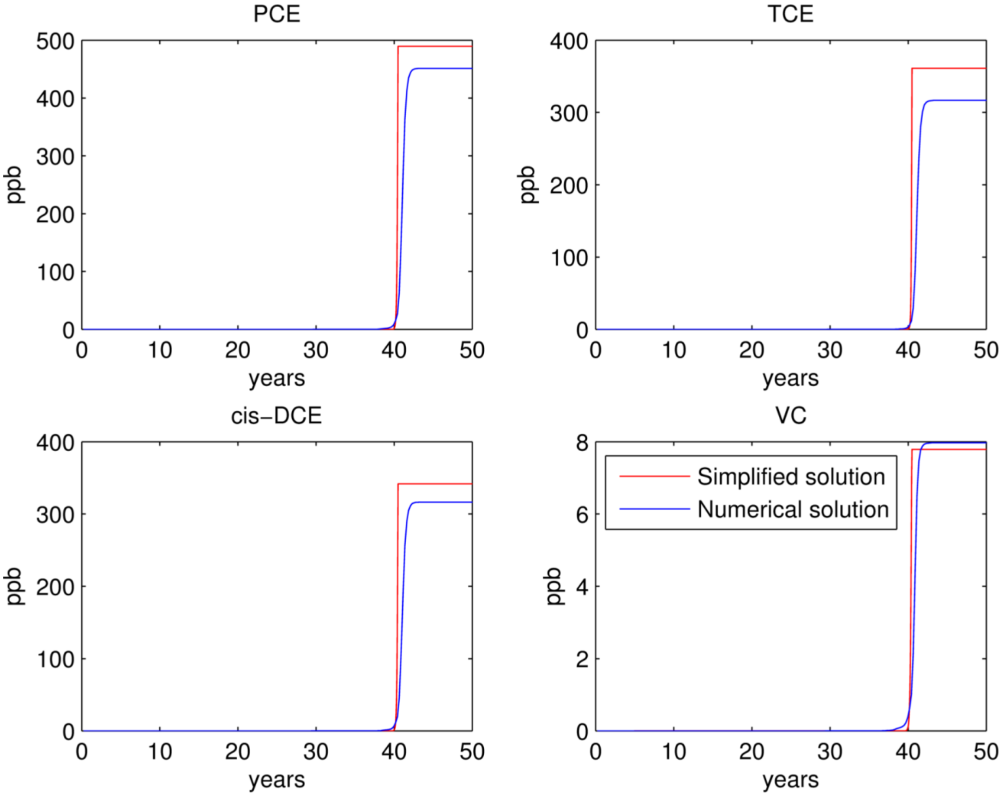


Figure 13. Contaminant breakthrough curves calculated with the full numerical model (blue solid line-method 3) and the simplified model (red solid line-method 4). These results refer to the column experiment performed within AQUAREHAB (DL7.2).

Table 8. Estimated PRB longevity under different flow and geochemical conditions. These results refer to the column experiment described in DL7.2.

Groundwater velocity (m year^{-1})	Ca^{2+} inlet concentration (mg L^{-1})	TIC inlet concentration (mg L^{-1})	Estimated longevity numerical model (years)	Estimated longevity simplified model (years)
0.5	187	95	41.14	40.40
5.1	187	95	4.28	4.01
50.6	187	95	0.71	0.44
0.5	1870	95	46.14	49.08
0.5	18	95	37.10	34.95
0.5	187	950	5.47.	3.54
0.5	187	9.5	>150	>150

5.5 PRB-CONCEPTS & DIMENSIONING

ZVI-barriers typically take advantage of the naturally present hydraulic gradient. Once installed, this passive regime is difficult to alter. Therefore the design and dimensioning of ZVI-barriers needs to be made with care taking into account site hydrology, contaminant type and extent, and minimal required hydraulic retention times.

- The groundwater water flow direction determines the direction of the ZVI-barrier. Barriers are preferentially installed perpendicular to the groundwater contamination plume. It is important to take seasonal variations of groundwater flow direction into account in the design phase. Flow directions may be altered in time, eg as a result of off-site groundwater extraction.
- The length of the ZVI-barrier is determined by the width of the contamination plume. Hydrological studies are advised to be performed to make sure that the barrier is able to capture the entire plume.
- The thickness of the ZVI-barrier is function of a number of parameters, comprising:
    - The minimal required hydraulic retention time (HRT) of the water in the ZVI-barrier (function of influent concentration and required effluent concentration and reactivity of the ZVI).
    - The groundwater flow velocity: the higher the flow, the thicker the ZVI-barrier needs to be to ensure a certain HRT. Groundwater flow velocity may vary significantly as a function of depth, depending on the permeability of different soil layers.
    - Porosity of the PRB.
    - The PRB-concept: for a funnel and gate concepts (see Figure 14) all water is funnelled through the gate which needs to be wider than in comparison with a continuous ZVI-barrier concept.

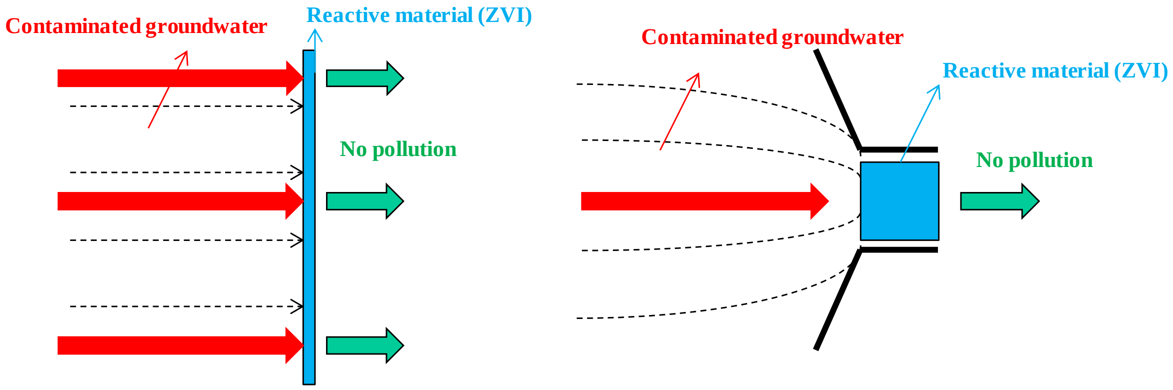


Figure 14 Schematic representation of a continuous (left) and funnel & gate (right) PRB concept

As an example, within AQUAREHAB different methods (see section 5.2.1) were used to derive the degradation rate constants, minimal required HRTs and minimal required thickness of the barrier. For the evaluated case, it was assumed that (1) the porosity in barrier is the same as the aquifer; (2) the groundwater flow velocity is 17.5 m/year, (3) and the barrier composition in the field would be as tested in the lab. The results obtained using method 1 & method 2, are given in Table 9.

These design parameters did not included data for accounting deactivation of the system. Generally, a safety factor of at least 2 is used for the final design of the barrier.

Table 9 Overview of ZVI-barrier design parameters for different scenarios using method 1 & 2 – AQUAREHAB case study

Simula-tion	influent	k-value*	Molar conversion model	target value	minimal required HRT (h)	Minimal required barrier thickness (cm)
1	belgian site	A1	Carniato et al., 2012	Flanders	36	7,23
2	belgian site	A1-1SDEV	Carniato et al., 2012	Flanders	59	11,85
3	belgian site	A2	Carniato et al., 2012	Flanders	28	5,62
4	belgian site	A2-1SDEV	Carniato et al., 2012	Flanders	38	7,63
5	belgian site	A2-1SDEV	I-sim5	Flanders	63	12,65
6	belgian site	A2-1SDEV	I-sim6	Flanders	63	12,65
7	belgian site	A2-1SDEV	II-sim8	Flanders	67	13,46
8	belgian site	A2-1SDEV	I-sim10	Flanders	35	7,03
9	belgian site	A2-1SDEV	II-sim14	Flanders	39	7,83
10	belgian site	B-I	I-sim10	Flanders	71	14,26
11	belgian site	B-I	II-sim14	Flanders	83	16,67
12	belgian site	B-II	I-sim10	Flanders	36	7,23
13	belgian site	B-II	II-sim14	Flanders	37	7,43

* "A" refers to method 1; while "B" refers to method 2.

Using the complex model (method 3), which does account for deactivation of the system, a thickness of 15 cm was calculated for a barrier performance of 30 years. For this calculation, data similar to simulation 12 in Table 9 were used. The minimum required thickness for a barrier that last 30 years was estimated at 15 cm, in line with the values reported in Table 9 for simulation 12 (7.23 cm, multiplied by a factor 2). For the studied situation, the results differ by a factor 2, but depending on the deactivation, the outcome of the two approaches followed may be different.

6 IMPLEMENTATION OF A ZVI-BARRIER (STEP 4)

6.1 INTRODUCTION

Within the AQUAREHAB project, no activities were included related to installation of permeable reactive barriers. Therefore this part is restricted to a brief to overview of a number of ZVI-implementation methods that have been reported in literature.
For more details, other information sources can be consulted like:

- ITRC 2011 – PRB technology update
- US EPA document EPA/600/R-98/125

6.2 OVERVIEW OF DIFFERENT INSTALLATION TECHNOLOGIES FOR PRB'S BASED ON ZVI

The techniques that can be used to install PRB's with ZVI include:

- Conventional excavation (unsupported or supported)

- Excavation by continuous trenching (up to 11 mbg and extendable to approx 14 mbg)

- Excavation with biopolymer trenching (hydraulic shoring, up to apprx 20 mbg).

Remark: temporary deactivation of ZVI may occur (Velimirovic et al., 2012)

- Excavation with sheet piling (up to apprx 9 mbg)
- Augered boreholes

- Caissons (up to 20 mbg)
- Clamshell excavation (up to 15 mbg)
- Injection techniques (to depths exceeding 30 mbg), comprising injection with pneumatic fracturing; injection with hydraulic fracturing, vertical hydraulic fracturing
- Deep soil mixing (up to 15 mbg)

7 GENERIC APPROACH TO MONITOR A ZVI-BARRIER (STEP 5)

7.1 INTRODUCTION

After implementation of a ZVI-barrier, its performance needs to be monitored over time. This implies the installation of monitoring wells and sampling of the groundwater for analyses at regular time points during the whole operational period of the ZVI-barrier. Generic guidelines for the type and amount of groundwater wells for different ZVI-barrier types are described in this document, as well as the parameters to be monitored and their sampling frequency. The guidelines are based on existing PRB-guidelines, literature and conclusions from AQUAREHAB research.

Occasionally, a more detailed monitoring event can help to analyse the condition of the ZVI-barrier. Within AQUAREHAB angled core samples were proven to deliver useful information related to porosity and reactivity of the ZVI-barrier. This approach is explained in section 7.3.

7.2 REGULAR MONITORING OF THE GROUNDWATER

7.2.1 Types and amount of groundwater sampling wells

Well types

The following types of monitoring wells can be distinguished based on their position relative to the ZVI-barrier

A: Wells type A are placed ≥ 10 m (for horizontal permeability, Kh, > 10^{-4} m/s) and 3 to 5 m (Kh < 10^{-4} m/s) upstream of the ZVI-barrier to monitor the quality of the upstream groundwater flowing towards the ZVI-barrier

B: Wells type B are located just upstream of the ZVI-barrier, being 1 to 2m (for horizontal permeability, Kh, > 10^{-4} m/s) and 0,3 to 0,8 m (Kh < 10^{-4} m/s).

C: Wells type C are situated within the ZVI-barrier, near the downstream aquifer or gravel section. It is advised not to install wells in the gravel part, as groundwater from the downstream aquifer part may re-infiltrate in the gravel zone (Gavaskar et al.,1999). In some occasions like for barriers with significant depths, 'multilevel' wells (C_1, C_2, C_3 , ...) can be considered. For funnel & gate configurations it is advised to place also C-type wells near the gate side walls of the gate as groundwater flow velocity may be the highest at these points (short-cut streams).

D: D-type monitoring wells are installed within the ZVI-barrier, upstream of well C to (I) estimate degradation rates and (II) as indicator for breakthrough of pollutants. It is advised to install D-wells in the barrier part with a thickness > 0,3 m where the highest groundwater flow velocity is expected. For ZVI-barrier with a thickness ≤ 0,3m another monitoring approach is recommended as described in section 7.3.

E: Wells type E are located just downstream of the ZVI-barrier in the aquifer part, being 1 to 2m (for horizontal permeability, Kh, > 10^{-4} m/s) and 0,3 to 0,8 m (Kh < 10^{-4} m/s).

F: Monitoring wells type F are situated further downstream of the ZVI-barrier and wells E, being at ≥ 10 m (for horizontal permeability, Kh, > 10^{-4} m/s) and 3 to 5 m (for Kh < 10^{-4} m/s).

G: To evaluate whether the barrier captures all pollutants and that pollutants are not flowing around the barrier, monitoring wells type G are placed sideward of the barrier.

H: Wells type H are installed upstream of an impermeable barrier part (funnel)

I: Monitoring wells type I are situated downstream of an impermeable barrier part (funnel) to evaluate whether the contamination plume is captured efficiently and is not flowing around or under the barrier.

A schematic representation of the different wells types for continuous ZVI-barriers, Funnel-and-gate configurations and in-situ vessel applications are given in Figure 15, Figure 16 and Figure 17, respectively.

Amount of monitoring wells for different ZVI-barrier configurations

The amount of wells that is advised for a continuous ZVI-barrier configuration (Figure 15) is summarised in Table 10. Guidelines are given for barriers with a length below 100 meter. For longer barriers, an indication of extra required wells is given.

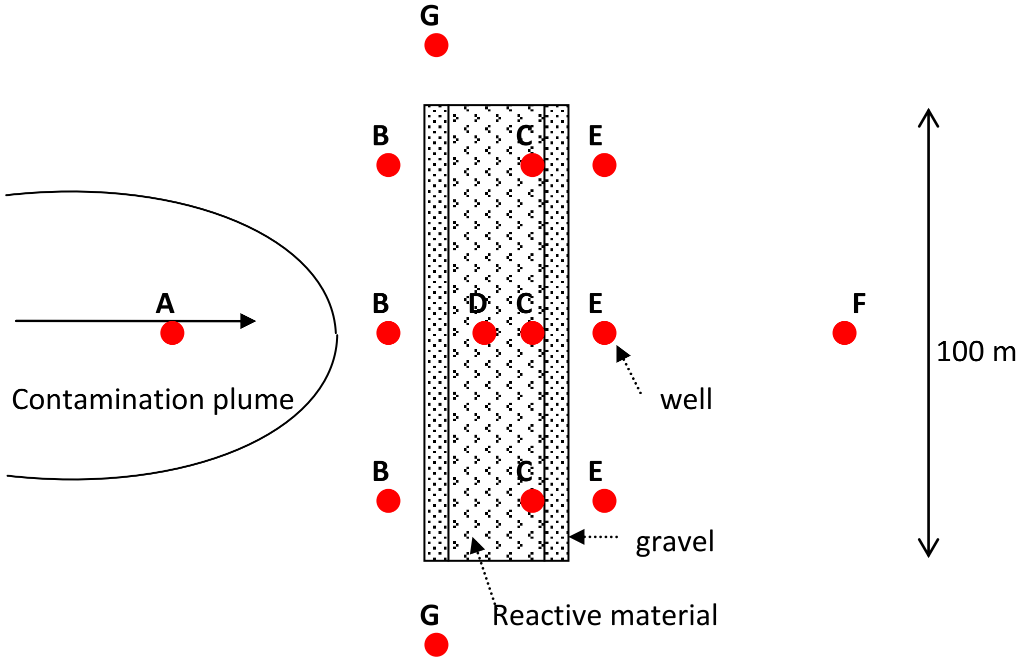


Figure 15 Schematic representation of a continuous ZVI barrier with indication of well types based on their location relative to the ZVI-barrier *(not to scale)*

Table 10. Guideline on amount of Wells to be installed for monitoring of a continuous ZVI-barrier with a length of (less than) 100m. +++: necessary; ++: important; + useful

Well type	*Amount of Wells**	*Extra*	*Importance*
A	*1*		*++*
B	*3*	*1 extra per extra 100 m*	*+++*
C	*3*	*1 extra per extra 50 m*	*++*
D	*1*	*For wide barriers > 30 cm*	*+*
E	*3*	*1 extra per extra 100 m*	*+++*
F	*1*		*+++*
G	*1 + 1*		*+++*

The amount of wells recommended for a funnel-and-gate configuration (Figure 16) is given in Table 11 for a configuration with 1 gate (< 25 m), with a total barrier length of less than 100 m. Further, some guidelines for extra wells are given when dealing with larger sized barriers.

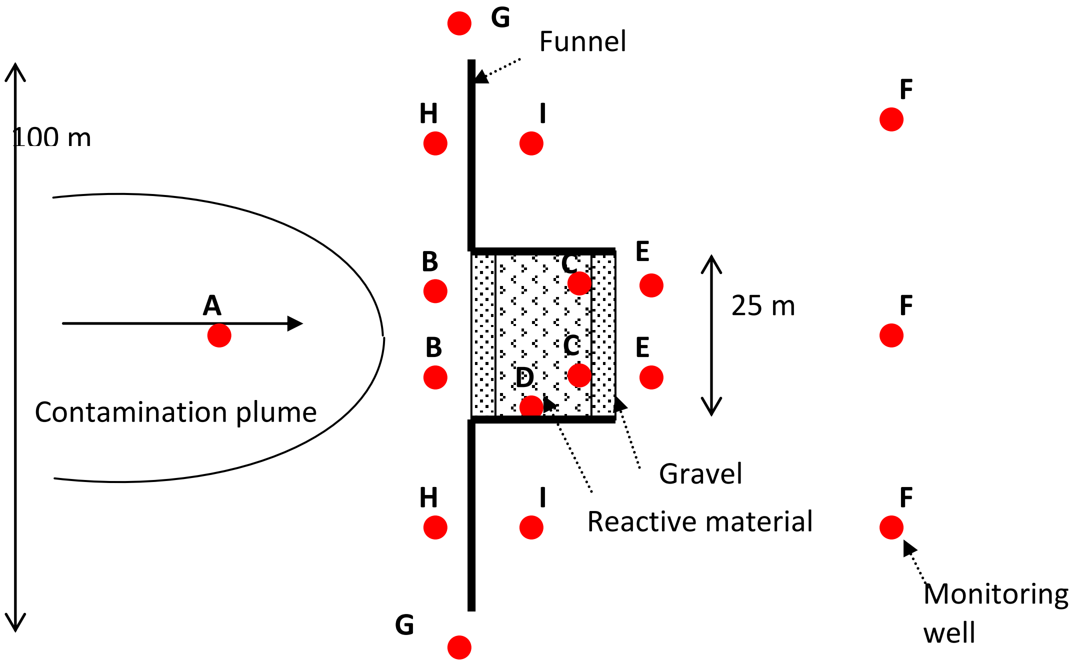


Figure 16 Schematic representation of a funnel-and gate ZVI-barrier with indication of well types based on their location relative to the ZVI-barrier *(not to scale)*

Table 11 Generic guidelines for amount of monitoring wells for a funnel-and-gate configuration. 100m. +++: necessary; ++: important; + useful

Well type	*Amount of Wells**	*Extra*	*Importance*
A	1		++
B	2 per gate	1 extra per extra 50 m	+++
C	2	1 extra per extra 25 m	+++
D	1	For wide barriers > 30 cm	+
E	2 per gate	1 extra per extra 50 m	+++
F	3 per gate		+++
G	1 + 1		++
H	1 per funnel	1 extra per extra 50 m	+++
I	1 per funnel	1 extra per extra 50 m	+++

- Total length of barrier < 100m; length of gate < 25 m.

A special type of funnel-and gate-configuration is the In-situ vessels barrier (Figure 17) where the gate consists of one or more vessels which are installed in the subsurface. The groundwater passes in a vertical way through the system instead of horizontally like the previous barrier types. Table 12 describes guidelines related to the number and types of wells that are required to monitor the in-situ vessel configuration. The prototype configuration for this study consisted of 1 vessel with a diameter below 5 m, and a total barrier length (funnel & gate) of 100m. Guidelines are also described in the table for different sized systems.

Table 12 Generic guidelines related to the amount of monitoring wells for an in-situ vessel configuration.
+++: necessary; ++: important; + useful

Well type	*Amount of Wells**	*Extra*	*Importance*
A	1		++
B	2 per gate		+++
C	1-2	1 extra per extra 2 m diameter	+++
D	1 multilevel	For large vessels	+++
E	2 per gate		+++
F	3 per gate		+++
G	1 + 1		++
H	1 per funnel	1 extra per extra 50 m	+++
I	1 per funnel	1 extra per extra 50 m	+++

- for vessel with diameter < 5 m; Total length of barrier < 100 m.

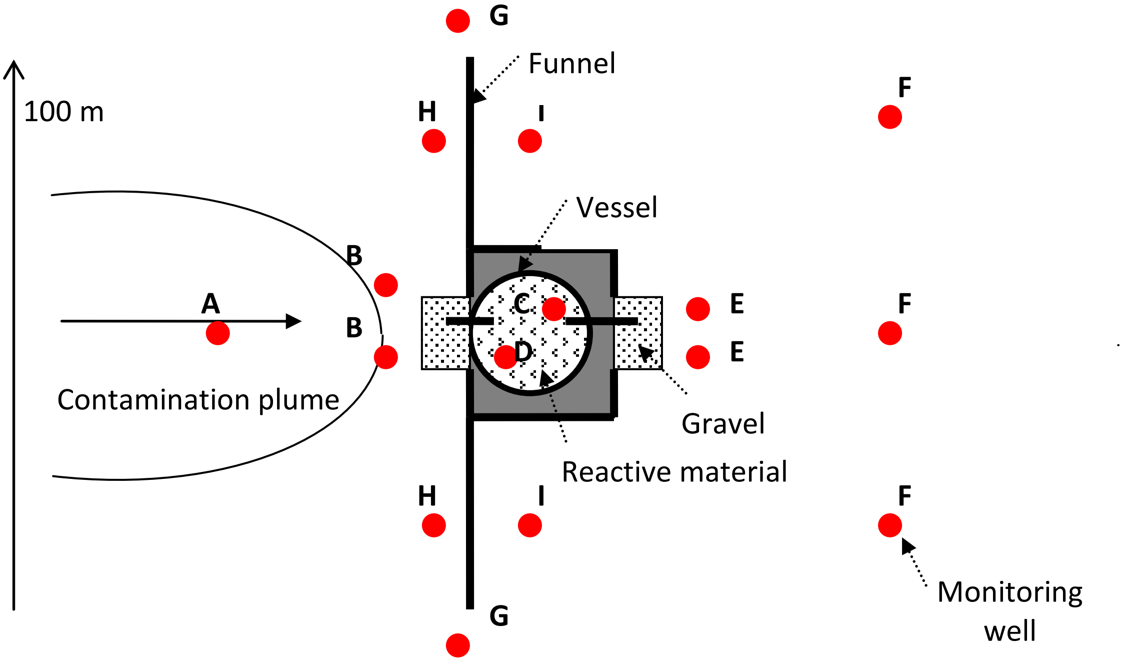


Figure 17 Schematic representation of a special type of funnel-and gate ZVI barrier configuration (in-situ vessel) with indication of well types based on their location relative to the ZVI-barrier *(not to scale)*

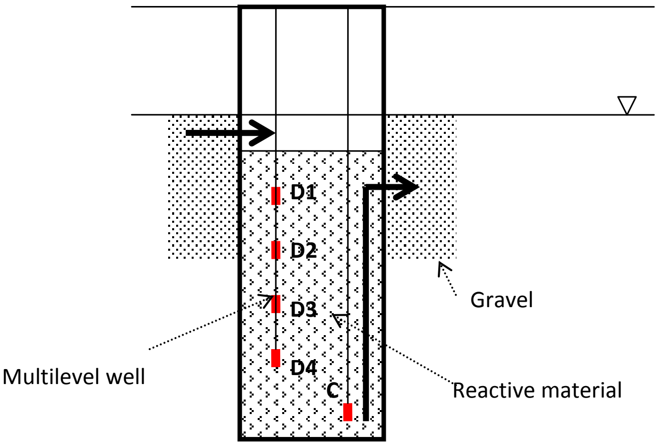


Figure 18 Cross section of an in-situ vessel Schematic *(not to scale)*

7.2.2 Monitoring parameters and monitoring frequency

Monitoring parameters

An overview of monitoring parameters for ZVI-barriers is given in Table 13**.** Groundwater levels are to be measured to evaluate the hydraulic properties of the system. Field parameters are especially useful for ZVI-barriers to monitor the redox conditions and pH in the subsurface. For organics, it is important to monitor not only the compounds that are present initially, but also possible breakdown products. Vinylchloride (VC), for instance, is an intermediate that may be formed during degradation of chlorinated ethenes and ethanes and requires special attention because of its high toxicity. Inorganic parameters (like calcium, magnesium, alkalinity, ..) can give an indication on (1) the precipitates formed in the barrier which influence the longevity of the system, or (2) compounds that can negatively influence the reactivity of the ZVI (like nitrate). Inorganic parameters are especially useful for wells in or near the ZVI-barrier (types B,C, (D), en E). When leaching of specific elements is expected from the reactive material, these parameters need to be included in the monitoring programme. Hydrogen gas is evolved in the barrier system as a result of the reaction of ZVI with water. This may block the pores in the barrier, resulting in a reduction of the groundwater flux through the barrier. It may also evolve as a gas above the ZVI-barrier, eg in in-situ vessel systems, where it should be evacuated in a safe manner.

Table 13: Recommended monitoring parameters for ZVI-barriers.

Monitoring parameters	
Groundwater level	
Groundwater velocity through the barrier	Eg conservative tracer test
Field parameters:	pH, redox potential (ORP),dissolved oxygen, electrical conductivity (EC), temperature
Organic analyses:	chlorinated compounds and other pollutants of concern Breakdown products
Inorganic analyses	Calcium Iron Chloride Magnesium Alkalinity Silicon in solution Manganese Nitrate and ammonium (when nitrate is present) phosphate sulfate
Other	Hydrogen gas

Monitoring frequency

The required monitoring frequency depends on the groundwater velocity through the ZVI-barrier, where a high groundwater flow velocity requires the most intensive monitoring. The generic recommendations described below (Table 14) are relevant for a groundwater flow velocity of 10 to 20 m/year, corresponding to 3 to 5 cm/day. For other flow velocities, the guidelines need to be adapted.

The subsurface is temporarily disturbed during the installation of a ZVI-barrier, which may still influence the monitoring performed within 3 months after installation (or longer) and may not reflect the ZVI-barrier performance. However, it is recommended to monitor during this period to document the disturbances and to monitor the hydraulic changes. An important question is whether the barrier catches the contamination plume. Increased pollutant concentrations in the groundwater just after the installation for a ZVI-barrier have been reported and are explicable by desorption of the contamination or changes in the groundwater flow direction.

During the remainder of the first year, 3-monthly monitoring campaigns are recommended to evaluate the functioning of the ZVI-barrier. The monitoring results need to be compared with the expectations (based on design & modelling) and it is advised to reconsider the monitoring strategy based on the results.

When the remediation objectives are met, the monitoring frequency can be reduced the next years to twice a year or even annual monitoring. It is known that processes do occur (eg inorganic precipitation, etc.) that may reduce the reactivity of the ZVI in the reactive barrier. Therefore, the monitoring frequency needs to be increased from the moment that first signs in that direction are seen.

Table 14: Recommended monitoring frequencies for ZVI-barriers.

Parameter	*Frequency*
Period: First 3 months	
Groundwater levels	Monthly
Field parameters	Monthly
Organic analyses	Monthly
Inorganic analyses	Monthly
Period: 3 months untill 1 year	
Groundwater levels	Every 3 months
Field parameters	Every 3 months
Organic analyses	Every 3 months
Inorganic analyses	Every 3 months
Period: 1 year untill 3 years	
Groundwater levels	Every 6 months
Field parameters	Every 6 months
Organic analyses	Every 6 months
Inorganic analyses	Every 6 months
Period: After 3 years	
Groundwater levels	Every 6 months to once a year
Field parameters	Every 6 months to once a year
Organic analyses	Every 6 months to once a year
Inorganic analyses	Every 6 months to once a year

The sampling frequency may differ between the well types. A more detailed indicative monitoring plan is given in annex A.4. for the first three years after the barrier installation.

7.2.3 Data interpretation

For a ZVI-barrier that performs well, the following is observed:

- the pollutant concentrations just downstream of the barrier (Well E) are lower than just upstream of the ZVI-barrier (wells B)
- A gradual decrease in concentration is observed from well B, to Well D, Well C and Well E.
- No pollution is detected at the barrier ends (wells G) or further downstream the barrier (well F).

The following observations are examples of monitoring results pointing towards an under-performing ZVI-barrier:

- Pollutant concentrations are measured just downstream of the ZVI-barrier (wells E) and are above the envisioned threshold values. These results indicate that the hydraulic retention time in the ZVI-barrier is too low to reduce the pollutants. More detailed monitoring is required to exclude/confirm short cut streams, reduction of the permeability in the ZVI-barrier or passivation of the ZVI. It may be necessary to sample filling material of the barrier for analyses (Gavaskar et al., 2000; see section 7.3). During the first years elevated concentrations of contaminants may persist as a result of desorption of contaminants from the soil.
- Pollution is detected at the barrier ends (wells G) and/or further downstream the barrier (well F). This points towards an inefficiency of the barrier system to capture the whole contamination plume. At that point, it is recommended to reconsider the hydrology of the site (Gavaskar et al., 2000).
- A rise in groundwater level in wells just upstream the barrier (B type) reveals that the permeability of the barrier is too low relative to the permeability of the surrounding aquifer layers.

7.3 ANGLED CORE SAMPLES

Occasionally, it may be useful or necessary to sample the barrier material to verify the ZVI-barrier thickness, to quantify the precipitates, to determine the barrier porosity, to compare the reactivity of the barrier filling with the reactivity of material before use, to study the microbial population, etc.

Within AQUAREHAB angled core samplings were performed across a 6 year old ZVI-barrier and these were proven to be a useful monitoring approach (Bastiaens et al., 2012). As shown in Figure 19, a Geoprobe drilling tool can be used to take 40° angled core samples comprising (1) aquifer upstream of the ZVI-barrier, (2) a transect of the ZVI-barrier as well as (3) aquifer material just downstream of the barrier. While pulling the probe after the core sampling, it is crucial to fill the drilling whole with bentonite (Figure 19, right) to prevent short-cut flow paths in the ZVI-barrier. After sampling, the core samples need to be frozen on the spot (dry ice) and stored afterwards at -80°C until use.

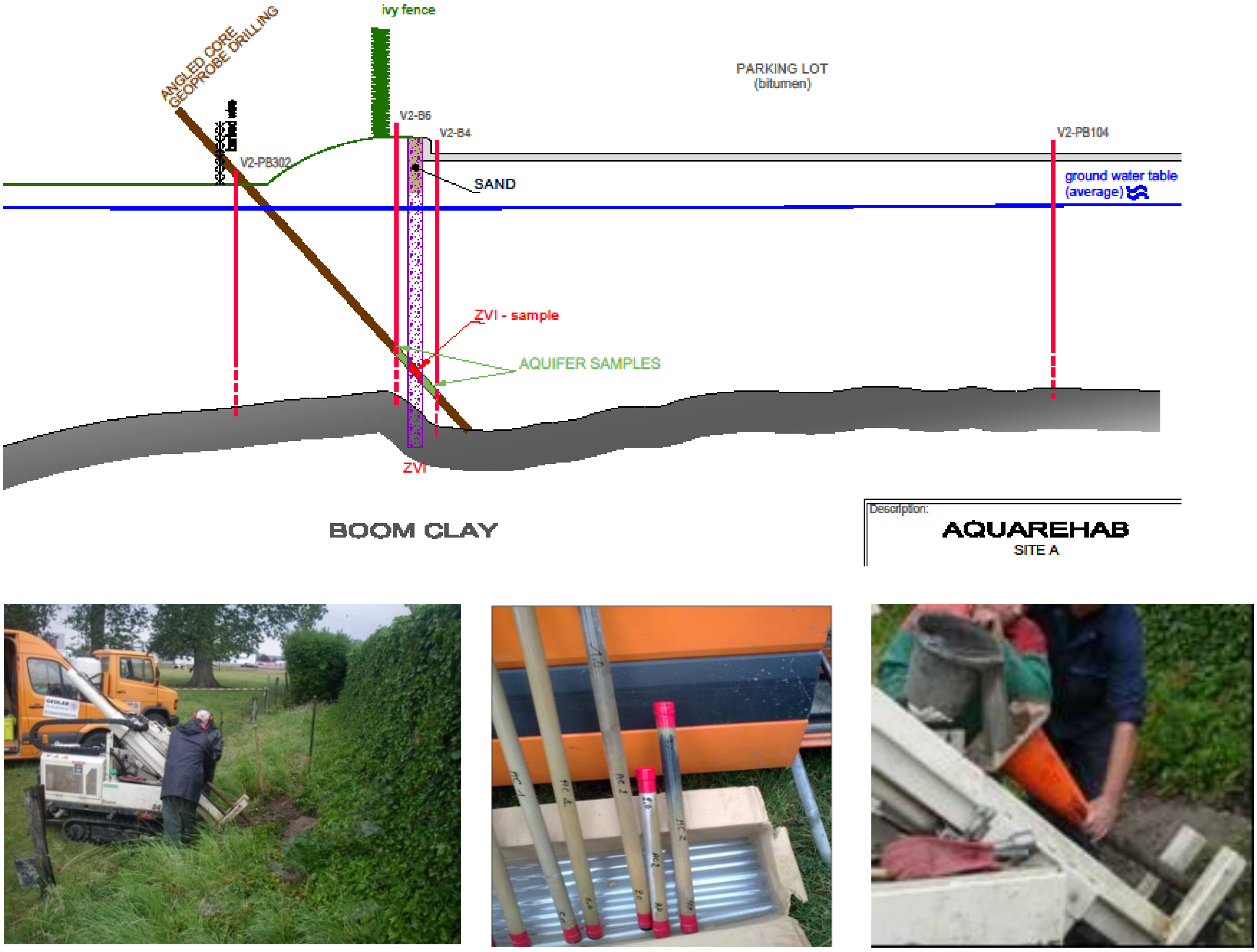


Figure 19. Angled core sampling.

Porosity measurements: The frozen cores (for instance diam. 3 cm) can be cut in to small pieces of 2 cm each. The porosity of each section can be determined by weight losses during drying under anaerobic conditions. An example of a porosity profile across a ZVI-barrier is given in Figure 20.

> *Note*: During core sampling the aquifer and barrier material is potentially being compressed somehow which may lead to an underestimation of the porosity.

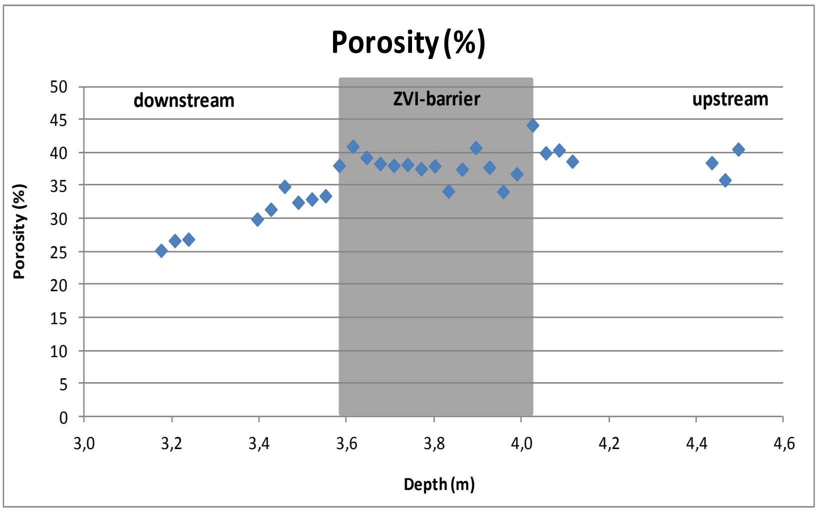


Figure 20. Porosity profile across a ZVI-barrier and adjacent aquifer material – porosity in ZVI-barrier is not lower than in the aquifer material

Characterisation of minerals: from the cores, about 4-6 cm sections can be defrosted and homogenized to get sufficient sample to be treated for microscopic analysis (SEM-EDX and EPMA). SEM-analyses can be used to identify elements and EPMA can reveal a number of different phases that are present. The mineral phase present can be revealed by XRD analyses.

> *Note*: the silica on the ZVI-particles can interfere with the XRD measurements, making identification of the minerals present difficult.

Alternatively, the different sections can be subjected to chemical analyses to quantify the inorganics in the different barrier sections. This will give an idea in which barrier sections the amounts of inorganics that were removed from the groundwater based on groundwater analyses (see section 7.2.2) are precipitated.

Reactivity determination of the ZVI: The reactivity of the iron from ZVI-barriers can be determined via the small scale lab degradation tests similar to the one described in 4.2 (for instance 37 ml bottles with Teflon lined crimp-caps with 2 g of ZVI and 20 ml of simulated anaerobic groundwater spiked with 10 ppm TCE). It is advised to test the reactivity of different barrier sections (for instance downstream part of ZVI-barrier, middle part of ZVI barrier and upstream part of ZVI barrier) and compare it with the reactivity of fresh (non-exposed) ZVI material (Figure 21). As ZVI-barriers may consist of ZVI/sand mixtures, it is recommended to use the original iron/sand mixture as control (when available).

> *Note*: Freezing was shown not to affect the reactivity of the iron significantly.

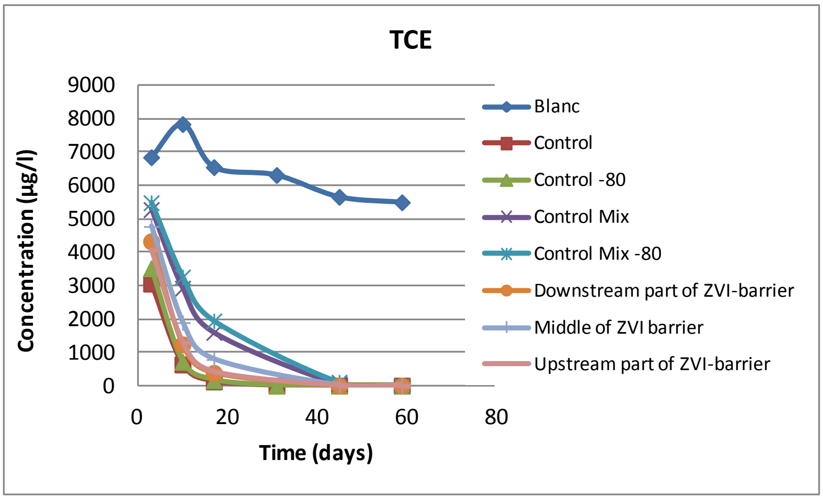


Figure 21: TCE degradation capacity of ZVI-iron mixtures taken from different parts from a 6 year old ZVI barrier. – The iron/Sand mixture from the ZVI-barrier was found to be more reactive than the control iron/sand mixture, and slightly less reactive than the 100% ZVI control.

Blanc = no ZVI
Control = fresh ZVI (100%)
Control Mix = original ZVI/sand mixture that has been stored (not been implemented in-situ)

Characterisation of the microbial community in the ZVI-barrier: Frozen core samples can be cut into small slices of 2 cm thickness. Out of each section a 2 g subsample can be taken for DNA or RNA-based molecular analyses. The microbial community can be characterized using PCR, and in addition it can be quantify when using q-PCR or 16S-tag Pyrosequencing. The type and detail of the analyses is function of the purpose of the tests. Detection of *Dehalococcoides* sp., and genes involved in anaerobic degracation of CAHs may indicate a contribution of biodegradion in and near the ZVI-barrier. Detection of active genes involved in sulphate reduction may explain sulphate decreases in the groundwater across the ZVI-barrier.

> *Note*: Extraction of RNA from ZVI-samples has been proven to be possible but challenging.

8 CONTACTS

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10 ANNEX 1: OVERVIEW OF PARAMETERS RELEVANT TO BE CONSIDERED DURING SITE INVESTIGATION

Groundwater chemistry

Pollutants	**Concentration expected at the barrier entrance (µg/l)**	**Regulatory limits (µg/l)**
PCE		
TCE		
Cis-DCE		
Trans-DCE		
1,1-DCE		
VC		
DCM		
…		

Inorganic components	**Concentration expected at barrier entrance (mg/l)**	**Inorganic components**	**Concentration expected at barrier entrance (mg/l)**
Barium		Chloride	
Calcium		Sulfate	
Dissolved Iron		Bromide	
Potassium		Nitrate	
Magnesium		Nitrite	
Manganese		Ortho-phosphate	
Sodium		Sulfide	
ammonium			
Silicon		Eh	
alkalinity		pH	
DOC		Temperature	
TOC		Conductivity	
Suspended solids		Dissolved oxygen	

Hydrogeological information:

Geology

- Soil type: ....
- Porosity of the aquifer: ....
- Hydraulic conductivity of the aquifer: ....
- Hydraulic gradient: ....
- Groundwater flow velocity: ....
- Layers with high hydraulic conductivity?
- Confining layer with limited permeability present? At which depth?:

Contamination plume:

- Depth of groundwater table: ....
- Width of contamination plume: ....
- Depth of the contamination: ....
  - Upper limit: ....
  - Lower limit: ....

Location:

- Hydraulic boundaries (rivers, wells, low-flow or no-flow boundaries)
- Adequate surface water recharge controls possible?
- Describe the location of the site: ....
  ....
  ....

Include a schematic map of the site (with indication of contamination plume, groundwater flow direction, ...)

Additional information:

....

....

....

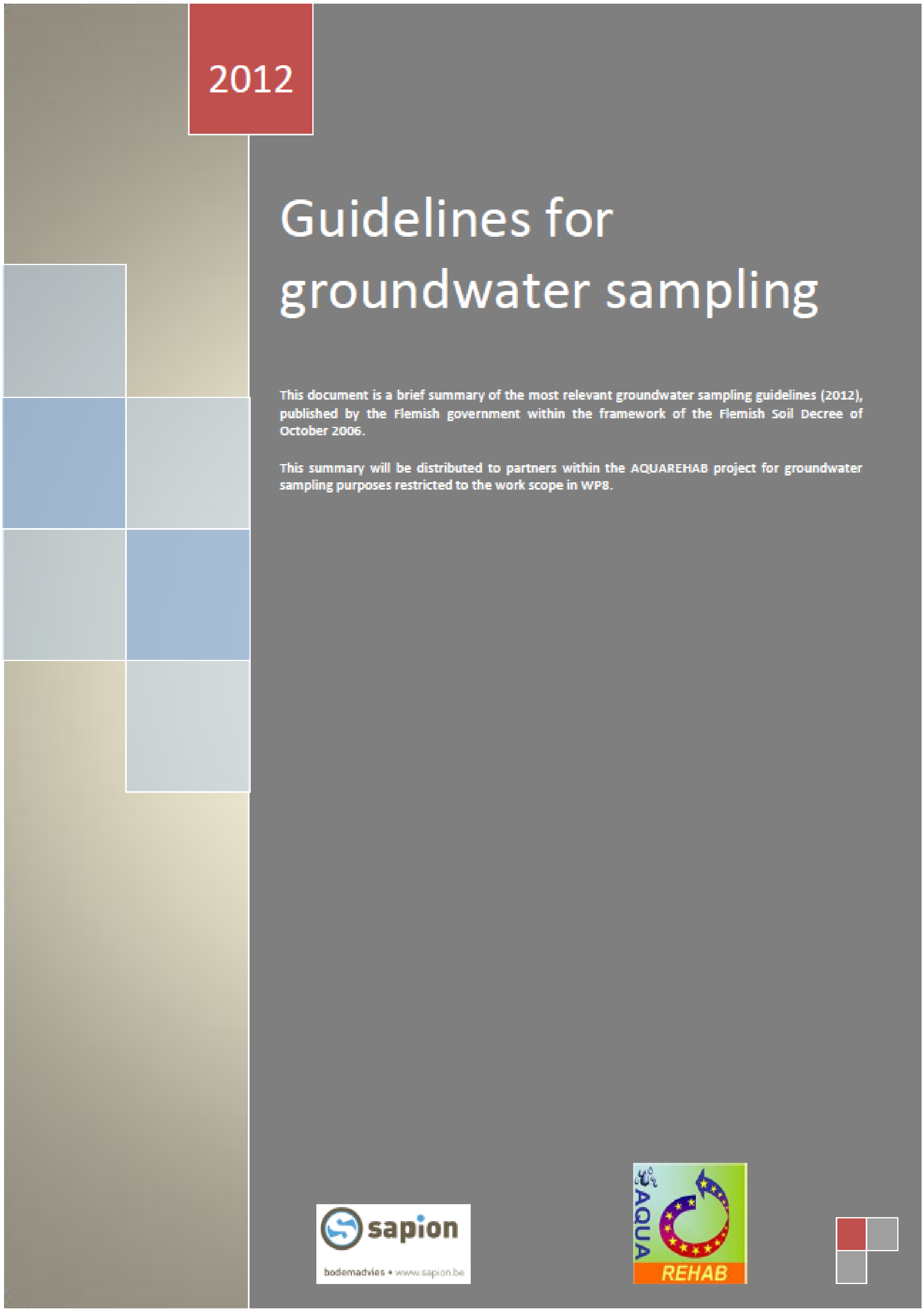
....

....

....

....

11 ANNEX 2: DETAILED GROUNDWATER SAMPLING PROCEDURE



2012

Guidelines for groundwater sampling

This document is a brief summary of the most relevant groundwater sampling guidelines (2012), published by the Flemish government within the framework of the Flemish Soil Decree of October 2006.

This summary will be distributed to partners within the AQUAREHAB project for groundwater sampling purposes restricted to the work scope in WP8.

TABLE OF CONTENTS

1. General criteria for groundwater sampling

1.1. Prior to sampling (existing piezometers)

1.1.1. Data prior to sampling

Using existing piezometers next data need to be available (it might be necessary to look up this information in prior investigation reports):

- exact location, plotted on a map – to be verified in the field.
- aquifer where the piezometer is installed.
- depth and length of the filter interval.
- piezometer tubing material (PE, PVC, stainless steel,…); diameter.
- depth and thickness of the coarse sand and the applied bentonite plug(s).
- drilling technique for installing the piezometer; diameter borehole.
- estimation of the piezometers yield.
- most recent previous sampling date.

1.1.2. Problems prior to sampling

- Is the aboveground finishing still intact (pipe covers, floor covers)? If not, sampling is only possible if this damage has no impact to the groundwater quality.
- Are the blind tubes still intact? If not, interference from the surface (e.g. influx of above ground (rain) water) can occur, and the piezometer should not be used.
- Did visible damage occur to the blind tube?
- Is piezometer ready to use (no dirt, opened cap,…)?
- Are monitoring characteristics (filter depth, application of coarse sand, depth bentonite plug) well known? If not, the piezometer can be sampled, but analysis results should be interpreted with caution.
- Piezometers that have not been sampled for at least 5 years, must be refreshed according to the procedures as for recently installed piezometers (cfr. "1.2.1 Refreshing"). Resampling can take place only as soon as 7 days after refreshing the piezometer.

1.2. Preparatory actions

1.2.1. Refreshing

First step in sampling, whenever physicochemical groundwater parameters should be analyzed, is refreshing in order to reach fresh groundwater from the aquifer for the actual sampling **1 week after** installing (new piezometers).

The minimum requirement is to refresh **5 times the actual water volume** of the piezometer. In case that extra water was used while installing the piezometer, this volume has to be increased by 5 times the volume of the extra water.

Total volume to be refreshed = [5 x water volume piezometer + 5 x volume working water]

1.2.2. Low flow sampling (micropurging)

While the sampling is being done by micropurging (low flow sampling LFS), refreshing takes place at a constant low flow rate:

- Refreshing at constant low flow rate of **0.1 – 0.5 l/min**.
- The natural groundwater inflow in the piezometer should not be exceeded.
- The groundwater level in the piezometer measured during micropurging should not drop more than 50 cm compared to the measured level before micropurging.
- During micropurging the groundwater level should not drop lower than the top of the filtered part of the piezometer.
- Deep piezometers (> 15 m-gl) can be pumped out at higher flow rates, if groundwater level drop doesn’t exceed 10 cm.

Refreshing by micropurging can be ended if:

- The EC value is stable and 5 times water volume piezometer has been refreshed;
  Or

- The EC an O2 values are stable;
  Or

- When turbidity value is 10 NTU (Nephelometric Turbidity Unit) or lower;
  Or

- If the above criteria cannot be met, at least 3 times the wet piezometer volume has been refreshed.

Short time after refreshing the groundwater by micropurging, the pump flow rate needs to be lowered **0.1 – 0.2 l/min**.

The pump must not be stopped between refreshing and actual groundwater sampling.

Geohydrological conditions, piezometer volume and installation characteristics must be known to avoid vertical inflow and creation of preferential canals.
Avoid dry pumping of the piezometers. The flow rate during micropurging has to be well defined so that the filtered piezometer part is never exposed to air.

The groundwater level should be recorded before and after refreshing and after sampling by micropurging.

2. Measuring field parameters

Field measurements (electrode determination of pH, EC, T, O2, ORP) may not be performed in bottles, buckets, jars, etc. where groundwater flow into the recipient from above may occur. In this case the measurement can be influenced from the outside.

The in situ measurements should be done using a so called **flow-through-cell**. The cell is designed to improve the in-line measurements of field parameters. The cell consists of a transparent cylinder. A constant bottom-up waterflow can be established. Accurate probes can be inserted for measuring pH, EC, T, O2, ORP,…

The same pump has to be used during the use of the flow through cell and the actual sampling. Before switching on the actual groundwater sampling, the flow-through-cell has to be removed.

Flow-through-cell

- Calibration:

Prior to the measurements all electrodes must be calibrated separately by means of calibration reagents.
All electrodes must be inspected at a regular basis on the presence of chemical precipitations and must be cleaned or changed if necessary.

- Gas bubbles

If small gas bubbles are present near the electrodes of the flow-through-cell, the flow rate of the pump has to be adjusted.

- Conversion redox-potential

The measured redox-potential in the field (Em) must be converted to the redox-potential according to the Standard Platina/Hydrogen electrode (Eh). The reference used for this conversion depends on the temperature and electrode type.

- Stabilization of measured parameters

The groundwater sample can only be taken after stabilization of the measured parameter. All values must be registered after stabilization, including failures and bad circumstances.

Measurements can be considered stable if (valuated during a period of 1 min.):

pH =	± 0.1
T =	± 5%
Ec =	± 5%
ORP/Eh =	± 10 mV
O2-value =	± 0.1 mg/l

3. Groundwater sampling for lab analysis

3.1. General sampling guidelines

- Sampling will be executed starting from the less polluted piezometer gradually advancing to the more polluted piezometers.
- The PE sampling tube has to be changed for all piezometer samplings.
- All recipients must be filled in one turn, without causing gas bubbles in the recipients.
- In case of prepared recipients with conservation reagents, no spills are allowed and a new sample must be taken in case of a reagent spill.
- Clean or change all parts of the sampling tool in contact with groundwater, after sampling.
- During sampling the PE sampling tube is being placed at least 50 cm above the bottom side of the filter.
- Turbulence must be avoided:
  - Flow rate: 0.1 – 0.2 l/min
  - Recipient must be held vertically during sampling
  - Put PE sampling tube to the bottom of the recipient and keep the PE sampling tube under the sample fluid level at all times.
  - Contact between PE sampling tube and sample fluid in the recipient must be kept as short as possible (max. 0.5 cm)
  - Lift the PE sampling tube gradually according to the sample fluid level in the recipient.

- After filling the recipient, cut the short part of the PE sampling tube that has been in contact with the conservation reagent. Do this every time you start filling a new recipient
- Volatile substances (e.g. BTEX and CAH): filling of recipients with head space is prohibited and a new sample must be taken in case of headspace
- Metals: filtration in the field of all separate samples and immediate acidification. A 0.45 µm teflon filter is preferred. A glass fiber filter is not recommended.

- Order of successive sampling:
  - Recipients without conservation reagent
  - Recipients with solid conservation reagent
  - Recipients with liquid conservation reagent
- Information that must be marked upon every recipient:
  - Piezometer code
  - Location code
  - Sampling date + hour
    (time between sampling and chemical analyses max. 3 days for CAH)
- Cooled conservation right after sampling during storage and transport until delivery at the laboratory (at 4°C).

3.2. Sampling piezometers with bad inflow

- Sampling has to be done within 24 hours after refreshing.

- If a bad inflow has been determined field measurements (pH, EC, T, O2, ORP) are useless. In this case measurements can be done at the laboratory (only samples without conservation reagents). The analysis results must be interpreted very cautiously.

4. Sample recipients and sample conservation

Parameter	Filtration over 0.45µm teflon filter	Conservation method	Conservation time	Recipient	Suggested min. volume
Chlorinated aromatic hydrocarbons (CAH)	NO	pH 1-2 with H_2SO_4 T 1-5°C no headspace and completely sealed	7 days	G with teflon lined air sealed cap	250 ml
As, Cd, Cr, Cu, Pb, Ni, Zn	YES	pH 1-2 with HNO_3	1 month	P or BG	100 ml
Cl^-, NO_3^-, SO_4^{2-}, $PO4^{3-}$	NO	-	Not specified in consulted literature	P or G	100 ml
CO_3^{2-}, HCO_3^-	NO	No headspace and completely sealed	Not specified in consulted literature	P with gas tight cap	250 ml
Fe^{2+}/Fe^{3+}, Mn, Ca^{2+}, Mg^{2+}	NO	pH 1-2 with HNO_3	Not specified in consulted literature	P	100 ml

Legend:
P: plastics (e.g. polyethylene, PTFE (polytetrafluoroethylene), PET (polyethylene terephthalate), PP (polypropylene)
G: glass
BG: borosilicate glass

12 ANNEX 3: DETAILS OF THE UPDATED FEASIBILITY TEST PROCEDURE TO PREDICT THE REQUIRED THICKNESS AND LONGEVITY OF A ZVI-BARRIER

12.1 INTRODUCTION

The use of **granular** zero-valent iron (ZVI) for in-situ remediation of groundwater contaminated with chlorinated solvents is a proven technology (see DL4.1). Chlorinated solvents like tetrachloroethylene (PCE) and trichloroethylene (TCE) can be degraded abiotically by reductive dehalogenation in the presence of zerovalent metals like iron. This iron can be installed in the subsurface as a permeable barrier (Figure 22). Contaminated groundwater flows through the barrier with the naturally present hydraulic gradient as driving force. While migrating through the barrier, the contaminants are degraded abiotically via reductive dehalogenation (see DL4.1).

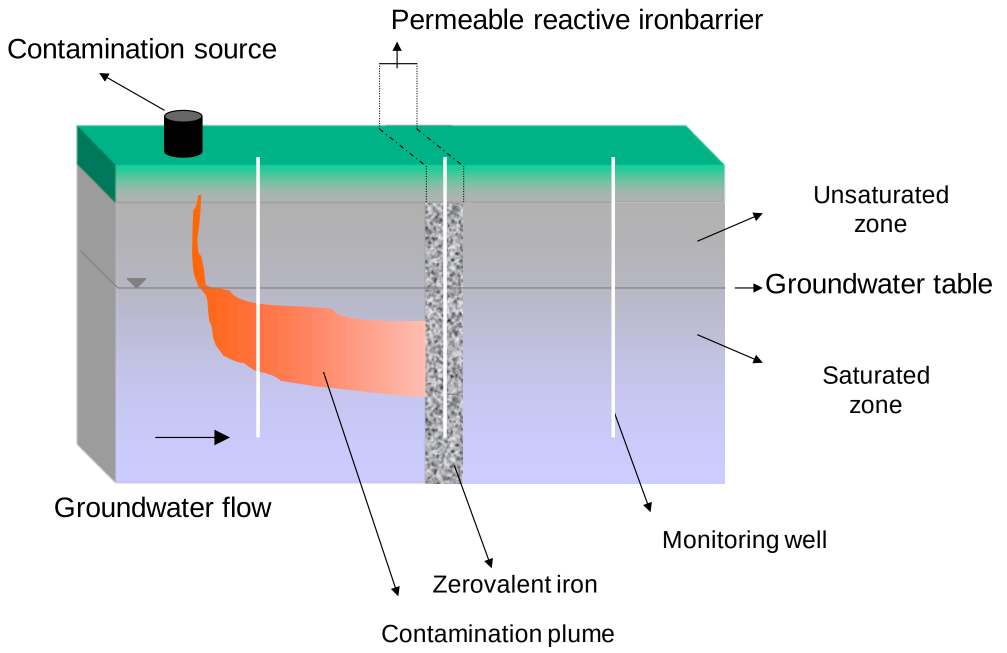


Figure 22: Schematic representation of a zerovalent iron barrier

Within AQUAREHAB WP4, efforts were made to determine parameters that influence the longevity of the ZVI-particles. Within AQUAREHAB (DL4.1), the following parameters were identified as crucial for the evaluation of the performance of ZVI-barriers:

- Groundwater flow rate
- Composition of the groundwater (organic and inorganic)
- CAH-degradation rates (first order degradation constants k)
    - k_{PCE}, $k_{TCE,}$ k_{cDCE}, k_{tDCE}, $k_{VC,}$ …
- Anaerobic corrosion rates of the ZVI
    - k_{IrC}
- Mineral precipitates in the barrier, to be determined in a longer-term column test

    - Type, k_{IH}, k_{IC}, k_{CC}, …
- Deactivation parameters
    - α_i

A numerical model describing in detail the functioning and aging of the particles has been elaborated within AQUAREHAB. To be able to predict the reactivity of ZVI-barriers in time, the numerical model needs to be fed with a number of parameters. This document describes a test procedure to derive the parameters required for ZVI-barrier design and for the model input.

More in detail, the aim of the feasibility test procedure is
- to determine pollutant degradation rates for the compounds present in the groundwater and their breakdown products,
- To estimate the required minimal hydraulic retention time to reduce the concentration of all pollutants (and their breakdown products) below the regulatory limits, and
- Have a first indication of the impact of mineral precipitates and ZVI-corrosion rates on the ZVI-process, i.e. on the longer term performance of the ZVI-barrier.

The procedure consists of the following phases:
- Phase A: Sampling of representative groundwater from the site (see section 4.3.1)
- Phase B: Set-up of a lab scale experiment & monitoring
- Phase C: Data processing
- Phase D: Determination of minimal required hydraulic retention time
- Phase C: Estimation of longevity

Phases B and C are explained in more detail in the following parts. The targeted audience are mainly feasibility test labs.

12.2 LAB SCALE COLUMN TEST (PHASE B)

12.2.1 Assumptions made

Flow rate

The main assumption for predicting site-specific iron barrier longevity based on a column test is that all model reaction parameters (i.e., rate coefficients for VOC degradation, corrosion, and mineral precipitation) are assumed to be constant and independent of differing flow conditions (e.g., flow velocity) between column tests and field site.

It should be emphasized that there are uncertainties in extrapolating from column to field conditions, especially when processes that may be relevant in the field are not observed under accelerated flow conditions in the column. For example, if the column test is performed under accelerated flow conditions compared to the field site, then minerals with a relatively slow precipitation rate may not precipitate in the column-scale iron barrier, whereas under field conditions they can still precipitate and contribute to a decrease in longevity. Another example relates to uncertainty in the exact mechanism for the iron deactivation process: different models have been proposed for this process; a recent study shows that these models are equally able to reproduce measurements from column experiments, yet they yield significantly different predictions of PRB longevity under field conditions (Carniato et al. 2012).

Degradation kinetics

Degradation of the pollutants by the ZVI is often described by a pseudo first-order approach.

$dC/dt = -k\,C$ (eq. 1)
with C = pollutant concentration
t = time
k = First order degradation rate constant (h^{-1})

$t_{1/2} = \ln(2)/k = 0.693/k$ (eq. 4)
with C_0 = pollutant concentration at the start ($t = t_0$)
C = pollutant concentration at time t
$t_{1/2}$ = half live (h)

Different approaches are available to model the degradation of chlorinated hydrocarbons on zero-valent iron. The most general approach is the Langmuir–Hinshelwood-Hougen Watson kinetics with a limited number of sites for the adsorption and desorption of chlorinated hydrocarbons on the reactive iron surface (Fogler, 1992; Zepp and Wolfe,1987).

If the degradation is limited by adsorption, contaminant concentrations on the iron surface are small, and degradation follows a pseudo first-order law with respect to the dissolved concentrations. If adsorption is much faster than degradation, the whole reactive surface is loaded and the contaminant concentrations on the iron surface are constant, and the pseudo first-order law switches to a pseudo zero-order law. Between these extremes a mixed kinetics is observed:

$$\frac{dC}{dt} = -kS\frac{C}{K_{1/2} + C}$$

where k is the rate coefficient per unit iron reactive surface area (mol m^{-2} s^{-1}), S is the iron reactive surface area per unit water volume (m^2 L^{-1}), and $K_{1/2}$ is the half-saturation constant (mol L^{-1}).
This is a more general approach than the pseudo-first order kinetic law since it can describe the degradation kinetic in the cases of high and low contaminant concentrations (Wüst et al., 1999).

ZVI-barrier composition

It is assumed that there is a linear correlation between the % iron in the column filling and the pollutant degradation rates.

12.2.2 General set-up

The experiments can be performed in for instance 0.5 m long columns with intermediate sampling points for the liquid phase for instance at 5 cm, 10 cm, 15 cm, 20 cm, 30 cm, 40 cm from the inlet (see Figure 23). The columns are filled homogeneously with ZVI or a ZVI/sand mixture by adding aliquots of dry ZVI or ZVI/sand mixtures into empty columns and compacting the filling after each addition using a solid rod. When the filling contains also sand beside ZVI, it is important to prepare the ZVI-sand mixture at the required ratio separately for each aliquot. In this way,

separation of the heavy and lighter particles in the column can be reduced to the layer level. Once the column is completely filled and the sampling ports are inserted and closed, the column needs to be filled with carbon dioxide gas (CO_2). In a next step, influent water is pumped from a Teflon bag into the column (from bottom to top) to saturate the pores (see Figure 23). The parameters listed in Table 15 need to be determined before the start of the experiment.
It is important to perform the column experiment at groundwater temperature representative for the considered site (for instance typically 12°C in Belgium).

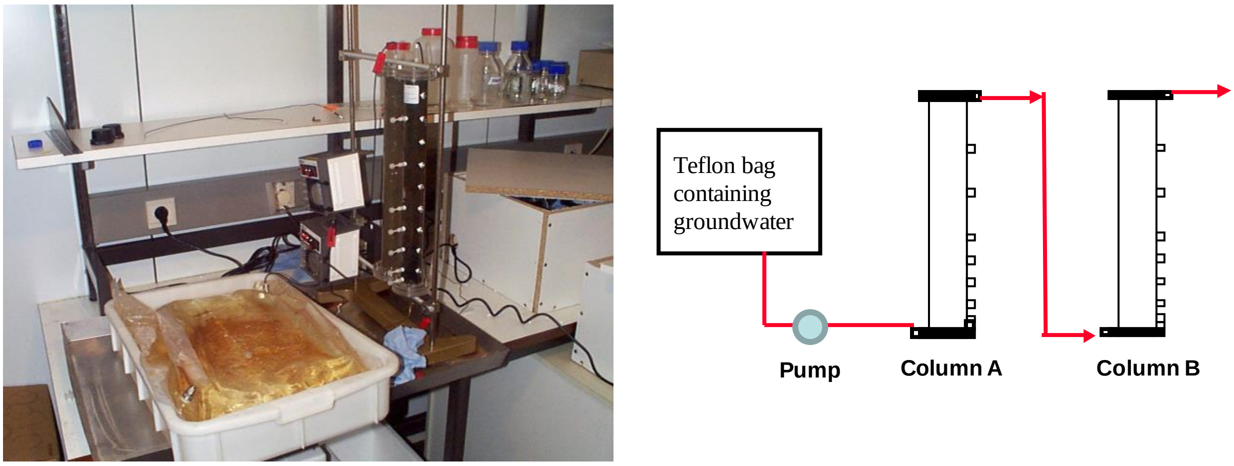


Figure 23: Experimental set-up

Table 15: Column parameters to be determined at the start of the column test.

Characteristics of the ZVI—material:	
Specific surface area of the iron	X m^2/g
Experimental parameters:	
Flow velocity of the groundwater	X cm/day
Hydraulic retention time	X hours
Pore volume	X ml
Porosity	X
Bulk density	X g/cm^3
Iron/liquid-ratio	X g: 1 ml
Surface area of iron per volume of liquid	X m^2 : 1 ml
Temperature	X °C

Once the column is saturated, the desired groundwater flow velocity can be set. Pore volumes mentioned here are 0.5 m pore volumes, being the pore volume of a column with a length of 0.5 m.

In phase 1 of the test (first 40-50 pore volumes), the rate at which groundwater is pumped through the column is to be set as close as possible to groundwater flow velocity in the field. However, in case groundwater flow velocity is very small, column flow rates may be much larger than on-site conditions, such as to limit the time needed to perform the column experiment. A key assumption is then that this higher flow velocity does not significantly affect the relevant reaction rates. Care should be taken to feed the column with a more or less constant feed solution: fluctuations in inflowing groundwater composition makes it hard to interpret measurements in the column and estimate parameters. Preferably, groundwater for the column test is to be collected from a single field visit.

In phase 2 of the test, a larger flow velocity is applied to study the longer-term iron deactivation of the ZVI in a shorter experimental time. The required amount of PVs that need to be pumped through the column to observed deactivation can be very high (> 500 PV) for good ZVI-types.

12.2.3 Sampling & analyses

As a function of time, liquid samples need to be taken along the column. The following measurements are needed to reliably determine reaction parameters in the model:

- **Rate coefficient for iron corrosion**: several (2-3) pH profiles and measurement of hydrogen production rates in the column.

- **Rate coefficients for mineral precipitation**:
  - geochemical concentration profiles (comprising at least 5 measurement point along the column) are needed for ions typically involved in mineral precipitation in iron barriers, namely, Ca^{2+}, Mg^{2+}, Fe^{2+}/Fe^{3+}, Mn, (bi)carbonate, and sulphate. Two profiles should be determined during steady state (between 30 & 50 PV) with at least 10 PV difference to give more information on the ZVI-deactivation processes.
  - Measurements of geochemical concentrations in groundwater may provide an initial assessment of how much mineral precipitation is to be expected. For example, a conservative estimate can be made by assuming all calcium and or (bi)carbonate in groundwater will precipitate in the barrier (see also simplified model below).
  - Measurements of pH profiles are also useful in this context, as mineral precipitation results in a decrease in pH (precipitation reactions buffer pH increases caused by iron corrosion).
  - Additional mineral analysis of the reactive solid material from the column at the end of the flow-through test (by XRD, XRF and SEM) is also very valuable for qualitative identification of precipitated minerals (location to be determined based on profiles).

- **Rate coefficients for pollutant degradation**: several (2-3) good quality pollutant concentration profiles are needed. Preferentially 4-5 ‘steady state’ pore volumes are collected when 30-40 PV are pumped through the column.

- **Iron deactivation parameters**: the rate of iron deactivation can be monitored by evaluation of repeated concentration profile measurements (for both pollutant and if time/money is available also geochemical species). In principle, these measurements should be repeated until a clear shift in the concentration profiles is observed, which is indicative of iron deactivation.

- **Mixing and hydraulic retention time (HRT):** tracer tests can be used to estimate mixing (dispersion) in the column, and average residence times. Lithium is a good conservative tracer for this purpose, as it does not react with the iron barrier material (Lai et al., 2006). Ideally, tracer tests should be performed at the start and at the end of the column experiment. The second tracer test may provide information on any changes in porosity and residence time that have occurred due to secondary mineral precipitation or accumulation of hydrogen gas in the column or any preferential flow paths that may have developed in the column.

When to measure concentration profiles:

- Several profiles are measured during the first 40 PV: these measurements represent initial conditions, before iron deactivation effects come into play.
- For monitoring gradual iron deactivation and its feedback effects on pollutant degradation and mineral precipitation, additional profiles (after the first 40 PV) need to be measured: these profiles may typically manifest a gradual shift indicative of gradual iron deactivation.

Table 16 Recommended monitoring parameters and frequency.

Parameters	Recommended for phase I	Recommended for phase II
pH & ORP profiles	3	3 profiles
CAH-concentration profiles	4-5	4-5 profiles
Geochemical concentration profiles	2 (between 30-50 PV), with 10 PV in between	0-1 profiles
Hydrogen production	over time	over time
Li tracer test	Option – not easy to perform	-
Ecotoxicological analyses	Influent and effluent At 2 time points (during startup & later in the experiment)	-

Taking into account that the time for performing feasibility tests may be limited, the following alternative options are available:

- Estimate iron deactivation parameters from literature: this would circumvent the need for additional profile measurements (after the first 40-50 PV), but this is likely to be less accurate.
- After the initial profile measurements, switch to a larger flow velocity (12.2.2, phase 2). This will lead to faster iron deactivation and therefore shorten the total time of the experiment.
- A possible approach could be to first get a rough estimate of the deactivation parameters from literature (which can also provide a first rough barrier design that accounts for longevity), and use these estimates to design the flow experiment in such a way that deactivation is expected to occur; data from that experiment can then be used to refine the deactivation parameters (and the design).

12.3 DATA PROCESSING & PARAMETER ESTIMATION

Based on the chemical analyses mentioned above, concentration profiles can be prepared for each of the pollutants (and breakdown products). The concentration profiles at 'steady state' (=equilibrium between transport and degradation of the pollutants) are used to calculate degradation rates. These calculations can be performed in different ways:

Method 1: Determination of degradation rates by linear regression of LN-transformed data based on a pseudo first order degradation kinetic as illustrated in Figure 24.

Eq. 1 can be transformed into the next equation:

$C = C_0 e^{-kt}$ (eq. 2)

$\ln (C/C_0) = -kt$ (eq. 3)

With C_0 = pollutant concentration at start ($t = t_0$)
C = pollutant concentration at time t
k = First order degradation rate constants (h^{-1})

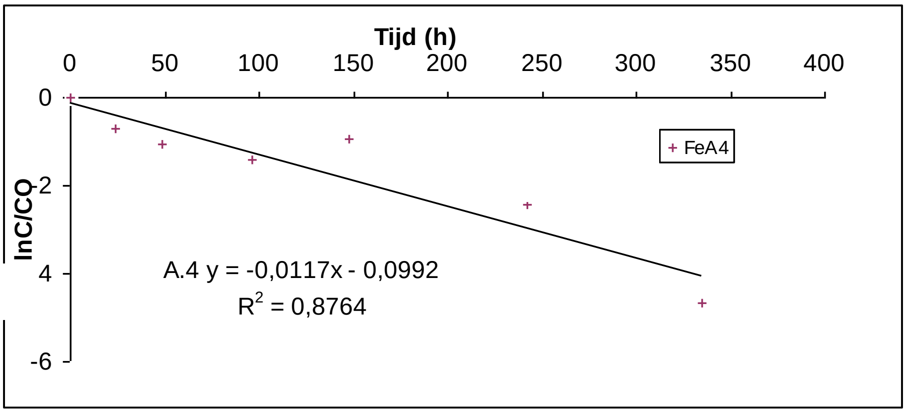


Figure 24: Determination of K-value ($k = 0.0117\ h^{-1}$) via linear regression of LN-transformed data (pollutant concentration in function of contact time in the column = concentration profile at 1 time point)

Method 2: Degradation rate constants can also be determined via fitting of the concentration profiles based on a pseudo first order degradation kinetic. During this fitting process, also molar conversion factors (f-values) need to be estimated. These factors are related with the degradation pathways (mostly mixture combination of degradation pathways) followed, which differ significantly between particles and the geochemical conditions as described in section 2.3. Figure 30 displays an example of a molar conversion model.

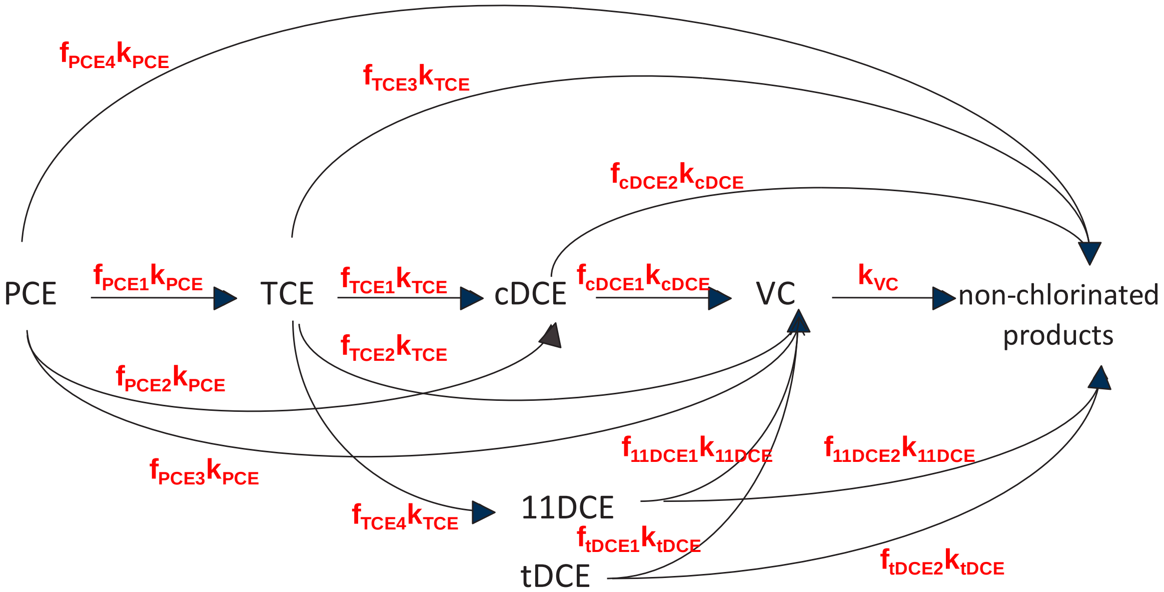


Figure 25: Generic reaction pathway and molar conversion model for degradation of chlorinated ethenes by ZVI (f = mole fractions; k = first order degradation rate constants).

The formula behind the fitting are listed below with concentrations of pollutants represented by PCE, TCE, cDCE, VC, tDCE, 11DCE; with f representing mole fractions and k first order degradation rate constants:

$dPCE/dt = - k_{PCE} * PCE$

$dTCE/dt = (f_{PCE1} * k_{PCE} * PCE) - (k_{TCE} * TCE)$

$dcDCE/dt = (f_{PCE2} * k_{PCE} * PCE) + (f_{TCE1}\, k_{TCE} * TCE) - (k_{cDCE} * cDCE)$

$dVC/dt = (f_{PCE3} * k_{PCE} * PCE) + (f_{TCE2}\, k_{TCE} * TCE) + (f_{cDCE1}\, k_{cDCE} * cDCE) + (f_{tDCE1}\, k_{tDCE} * tDCE) + (f_{11DCE1}\, k_{11DCE} * 11DCE) – (k_{VC} * VC)$

$d(\text{non-chlorinated products})/dt = (f_{PCE4} * k_{PCE} * PCE) + (f_{TCE3} * k_{TCE} * TCE) + (f_{cDCE2} * k_{cDCE} * cDCE) + (k_{VC} * VC) +(f_{tDCE2} * k_{tDCE} * tDCE) + (f_{11DCE2} * k_{11DCE} * 11DCE)$

$dtDCE/dt = - k_{tDCE} * tDCE$

$d11DCE/dt = - k_{11DCE} * 11DCE$

$f_{PCE1} + f_{PCE2} + f_{PCE3} + f_{PCE4} = 1$

$f_{TCE1} + f_{TCE2} + f_{TCE3} + f_{TCE4} = 1$

$f_{cDCE1} + f_{cDCE2} = 1$

$f_{tDCE1} + f_{tDCE2} = 1$

$f_{11DCE1} + f_{11DCE2} = 1$

Method 3: Within AQUAREHAB a methodological protocol was elaborated for estimating model parameters (iron corrosion rates, mineral precipitation rates, pollutant degradation rates and iron deactivation parameters) from the measurements. The protocol relies on an automatic parameter estimation tools, such as PEST (Doherty, 2007) to perform model calibration: during this process parameter values are automatically adjusted to obtain a good fit between simulated and measured concentration profiles. The “fit” between simulated and measured concentrations is typically quantified by the total sum of the squared deviations between all laboratory measurements and their corresponding model-predicted values; these deviations should be as small as possible.

The methodology consists of three consecutive steps:

- Step 1: (manual) estimation of initial parameter values.
- Step 2: (automatic) estimation of geochemical parameters.
- Step 3: (automatic) estimation of pollutant degradation and iron deactivation parameters.

The added value of this procedure compared to the method using linear regression of log-transformed data (section x) is that (i) it accounts not only for degradation but also for production from parent products, and hence can handle complex degradation pathways, and (ii) it accounts for interactions or correlations between parameters.

Indeed, the rationale for these steps is as follows. Initial parameter values may be estimated by linking each parameter to a particular concentration profile. For example, the rate coefficient of TCE degradation can be estimated from initial TCE concentration profiles. Similarly, measured calcium concentration profiles provide estimates of aragonite precipitation rates. However, it should be noted that these only provide rough estimates, since interactions between parameters are ignored. For example, TCE profiles may be also be affected by PCE degradation rates (PCE can partially degrade to TCE, as shown in figure 30), and measured calcium concentrations are likely affected by precipitation rates of other minerals. Therefore, these initial parameter estimates are subsequently refined using an automatic calibration tool, which adjust the initial parameter values to take parameter interactions into account. Due to the large number of parameters, the calibration is divided into two steps, as discussed below.

Step 1: (manual) estimation of initial parameter values

Initial parameter values for pollutant degradation (k_{VOC} and $K_{1/2}$) can be estimated from initial pollutant concentration profiles by manually fitting the first part of the profile with a zero-order kinetic model (yielding an estimate for parameter k_{VOC}) and the last part of the profile with a first-order kinetic (yielding an estimate for parameter $K_{1/2}$), as suggested by Wüst et al. (1999).

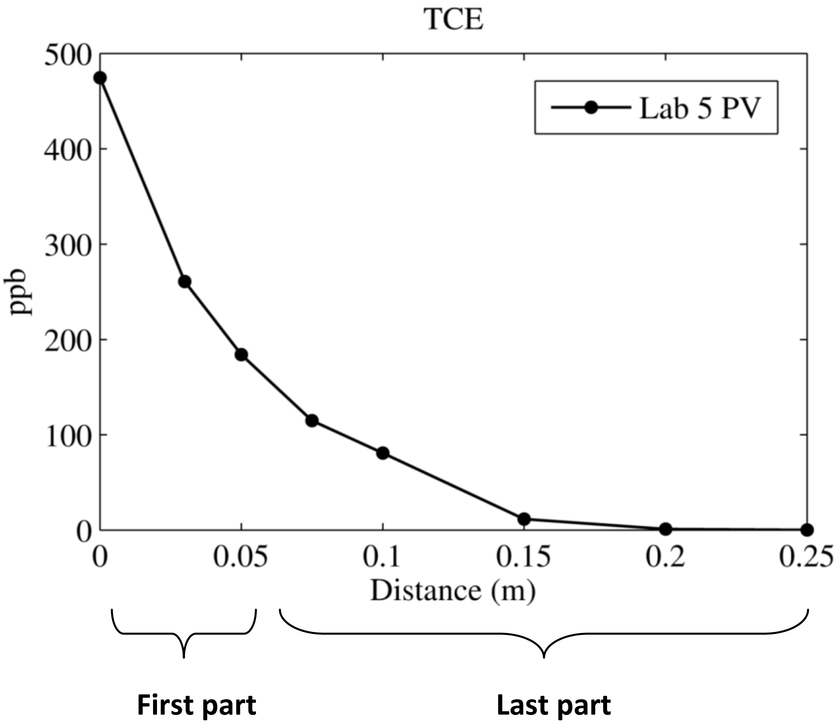


Figure 31: Example of initial estimation of parameters k_{VOC} and $K_{1/2}$ of a mixed-order pollutant degradation model: the first 3 measurements (first part) can be used to estimate degradation rate k_{VOC}, while the last measurements (last part) can be used to estimate parameter $K_{1/2}$.

The pollutant degradation model also requires specification of the molar conversion model (the reaction pathways). An initial model may be based on published reaction networks for zero-valent iron (Arnold and Roberts, 2000). As the reaction network depends on the type of iron used, it is important to use a reaction network for an iron type that is as similar as possible to the one used in the application. The degradation pathways may in principle also be estimated from measured pollutant profiles in the column, using for example an automatic parameter estimation tool. However, it remains to be seen whether this will result in reliable results; this is currently being investigated.

An initial value for the rate coefficient of iron corrosion (k_{IrC}) can be estimated from the measured rate of gas production in the column, using the method of Reardon (1995).

Initial estimates for rate coefficients of mineral precipitation reactions and iron deactivation parameters can be made from existing literature (Jeen et al., 2007; Li et al., 2006). Alternatively, initial measured concentration profiles can be used to get initial parameter values: for example, measured calcium concentration profiles provide estimates of aragonite precipitation rates, whereas measured dissolved iron concentration profiles provide estimates for precipitation rates of Fe-bearing minerals such as iron hydroxide and iron hydroxy carbonate.

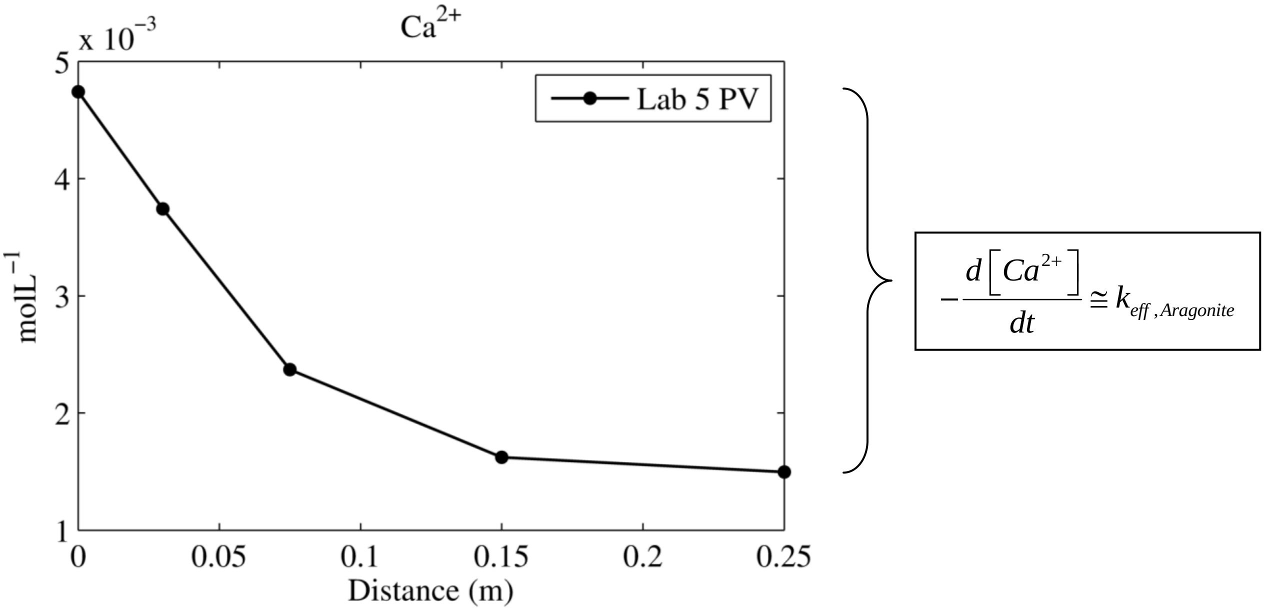


Figure 32: Example of initial estimation of the rate coefficient for aragonite precipitation. An estimate is obtained by dividing the measured change in calcium concentration between column inlet and outlet by the residence time in the column.

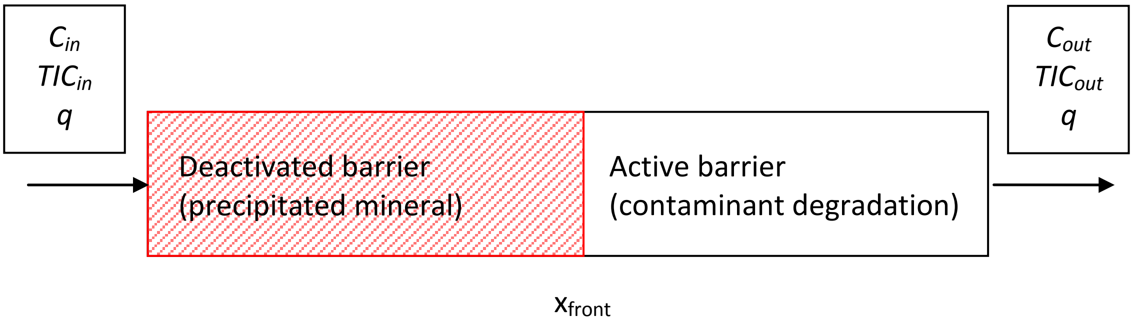
Step 2: (automatic) estimation of geochemical parameters

Initial parameter values should ideally be refined using automatic calibration. Due to the large number of parameters to be estimated, it is useful to tackle this in two steps. In this first step, only the geochemical parameters are estimated. This is done using measured inorganic profiles up to 50 PV, namely measured profiles of calcium, dissolved iron, (bi)carbonate, and pH. It is assumed that pollutant degradation and iron deactivation parameters do not influence these initial inorganic profiles, and their values are kept constant at the initial estimates from step 1. Note that all geochemical parameter are estimated together, thereby accounting for possible parameter interactions, not accounted for in step 1. However, when jointly estimating geochemical parameters, one often encounters strong correlations between parameters (for example, when estimating rate coefficients for precipitation of several, related minerals, such as calcium carbonate and iron carbonate). In that case, it may be necessary to fix one of these parameters and only estimate rate coefficients for the remaining reactions. A preliminary sensitivity analysis may be very helpful in identifying correlated parameters.

Step 3: (automatic) estimation of pollutant degradation and iron deactivation parameters

In the second calibration step, geochemical parameter values are fixed at their values determined in step 2, and the pollutant degradation and iron deactivation parameters are jointly estimated (refined from step 1) using measured pollutant profiles. Again, joint estimation allows one to account for possible parameter interactions not accounted for in step 1. In order to obtain reliable estimates of the deactivation parameters, it is necessary to have measured profiles after 50 PV, as only these later profiles will exhibit a gradual shift in the concentration profiles due to gradual iron deactivation caused by mineral precipitation.

Method 4: The estimation procedure described above is quite elaborate and may require significant technical input. A simpler approach, based on a simplified model to estimate the PRB longevity under field condition was explored. The input parameters required by the simplified model are estimated on a short-term column experiment (phase 1 only) using the methodology proposed above. This simplified model assumes that a mineral front develops in the PRB under low flow velocities (field conditions) and that before the front all the reactive surface area is depleted. Hence, only behind the deactivation front contaminants are actively degraded. The mineral front advances with the aging of the barrier according to the formula reported in figure 33.



$$\frac{dx_{front}}{dt} = \frac{(TIC_{in} - TIC_{out}) \cdot \phi \cdot 1000 \cdot mv \cdot q}{S_0 \cdot T_c}$$

Figure 33. Simplified model conceptualization. *C* is the contaminant concentration (mol L^{-1}), *TIC* is the total inorganic carbon concentration (mol L^{-1}), *q* is the darcy velocity (m_{bulk} s^{-1}), ϕ is the porosity (-), *mv* is the average mineral volume of carbonate minerals ($m^3_{mineral}$ mol^{-1}), S_0 is the reactive surface ($m^2_{reactive\ surface}$ m^{-3}_{bulk}) and *Tc* is the thickness parameter ($m^3_{mineral}$ $m^{-2}_{reactive\ surface}$).

The main advantage of using the simplified model instead the full numerical model is that the barrier longevity under different conditions (e.g. groundwater velocities, carbonate concentrations) and design parameters (e.g. barrier thickness) can be much more rapidly assessed. Hence, it may provide a useful screening and design tool.

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13 ANNEX 4: DETAILED INDICATIVE MONITORING PROGRAM FOR A ZVI-BARRIER

Table 17. Detailed generic guideline for monitoring of ZVI-barriers in function of time and well types.

	Monitoring well type								
	A	B	C	D	E	F	G	H	I
1 month after installation									
Groundwater levels	+	+	+	-	+	+	+	+	+
Field parameters	+	+	+	-	+	+	+	+	+
Organic analyses	+	+	+	-	+	+	+	+	+
Inorganic analyses		+	+	-	+	-	-	-	-
2 months after installation									
Groundwater levels	+	+	+	-	+	+	+	+	+
Field parameters	-	+	+	-	+	-	+	+	+
Organic analyses	-	+	+	-	+	-	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-
3 months after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	+	+	+	+	+	+	+	+	+
Organic analyses	+	+	+	+	+	+	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-
6 months after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	-	+	+	+	+	-	+	-	+
Organic analyses	-	+	+	+	+	-	+	-	+
Inorganic analyses	-	+	+	-	+	-	-	-	-

Generic guideline proposed for groundwater flow velocities of 10 to 20 m per year
Well types are explained in section 7.2.1.

Table 17. Detailed generic guideline for monitoring of ZVI-barriers in function of time and well types. ***(Cont.)***

	Monitoring well type								
	A	B	C	D	E	F	G	H	I
9 months after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	-	+	+	+	+	-	+	+	+
Organic analyses	-	-	+	+	-	-	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-
1 year after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	+	+	+	+	+	+	+	+	+
Organic analyses	+	+	+	+	+	+	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-
1.5 year after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	-	+	+	+	+	-	+	-	+
Organic analyses	-	+	+	+	+	-	+	-	+
Inorganic analyses	-	+	-	-	+	-	-	-	-
2 years after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	+	+	+	+	+	+	+	+	+
Organic analyses	+	+	+	+	+	+	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-
2.5 years after installation									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	-	+	+	+	+	-	+	-	+
Organic analyses	-	+	+	+	+	-	+	-	+
Inorganic analyses	-	+	-	-	+	-	-	-	-
3 years after installation and afterwards once a year									
Groundwater levels	+	+	+	+	+	+	+	+	+
Field parameters	+	+	+	+	+	+	+	+	+
Organic analyses	+	+	+	+	+	+	+	+	+
Inorganic analyses	-	+	+	-	+	-	-	-	-

Generic guideline proposed for groundwater flow velocities of 10 to 20 m per year
Well types are explained in section 7.2.1
It is advised to reconsider the monitoring plan from the moment the results are not in line with the expectations.