Injectable reducing iron particles

Generic guideline

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

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Project website address: aquarehab.vito.be

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List of abbreviations

bgs	Below groundsurface
CAH	Chlorinated aliphatic hydrocarbons
DCE	Dichloroethylene
DNAPL	Dense non-aqueous phase liquid
DO	Dissolved oxygen
iZVI	Injectable zerovalent iron particles
mZVI	Micro-scale zerovalent iron
NAPL	Non-aqueous phase liquid
nZVI	Nano-scale zerovalent iron
ORP	Oxido-reduction potential = redox potential
PCE	Tetrachloroethylene
PRB	Permeable reactive barrier
TCE	Trichloroethylene
TOC	Total organic carbon
VC	Vinylchloride
ZVI	Zerovalent iron

1 INTRODUCTION

Reactive zones with injected reducing iron particles (iZVI technology) are an innovative in-situ remediation technology for contaminated aquifers. This guideline aims at assisting prospective users of the iZVI technology through the various steps, which have to be performed in order to use the injectable ZVI technology in an optimal way. More specifically, information is provided for supporting consultants, authorities and scientists to evaluate the feasibility and the impact of the iZVI-zone technology to remediate contaminated sites, as well as for designing, implementing and monitoring iZVI-zones.

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 IZVI-ZONE TECHNOLOGY

2.1 Concept

The use of zero-valent iron (ZVI) as a nontoxic material has been shown as one of the most promising remediation techniques for in situ passive removal of chlorinated hydrocarbons via abiotic reductive dehalogenation (Gillham and O'Hannesin, 1994; Mathenson and Traynek, 1994). Since early 1990s ZVI has been used for site remediation in permeable reactive barriers (ZVI-barriers) because of its low cost, availability, and high ability to dehalogenate chlorinated organic compounds over a wide concentration range (EPA, 1999). ZVI-barriers are established in the subsurface by excavating trenches that are refilled with granular (mm-size) ZVI. The contaminants are degraded while the groundwater flows through the ZVI barrier.

Groundwater and aquifer rehabilitation with injectable Fe-based materials (iZVI technology) may be attained using ZVI as micro scale (100 nm < d < 100 µm) or nano-scale (< 100 nm) particles in a specifically designed suspension. The general idea of this method is to inject small sized ZVI particles into the subsurface to spread them over a certain distance before sedimenting or adsorbing to the aquifer matrix (Figure 1). Subsequently, contaminants present in the injection zone as well as contaminants that are transported by the groundwater in the reactive zone can be degraded after contact with the ZVI-particles.

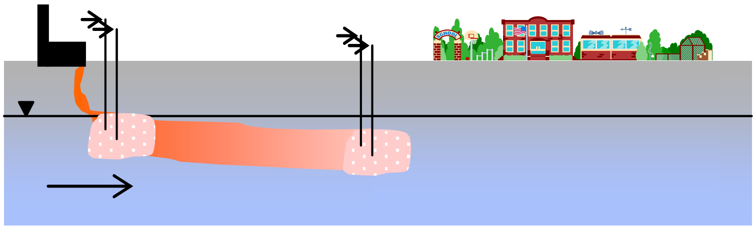


Figure 1 Schematic representation of the groundwater and aquifer rehabilitation with injectable ZVI particles.

Injection of ZVI more closely to the source zone actively removes the contaminants and thus results in a decrease in remediation time, whereas injecting particles for plume control (reactive barrier) may be efficiently prevent contaminants from migrating from a site. However it is unlikely to result in a remediation of the source when significant amounts of DNAPL are present.

Compared to the more established ZVI-barrier technology, a major advantage of the iZVI technology is that the reactive zone may be installed via injection, hence no expensive construction techniques are required. The reactive zone may even be installed underneath buildings and at deeper levels (Figure 2).

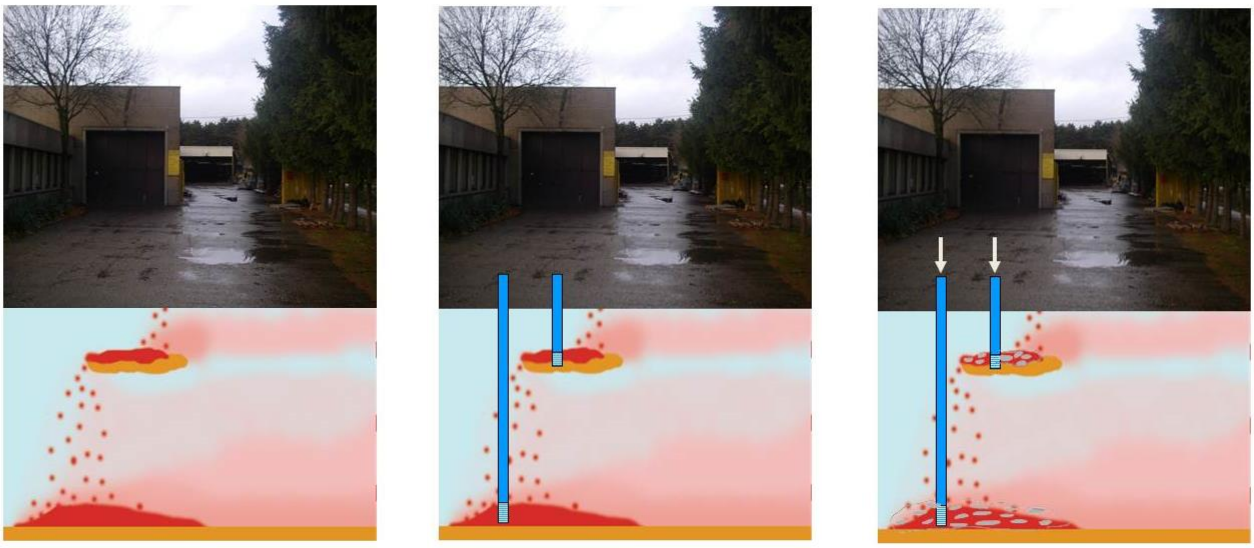


Figure 2 Contamination underneath buildings - Drilling of injection wells – Injection of iZVI particles. (pollutants are represented by the red colour; the darkest red colour represents small droplets of residual phase).

In addition, smaller sized ZVI particles are more reactive and can be applied closer to the source zone of the contamination, which potentially leads to a great reduction of the time necessary for remediation. The mobility of the particles in the subsurface is inversely correlated with their size. On the other hand, the life-time of fine sized particles is lower and the price increase significantly with reduced size (Figure 3).

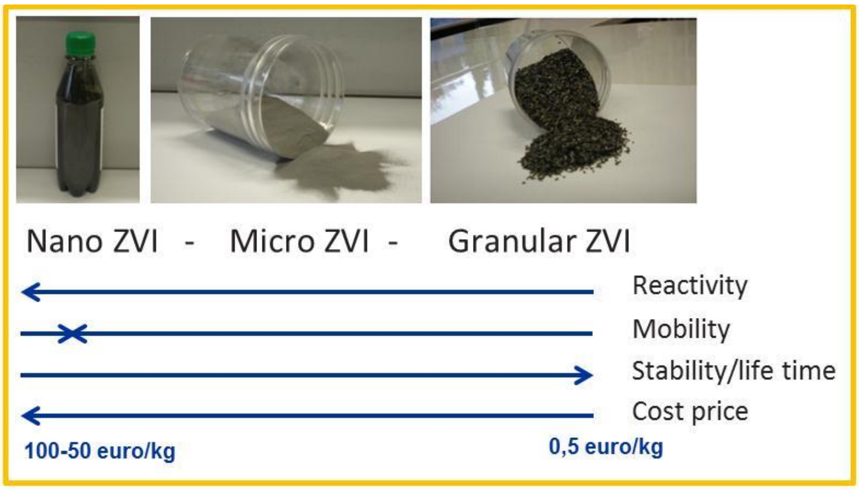


Figure 3 Comparison of different sized ZVIs.

2.2 Targeted substances

An overview of the substances that can be targeted by the iZVI technology is given in Table 1 (adapted from Zhang 2003). While this table is not conclusive, it clearly shows that the potential uses of the iZVI technology are very versatile and ZVI can be applied to many sites where hazardous substances have to be treated.
A part of the compounds that are mentioned is completely degraded by the ZVI, while others are only transformed (dyes, chloro-aromatics, etc.) or immobilised (metals, etc.). This document mainly focusses on chlorinated ethenes that can be completely degraded by the ZVI.

Table 1 Detailed overview of substances that can be targeted by ZVI particles.

Substance	Substance
Chlorinated methanes	**Trihalomethanes**
Carbon tetrachloride (CCl4)	Bromoform (CHBr3)
Chloroform (CHCl3)	Dibromochloromethane (CHBr2Cl)
Dichloromethane (CH2Cl2)	Dichlorobromomethane (CHBrCl2)
Chloromethane (CH3Cl)	**Chlorinated ethenes**
Chlorinated benzenes	Tetrachloroethene (C2Cl4)
Hexachlorobenzene (C6Cl6)	Trichloroethene (C2HCl3)
Pentachlorobenzene (C6HCl5)	*cis*-Dichloroethene (C2H2Cl2)
Tetrachlorobenzenes (C6H2Cl4)	*trans*-Dichloroethene (C2H2Cl2)
Trichlorobenzenes (C6H3Cl3)	1,1-Dichloroethene (C2H2Cl2)
Dichlorobenzenes (C6H4Cl2)	Vinyl chloride (C2H3Cl)
Chlorobenzene (C6H5Cl)	**Other polychlorinated hydrocarbons**
Pesticides	PCBs
DDT (C14H9Cl5*)*	Dioxins
Lindane (C6H6Cl6*)*	Pentachlorophenol (C6HCl5O)
Organic dyes	**Other organic contaminants**
Orange II (C16H11N2NaO4S)	N-nitrosodimethylamine (NDMA) (C4H10N2O)
Chrysoidine (C12H13ClN4)	TNT (C7H5N3O6)
Tropaeolin O (C12H9N2NaO5S)	**Inorganic anions**
Acid Orange	Dichromate ($Cr2O^{2-}7$)
Acid Red	Arsenic ($AsO^{3-}4$)
Heavy metal ions	Perchlorate ($ClO^{-}4$)
Mercury (Hg^{2+})	Nitrate ($NO^{-}3$)
Nickel (Ni^{2+})	
Silver (Ag^{+})	
Cadmium (Cd^{2+})	

2.3 Reaction mechanism

2.3.1 Reaction pathways for chlorinated ethenes

The degradation of chlorinated compounds by ZVI into less toxic compounds is based on electron transport from the ZVI to the pollutant. Figure 4 presents three possible mechanisms for this electron transport (Matheson and Tratnyek 1994).

The first mechanism involves direct electron transfer from the ZVI surface to the chlorinated compound, and is considered to be the main mechanism :

$Fe^0 + RCl + H^+ \dashrightarrow Fe^{2+} + RH + Cl^-$ (1)

The second mechanism involves ferrous iron (Fe^{2+}) formed by iron corrosion with water:

$2Fe^{2+} + RCl + H^+ \dashrightarrow 2Fe^{3+} + RH + Cl^-$ (2)

The third mechanism involves molecular hydrogen which is a product of iron corrosion with water:

$H_2 + RCl \dashrightarrow RH + H^+ + Cl^-$ (3)

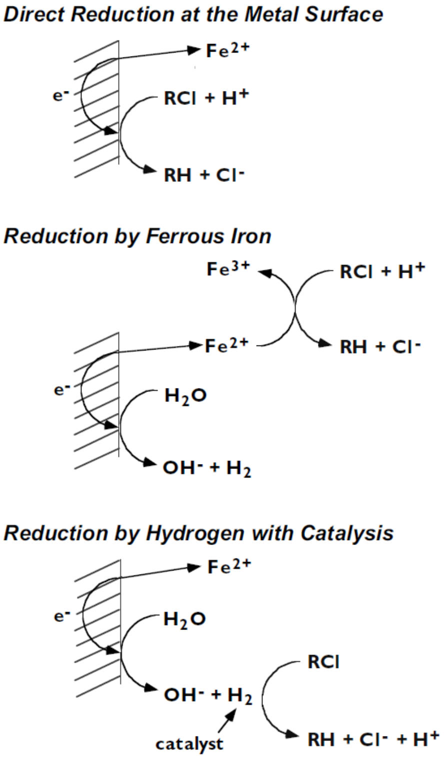


Figure 4 Possible mechanisms for reduction of CAHs by ZVI (Matheson and Tratnyek, 1994).

Different reaction pathways have been reported for degradation of chlorinated compounds involving β-elimination, hydrogenolysis, α-elimination, and/or hydrogenation (Arnold and Roberts 2000). The main degradation pathways of chlorinated ethenes are presented in Figure 5**.**

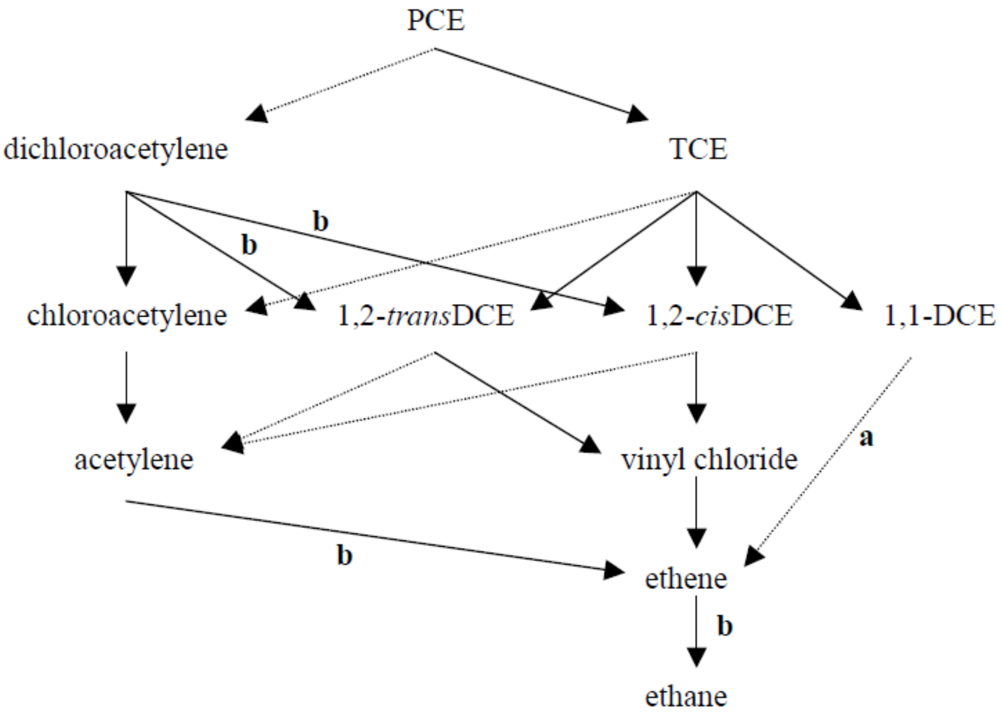


Figure 5 Transformation pathways of chlorinated ethenes in anaerobic conditions (full arrows represent hydrogenolysis reactions, dotted arrows represent reductive *β-elimination* reactions, reaction "a" proceeds via *α-elimination*, and reactions "b" are hydrogenation reactions (Arnold and Roberts 2000).

2.3.2 ZVI corrosion

ZVI is an active agent that rapidly reacts with oxygen (**aerobic corrosion**):

$$4\,Fe + 3\,O_2 + 6\,H_2O \rightarrow 4\,Fe(OH)_3 \downarrow \qquad \textbf{(4)}$$

For this reason, use of the iZVI technology in the unsaturated zone is rarely possible, due to the presence of air containing oxygen. In the saturated zone, the technology is most efficient in oxygen free groundwater.

Under anaerobic conditions, ZVI will undergo **anaerobic corrosion** implying reaction with water:

$$Fe + 2\,H_2O \rightarrow Fe^{2+} + H_2 + 2\,OH^- \qquad \textbf{(5)}$$

The solubility of oxygen in water is very limited and, thus, aerobic corrosion will cease fairly quickly, as soon as the dissolved oxygen is consumed. The anaerobic corrosion, however, will be a persistent reaction which is competing with the desired reaction with the contaminants.

Although the reactions and reaction mechanisms for the various potential contaminants are quite different, the competing corrosion reactions remain. This requires a stoichiometric excess of iron compared to the quantity of contaminants present in the aquifer. This aspect emphasizes that most likely it is economically better to implement this technology in areas with higher pollutant concentrations (mg/L range).

ZVI corrosion rates are strongly depending on the hydro-chemical characteristics of the groundwater. Anaerobic corrosion is greatly influenced by the pH, with higher corrosion rates at neutral and even more at acidic pH values. Also other electron acceptors (beside oxygen and water) present in the ground water such as nitrate can consume ZVI. Therefore, a detailed characterisation of the groundwater chemistry prior to the application of ZVI suspensions is needed.

2.3.3 Points of attention related to source zone treatment

The National Research Council (NRC 2004) defines a groundwater contamination source zone as follows:

> "…a saturated or unsaturated subsurface zone containing hazardous substances, pollutants or contaminants that acts as a reservoir that sustains a contaminant plume in groundwater, surface water, or air, or acts as a source for direct exposure. This volume is or has been in contact with separate phase contaminant (NAPL or solid). Source zone mass can include sorbed and aqueous-phase contaminants as well as contamination that exists as a solid or NAPL.

As such, a source zone is the zone where a groundwater contamination plume is being created. It could be NAPL pool, residual NAPL (both require NAPL as a separate phase) or back-diffusion from "impermeable" layers (Figure 6). Usually, in the source zone the concentration is higher than in a plume. The contamination plume has contaminants that are dissolved in the groundwater at a location where there is no recharge.

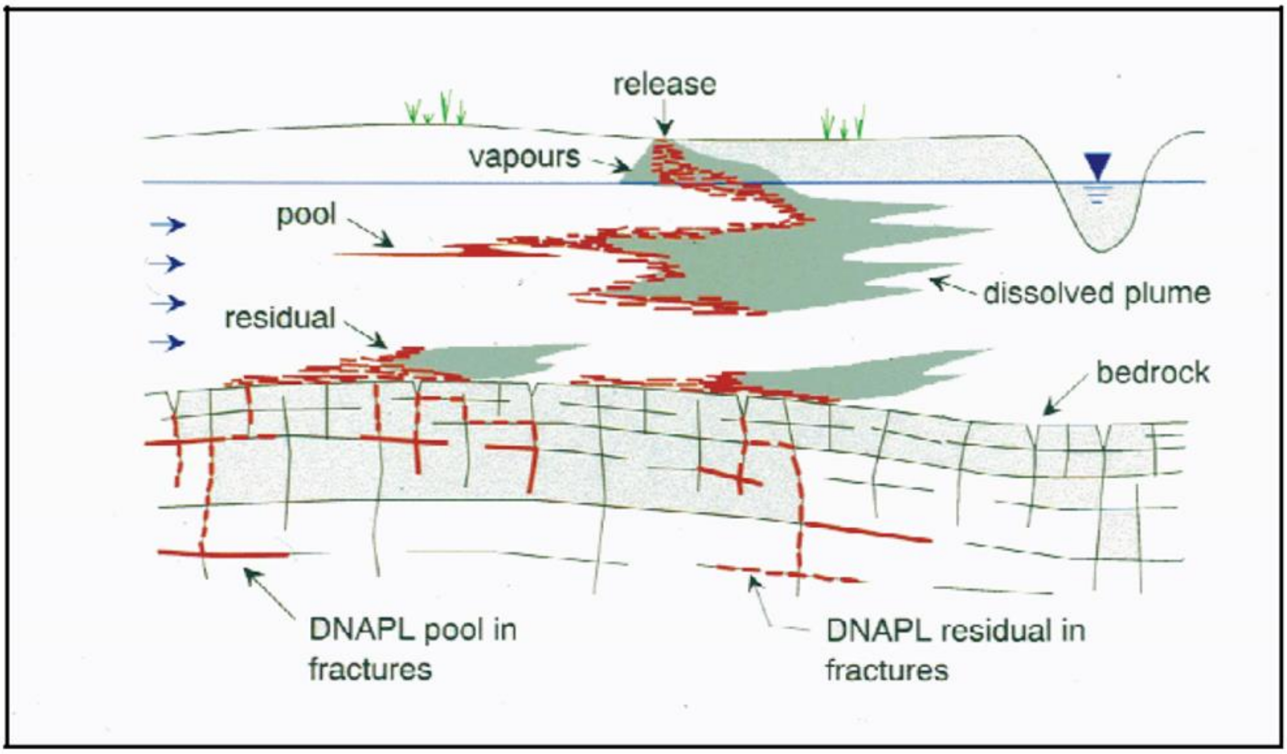


Figure 6 Conceptual site model of a DNAPL source zone (UK environmental Agency, 2004)

There is quite some discussion and confusion related to the applicability of the iZVI-technology in source zone.

Considering the fact that (1) iZVI particles do have a limited mass, (2) do have a relatively short life time, and (3) competing reactions in the subsurface cannot be avoided (mainly anaerobic corrosion), a higher pollutant concentration is expected to result in a higher pollutant removal per mass of injected iZVI. From this perspective, source zones may be an interesting application area for iZVIs.

However, because the chemical reduction of chlorinated solvents by ZVI is based on the anaerobic corrosion of ZVI by water (with the release of reducing equivalents such as molecular hydrogen), the contact of ZVI with water is a prerequisite for successful dechlorination. That infers that it can be expected that ZVI-particles cannot be effective within a separate DNAPL phase. For that reason, ZVI particles have been formulated as emulsified ZVI for the treatment of DNAPL pools in source zones (EZVI, patented by NASA). Such EZVI has the ZVI surrounded by water within a micelle that is present in an oil in water emulsion as represented in Figure 7.

When no DNAPL pools are present anymore in the subsurface, only sorbed NAPL or a limited amount of residual NAPL, the iZVI technology with non-emulsified ZVI may be successful. Since the time frame of back diffusion (many years) is much longer than the longevity of iZVI the treatment of this kind of source would require (as in the case of plume treatment) frequent reinjection of particles which might render the application of iZVI for some of these sources uneconomic.

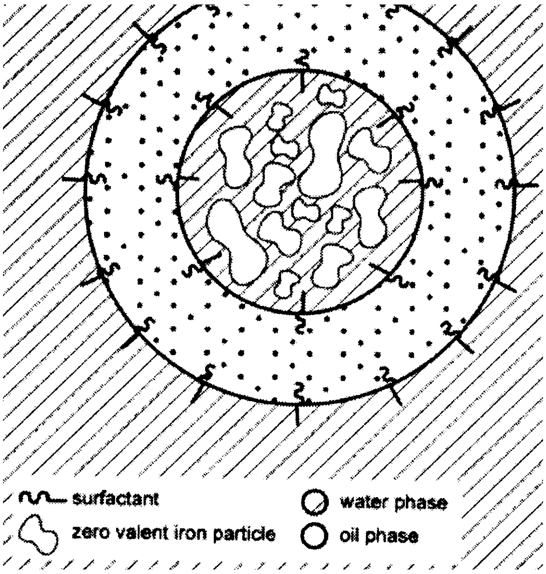


Figure 7 Schematic representation of an emulsified nZVI droplet (Quin et al., 2005).

2.3.4 Reaction rates

The reactivity of ZVI materials towards chlorinated compounds can be quantified by dechlorination rates calculated using the pseudo-first order rate equation:

$$C = C_0 \cdot e^{-kt} \qquad \textbf{(6)}$$

with C the concentration at any time, C_0 initial concentration, k the first order decay constant [day^{-1}] and t the reaction time [days]. Half-lives can be calculated as:

$$t_{1/2} = \ln 2/k \text{ [days]} \qquad \textbf{(7)}$$

First order rate constants and half-lives of different CAHs obtained with a variety of ZVI-types are reported in Table 2, and are mostly deduced based on laboratory batch studies. Due to possible pH-increases in the batch bottles, the listed rates may be an underestimation of the field rates. From the field, however, very few reliable data is available to date.

Table 2 The first order decay constant k (h^{-1})and half life times $t_{1/2}$ (h) for reaction of different chlorinated compounds with ZVI particles, adapted from Gillham and O'Hannesin (1994) and Song and Carraway (2005).

Compound	*Treatment*	*Specific surface area (m^2 g^{-1})*	k (h^{-1})	$t_{1/2}$ (h)	*Reference*
Methanes					
Tetrachloromethane	*Fisher electrolytic*	*0.287*	2.77×10^0	0.25	a)
Trichloromethane	*Fisher electrolytic*	*0.287*	2.10×10^{-2}	33.0	a)
Ethanes					
1,1,2,2-tetrachloroethane	*Fisher electrolytic*	*0.287*	3.61×10^{-2}	19.2	a)
	Nanosized iron	*27.9 ± 1.7*	6.82×10^{-2}	10.16	b)
1,1,1,2-tetrachloroethane	*Fisher electrolytic*	*0.287*	1.57×10^{-1}	4.4	a)
	Nanosized iron	*27.9 ± 1.7*	1.21×10^0	0.57	b)
1,1,1-trichloroethane	*Fisher electrolytic*	*0.287*	1.31×10^{-1}	5.3	a)
	Nanosized iron	*27.9 ± 1.7*	3.40×10^{-1}	2.04	b)
	Nanofer25s	*25*	1.2×10^{-1}	5.77	c)
	Höganäs irons	*0.06-3.98*	1.6×10^{-2} - 1.6×10^{-5}	43 - 43312	c)
1,1-dichloroethane	*Nanosized iron*	*27.9 ± 1.7*	2.41×10^{-4}	2875	b)

Compound	***Treatment***	***Specific surface area (m^2 g^{-1})***	***k* (h^{-1})**	**$t_{1/2}$ (h)**	***Reference***
Ethenes					
Tetrachloroethene	*Fisher electrolytic*	*0.287*	3.87 x 10^{-2}	17.9	a)
	Nanoscale Pd/Fe	*35*	2.13 x 10^{0}	0.32	d)
	Iron filings		1.6 x 10^{-1}		e)
	Nanofer25s	*25*	1.4 x 10^{-2}	49.5	c)
	Höganäs irons	*0.06-3.98*	2.3 x 10^{-2} - 9.6 x 10^{-5}	30.1 - 7219	c)
Trichloroethene	*Fisher electrolytic*	*0.287*	5.1 x 10^{-2}	13.6	a)
	Fisher electrolytic	*1.635*	4.25 x 10^{-1}	1.63	f)
	Nanoscale Pd/Fe	*33.5*	6.70 x 10^{1}	0.01	g)
	Riedel powdered Fe^0	*n.a.*	2.7 x 10^{-4}	2589	h)
	Nanoscale Pd/Fe	*35*	3.18 x 10^{0}	0.22	d)
	Fisher Fe^0	*1.1*	(7.5±0.2) x 10^{-3}	92.4	*i)*
	nano	*18*	1.98 x 10^{0}	0.35	*j)*
	nine types of granular ZVI*	*n.a.*	*n.a.*	*n.a.*	*k)*
	ZVI powder	*0.71*	7.6 x 10^{-2}	9.1	*l)*
	Microscale iron	*1.8*	8.0 x 10^{-2}	8.7	*m)*
	Fe/B nanoscale	*36.5*	1.02 x 10^{-1}	0.68	*n)*
	RNIP Toda	*23*	3.45 x 10^{-2}	20.08	*n)*
	Iron filings	*n.a.*	2.7 x 10^{-1}	*n.a.*	*e)*
	Nanofer25s	*25*	1.2 x 10^{-2}	*58*	*c)*
	Höganäs irons	*0.06-3.98*	1.1 x 10^{-2} - 4.2 x 10^{-5}	*63 - 16500*	*c)*
1,1-dichloroethene	*Fisher electrolytic*	*0.287*	1.73 x 10^{-2}	40.0	a)
	Nanoscale Pd/Fe	*35*	2.01 x 10^{0}	0.34	d)
Trans-dichloroethene	*Fisher electrolytic*	*0.287*	1.26 x 10^{-2}	55.0	a)
	Nanoscale Pd/Fe	*33.5*	0.7 x 10^{-1}	0.1	o)
	Microscale Fe (Aldrich)	*0.9*	1.8 x 10^{-3}	385	o)
	Nanoscale Pd/Fe	*35*	2.64 x 10^{0}	0.26	d)
Cis-dichloroethene	*Fisher electrolytic*	*0.287*	1.60 x 10^{-3}	432.0	a)
	Nanoscale Pd/Fe	*35*	3.08 x 10^{0}	0.22	d)
	Nanofer25s	*25*	1.0 x 10^{-2}	69.3	c)
	Höganäs irons	*0.06-3.98*	1.2 x 10^{-3} – 3.3 x 10^{-5}	533 - 21000	c)
Vinyl chloride	*Fisher electrolytic*	*0.287*	1.85 x 10^{-3}	374.0	a)

* Aldrich powder (Milwaukee, WI, 97%), Fisher electrolytic powder (Pittsburgh, PA, 99%), EM Science degreased filings (Cherry Hill, NJ), Fluka filings (Milwaukee, WI, 99+%), Baker chips (Phillipsburg, PA, 99.9%), Fisher filings (Pittsburgh, PA, >97%), Master Builders (Cleveland, OH), Peerless Powders and Abrasives (Detroit, MI, “PMP Traditional” Size 8/50, >90%), and Connelly (Chicago, IL, ETI CC-1004, 90%). ** the average k_{SA}’s

a) Gillham and O’Hannesin, 1994; b) Song and Carraway, 2005; c) Velimirovic et al. 2013; d) Lien and Zhang, 2001; e) Dries et al., 2005; f) Johnson et al., 1996; g) Wang and Zhang, 1997; h) Cheng and Wu, 2000; i) *Tratnyek et al., 2001;j) Schrick et al., 2002; k) Miehr et al., 2004; l) Lookman et al., 2004; m) Jung Lin and Lo, 2005; n) Liu et al., 2005; o)* Zhang et al., 1998

The dechlorination rate of ZVI is strongly dependent on characteristics of the ZVI particles, comprising (1) specific surface of the particles; (2) particle size; and (3) composition of the particle (pure iron vs. iron alloys, bimetallic particles) (Velimirovic et al., 2013a, 2013b). Further, also the composition of the suspension (Velimirovic et al., 2014a)and surface treatments of the ZVI particles influence the ZVI reactivity. This makes it on one hand difficult to predict the efficiency in a specific field situation, but on the other hand opens a variety of measures to optimize particles for specific conditions in an aquifer.

2.4 Mobility of iZVI

For successful field applications, the iZVIs need to be mobile to a certain extent to allow them to be distributed around the injection points. In contrast to earlier thoughts, iZVIs are much less mobile due to aggregation and sedimentation. Therefore, the radius of influence that can be reached around injection points is smaller than initially estimated.

2.4.1 Aggregation & sedimentation of iZVIs

The stability against sedimentation is a critical point, because experimental results indicated that all mZVI and nZVI particles (Tiraferri et al., 2008; Tiraferri and Sethi, 2009), when dispersed in pure water, do not form a stable colloidal suspension, due to their large size. The fast sedimentation of the particles in the water has an extremely negative impact on their injectability and also on the mobility in the porous medium: iron micro-particles in pure water sediment inside the tanks where the water/particles dispersion is stored before the injection, as well as inside the pumps and tubing of the injection machines. Also, fast sedimentation occurs in the porous medium, thus resulting in an extremely limited radius of influence of each injection point.

As a consequence, when working with mZVI particles, the stability of the dispersions has to be improved. A successful approach consists in increasing the viscosity of the dispersion by means of addition of “green” biopolymers, eg. xanthan gum and guar gum (Cantrell et al., 1997; Comba et al., 2011; Comba and Braun, 2012; Gastone et al., 2014a; Luna, 2013; Saleh et al., 2007; Tiraferri and Sethi, 2008; Xue and Sethi, 2012), thus providing the so-called viscous stabilization (Figure 1). This approach is effective in increasing both stability against sedimentation and mobility in the porous medium (Dalla Vecchia et al., 2009).

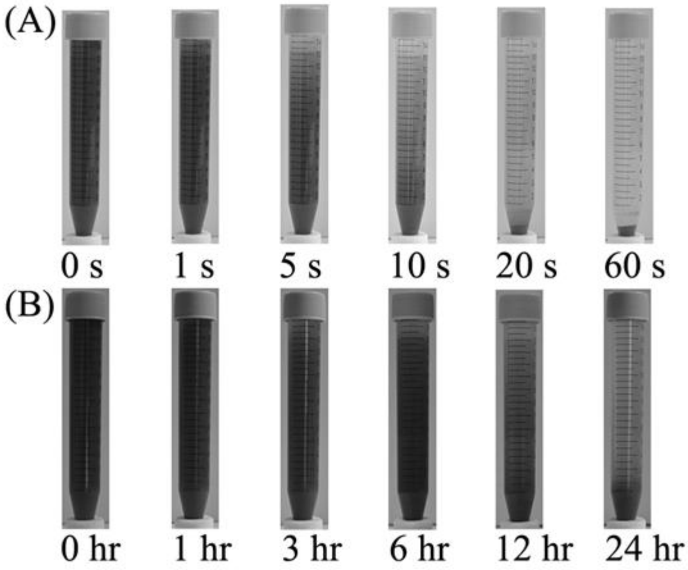


Figure 8 Sedimentation of (A) non-stabilized mZVI (50 g L^{-1}) and (B) mZVI (50 g L^{-1}) stabilized by guar gum (6 g L^{-1}).

2.4.2 Transport of iZVIs

Some data on the radius of influence (ROI) that have been observed within the AQUAREHAB project are summarised in Table 3. They indicate that iZVIs are limited mobile and that the mobility is influenced by the particle size, injection flow rate, granulometry of the soil, etc. More detailed calculation of ROI are part of appendix D.

Table 3 Radius of influence of a single iZVI injection.

Particle	Test conditions	Radius of influence	Reference
nZVI (D50 = 3-9 µm aggregates of 70 nm particles)	Tank experiment, permeation, coarse sand,	0.5-1 m (1 m^3/h) > 1.5 m (3-6 m^3/h)	De Boer, C, 2012
mZVI (D50= 50 µm) – guar gum stabilised	Field, direct push, high pressure & high volume injections	Very heterogeneous distribution, up to 2-4 m from injection well	Velimirovic et al., 2014c (AQUAREHAB)
mZVI (1-2 µm) – guar gum stabilised	Field, injection well, permeation, low pressure injection, fine sand	0.8 m (9 m^3/h)	Gastone et al., 2014b (AQUAREHAB)
mZVI (50 µm) – guar gum stabilized	Field, direct push – high pressure low injection volume, fine sand	0.5 m (with hetergeneous distributions observed further from the injection points)	(AQUAREHAB)

Within the AQUAREHAB project, the mobility of guar gum stabilized mZVI was assessed from a both experimental and numerical point of view.

Column transport tests performed within AQUAREHAB (Tosco et al., 2014) evidenced that both flow rate and guar gum concentration have a great impact on the mobility of the iron particles in porous media, and consequently on their fate in the environment in the short term (i.e. just after the injection in the field, during the remediation activities) as well as in the long term, when evaluating the final fate of the injected particles. Also, in the short term the residual undissolved guar gum can play a role in porous medium clogging. Concerning the long-term fate, no specific tests were performed. However, basing on the experimental results the long-term re-mobilization is expected to be a minor issue formZVI, due to their large size, as suggested by column transport tests, where reduced particle release was observed after injection, when the column was flushed with particle-free solution.

nZVI and mZVI field injection can be performed following a permeation injection or a fracturing injection approach. The modelling for permeation injection can be faced using advection-dispersion equations, modified on purpose to include deposition and release phenomena, clogging, and other specific processes, as detailed below. Conversely, modelling fracturing injection in shallow systems (like typical contaminated aquifers) is an extremely critical issue, and is usually not faced for the field-scale application design. In reality, at most injection sites, preferential flow paths are created during injection of iZVIs due to the pressures used to implement the material within a reasonable time.

2.4.3 Modelling of iZVI mobility

Considering permeation injection, a reliable estimate of particles mobility requires a modelling approach based on the numerical solution of a modified form of the advective-dispersive transport equations. Porous media transport models for mZVI and nZVI are usually based on advection-dispersion equations, modified on purpose to include deposition and release phenomena, clogging, and other specific processes, as detailed below. In both one-dimensional and radial models (suitable for the simulation of field injection of mZVI and nZVI), the key aspects included in the model are clogging phenomena (i.e. reduction of porosity and permeability due to particles deposition), and the rheological properties of the carrier fluid (in this project, guar gum solution) for a correct estimate of pressure drops. Moreover, in radial geometry, the flow rate is not constant, but decreases hyperbolically with increasing distance from the injection point. For this reason, a space-variable flow velocity is to be considered, affected both by reductions in porosity and by increasing distance from the injection point. As all model equations are strictly coupled, changes in flow rate affect the non-Newtonian viscosity of the carrier fluid, and consequently the pressure drop, as well as the deposition and release kinetics, which depend on flow rate and fluid viscosity.

2.5 Development stage of the iZVI technology

2.5.1 Field applications

Although quite a number of field applications have been conducted worldwide (Table 4), the technology still lacks a sound scientific proof. Most of the applications have been conducted in North America and reliable data on success or failure are only publically available to some degree. Therefore, the technology can be categorized **"becoming transferable"** until additional field data are made available and further proof of success has been shown.

Table 4 Literature review about pilot tests with mZVIs and nZVIs with efficiency, adapted from Karn et al. (2009) and from Muller et al.(2012)

Site	Year	Target compounds	Iron particles	Injection technology	Iron efficiency	Ref.
Trenton	2001	PCE, TCE, c-DCE, vinyl chloride, chloroform, carbon tetrachloride, 1,1-DCE	BNP	Gravity + recirculation	Contaminant concentrations reduced by 1.5% to 96.5%	a)
Launch complex 34, Cape Canaveral (FL) – U.S.A.	2002	TCE and corresponding daughters corresponding daughters	EZVI	Pressure Pulse Technology	Contaminant concentrations reduced by 99%	b)
Research Triangle Park (NC) – U.S.A.	2002	TCE & cis-1,2-DCE	BNP	Gravity + recirculation	90 percent reduction of total VOCls concentrations	c)
Klockner Road Site, Hamilton (NJ) – U.S.A.	2004	TCE, DCE, TCA, DCA	nZVI	Direct push	Contaminant concentrations reduced up to 99%	d)
NAS Jacksonville (FL) – U.S.A.	2005	TCE, TCA, DCE, vinyl chloride	BNP	Direct push + recirculation	Rapid reductions by 65% to 99%	e)
NAES Lakehurst – U.S.A.	2005	Soil: PCE, TCE, 1,1,1-TCA Groundwater: PCE, TCE, cis-DCE	BNP	Direct push	The average decrease in total VOCls concentrations was 74%.	e)
Marshall Space Flight Center, Huntsville (AL) – U.S.A.	2000	TCE	mZVI	Pneumatic fracturing	90% of TCE reduction, increase in cis-1,2-DCE	f)
Hunter Point Shipyard (CA) – U.S.	2002	TCE	mZVI	Pneumatic fracturing	99% of reduction	e)
DuPont's Kinston Plant, Ontario, CAN	1999	TCE	Granular ZVI	Clay-soil mixing	95% of reduction	g)

Site	Year	Target compounds	Iron particles	Injection technology	Iron efficiency	Ref.
Camp Lejeune (NC) – U.S.A.	2005	PCE (soil & groundwater)	Granular ZVI	Clay-soil mixing	Significant decrease of 67-90%	h)
Goodyear (AZ) – U.S.A.	2007	TCE, PCE, Perchlorate	nZVI	Jetting	n.a.	i)
Marine Corp Logistic Base, Albany (GA) – U.S.A.	2002	TCE, PCE, DCE, TCA, and VC	ZVI Ferrox	Pneumatic fracturing	n.a.	j)
Palo Alto (CA) – U.S.A.	2006	PCE, TCE, Freon	nZVI	Push Pull	n.a.	k)
Bornheim, Germany	2007	PCE	nZVI + mZVI	Sleeve pipe injection	approximately 90% reduction of the concentration of total chlorinated compounds.	l)
Horice, Czech Republic	2008	PCE, TCE, DCE	nZVI	Direct Push	Reductions of 60–75% of the original contaminant concentration were achieved	l)
Pisecna, Czech Republic	2009	Chlorinated ethenes	nZVI	?	Significant decrease of 40-80%	l)
Biella, Italy	2005	TCE & cDCE	nZVI	Gravity infiltration	20-50% reductions in total chlorinated solvent concentrations after one month	m)
Former USAF “Atlas 12” Missile Site, Colorado, USA	2009	TCE	MicroMicroiron/carbon (Adventus EHC) - “EHC-G”	Fracturing	TCE reduction with first 90 days cis-DCE increased Ethene detected at low levels	n)
Belgium		TCE	mZVI	Injection well	Pilot Failure due to sedimentation of the mZVI	o)
Belgium (AQUAREHAB)	2012	1,1,1-TCA	mZVI (guar gum stabilised) (Höganäs)	Direct push	Pilot– focus on injectability In-situ degradation of 1,1,1-TCA observed	p)
Belgium (AQUAREHAB)	2013	TCE	mZVI (1-2 μm) (guar gum stabilised) (Höganäs)	Injection well	Pilot – focus on injectability In-situ Incraeses in ethene & cDCE concentrations observed	q)
Belgium (AQUAREHAB)	2013	TCE	mZVI (50 μm) (guar gum stabilised) (Höganäs)	Direct push (MIP-IN)	Pilot – focus on injectability In-situ Incraeses in ethene & cDCE concentrations observed	r)
Belgium	2013	TCE	mZVI (guar gum stabilised) (Höganäs)	Soil mixing	Pilot test Smooth injection Increases in ethene & cDCE observed	s)

<table>
<tr><th>Site</th><th>Year</th><th>Target compounds</th><th>Iron particles</th><th>Injection technology</th><th>Iron efficiency</th><th>Ref.</th></tr>
<tr><td colspan="7">n.a. information not available, a) Elliot and Zhang, 2001, b) Quinn et al., 2005, c) Zhang and Elliot, 2006, d) Varadhi et al., 2005, e) Gavaskar and Condit, 2005, f) USEPA, 2003, g) Kavanaugh and Rao , 2003, h) Bozzini, 2005, i) Chang, 2010, j) Sprinkle, 2004, k) Bennett, 2010, l) Muller et al., 2012, m) http://www.nanotechproject.org/inventories/remediation_map, n) North Wind Inc., 2010; o) unpublished; p) Velimirovic et al., 2014c; q) Luna et al., submitted; (r) Velimirovic et al., in preparation; s) unpublished VITO and A+E</td></tr>
</table>

BNP: bimetallic nanoscale particles with palladium shell
EZVI: emulsified zerovalent iron
mZVI: microscale zerovalent iron
nZVI: nanoscale zerovalent iron
ZVI Ferox: microscale iron particles (commercial product, ARS Techonlogies)

Up to now, most field applications of the iZVI technology have been performed with nZVI (Table 4), while the use of mZVI is more recent and it is less evaluated with field trials. The AQUAREHAB project contributed here by performing and documenting 3 pilot tests with micro-scale ZVI injections.

2.5.2 Acceptability

Technical acceptability

With respect to the "acceptability of the technology", it needs to be mentioned that larger ZVI particles (mm-range) have been extensively used during the past decades for the remediation of chlorinated hydrocarbons, as well as of a wide range of other contaminants. In particular, the use of granular ZVI filings in permeable reactive barriers (PRBs) is a consolidated technology which has been applied at a number of sites and it is well-accepted (see generic guideline ZVI-barrier).
Injection of ZVI particles for in-situ aquifer remediation is less accepted than the PRB technology, because of the lack of scientific proof of the performance in the field. The performance of the technology on the lab scale has been improved considerably. In the field, the subsurface is usually heterogeneous or at best anisotropic, resulting in an inhomogeneous distribution of iron after injection. In other words, the exact position of the injected iron is often not known, creating an uncertainty. In addition, the evaluation of the impact of the injected particles on the pollutant concentration has been shown to be challenging.

Safety issues

The use of fine ZVI particles, and especially nanoscale zerovalent iron (nZVI) particles, raises questions regarding (1) their fate after injection in the subsurface and (2) environmental safety in general. Micro-scale zerovalent iron (mZVI) particles are of less of concern with respect to environmental safety as they are nearly immobile after injection.

Mobility. During the last years, the mobility of fine ZVI particles has been studied by several groups. The main conclusions from these studies are that the bare particles (even though they are nano sized) are not very mobile, often even insufficiently mobile to inject them in the subsurface (Dalla Vecchia et al., 2009; Tosco et al., 2014). With respect to fate of mZVI in the subsurface, it can be concluded that mZVIs are not expected (1) to migrate far from the injection well during the injection nor (2) to migrate after the injection. As such, the impacts of mZVI are very local.

Environmental risks. Although the injectable ZVI-particles are not very mobile, the environmental concern remains to some extent. Potential risks of fine iZVI could be direct or indirect toxic effects towards non-target organisms within both aquatic and soil environments. In some EU countries the injection of nZVI particles is currently prohibited, pending positive proof of their environmental safety (Hansen & Braun, 2012).

Within the AQUAREHAB project, potential ecotoxic impacts of ZVI particles (and acidic Fe materials) on both aquatic and soil biota were examined. The main aim was to examine whether iZVIs do not pose a threat when used in large scale field application.

- **Ecotoxicity to aquatic and soil biota** was tested with the bioassays corresponding to available standards and feasibility. In total five bioassays have been used including aquatic tests (bioluminescent bacteria, algae) and soil models (plants - two species, annelid worms). Some effects on model organisms have been observed at high doses of specific batches of ZVI particles, but they were rather short-term and were eliminated during aging experiments. The overall benefit-to-risk ratio was concluded to be positive, considering the minor and local scale of ecotoxicological impacts (a few square meters for the worst case situations, in case daylightening of the injection fluid would occur).
- **Soil micro-organisms**: An ATP bioluminescence assay approach was done to evaluate the worst case scenario of potential impacts of iZVIs on CAH-degrading enrichment cultures (Velimirovic et al., in preparation). Stimulating effects on the bacterial activity have been observed, as well as reduced activities when high doses were applied. The experimental data suggest that nZVI have more negative influence on CAH-degrading enrichment cultures than mZVI particles. The observed inhibiting effects could be related to pH increases above pH7.5, which are induced by the ZVI. Whether the cells are killed or only temporarily reduced in activity cannot be concluded from the test. In any case, the presence of aquifer material is expected to act as a buffer protecting the bacteria. As such the impact in the real environment is expected to be minimal.

These tests, as all the other tests, did not reveal elements that are conflicting with the use of ZVI particles as reactive material for in situ application. Within AQUAREHAB environmental risks were assessed and a positive benefit/risk was found, especially for mZVI particles.

2.6 Applicability and boundary conditions of the technology

Table 5 gives an overview of possible uses of the injectable ZVI technology. It names the parameters controlling the application, rates their suitability and briefly comments on their importance and influence.

Table 5 Parameters controlling the applicability of injected ZVI technology

Parameter	State	Suitability*	Comments
Unsaturated zone		--	Competing reactions with oxygen dominate: extremely high oxidation rate of ZVI particles, reduction of contaminant negligible - reaction takes place in aqueous phase
Saturated zone	Aerobic	+	Competing reactions with oxygen, high oxidation rate of particles at low reduction of contaminant
	Anaerobic	+++	No aerobic corrosion
pH	High	+++	Slow anaerobic corrosion
	low	--	Economically not interesting due to increased corrosion
Hydraulic conductivity	High	+	Potential problems due to high ground water velocity often associated with aerobic conditions
	Moderate	+++	

Parameter	State	Suitability[*]	Comments
	Low	+	Delivery of the iZVI via permeation not possible - fracturing is an option
Contaminant concentration	bulk amounts of free product (DNAPL)	--	Reaction needs the presence of water; Very high doses of ZVI would be needed to cope with the pollution
	Residual free product	++	Source zones; special attention needed for accumulation of metabolites (partial degradation)
	High dissolved concentrations	+++	Source zones or plumes with high soluble concentrations
	Low dissolved concentrations	-	Economically not interesting

[*] -- : Not suitable; - : Not interesting; + possible; ++ interesting; +++ very interesting.

The iZVI-zone technology is recommended under the following conditions:

- The pollutants present in the groundwater are degradable by ZVI, and do not result in accumulation of non-degradable harmful metabolites.
- Pollutants are dissolved in the groundwater or present as very small droplets of separate fluid phase surrounded by groundwater.
- In principle, there is no depth limitation to the application but injection into deeper source zones or plumes will increase cost for drilling. However, this is partially offset by the additional injection safety as injection in deeper zones will allow higher injection pressures without blow-outs (day lighting).
- With respect to the hydrogeological characteristics of the site:
  - The groundwater flow direction, the gradient and the velocity are known and are relatively stable during the year.
  - In principle, the iZVI-zone technology is applicable for a wide range of groundwater flow velocities. For higher flow velocity, larger dimensions of the iZVI-zones are generally needed (to ensure sufficient contact time). High groundwater velocities will enhance competing reactions (like corrosion of the ZVI) and reduce the longevity/ reactivity of the injected particles, resulting in more frequent reinjections and an increase in remediation cost.
  - The hydraulic conductivity of the injected zone is to be fairly high ($K > 10^{-4}$ m/s) for injection utilizing porous (Darcian) flow. For lower hydraulic conductivities an efficient injection is only possible with the creation of artificial preferential flow paths (fractures). This high pressure application cannot be applied in very shallow (a few m bgs) because of the risk for blow outs.
- The site or the basements of above ground structures is temporarily accessible for drilling equipment and associated infrastructure (mixing/ injection equipment, tanks, etc.). After the injection phase (approx. 2-4 weeks) no above ground installations will impede the beneficial use of the property. At appropriate and predefined locations, well heads should remain accessible for monitoring.
- The geochemical characteristics of the groundwater do not lead to excessive competing redox reaction or large quantities of precipitates that can block the injected reactive zone over time.

The use of iZVI-zones is not recommended in the following cases:

- In the unsaturated zone (ZVI would be consumed predominantly by atmospheric oxygen).

- For pollutants that have not been shown to be degradable, or that are transformed in harmful reaction products.
- For treatment of zones with bulk amounts of free phase (DNAPL).
- For sites with a shallow contamination in low permeability soil (high injection pressures may lead to daylightening).
- High oxygen concentrations and fast groundwater flow will lead to aerobic corrosion of the ZVI particles. This may reduce the longevity of the particles, requiring more frequent reinjection.

2.7 Secondary effects linked to the iZVI technology

2.7.1 Positive effects

Oxidation of ZVI by water will produce hydrogen gas. This may decrease the **hydraulic conductivity** in the treatment zone. On the one hand this may prevent uncontaminated water from entering the source zone and on the other hand it may reduce the flow velocity in the source zone and therefore increase the residence time and the effectiveness of chemical reduction.

After the iron is consumed, a highly reducing environment in the aquifer will persist, which can **promote biodegradation** of the residual contaminants by reductive dechlorination. This effect may be supported by the hydrogen gas which is formed by the anaerobic corrosion of the ZVI particles in the aquifer. Those two effects may also be supportive downstream of the area where the iron actually has been applied. This means that the radius of influence of application of iZVI might be extended beyond the space where iron is present, by influencing the redox conditions downstream of the injection area.

2.7.2 Negative secondary effects

Reduced permeability of the aquifer could arise from precipitation products of the iron, i.e. iron oxides, which can lead to clogging of the aquifer. Although the first reaction step leads to Fe(2+), which is soluble in water, further downstream from the injection area, where oxygen may be present in the ground water, an oxidation of the soluble iron(II) to the insoluble iron(III) will occur. A clogging of the aquifer may also result from the hydrogen gas bubbles that are generated from ZVI (hydrogen gas has a low solubility in water). The latter can be avoided by conditioning of the aquifer such that the pH is kept high (pH>10). However, most often, the hydrogen is readily consumed by the soil micro-organisms.

The iZVI may (temporarily) **impact soil micro-organisms** in a direct or indirect way.

- The injection of iZVI can cause changes in the field conditions, comprising pH-increases and more reducing conditions, that indirectly impact the soil biota. This impact is expected to be minor in buffered aquifer systems (see 2.5.2)
- A direct way would be by direct contact between the micro-organisms and the iZVI-particle. For nano-materials, such direct effect has been reported for sulphate reducing bacteria (Kumar et al., 2014).

The iZVI may temporarily **impact biota in the surface soil** in case of daylightening of the injection fluid.

Accumulation of lower chlorinated compounds (cDCE and VC) has been reported in a number of field studies. Degradation of chlorinated ethenes by fine sized ZVI particles follows mainly the beta-elimination pathway, hereby avoiding the production of cDCE and VC. However, when the redox potential is insufficiently lowered, TCE may be degraded by hydrolyses or biodegradation (ITRC, 2011).

2.8 Longevity of the technology

Long-term performance of iZVI zones is influenced by (1) the composition of the groundwater, (2) the groundwater velocity through the injected zone and (3) the type, size and specific surface area of the ZVI used.

Within AQUAREHAB, standardised lab scale batch experiments were used to compare the longevity of commercial and new produced ZVIs. The corrosion rates were determined and converted into lifetimes. Overviews of the findings as well as literature data are presented in Table 6. Although the corrosion rates may be different in the field (mainly due to pH-effect and the buffering properties of the aquifer) the data are useful for a relative comparison. nZVIs do have the highest corrosion rates, and are expected to be consumed very fast in the field (weeks), while the life time of mZVIs is longer (months-years). Granular ZVIs usually have a lifetime of decades.

Table 6 ZVI corrosion rate with life time of particles (Velimirovic et al., 2014b)

Iron manufacturer	Iron name	PSD[D_{10}, D_{50}, D_{90}][a] [µm]	R[b] [mmol kg^{-1} d^{-1}]	Estimated longevity [years]
Gotthart Maier (DE) – granular ZVI	FeA4	300-1300 mm	0.36	137.8
Höganäs (SE) - mZVI	FeH3	36, 84, 168	0.43	113.8
	FeH4	22, 41, 62	1.86	26.32
	FeH6	41, 98, 162	0.64	76.76
	FeH7	44, 96, 158	0.20	249.3
	FeH8	34, 63, 97	3.00	16.37
	FeH10	9, 22, 42	0.04	1358
	FeH11	6, 19, 38	2.65	18.53
	FeH12	6, 17, 32	1.14	43.14
	FeH13	7, 18, 34	0.48	102.8
	FeH14	21, 79, 162	3.05	16.06
	FeQ2	8, 26, 44	4.24	11.58
BASF (DE) - mZVI	BASF		1.59	30.93
	MS200	2.1, 4.2, 7.2	1.67	29.45
	BASF	1.7, 3.7, 7.1	0.20	245.4
	MS200+	1.4, 2.5, 4.1	2.87	17.08
	BASF SM	0.6, 1.2, 2.4		
	BASF HQ			
NANOIRON (CZ) - nZVI	Nanofer25s	$D_{50}< 0.05$[c]	143	0.342
TODA (JP) - nZVI	RNIP	$D_{50}< 0.07$[c]	30.3	1.620
Master Builders Inc., U.S.A. – granular ZVI		$D_{50}< 1000$	0.39[d]	
Fisher Scientific (Electrolytic) U.S.A. - mZVI		$D_{50}< 149$	79.0[d]	
Connelly GPM Inc., U.S.A. - granular ZVI		74-1680	0.27[d]	
Peerless Metal Powders and Abrasives, U.S.A. - granular ZVI		297-2380	0.14[d]	
ISPAT Sidbec-Dosco, Quebec, Canada - Granular ZVI		74-1680	3.13[d]	

[a]Particle Size Distribution. [b]Corrosion rate. [c]Producers data, [d]Based on Reardon, 2005.

Considering the limited lifetime of iZVIs, reinjections may be needed during a remediation. The required frequency Generally, the time period the technology can be operational before reinjection is approximately 6-12 months (strongly dependent on hydro-geochemistry, contaminants to be treated and type of particle used).

The mZVI-particles are typically suspended with an organic agent that stabilizes the suspension, eg guar gum. The guar gum is biodegradable and the reducing conditions that result may affect the lifetime of the ZVI by scavenging natural oxidants such as oxygen and nitrate. The anaerobic microbial activity that is expected to develop may be synergistic with the inorganic dechlorination by ZVI.

2.9 Cost of the iZVI technology

Cost drivers for iZVI-zone technology include (1) detailed site assessment, (2) preliminary lab tests to match ZVI particles and injection technology to the hydrogeology and chemistry of the site, (3) geometry of the injected zone (depth, length, width, height) and spacing of injection wells, (4) price of the injectable ZVI particles and suspension, (5) loss of reactive particles in the subsurface due to soil heterogeneities or competing reaction (oxygen), (6) the local situation on the site (accessibility, surroundings buildings, underground constructions, type of subsurface ...), (7) installation and maintenance of monitoring equipment, (8) mobilization of equipment and (9) skilled work force and machinists (country dependent).

Cost of ZVI: The initial investment cost for the injection of a reactive zone is strongly dependent on the price of the particles that is determined by its size/shape (Figure 3), composition, performance:

- 5-40 €/kg for micro-sized ZVI
- Up to 150 €/kg for nano-ZVI.

Due to the limited life-time of the fine ZVI particles, reinjection may be needed.
Maintenance cost: is limited to maintenance of injection wells and monitoring of the pollution.
Field application costs: The iZVI-zone technology is an emerging technology. Currently there are no sites which offer both a conclusive proof of achieved remediation goals and sufficient information with respect to cost incurred. Hence, no cost estimation supported by sustainable data can be offered to date.

2.10 Performance, Abatement Rate and Efficiency Drivers of iZVI Zone

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 iZVI-zone technology aims at an abatement rate close to 100%, in other words at an almost total reduction of effluent concentration downstream of the treatment zone. However, as the distribution of iZVIs in the subsurface is rarely homogenous and rebound of the pollutants may occur, the actual abatement rate is often lower than 100%. Table 4 lists abatement rates ranging between 2 and 99%, which shows the success is strongly case-dependent. A good design of the technology as well as more field experience is expected to increase the average abatement rate.

In addition to the targeted reduction in effluent concentration, the iZVI-zone technology can also aim at a reduction of the contaminant mass in source zones with small droplets of residual free phase. This source reduction is driven by an increased dissolution of the free phase caused by an increased diffusion gradient due to the fact that chemical reduction takes place immediately after diffusion, i.e. the ZVI particles keep the contaminant concentration in the water between the free phase globules very low.

Efficiency drivers are (1) the degradation rates of the different pollutants and their breakdown products, (2) the distribution (transport distance) and availability of ZVI particles, (3) the type of ZVI particle used and (4) the composition of the suspension and groundwater/aquifer.

3 GENERIC APPROACH TO DETERMINE THE APPLICABILITY OF THE IZVI-TECHNOLOGY FOR A SPECIFIC SITE OR AREA

For a successful application of the iZVI-zone technologies, the following steps, illustrated in Figure 9, are to be followed:

Step 1: Site characterisation

A site characterisation is required for checking the application and boundary conditions associated with the technology. The site characterisation includes:

- Identification of the type, quantity and distribution of contaminant in phase
- Geometry and concentration of contaminant dissolved in plume
- Determination of the location of the pollution (saturated/ unsaturated zone, depth, ...)
- Collection of information on the hydro-geology (permeability, heterogeneity, layers, anisotropy, temperature, gradients, main flow direction and velocity, etc.)
- Collection of geochemical data (pH, Eh, dissolved oxygen, total organic carbon, etc.)
- Evaluation of the accessibility of the site

Important: Involvement of regulatory agencies is of utmost importance at an early stage of the investigation, especially, when suggesting an emerging technology.

Step 2: Selection of injection approach

ZVI-particles can be implemented via (1) injection targeting permeation (Darcian flow), (2) high pressure injection leading to preferential flow paths (fracturing), and also (3) soil mixing (Figure 10). It is advised to evaluate the possibilities for a specific site and decide on the injection approach in an early stage, as it determines the activities in next steps. The soil type and hydraulic conductivity determined in step 1, can be used to evaluate whether permeation is possible for a certain size of ZVIs.

Step 3: Feasibility tests at lab scale

Lab scale tests can be used to (1) select appropriate ZVI-types, (2) deduce site relevant transport properties and needs for stabilising the ZVI suspension, (3) calculate degradation rates of the pollutants, and (4) other parameters needed as input parameters for the design of the iZVI-zone (eg required minimal dose).

For the transport tests, column tests with porous media obtained from the site or material with matching grain size distribution can be performed to evaluate the expected mobility of the particles when injected at the site (Comba & Braun, 2012; Dalla Vecchia et al., 2009). For the reactivity tests, batch tests with groundwater from the site can be performed to verify the degradability of the pollutants or the reactivity of selected ZVI-types (Velimirovic et al., 2013). It is preferred to use also aquifer from the site for dose tests and determination of minimal required contact times between the pollutants and ZVI particles to meet the regulatory requirements. The latter tests are preferably performed as column tests (Velimirovic et al., 2014b). A time period of 6 to 12 months is generally needed for these tests.

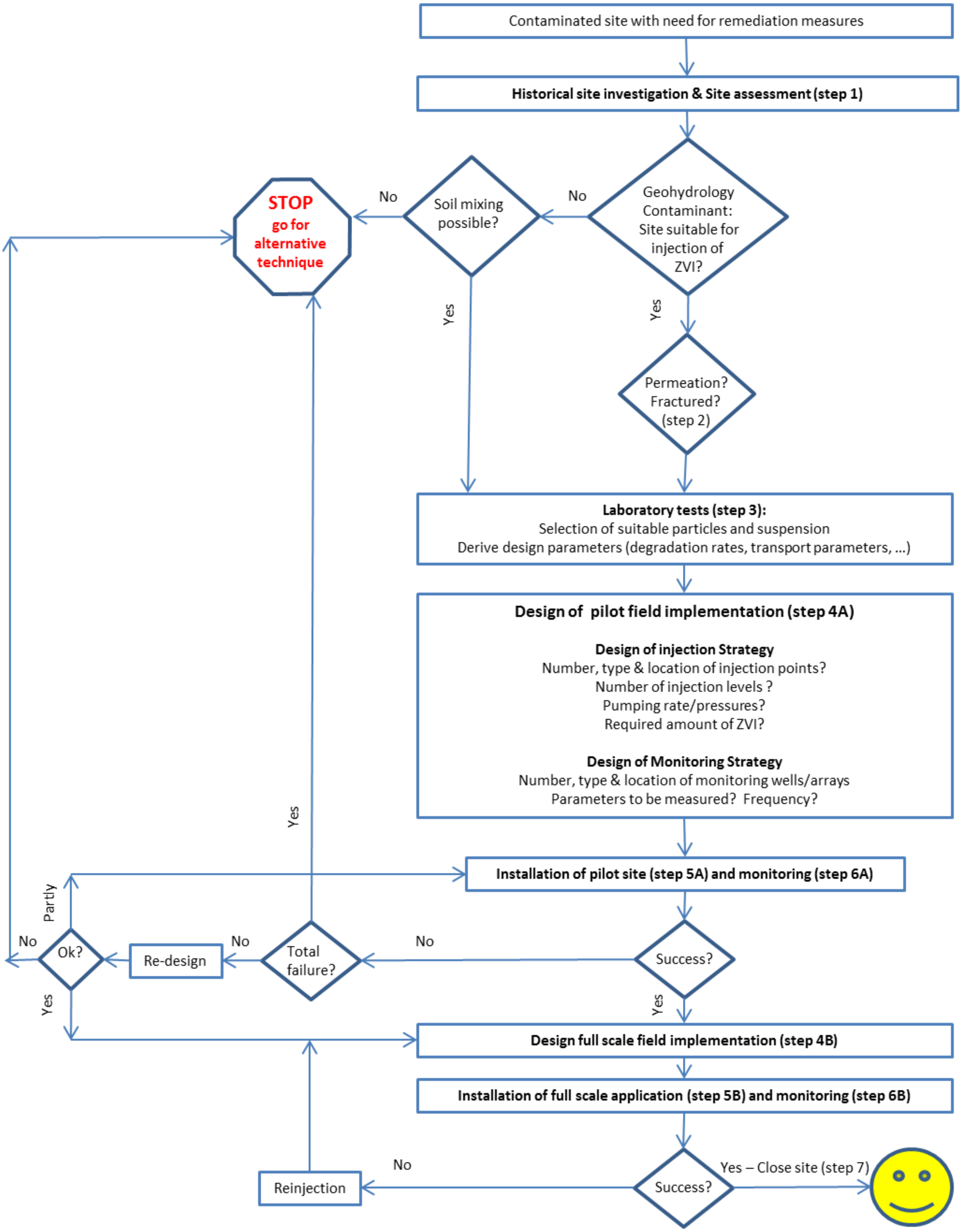


Figure 9 Flowchart for the application of iZVI technology application.

Step 4A: Design & dimensioning of pilot scale

As the iZVi-technology is still in the ‘becoming transferrable’ stage, a pilot test is advised as an intermediate step before a full scale implementation. The goals of a pilot test can comprise evaluating (1) injectability of the selected ZVI-particles, (2) the distribution of the particles in the subsurface in function of injection parameters (radius of influence), and (3) evaluate the impact on the pollutant concentrations. Based upon information from steps 1 and 3, and the decision made on the injection modus (step 2), a pilot test design can be made taking into account the stated goals.

Even though qualitative information on iron particles mobility can be inferred directly from the experimental results of column transport tests, a quantitative analysis via numerical modelling of the test results from step 3 is necessary for a preliminary design of a field application. In particular, numerical modelling of the results provides information for the design of the iZVI slurry (particles concentration, eventual needs for amendments to improve colloidal stability of the slurry)(Xue & Sethi, 2012; Gastone et al., 2014), the most suitable discharge rate, and the expected radius of influence, attainable iron distribution, and possible porous medium clogging(Tosco and Sethi, 2010; Tosco et al., 2014).

Step 4B: Design & dimensioning of a full scale application

Based on the pilot test results, a final decision on injection equipment (injection wells, direct push, or soil mixing), injection fluids, and injection pressures can be made for the full scale application. The radius of influence that can be reached will determine the spacing of the injection points. In permeable flow the vertical distribution around the well is more homogeneous whereas high pressure injection results in a more heterogeneous radial iron distribution. This needs to be taken into account as well.

The amount (mass) of iron particles to be injected is based upon the mass of contamination on site, its distribution (availability for reaction) and hydrochemistry (competing reactions). For example: Stoichiometrically approximately 1.2 kg of ZVI is necessary to reduce 1 kg of PCE, but side reactions like anaerobic corrosion will also consume ZVI. Dependent of heterogeneities and side reactions, a three to ten-fold overdose of ZVI might be required in total for successful site clean-up. Therefore, once the pattern of injection wells has been established the mass injected at each point can be determined on the expected reaction rate and the longevity of the particles injected.

Step 5: Implementation of the iZVI-zone

This step comprises the injection of the iZVI-zone according to the design parameters derived in step 4. To avoid sedimentation of the iZVI-particles, it may be needed to stabilise the particles in a more viscous suspension (for instance guar gum solutions). Many iZVI particles are, due to their size, not air stable. Thus sufficient vessels have to be held available to ensure a continuous availability of sufficient suspension to keep the injection pumps operational. Particles are injected either via direct push technology or via “conventional” wells. Soil mixing is another possibility. For the conventional well injection approach, an additional field action is needed before the first injection event to install the injection wells. Packers can be used to close off most of the well screen to inject from a fairly small well section. The direct push injection approach can be made in 1 implementation event (to be repeated for each injection event) and offers flexibility at the site during the injection in terms of location of the injection points.

Step 6: Monitoring of the iZVI-zone

Any remediation measure used for a specific site needs some kind of verification or an evaluation of the success. In the case of the iZVI technology, monitoring efforts aim at (1) verifying the distribution of the ZVI particles in the subsurface during and after the injection and (2) evaluating the reactivity of the ZVI for reducing contaminant concentrations. Monitoring results will also give indications whether reinjections are needed.

The distribution of the particles in the subsurface can be evaluated via in-situ methods (susceptibility measurements), or by analyses (susceptibility measurements, chemical analyses) on undisturbed aquifer cores. The impact of the ZVI on the pollution is generally followed by chemical analyses on groundwater samples taken from monitoring wells or passive samplers. Monitoring arrays equipped with ZVI-sensors and groundwater sampling ports were evaluated within AQUAREHAB for combining both monitoring aspects.

Step 7: Closing the site

Generally, the monitoring wells/arrays will remain in the subsurface after the remediation is concluded. Injected ZVI will corrode forming Fe(II) and eventually Fe(III), an ubiquitous component of the subsurface. Chemicals for creating suspensions of ZVI are to be selected such that they are biodegradable (eg guar gum).

More details on Steps 1 to step 6 are described in the following sections.

4 SITE CHARACTERISATION (STEP 1)

4.1 Contaminant type

The first criterion for considering an application of injectable iron particles as an appropriate remediation technique, is the type of compounds that need to be targeted at a specific site. It needs to be checked that these compounds can be degraded by the ZVI. In Table 1 a list of such compounds is presented. The compounds must allow for a reductive reaction that converts them into environmentally benign products.

4.2 Contaminant mass

For chemical in-situ remediation methods, the effort to investigate the exact mass of the contaminants must generally be much higher than for e.g. hydraulic in-situ methods using surfactants or alcohols. This is caused by the stoichiometry of the specific reaction used. For the use of zerovalent iron the theoretical ratio is around 1 kg of ZVI is needed for 1 kg of contaminants, at least for the most prominent contaminants such as chlorinated ethenes. For reasons that are discussed above (see chapter 3) and due to the anaerobic corrosion of ZVI, the effective mass required is considerably higher.

4.3 Contaminant distribution

The distribution of the contaminants is an important criterion for the decision for or against the use of iron colloids. Because the reaction mechanism is heterogeneous, involving a solid phase (iron) and usually a liquid phase, the boundary surface of the NAPL phase (i.e. the ratio between the surface of the NAPL phase and its volume) is important for the efficiency of the reaction. While for a distribution of the NAPL phase as fine droplets in the aquifer, a reasonably effective reaction can be expected, for a pool type distribution with a low surface to volume ratio an ineffective situation might arise, i.e. a low reaction kinetic may unfold. The lower the kinetic will be, the more competing corrosion will occur and more iron will be needed.

A last important parameter for planning a remediation is the volume of the contaminated aquifer. This factor will particularly affect the effort and the cost for the injection of the particles. Due to the limited radius of influence of the particles, very large volumes might turn the application of iron economically unfeasible. The same is true for the depth of the contaminated volume. These two factors, however, hold also for other remediation methods. Therefore, the use of iron colloids might still be an option for a given site, despite of a fairly large volume, which is considerably deep, if other factors are favourable.

4.4 Hydrogeology

Important hydrogeological information in this perspective comprises:

- Geology, geometry and parameters (conductivity) of affected aquifers.
- Heterogeneities (fractures, low or high permeable lenses…)
- Ground water table (piezometric surface, hydraulic gradients and their (seasonal) fluctuations)

- Ground water flow velocity and direction
- Anthropogenic disturbances (building foundations, pipes and cables).

Beyond this general knowledge about the hydro-geology at the site, the following specific information is needed for the design and application of the iZVI technology:
- Porosity,
- Content of organic carbon in the soil which may affect the transport,
- the anisotropy (the ratio between the conductivity in vertical direction to the conductivity in horizontal direction), and
- heterogeneity (which can be responsible of preferential migration pathways).

The effects of these elements will appear during a pilot test application, but if the knowledge is available sooner, then early decisions could avoid useless efforts and cost.

4.5 Groundwater Chemistry

Besides groundwater pollutants, other parameters related to the geochemistry of the groundwater must be evaluated. They may have an influence of the technology performance and, as such, on the reactive zone design. An overview of relevant groundwater chemistry parameters, in addition to groundwater pollutants, is given in Table 9.

Samples should be taken from spots representative for the examined site (e.g. sampling points uniformly distributed, several samples from the same depths). Analysis essential for geochemical characterization comprise routine analyses for soil and groundwater contaminants and have been described more in detail by USEPA (1998) and UK environment Agency (2002).

To characterize the geochemistry of the subsurface, measurements of field parameters on groundwater can be very informative. The following field parameters are strongly recommended to be measured in the area where injection of reducing iron particles is foreseen:
- **Temperature** is measured as it influences degradation rates and the viscosity of stabilisers
- **pH:** the hydrogen ion concentration (expressed in pH units) influences the corrosion rate of the iron particles.
- **ORP:** Chemical reactions that involve the transfer of electrons from one ion to another are redox reactions. The reductive dehalogenation of CAHs by ZVI is favored by a low redox potential. In aquifers with a high redox-potential, a part of the reducing iron particles will be consumed to reduce the subsurface.
- **Conductivity** is a general water quality parameter used as a marker to verify that site samples are obtained from the same ground-water system.
- **Dissolved oxygen** concentration is an important parameter to distinguish aerobic and anaerobic field conditions. Concentrations lower than 1 mg/L generally indicate anaerobic conditions (USEPA, 1998). When oxygen is present, a part of the ZVI particles will be consumed by aerobic corrosion and will not be available for degrading the pollutants. Anaerobic conditions are most favorable for the ZVI technology.

A number of analyses of relevant inorganic and organic secondary parameters are listed inTable 9. Inorganic parameters play an important role in reactive zones design as they provide information on redox conditions. The typical list of geochemical parameters present at concentrations in the range of few mg/L to several hundred mg/L includes the following (USEPA, 1998):

- **Chloride:** This parameter is used to verify that the samples are obtained from the same groundwater system. Chloride is also a final product of CAHs reduction, but in many cases the chloride concentration from dechlorination is not significant when compared with the background concentration.
- **Nitrate and nitrite**: Nitrate is reduced by ZVI particles to ammonium, consuming a part of the iron particles. In addition nitrate is known to accelerate the inactivation of reducing iron particles. The absence of nitrate is favorable for the reducing iron technology. The nitrogen gas which is produced by ZVI can lead to a reduced hydraulic conductivity.
- **Sulfate** can be an electron acceptor for sulfate reducing bacteria which are omnipresent in the subsurface. It has been shown that these bacteria benefit from the presence of reducing iron particles. When sulfate is reduced, iron sulfides are precipitated. In general, precipitates are not favorable as they reduce the hydraulic conductivity. Iron sulphides, however, are reducing particles themselves and at least a number of biogenic iron sulfides have been shown (among others in the AQUAREHAB project) to be reactive towards chlorinated compounds (Velimirovic, in preparation).
- **Dissolved iron** may not be very relevant for reducing iron particles applications, nevertheless Fe^{2+}may be an indicator for anaerobic degradation processes.
- **Manganese** is considered as not important but “nice to have” since it is an indicator for potential precipitate formation.
- **Total organic carbon (TOC)** is useful to measure, since organic compounds can bock the reactive sites of reducing iron particles. High TOC concentrations are not favorable for the reducing iron particles technology, especially when the pollutant concentrations are low. In addition, TOC is used to indicate if reductive dechlorination is possible in the absence of anthropogenic carbon.
- **Alkalinity** is used to measure buffering capacity of the groundwater system.

In addition to these parameters, more sophisticated techniques include measurement of stable isotopes $\delta^{13}C$. Degradation of chlorinated aliphatic hydrocarbons favors the 12C with respect to the 13C isotopes, which results in an enrichment of $\delta^{13}C$ in the residual fraction (Suthersan and Payne, 2005). However, these methods are more useful for the determination of remediation success than for preliminary site investigation.

5 SELECTION OF THE INJECTION APPROACH (STEP2)

5.1 Permeation, fracturing & soil mixing

ZVI-particles can be implemented via (1) injection targeting permeation (Darcian flow), (2) high pressure injection leading to preferential flow paths (fracturing), and (3) soil mixing (Figure 10).

Permeation can be realised when the applied injection pressure is lower than the critical one (i.e. the pressure that destroys the structure of the porous medium, which is a function of field stress conditions and soil geotechnical properties). The delivery of a reagent in the subsurface is performed using low pressure. A small injection flow rate and a high injection volume need to be applied. This results in a fairly homogeneous distribution of the injected reagent into the porous medium.
The permeation injection approach is feasible for high permeability aquifer systems and for small sized particles. For low permeability formations, the radius of influence which can be obtained using permeation delivery is usually too small to be economically feasible.

During **fracturing** the pressure exceeds the critical value and the injected reagent is distributed in the porous medium through single or multiple fractures. Therefore, fracturing requires higher pressures and injection rates, while the volume of the reagent may be significantly reduced. The generation of fractures guarantees on the one hand the penetration of the reactive material in the subsurface, and on the other hand improves the total permeability of the formation.

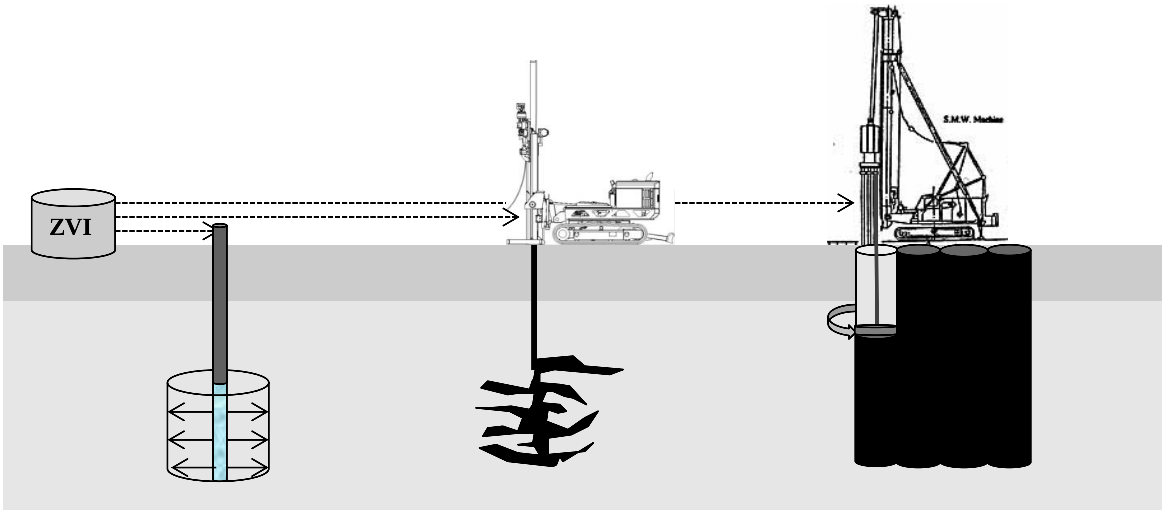


Figure 10 Simplified schematic representation of ZVI-injection via permeation (left), injection via fracturing (middle) and soil mixing (right).

With **soil mixing**, chemicals are directly mixed with the soil. Soil mixing technologies allow the use of a greater particle size of the ZVI and they can realise a fairly homogeneous distribution of the ZVI in the subsurface. On the other hand, they severely disturb the soil structure and create stability issues that may prevent construction development using conventional foundations.

5.2 Selection of injection approach

Based on the characteristics of the iron particles (in particular, the size) and of the contaminated site (permeability, grain size distribution of the deposits, etc), a delivery approach is to be identified. A comparison between injection via permeation (i.e. porous flow, with low pressures and low injection rates) and fracturing (high pressures and injection rates) is given in Table 7. The main differences between the two approaches consist in the volume injected, and the pressure and time needed for the injection.

Permeation injection can be performed in medium to highly permeable aquifers, and is suitable for fine iron particles (mZVI in the order of few microns, and nZVI) otherwise filtration and clogging of the porous medium will occur (Luna 2013; Luna et al., submitted). Conversely, the fracturing approach is usually adopted for medium to low permeable formations, and is suitable for both medium size and small particles. Different screening tests can be performed depending on the chosen strategy.

Table 7 Comparison between permeation and fracturing.

	Permeation (porous flow)	**Fracturing (preferential flow paths)**
Advantages	- "uniform" distribution of particles - control of iron distribution possible	- larger volumes injectable - larger particle sizes injectable - high viscosity suspension injectable - fractures generate higher permeability zones where ZVI and contaminants are both present
Disadvantages	- Slow process - High injection volumes needed - limited radius of influence - only for small particles - only for small viscosity suspensions - high variability in iron concentration	- heterogeneous distribution of ZVI - limited control of iron distribution - danger of day-lighting - structural danger to buildings - iron only in fractures

As a general rule, permeation is preferred when the diameter of the injected particles is much smaller than the soil particles, otherwise the injected particles can be filtered in the porous medium, thus significantly reducing their travel distance. It is suggested in the literature that, if the ratio of average particle size $d_{50,part}$ to average soil grain size $d_{50,soil}$ exceeds a fixed limit, filtration and/or straining can be relevant phenomena. As a consequence it is possible to adopt a limit ratio of particle to grain size for the applicability of permeation injection (Bradford, S.A., et al., 2006):

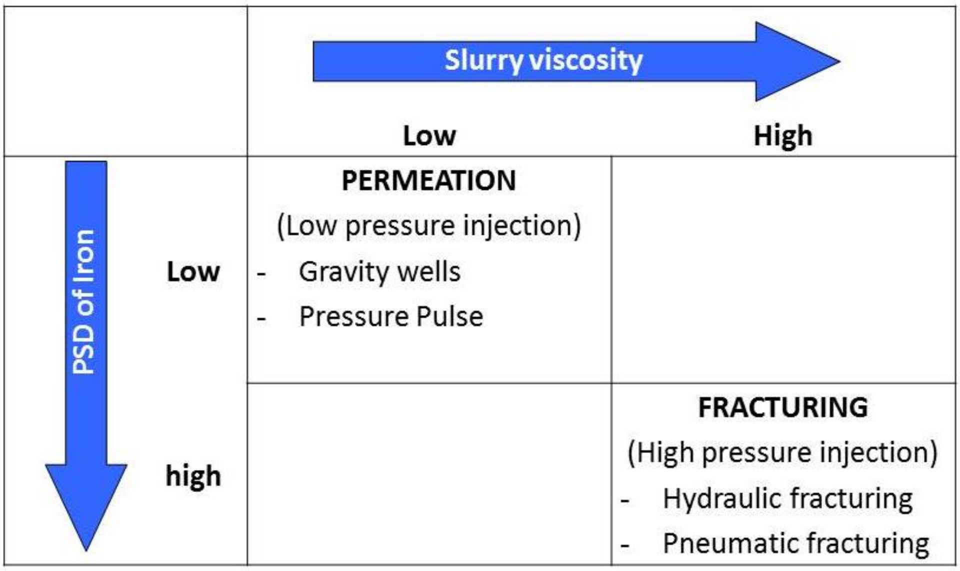
$$\frac{d_{50,part}}{d_{50,soil}} < 0.5\% \qquad \textbf{(8)}$$

Here we also suggest a modified expression, which is more suitable for particles and soils with a broad particle size distribution, comparing the maximum size of particles to be injected and the minimum size of soil deposits:

$$\frac{d_{90,part}}{d_{10,soil}} < 1\% \tag{9}$$

where $d_{90,part}$ is the 90th percentile of particle size distribution and $d_{10,soil}$ is the 10th percentile of soil grain size distribution.

Viscous solutions of biopolymers can be used for dispersing nZVI and mZVI particles, to improve colloidal stability and hinder particle sedimentation and aggregation. This facilitates handling and injection operations of the iron slurries (Tiraferri, A., et al., 2008; Dalla Vecchia, E., M. Luna, and R. Sethi, 2009). As a general rule, larger particles require higher polymer concentration, and mZVI cannot be injected without using a stabilizing agent, due to its fast sedimentation in water. This implies that mZVI is to be injected with highly viscous fluids, and consequently requires higher injection pressures. In Figure 11 permeation and fracturing technologies are classified according to particle size and fluid viscosity.



PSD of Iron	Slurry viscosity: Low	Slurry viscosity: High
Low	**PERMEATION** (Low pressure injection) - Gravity wells - Pressure Pulse	
high		**FRACTURING** (High pressure injection) - Hydraulic fracturing - Pneumatic fracturing

Figure 11 Influence of particles size distribution (PSD) and slurry viscosity on the selection of the proper injection technology

6 FEASIBILITY TESTS AT LAB SCALE (STEP 3)

The iZVI suspension that is injected to create a reactive zone is fairly expensive. Therefore it has to be ensured that both the suspension fluid and the particles are perfectly suited to the given contaminant (reactivity) and hydrogeological conditions (reactivity and transport).
Different types of feasibility tests exist to answer a variety of questions, for instance:

- In case a new type of iron is envisioned, it is advised to test its reactivity in 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).
- When a ZVI-application is considered for non-regular pollutant types or groundwater chemistries (e.g. high salinity), lab scale feasibility tests are strongly recommended.
- Results of dose tests can be a help to determine the required dose of ZVI to degrade the pollutants that are present.
- For each iZVI zone implementation, a lab scale column reactivity test is recommended for deriving design parameters (degradation rates, minimal required retention times, etc.).
- Additional column tests may be performed to predict transport parameters and to derive input parameters for the numerical model.

In the section below, feasibility tests related to iZVI reactivity and iZVI mobility are described in more detail.

6.1 Reactivity tests

Reactivity tests can be performed to answer a number of reactivity related questions, comprising:

- Is a specific ZVI particle reactive (degradation, not only sorption)?
- Is a specific ZVI particles able to degrade the contaminant types present at a specific site?
- Which degradation rates can be expected?
- How long are the ZVI particles expected to be reactive?
- Does a stabilizer (like guar gum) impact the reactivity of ZVI-particles envisioned for the site remediation?
- What is the minimal required dose of the reducing iron particles to target contaminants in the specific matrix of the site?

6.1.1 Standardized lab scale reactivity screening test

Prior to an in situ application, screening experiments can indicate whether ZVI particles are efficient or not for sustainable remediation of contaminants of concern. Especially when no reactivity data are available yet for the envisioned iron or less common pollutants are present at the site, a reactivity screening test is recommended to evaluate the CAHs removal efficiency of the ZVI material. By doing this under standardized conditions, the results can be compared directly with the results of other iron types tested with the same procedure. The ZVI types that are relevant to test are materials that are compatible with the injection approach selected in step 2.

Within the AQUAREHAB project, a standardized procedure was worked out (Velimirovic et al., 2013a; Appendix A) that can be used to determine degradation rates of CAHs using an artificial groundwater. During such test, ZVI iron particles are contacted with polluted water. In function of time, the evolution of the pollutant concentration (and of breakdown products) is quantified. For evaluating the ZVI-reactive properties it is important to distinguish between 2 removal mechanisms that can cause CAH concentration reductions, being:

- **Removal by sorption to the ZVI:** The occurrence of sorption can be deduced from mass balances calculations. When the molar sum of mother products & breakdown products (including ethane, ethane and acetylene) is significantly decreasing over time, sorption is ongoing, which is not considered interesting for a reactive material.
- **Removal by degradation catalyzed by the ZVI (reductive dehalogenation):** Decreased concentrations of the selected mother compounds should be observed with detection of degradation intermediates and end-products, as illustrated in Figure 12. The molar mass balance is expected to be above 80%. A decrease of the redox-potential (ORP) will indicate reducing conditions which are required for reductive dehalogenation.

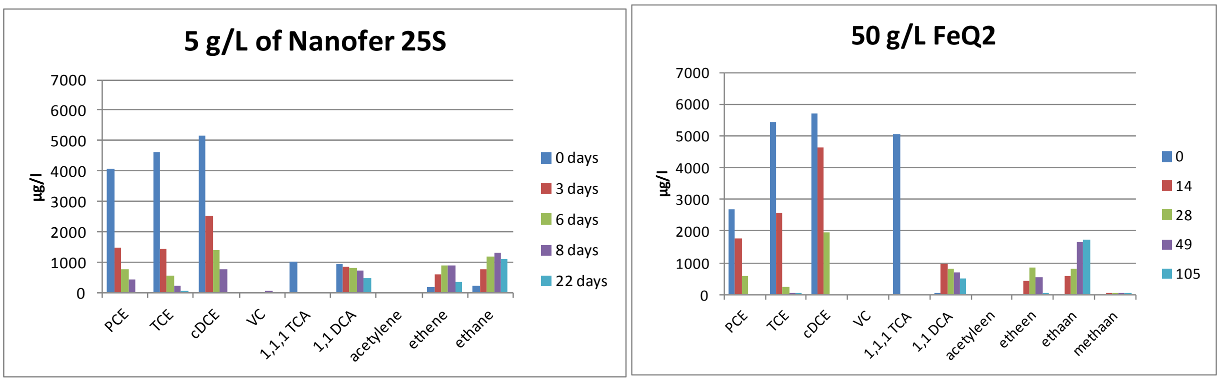


Figure 12 Example of the evaluation of CAHs and breakdown products in the presence of nZVI (Nanofer 25S) and mZVI (FeQ2).

More details are described in Appendix A.
Further, the reactivity of ZVI materials can be quantified by dechlorination rates using the pseudo-first order rate equation as explained in 2.3.4. When examining the degradation potential and rates a specific site, the ZVI screening test can be performed with real groundwater and with the relevant pollutants.

6.1.2 Estimation of corrosion rates and life time for ZVI particles

In addition to reactivity and mobility, another fundamental parameter for a successful application of injectable ZVIs is the lifetime of the ZVI particles. The site clean-up time following injection of mZVI will depend on iron reactivity as well as ZVI aging. It is confirmed that the long-term performance of ZVI remedial systems depends on the continued effectiveness of the ZVI to serve as an electron donor (Farell et al., 2000).
ZVI is not only consumed for degrading the halogenated hydrocarbons in groundwater, but also by oxygen (aerobic corrosion), water (anaerobic corrosion) and other competing compounds (like nitrate). In absence of oxygen, water can be considered as the main competitor. During the anaerobic corrosion water reacts with the ZVI and hydrogen is produced. Hence, corrosion rates of the ZVI can be estimated via measurements of hydrogen production rates.

During for instance a batch degradation experiment as described in chapter 6.1.1, hydrogen formation can be analysed with GC-TCD. The corrosion rate (mol of Fe g^{-1} s^{-1}) can be calculated assuming that 1 mol of $H_2(g)$ in the headspace is produced for every mole of iron corroded (Reardon, 1995). As the test conditions in batch tests are different from field conditions (pH, aquifer/liquid-ratio's, refreshment of groundwater, etc.), the deduced corrosion rates may differ from the ones that will occur in the field. However, the calculated corrosion rates may give a first indication, and the method allows for comparison of different ZVIs.

One can go one step further by using calculated iron corrosion rates as indicator for the life time of iron particles. Data in Table 6 show that the ZVI-particles with the highest reactivity usually have the highest corrosion rates and the lowest longevity.

6.1.3 Reactivity test for stabilized iron particles

Stabilizers like guar gum and xanthan are used to keep Fe-based particles in suspension for a longer time. This is especially required for micro-scale particles to prevent sedimentation in the tubing and injection wells during injection. Stabilizers have mainly been studied to improve technological and environmental performance of ZVI, mostly considering mobility and stability of ZVI particles. AQUAREHAB results revealed clearly that these stabilizers can reduce the reactivity of the ZVI significantly as long as the stabilizer is present (Velimirovic et al., 2012). Subsequent addition of commercial enzymes (e.g. Ranteccorp) resulted in cleavage of guar gum into lower molecular fragments. The reactivity, however, only restored after removal of the guar gum and its breakdown products by intensive rinsing. By doing this, in situ conditions were simulated and it was clearly observed that the negative impact on iron reactivity of the guar gum was only temporary.

Before proceeding with a pilot test, it is therefore advised to verify the reactivity of the stabilized particles towards the contaminants of concern. The impact of stabilizers on the CAHs removal by mZVI particles can be evaluated via batch degradation experiments or column experiments.

Option 1: Reactivity batch tests can be performed in a similar way as described in 6.1.1, only stabilizers are to be additionally supplied in the concentration proposed based on transport tests. At this stage there is no need to use aquifer material as no impact of the presence of aquifer was observed in AQUAREHAB tests. The degradation and removal of the stabilizer can be enhanced by addition of enzymes and a number of rinsing steps (Velimirovic et al., 2012).

Screening batch tests are relatively fast and do not require much manipulation. A disadvantage is, that it not a continuous system, and as such it can overestimate effects, as has been observed in AQUAREHAB experiments.

Option 2: Another way of testing the reactivity of stabilized iron particles is to simulate in situ conditions in a **continuous column** at lab scale. Aquifer material and groundwater collected from the contaminated site are used to fill the columns and to simulate the effect of groundwater flow through the system. Within the AQUAREHAB project, a test procedure was elaborated (Velimirovic et al., 2014a) using Plexiglas columns containing the collected aquifer material mixed with ZVI and stabilizer (Figure 12, See Annex A for more details). Different test conditions can be considered, for instance:

- Controls with only aquifer material to evaluate biodegradation & soil adsorption properties (no ZVI, columns may be poisoned)
- Control with aquifer material and stabilizer to evaluate enhanced biodegradation in the presence of the stabilizer (no ZVI)
- Test column with aquifer material mixed with ZVI

- Test column with aquifer material mixed with stabilised ZVI.

The groundwater is pumped into the column in an up flow direction. For monitoring purposes (CAHs, their breakdown products, pH, ORP, H_2 production), liquid samples are collected from the effluent and/or along the column. The duration of such tests is typically 3-6 months, and may be longer when one is interested in longer-term effects. The pollutant removal capacity of the column systems can be quantified by calculating degradation rate constants and half-lives.

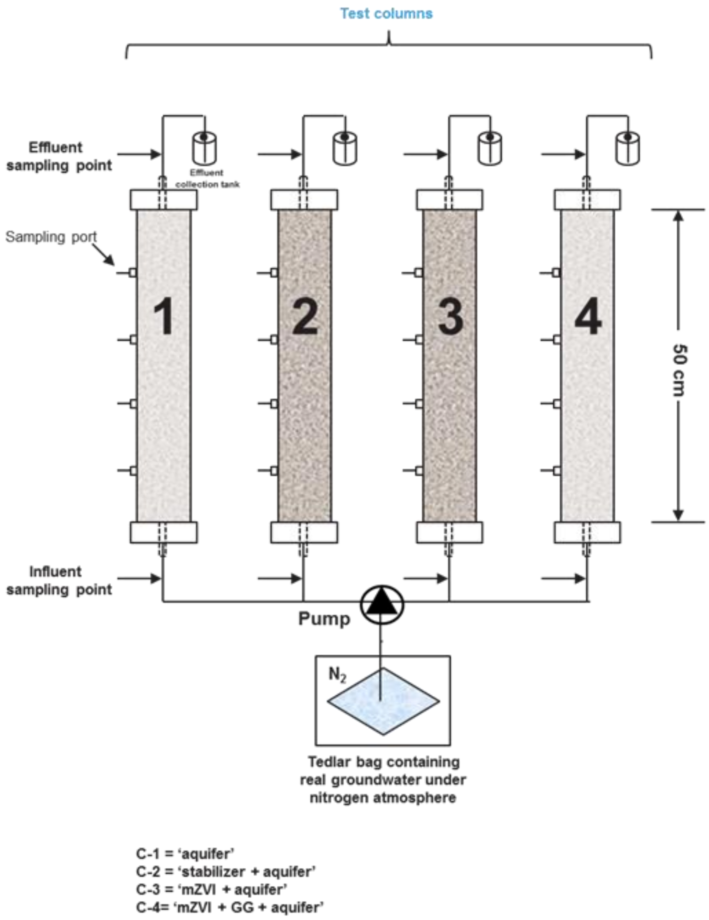


Figure 13 Schematic overview of the laboratory continuous flow column test set up (Velimirovic et al., 2014a).

Although column tests can be long lasting and do require a lot of manipulation, they can be considered as favorable for simulation in situ conditions with continuous groundwater flow

6.1.4 Determining minimal required concentrations of ZVIs

To determine the minimal required dose of ZVI for CAHs removal, batch screening tests can be performed with different doses of ZVI in the presence of aquifer material and groundwater sampled at the studied site. Details are described in Appendix A while a test result is given in Figure 14 as illustration. Site specific minimal required concentrations of ZVIs needed for efficient remediation of selected pollutants in situ can be calculated based on the amount of (a) slurry, (b) aquifer or (c) groundwater present in the flasks during the batch degradation experiment. In case the majority of the pollution at the site is present in the groundwater, the groundwater approach may be the preferred one for designing the pilot test in the field.

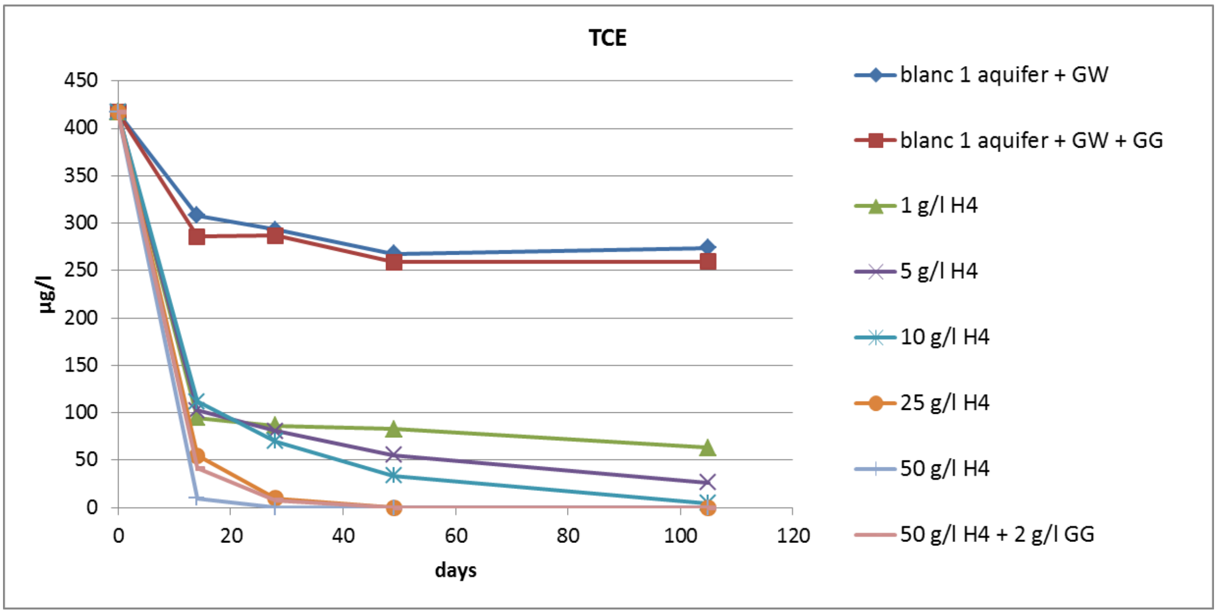


Figure 14 Results of a dose test performed within AQUAREHAB with mZVI H4 (50 µm) in a slurry with aquifer material and groundwater (GW) from the site. The impact of guar gum (GG) was investigated.

6.2 Stability of ZVI suspensions and transport of ZVI

When the most appropriate particles have been selected for their reactivity, two further key aspects are to be assessed, i.e. (1) the stability against sedimentation of the particles when dispersed in the carrier fluid, and (2) their mobility in the porous medium (during injection and later under natural flow).

To avoid sedimentation, the use of a stabiliser like guar gum is necessary. Lab scale experiments are useful to identify the most suitable stabilizing polymer, as well as the most effective concentration. They may include sedimentation tests, rheological tests and column transport tests, which will be discussed in details in the next paragraphs.

Requirements for a successful delivery of Fe-based particles in the subsurface via **permeation** are:

- Fe-based particles must be smaller than a few microns, to avoid mechanical filtration and/or straining. A ratio of average particle diameter D_{50} to average grain size D_c not larger than 0.5% is usually accepted (therefore, the maximum size of suitable iron particles depends on the grain size distribution of the aquifer). This is not restrictive for nZVI, but it is a limiting condition for mZVI.
- Slurry viscosity must be high enough to prevent particle sedimentation (a sedimentation half-time equal to or higher than 1.5 hours is usually an acceptable target), but it should be as low as possible to minimize the injection pressure.
- Residual guar gum particles, which may result from imperfect dissolution during the fluid preparation, should be avoided because they can plug the porous medium. This target can be achieved using a specific protocol for the preparation of the guar gum solution, which can include centrifugation or filtration of the fluid (to remove residual undissolved guar gum particles and other impurities), and eventually dissolution in warm water (to improve dissolution).

If the chosen delivery approach is permeation injection, the screening tests to be performed include:

- *sedimentation tests*, in order to assess whether a stabilizing agent (eg, guar gum) is required to improve the colloidal stability of the dispersion, and, if so, which is the correct concentration of the stabilizer.
- *rheology tests*, for the characterization of the iron suspension, when stabilizing polymers are used. This information is especially required for modelling.
- *column transport tests* assess the mobility of selected iron particles when injected in sand-packed columns at flow rates similar to those which could be employed in the field during permeation injection.

Conversely, the requirements for a successful delivery of Fe-based particles in the subsurface via **fracturing** are:

- Fe-based particles are not strictly limited in size. Therefore, larger particles can be used (D_{50}/D_c> 0.5%), which require a higher concentration of guar gum.
- Slurry viscosity should be high, to facilitate fracturing of the porous medium, which is in agreement with the previous point.
- The presence of residual guar gum particles is not so critical.

If fracturing injection is chosen as technology for delivering mZVI, the screening tests to be performed include:

- *sedimentation tests*, to identify the correct concentration of the stabilizer.
- *rheology tests*, for the characterization of the iron suspension, which is, in case of large particles, obtained with a high concentration of polymers, thus resulting in complex non-Newtonian rheological properties of the slurry.
- *Column transport tests* are not required in this case, because fracturing injection cannot be reproduced at laboratory scale.

6.2.1 Sedimentation tests

Sedimentation experiments are a fast and easy way to check the colloidal stability of the iron suspensions. They can be used as preliminary tests to identify the most appropriate polymer concentration (Gastone et al., 2014a). They are performed preparing a dispersion of iron particles in water, or in an aqueous solution of the stabilizing biopolymer (eg. guar gum). The sedimentation velocity of the particles in static conditions is measured. Possible experimental protocols include:

- The dispersion is put in a transparent cuvette, or in a beaker or any similar transparent container, and the sedimentation of the particles is periodically monitored with photographs, other optical devices, or magnetic sensors (suitable for iron-containing particles).
- For dispersions at low iron concentration, a continuous monitoring of the sedimentation process can be performed using UV-vis spectroscopy

The tests can be repeated for different combinations of polymer and iron concentrations.

The experimental results (see example in Figure 15) can be qualitatively evaluated, or a characteristic parameter can be obtained from a quantitative analysis of the results. A suitable parameter which can be derived for a quantitative analysis can be the **sedimentation half time (t_{50}),** corresponding to the time required for the sedimentation of half of the particles dispersed in the suspension. This value can be compared to a fixed limit time. A minimum time of 1.5 hours is a reasonable target for field injection, which allows keeping the particles suspended during slurry preparation, injection and, in case of permeation delivery, early stages of migration in the subsurface. The sedimentation half time is expected to be directly proportional to the particles size and concentration, and inversely proportional to the polymer concentration. Empirical relationships were derived for suspensions prepared using guar gum (Gastone et al., 2014a). These or similar relationships can be used prior to sedimentation tests for a first estimate of sedimentation half times, in order to optimize the number of the experiments.

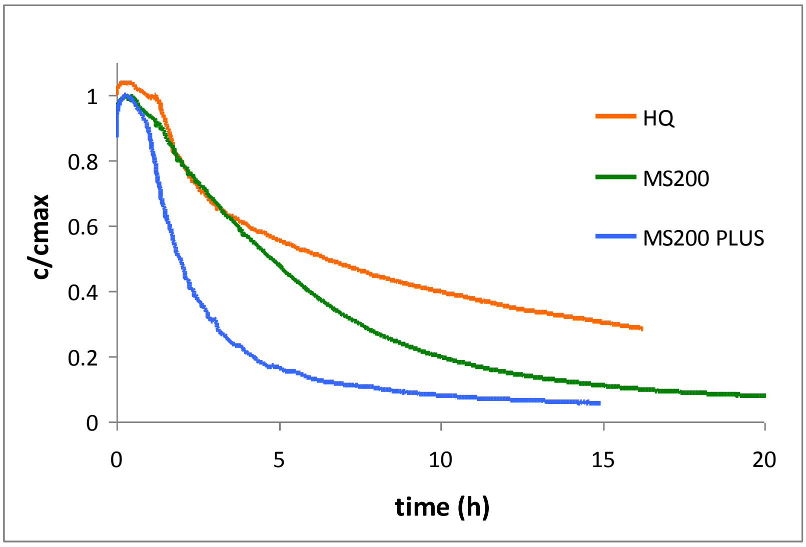


Figure 15 Sedimentation tests results for three different particles: HQ (1-2µm); MS200 (4 µm) and MS200+ (4 µm) for a guar gum concentration of 3 g/l.

6.2.2 Rheological tests

Rheological tests consist in the measurement of the viscosity of the polymeric fluid in which the particles are to be dispersed, or of the dispersion itself, as a function of the shear rate. Viscosity at low shear rates provides information on the viscosity of the dispersion in static conditions, for example during storage of the suspension after preparation and before injection in the subsoil, and is directly related to the sedimentation half time (Gastone et al., 2014a). Conversely, measurements at high shear rate are related to the viscosity of the suspension during injection, and which can be used for an estimate of pressure injections in the modelling step. For example, iron suspensions prepared using guar gum as a stabilizing agent exhibit shear thinning properties, that is, the viscosity is high at low shear rates (static conditions) and lower at high shear rates (dynamic conditions). This is particularly positive for the application to micro-scale iron, because these suspensions can provide high viscosity during storage, thus increasing stability against sedimentation, and lower during injection, thus limiting the pressure injection (Gastone et al., 2014b). Viscosity curves can be measured using rheometers.

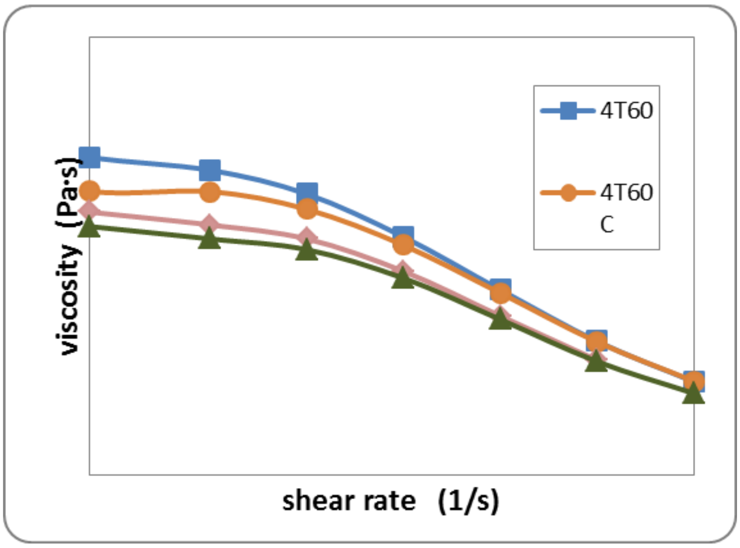
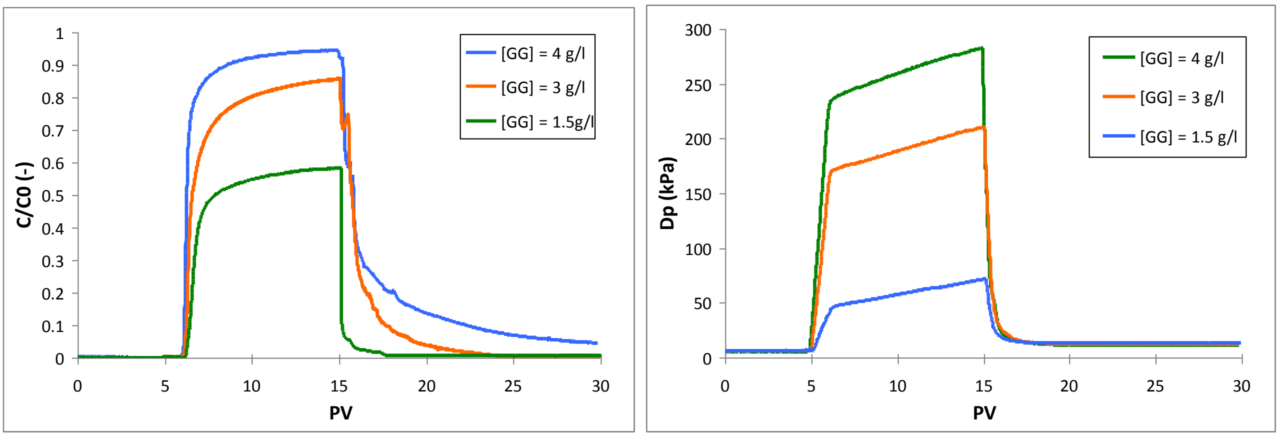


Figure 16 Viscosity as a function of shear rate for different guar gum suspensions.

6.2.3 Column tests

Column transport tests provide information on the mobility of the iron particles in porous media. They are usually performed after sedimentation and viscosity tests as they are more complex. Consequently, they should be performed on a limited selection of iron particles and of iron and guar gum concentrations, which were indicated by the previous tests as the potentially suitable ones.

Column tests are performed by injecting the suspension of iron particles through columns packed with a porous medium (typically, a sand) and saturated with water. Column length typically varies from 10-20 cm to 1 m. If available, the soil obtained from the contaminated site can be used, otherwise other sand is used with characteristics similar to those of the site (porosity, grain size distribution, etc). Iron suspensions are typically injected in horizontal columns, to minimize gravity effects. The flow rate can be chosen as representative of the injection close to the well (i.e. column tests at high flow rates) or of long-term migration (i.e. column tests at low flow rates, similar to the undisturbed groundwater flow).



(a) (b)

Figure 17 (a) Breakthrough curve and (b) evolution of pressure drop at column ends over time for mZVI particles dispersed in a guar gum solution (4 g/l) and injected in sand packed columns.

The inlet and outlet concentration of iron particles can be continuously monitored with different techniques (e.g. susceptibility measurements, chemical analysis of iron content, etc.). Also the monitoring of the pressure injection can be useful to obtain information on the clogging of the porous medium due to iron particles filtrated or deposited inside the column (Tosco et al., 2014).
A typical experimental result is reported in Fig. 3. Test results at different flow rates and with changing iron and polymer concentration can help in the design of the field injection.

7 DESIGN & DIMENSIONING OF PILOT/FULL SCALE FIELD TESTS (STEP 4)

7.1 Introduction

During the design phase, different types of information collected in earlier steps are to be considered jointly to elaborate an approach that meets with (1) the remedial objectives or test aims, (2) the site specific conditions, (3) regulatory concerns, (4) available technologies and materials, and (5) safety issues.

Based on information from step 1 (site characterisation) and step 3 (feasibility tests), final decisions need to be made on the injection mode (linked to step 2) and the iron type (and size) to be used. Next, the following is to be defined for pilot tests as well as full scale field implementations:

- Selection of a location at the test site for a relevant field test
- Number & configuration of injection points
- Required equipment & amounts of ZVI-suspension (ZVI dose)
- Injection strategy
- Monitoring plan
- Planning of the execution.

7.2 Pilot tests

As the iZVI-technology is still in the ‘becoming transferrable’ stage, a pilot test is advised as an intermediate step before a full scale implementation. The goals of a pilot test can comprise evaluating (1) the injectability of the selected ZVI-particles, (2) the distribution of the particles in the subsurface in function of injection parameters (radius of influence), and (3) the impact if the injected iZVI-suspension on the pollutant concentrations.

7.2.1 Selection of a test location

Pilot tests are to be performed at a representative part of the site. In general the pilot test is performed within the contaminated area, although it may also be performed outside the contaminated area when mobility and injectability are the focus of the test. It is preferred to select an accessible spot where monitoring within, upstream and downstream of the injection area can be performed.
When the presence of the pollutants is crucial, it is advised to verify the pollution at potential spots with existing monitoring wells, MIP-probing or temporary piezometers. Soil and groundwater pollution is known to be heterogenic. Most often pilot tests are performed at a representative location and at rather shallow depth, as monitoring costs increase significantly with depth.

7.2.2 Pilot test configurations

Pilot test configurations are to be elaborated in function of the defined test aims and the characteristics of the site.

When the aim is **to verify the on-site preparation procedures or to evaluate the injectability of a ZVI-suspension,** the major requirement is to select a representative geology and depth for the injection. One or two injection points at a representative depth may be sufficient. No in-situ monitoring is to be performed after the injection.

For **evaluating the distribution of the ZVI-particles in the subsurface** and deducing the radius of influence, in principle a single injection point is required as well as a (post-)injection monitoring. To allow the implementation of monitoring devices and soil corings after the injection, an accessible area is needed of at least 3-4 m distance from the injection point in all directions. The accessibility is related to (a) no above ground constructions or barriers, but also (b) no utilities (cables, pipes, etc.) in the subsurface that make drilling impossible. To prevent preferential flows, this area around the injection point is preferable undisturbed by previous field activities (no presence of monitoring wells). When for monitoring purposes the installation of monitoring equipment (like sensors) is needed before the injection, care should be taken to seal the drilling points properly.
The distribution of ZVI in the subsurface after the injection can be investigated by evaluating the presence of ZVI and/or injection fluids at distinct spots around the injection well (see 9.2). It is recommended to select monitoring spots at different distances from the injection well, and this in different directions. An example of a monitoring strategy with a single injection point is given in Figure 18. In case more than one injection point is envisioned, it is advised to install these at a distance at least as high as the sum of their radius of influence.

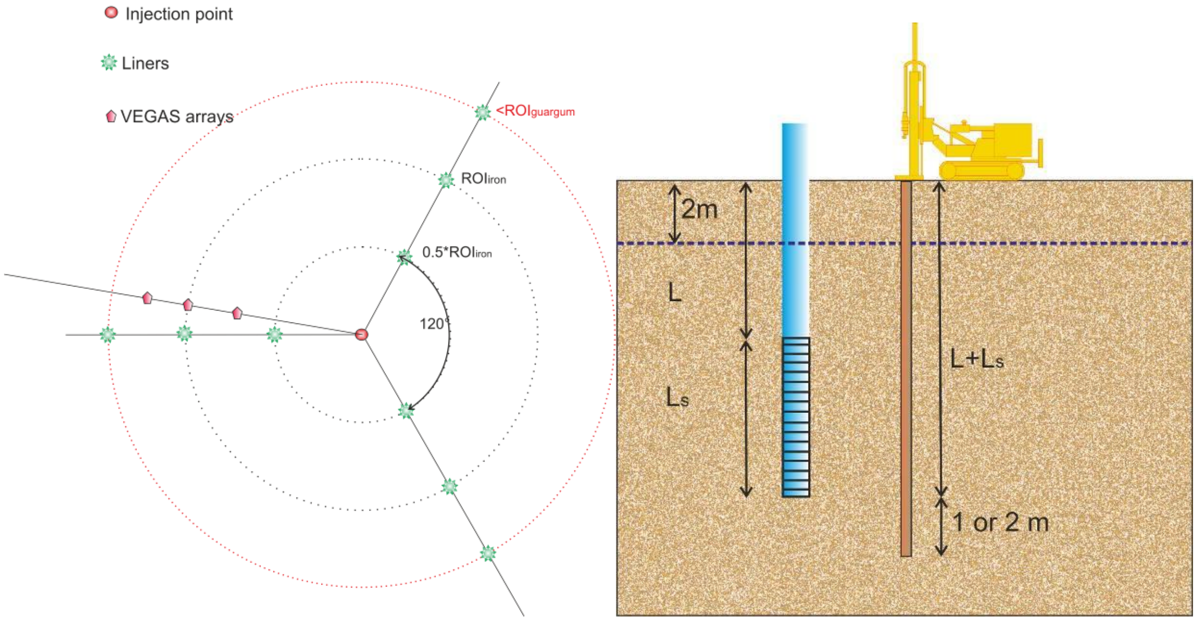
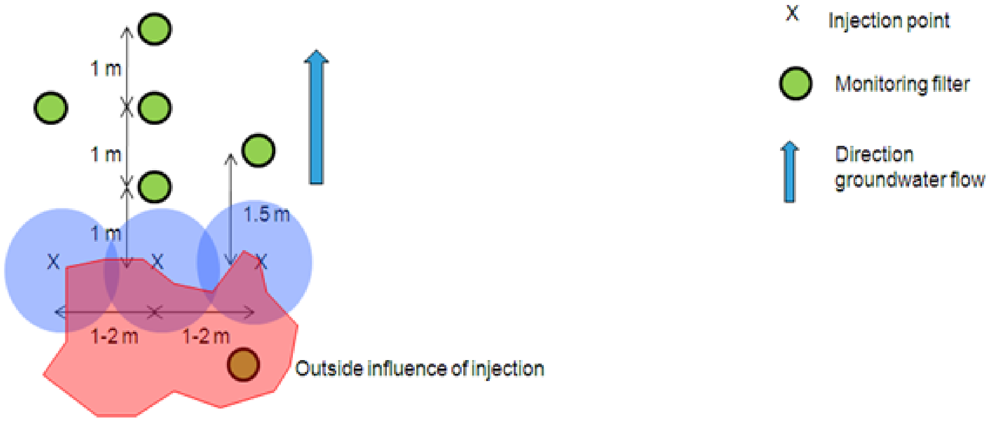


Figure 18 Example of pilot test configuration with a single injection point and multiple monitoring lines around the injection point (AQUAREHAB).

When the aim is in addition to **evaluate the impact of the injected iZVI-suspension on the pollutant concentrations in the subsurface**, also hydrogeological parameters like groundwater flow velocity and direction of the groundwater flow are to be taken into account. To create a measurable impact on the groundwater pollutants, more than 1 injection point is needed, preferable at least 5 injection point. Many configurations of injection points and monitoring points are possible. A few examples are given below.

The most straight forward pilot test configuration is depictured in Figure 19, and consists of (1) a row of injection points perpendicular to the groundwater flow direction, and (2) groundwater monitoring wells in the downstream area at different distance of the injection row, and (3) an upstream monitoring well. The performance of the iZVI zone can be evaluated by comparing the evolution of the pollutant concentration in the upstream and different downstream wells. During the design phase it is important to fix the distance between the injection points and downstream wells based on the groundwater flow velocity. The flow distance of the groundwater needs to match with the envisioned monitoring time period. The evaluation of the iZVI distribution after the injection is possible in the configuration when focussing on non-overlapping areas of influence.



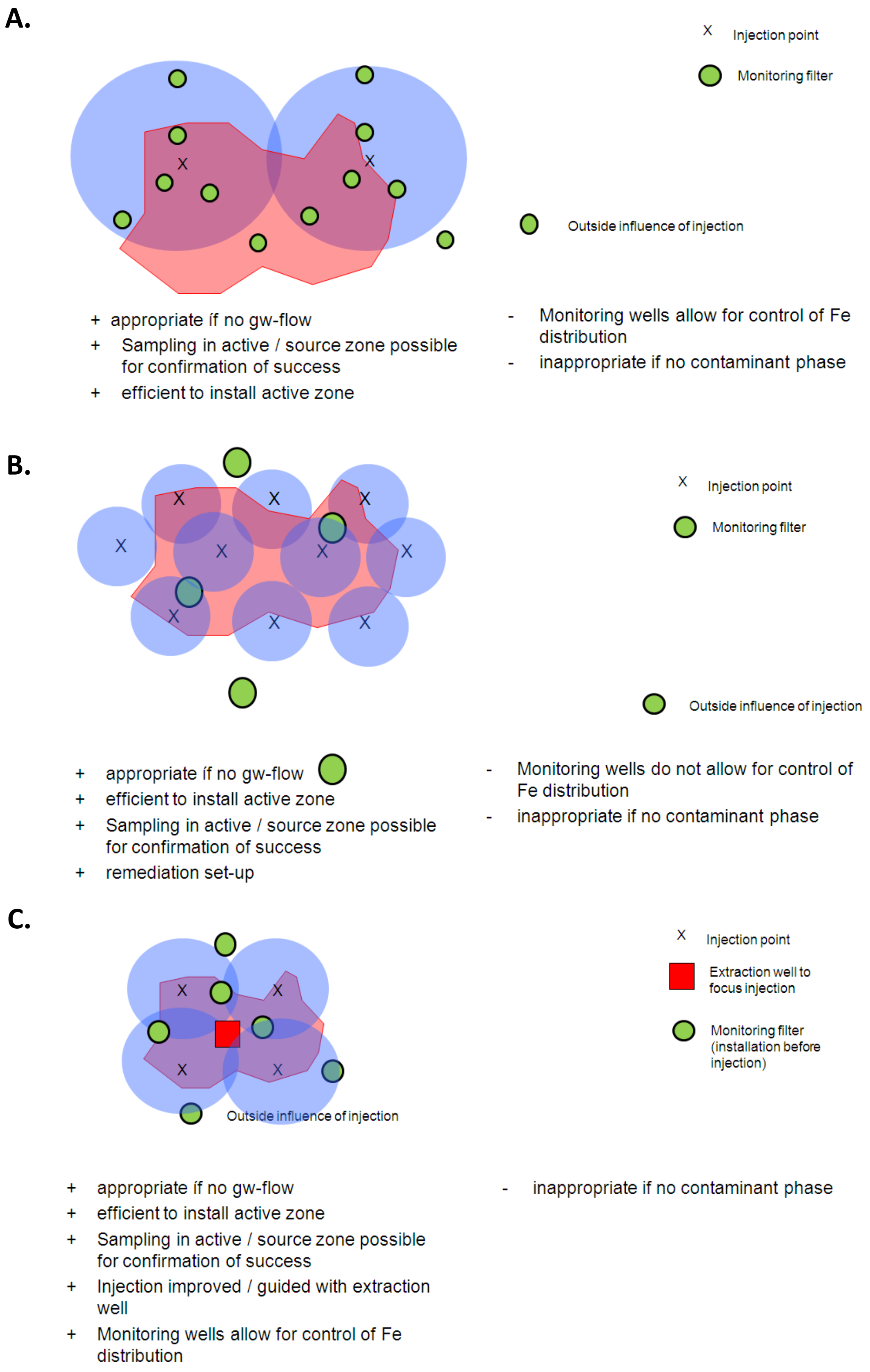
+ most efficient monitoring method if appreciable gw-flow
+ efficient to combine active zone and plume cut-off

- not applicable for aquifers with very small gradient / very small flow velocities
- monitoring wells for contaminant control only (unless transport of particles with gw)

Figure 19 Pilot test configuration for site with significant groundwater flow velocities and a dominant groundwater flow direction.

When the groundwater flow velocity is low (few m/Year) or the available monitoring period limited, other monitoring strategies are needed as the groundwater will not reach downstream monitoring well (Figure 20). A possible approach may be to evaluate the changes of the pollutant concentrations within the reactive zone over time. A clear decline in concentrations would be an indication for pollutant removal. The impact of the inject amount of (non-polluted) suspension in the subsurface needs to be taken into account when designing a pilot configuration. Re-extraction of a groundwater volume (x time the injection volume) may deal with this aspect, and transport pollutant from the surrounding area in the reactive zone (Figure 20C).

In contract to ZVI-barriers (excavating and refilling trenches), the distribution of iZVI in the subsurface can be less controlled leading to a more heterogeneous distribution of the iZVI. Therefore, for a remediation set-up at pilot scale, multiple injection rows are recommended (Figure 20B). Within AQUAREHAB a high pressures and low flows injection method (aiming at limited injection radius) was shown to realise less heterogeneity of mZVI in the subsurface as compared to high pressure high volume direct push injections.



A.

+ appropriate if no gw-flow
+ Sampling in active / source zone possible for confirmation of success
+ efficient to install active zone

- Monitoring wells allow for control of Fe distribution
- inappropriate if no contaminant phase

B.

+ appropriate if no gw-flow
+ efficient to install active zone
+ Sampling in active / source zone possible for confirmation of success
+ remediation set-up

- Monitoring wells do not allow for control of Fe distribution
- inappropriate if no contaminant phase

C.

+ appropriate if no gw-flow
+ efficient to install active zone
+ Sampling in active / source zone possible for confirmation of success
+ Injection improved / guided with extraction well
+ Monitoring wells allow for control of Fe distribution

- inappropriate if no contaminant phase

Figure 20 Pilot test configuration for site with low groundwater flow velocities (few m/year).

7.2.3 Required doses

As the impact of a specific dose is site dependent, determination of the exact required dose is difficult. Different approaches have been reported to get a best estimate:

1. Firstly, a stoichiometric approach based on pollutant mass present has been reported. For example, stoichiometrically approximately 1.2 kg of ZVI is necessary to reduce 1 kg of PCE, but side reactions like anaerobic corrosion will also consume ZVI. Dependent of heterogeneities and side reactions, a three to ten-fold overdose of ZVI might be required in total for successful site cleanup.
2. The required doses may be estimated based on minimal required doses determined via labscale batch tests (Appendix A).

   Batch dose testes (at groundwater temperature): The test results reveal the impact of different dose on the pollutants as tested. The outcome of the test (a minimal required dose) needs subsequently be extrapolated to the field conditions, where the solid/liquid ration is generally different compared to the lab scale tests.

   - For contaminants that are predominantly present on the aquifer material, extrapolations from lab to field may be calculated based on amount of contaminated aquifer.
   - On the other hand, when the pollutants are predominantly present in the groundwater, the extrapolation may be better based on the amount of groundwater?
   - Another approach may be to deduce the required iron amount needed to create strong reducing environment (ORP <−400 mV)

   Column test (at groundwater temperature): As the test conditions are closer to field conditions (continuous system & solid/liquid-ratio) column tests are preferred for deriving design parameters.
3. Next, guideline concentrations mentioned in literature may be used to set required doses of iZVI. Gavaskar (2005) reported that a ZVI-to-soil mass ratio of 0.4% (4 g ZVI/ kg aquifer) is minimally necessary to achieve a sufficient reductive environment for the abiotic degradation of TCE. Others mention 0.4%-0.8% of ZVI by mass of soil (ITRC, 2011)
4. Another more practical approach is to implement the maximum amount that is injectable.
5. Finally, in reality, often the above mentioned approaches are combined with the ‘trial and re-inject’ approach.

7.2.4 Equipment & materials required

It is crucial to prepare iZVI-slurries on site just before the injection to avoid corrosion and aggregation/sedimentation of the ZVI particles and degradation of stabilisers. This requires the availability of sufficient mixing equipment, pumps and storage vessels. These needs as well as the availability of electric supply and access to tap water are to be taken into account already in the design phase.

As an example, appendix D describes the design and need materials (such as iZVI-suspension) and equipment related to 2 pilot tests performed within AQUAREHAB. It is recommended to design injection wells with care.

7.2.5 Planning execution

The implementation of field test requires different steps that are often performed by different parties. Therefore, a good planning of the different steps increases the change for a successful and efficient field test. These steps may comprise:

- ➔ Preparation of the field: installation of wells/devices in the subsurface, making the site accessible, etc.
- ➔ Pre-injection monitoring
- ➔ Mobilising the necessary above ground equipment and reactive material (dry storage place at the site needed)
- ➔ Preparation of injection fluid
- ➔ Injection of the fluids
- ➔ Groundwater extraction events
- ➔ Post-injection monitoring

7.3 Full scale tests

Based on the pilot test results, a final decision on injection equipment (injection wells, direct push, or soil mixing), injection fluids, and injection pressures can be made for the full scale application. The radius of influence that can be reached will determine the spacing of the injection points. In permeable flow the vertical distribution around the well is more homogeneous whereas high pressure injection results in a more heterogeneous radial iron distribution. This needs to be taken into account as well.

The amount (mass) of iron particles to be injected is based upon the mass of contamination on site, its distribution (availability for reaction) and hydrochemistry (competing reactions). Once the pattern of injection wells has been established, the mass to be injected at each point can be determined.

7.4 Safety issues

Safety issue related point of attention to be taken into account when designing a iZVI technology field implementation comprise:

- Fine Iron dust, and
- Formation of hydrogen when ZVI is contact with water

7.5 Constitutive relations & modelling

Efficient design and dimensioning of pilot and/or full scale applications may benefit from dedicated numerical models. For the iZVI technology these models were, prior to AQUAREHAB, virtually non-existent. Hence, the model development had to include the determination of constitutive relations.

Simple empirical equations can be derived from small-scale laboratory test results, and can be can be useful in extrapolating preliminary information on stability and mobility of the particles at lager scales and for different delivery strategies, namely:

- For injection via permeation, the results of column transport tests can be used to estimate the dependence of transport parameters on flow properties (flow rate) and fluid properties (viscosity, polymer concentration);
- For injection both via permeation and fracturing, the results of rheological measurements and sedimentation tests can be used to estimate the dependence of the particle stability against sedimentation on polymer concentration.

Some examples of empirical constitutive relationships are proposed in the following. It is worth to recall that, being transport tests in 1D columns performed at constant flow rate, empirical constitutive equations derived from such experimental results are to be carefully considered and evaluated when applied to multi-dimensional geometries, where flow parameters are not constant in space, and need to be confirmed by large-scale experiments.

7.5.1 Constitutive relations for permeation injection of fine ZVI particles

An important parameter for a correct dimensioning of full scale injection is the spatial distribution of the iron particles retained in the porous medium. Even if the particles distribution should be predicted using numerical solutions of modified advective-dispersive transport equations, a first estimate can also be obtained using empirical relationships, derived from small scale laboratory tests.

As an example, experimental results (Tosco et al., 2012) suggested that the dependence of the mass of iron retained inside the column as a function of polymer concentration can be empirically modelled using a power function.

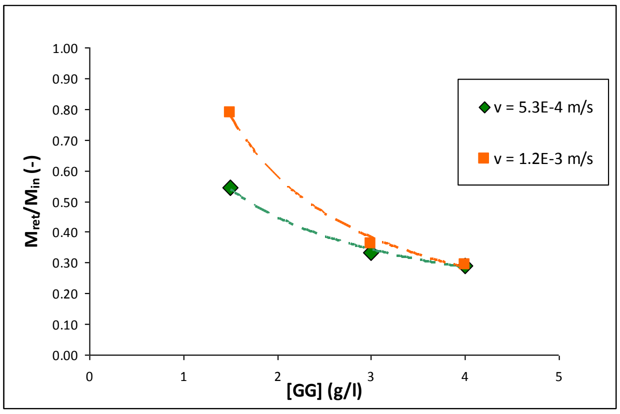


Figure 21 Dependence of the fraction of particles retained inside the column after injection reported as functions of the guar gum concentration, for different flow rates

7.5.2 Constitutive relations for fracturing injection of fine ZVI particles

If the delivery strategy is fracturing, empirical relations that predict transport parameters cannot be derived from small-scale tests, but it is possible to derive constitutive equations for some important parameters, for example the viscosity of the iron slurries and the particles sedimentation time.

When evaluating the capability of polymeric solutions to keep iron particles suspended, the controlling parameter is the low-shear viscosity of the slurry, that is, the viscosity of the polymeric solution in static conditions. This parameter is obtained from rheological measurements of viscosity at low shear rate. The dependence of the low-shear viscosity on guar gum concentration can be modelled again by a power law (see example for guar gum solutions in Figure 22).

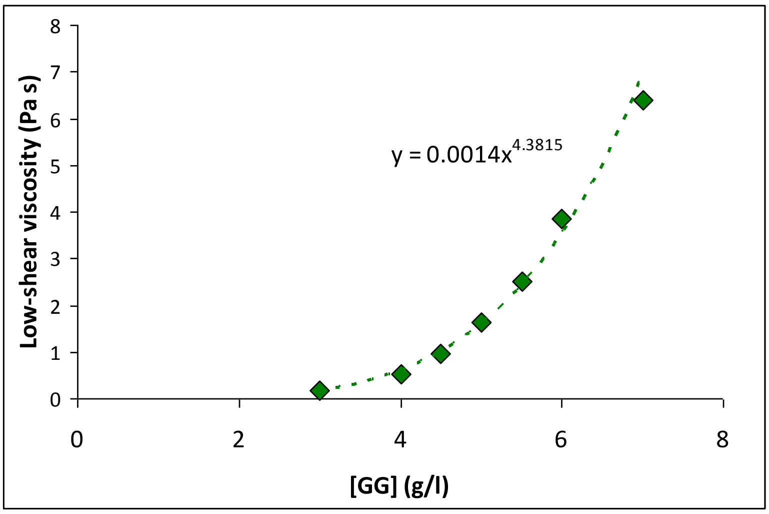


Figure 22 Measured data of low-shear viscosity for HQ mZVI dispersed in guar gum solutions as a function of guar gum concentration.

Experimental results of sedimentation tests can also be used to derive correlations to link the sedimentation half time of iron particles, t_{50}, to the particle size, as well as the polymer concentration to t_{50}.

7.5.3 Numerical Model

Numerical modelling of transport processes of iron particles transport in porous media, as well as of their reactivity towards the contaminants, is useful for the interpretation of the laboratory tests previously described, and for the simulation of injection and reactivity at the field scale. Concerning particles mobility, the modelling for permeation injection can be faced using advection-dispersion equations, modified on purpose to include deposition and release phenomena, clogging, and other specific processes, as detailed below. Conversely, modelling fracturing injection in shallow systems (like typical contaminated aquifers) is an extremely critical issue, and is usually not faced for the field-scale application design.

For permeation injection, the following within AQUAREHAB developed modelling approaches can be taken into consideration for the implementation of iron-based particles in a contaminated site:

- *Laboratory-scale modelling*: all tests previously discussed are to be interpreted for the up-scaling via numerical modelling, or applying constitutive relationships, in order to derive transport and reactivity parameters applicable to the field scale. In particular, modelling should include:
    - Numerical models for particles transport in porous media in one-dimensional systems, for the analysis of column tests;
    - Numerical models for particles reactivity towards contaminants, both in batch and in column reactivity tests.
- *Field-scale modelling*: For a correct design of a field injection of iron particles in porous media, it is necessary to predict both the final spatial distribution of the particles around the injection

point, and their reaction towards the contaminants present in the polluted subsoil. Consequently, the modelling at this stage should include:

- Transport modelling in radial and/or spherical geometry, to simulate the injection of the particles into the subsoil.
- Reactive transport modelling in three dimensional geometry, to simulate the short- and long-term reactivity of the injected particles towards the contaminants. This model should use as an input the spatial distribution of the particles after injection, that is, the results of the injection model should be used as initial condition for the reactive transport model.

Considering permeation injection, a reliable estimate of particles mobility requires a modelling approach based on the numerical solution of a modified form of the advective-dispersive transport equations. In particular, transport models are to be used, which implement both advection-dispersion transport (available in all freeware or commercial numerical models for transport simulation in porous media) and interactions of the particles with the porous matrix (deposition, filtration, clogging processes, etc.). The latter phenomena are usually not implemented in commercial codes. A description of an approach to colloid transport modelling suitable for iZVI injection design is described in the Appendix B and in Tosco and sethi (2010), Gastone et al. (2014a, 2014b), Tosco et al. (2014).

8 IMPLEMENTATION OF THE IZVI-ZONE (STEP 5)

8.1 Pilot versus full scale

Before a full scale application of reducing iron particles is performed, it is in most cases advisable to perform a pilot scale test on the respective site. A pilot test generates additional data which can reduce specific uncertainties and is useful to improve the injection design/approach elaborated based on lab scale test. The main focus of this pilot test should be to prove the achievable radius of influence of the particles during an injection, i.e. to verify the injection method and the selection of the particles and the formulation. But also the reactivity predicted by tests performed during the planning phase can be verified under the precise hydro-chemical and hydraulic conditions on site.

For the implementation of an iZVI zone, all available information from the preceding experiment and field experiments combined with the additional knowledge gained from the numerical models should be taken into consideration.

If performed in a proper way, a pilot study can be a valuable contribution in order to avoid mistakes and to optimize the approach for a full scale remediation. The data obtained from the distribution of the particles during the pilot injection can be used to layout the grid for the injection wells (horizontal distance of injection points) and to determine the number of vertical injection points per drilling (vertical distance of injections in each borehole). This latter information is difficult to obtain without a test injection, because it depends mainly on the anisotropy of the subsurface, a property which is usually not known.

But also for a prediction of the chemical efficiency, i.e. the time required for finishing a remediation or planning the number of reinjections required, a pilot application can be a valuable support to confirm or expand laboratory investigations. To determine reliable data about the reactivity and about potential unwanted side reactions a pilot application is essential in most cases. This type of data is required to really predict the amount of iron necessary for a given mixture and distribution of contaminants. It can also be used to estimate the number of reinjections necessary, depending of the homogeneity of the particle distribution that can be achieved and the mass and distribution of the contaminants present.

Finally, if a pilot application is conducted in a proper way and it shows promising results, the effort for the monitoring in a full scale application can possibly be reduced and, thus, the costs for the remediation reduced.

As mentioned in chapter 4.3, injection of a suspension in the subsurface will result either in Darcian type of flow or a preferential (fractured) type of flow. While Darcian flow is preferable for a homogeneous particle distribution, in some cases (low permeability, high viscosity suspension etc.) preferential flow must be the method of choice.

8.2 Implementation technologies

8.2.1 Permeation technologies

8.2.1.1 Gravity wells

Injection by gravity is usually accomplished in injection wells without using any pumping system. The migration of iron particles is then due to the small pressure gradient that develops between the injection well where the reagent is placed and the aquifer system.

8.2.1.2 Injection wells with recirculation

When reactants are injected into the aquifer using a pumping system, in some cases it is desired to to speed up their migration and limit the volume of reagents to be injected. This can be achieved using a recirculation circuit: the contaminated water is injected in a well and extracted in a downstream well, and further re-injected in the upstream well, thus creating a treatment zone where flow rate is increased thanks to the increased gradient, and the consumption of reagent and injected volume are limited (Figure 23). Also, the use of a recirculation system allows to control the migration of the reagent in the aquifer system, and to limit the losses of reagent. This is particularly useful when injecting iron colloids, for which uncertainties still exist on their final fate, and wide spreading in the environment could not be desired.

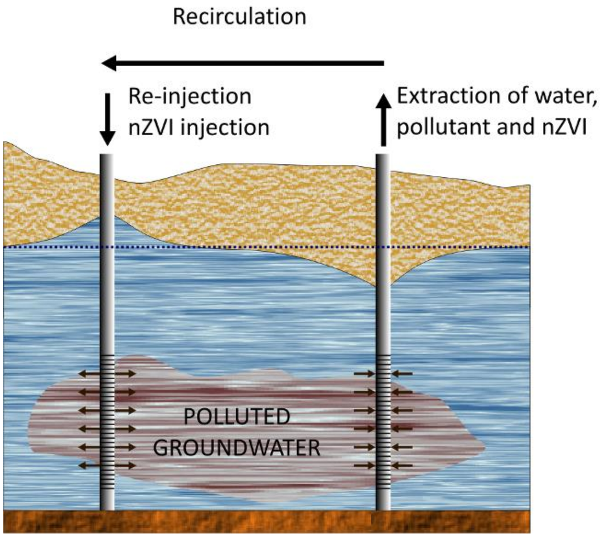


Figure 23 Scheme of nZVI injection with recirculation

8.2.1.3 Push-Pull injection for enhancing particles mobility

An injection strategy designed in order to improve the contact among reactant and contaminated water is the Push-Pull technology (Figure 24). In this case, a certain volume of reactant (i.e. the slurry of iron particles) is first injected into the aquifer, displacing the contaminated water around the injection point. Then, after a reasonable time interval, one or more pore volumes of water is extracted from the injection well to pull the contaminated plume back in the reactive zone in contact with the iron particles.

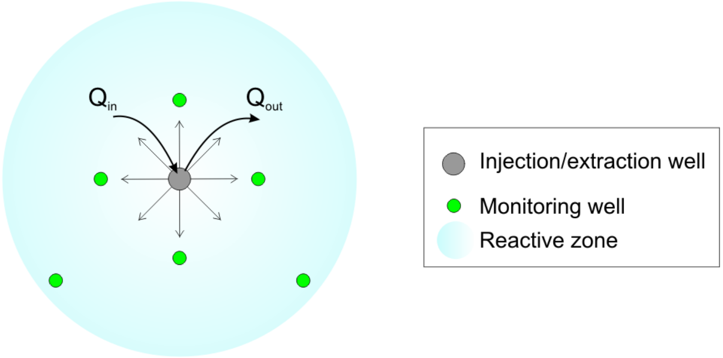


Figure 24 Sketch of Push-Pull injection

8.2.1.4 Pressure Pulse Technology

In the literature the use of Pressure Pulse Technology (PPT) is reported in a limited number of field tests. PPT, a patented technology (Wavefront Energy and Environmental Technologies) used for environmental and reservoir applications,provides an increase of the injection radius due to the generation of pressure waves in the subsoil. PPT disperses injected reagents at the pore scale by elastically dilating the matrix.

The distance at which the pressure pulse can propagate usually ranges between 5 and 300 m, depending on the magnitude of the applied over-pressure, the subsurface characteristics (such as permeability) and the viscosity of the injected slurry (Quinn, J., et al., 2005). However, it has to be noted that it has not been shown to date to which distance these pressure pulse have a positive influence on the transport distance of ZVI particles. It may be a save assumption that the positive effect of the pulses is very small as compared to the retaining gravitational forces due to the high density of the particles.

8.2.2 Fracturing technologies

Fracturing injection technologies consist in delivering the reactive material into the subsoil through fractures, which are generated previously or contemporary to the reagent injection. These technologies are suitable for the injection of larger particles and/or for low permeability formations. The fracture geometry and propagation depends on the geotechnical properties of the subsoil, in particular on the stress field at injection depth.

A first rough estimation of the pressure needed to crack a formation can be determined from the field vertical stress. For non-cohesive materials, porous media, the critical pressure approximately ranges from half to one times the effective vertical stress (σ_1'):

$$\begin{aligned} \sigma_1' &= \left(\rho_{b,dry} g h_{dry} + g h_{sat}\left(\rho_{b,dry} - \rho_w\right)\right) \\ p_{cr} &= [0.5 \div 1] \cdot \sigma_1' \end{aligned} \qquad \textbf{(10)}$$

where p_{cr} is the critical pressure (kPa), $\rho_{b,dry} g$ is the specific weight of dry soil (N/m^3), $\rho_w g$ is the water specific weight (N/m^3), h_{sat} is the saturated thickness (m), and $h_{dry}$is the height of the vadose zone (m).

This estimation does not take into account cohesive strength and over-consolidation processes. For this reason it is better to estimate the critical pressure from field tests, as discussed below.

The stress field of soil can be described with three principal stresses. The first is the effective vertical stress, equal to the lithostatic load at a certain depth z ($\sigma'_v = \rho_{b,dry} g z$). The effective horizontal stress is divided into maximum (σ_H) and minimum (σ_h) stress on the horizontal plane, and it is possible to define an average value of horizontal stress equal to

$$\sigma'_{Ha} = \frac{\sigma'_H + \sigma'_h}{2} \tag{11}$$

The horizontal stress depends both on vertical stress (and consequently on depth) and on a constant factor:

$$\begin{aligned} \sigma'_h &= K_h \cdot \sigma'_v \\ \sigma'_H &= K_H \cdot \sigma'_v \end{aligned} \tag{12}$$

The K factor depends on consolidation phenomena occurred, and is defined as the ratio of the mean horizontal stress to the vertical stress:

$$K = \frac{\sigma'_{Ha}}{\sigma'_v} \tag{13}$$

Several studies (Goodman, R.E., 1987; Hoek, E. and E.T. Brown, 1997; Brown, E.T., et al., 1984)report that the *K* factor follows a hyperbolic trend and field observations demonstrate that *K* may range from $\frac{100}{z} + 0.3$ to $\frac{1500}{z} + 0.5$ (Figure 25).

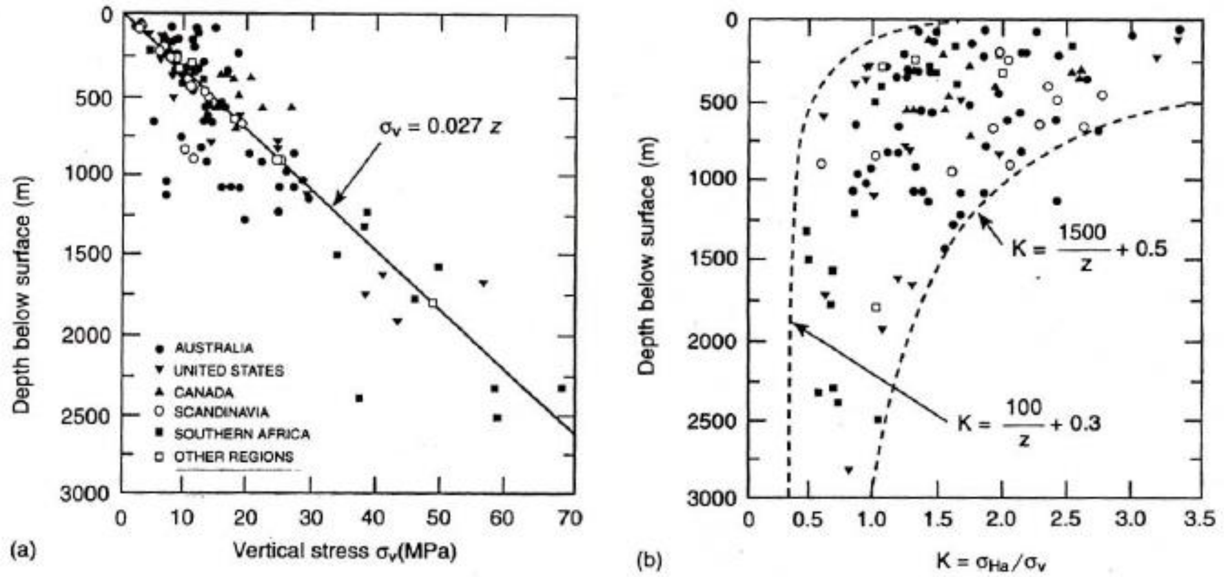


Figure 25 Relationship between depth and vertical stress (a) and *K* factor (b) [32]

According to the elasticity theory, the fractures develop in the plane of the maximum principal stress and are perpendicular to the minimum principal stress. After the fracture generation they tend to follow the direction of least resistance. If the vertical component is the maximum principal stress (which is realistic at great depth, e.g. in the case of oil reservoirs) the fracture propagates vertically, while in the case of horizontal maximum principal stress (which is likely to be the condition in environmental applications, in typical aquifer systems), the fracture will be vertically oriented near the borehole, and tends to develop in the horizontal plane during propagation at a certain distance from the well.

The pressure needed to crack a formation can be determined both with empirical formulas, which requires a precise knowledge of the geotechnical properties of the soil, such as internal friction angle, and cohesive strength. These parameters are obtained from laboratory tests, which often will not be representative of field conditions, because they do not take into account over-consolidation phenomena. As an alternative, a preliminary fracturing test can be performed. In this test, a fluid is injected with increasing discharge rate (Figure 26). The injection pressure, continuously monitored during the whole test, increases with increasing discharge up to a critical value (fracture generation), and then suddenly decreases even if the flow rate is further increased (fracture propagation).

Therefore, if the fluid is injected in the subsoil at a pressure lower than the critical one, permeation flow will occur, while a pressure higher than the critical value will result in fracturing of the porous medium.

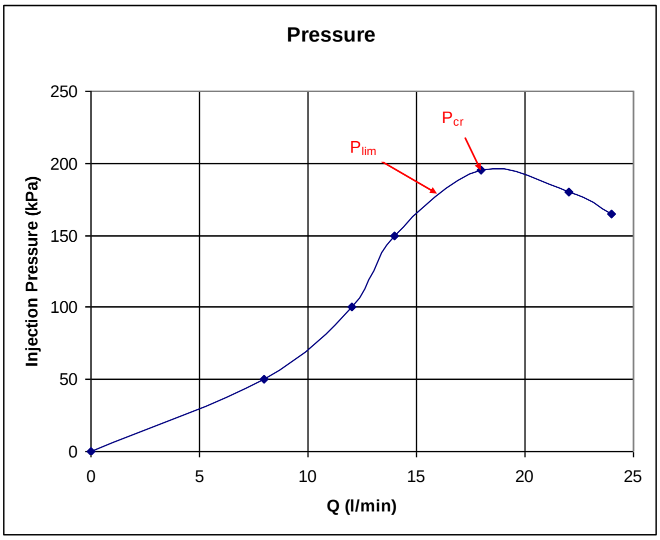


Figure 26 Field test for the determination of critical pressure

Fracturing injection technologies can be classified in hydraulic and pneumatic. Several studies reported in the literature show that, as a general rule, the injection pressure needed for hydraulic fracturing is usually lower than the one needed for pneumatic injection, while the radius of influence ranges approximately between 1 to 3 m(Christiansen, C.M., et al., 2010; Christiansen, C.M., et al., 2008).

8.2.2.1 Hydraulic fracturing

Hydraulic fracturing has been largely used for reservoir stimulation (Hossain, M.M. and M.K. Rahaman, 2007; Settari, A. and M. Cleary, 1984; Zhou, J., et al., 2010; Meng, C. and C.J. De Pater, 2010), but recently has been adapted for remedial extent (Castillo, L.M., C.J. Jablonoskwi, and J.E. Olson, 2010; Montgomery, C.T. and M.B. Smith, 2010; Huang, N.C. and S.G. Russell, 1985). It is a process creating fractures or a fracture network in a porous medium by injecting fluids under pressure. Fractures are usually generated with a lance advanced into a casing with a hammer down to the target depth (Figure 27). The fluid is first injected at a constant rate into a borehole, until the pressure exceeds the critical value and a fracture is nucleated.

A typical pressure required to create a fracture in shallow aquifers is about 5 to 10 bar. It decreases sharply when the fractures start to propagate. After the fracture is created, a fluid is injected at a lower pressure in order to promote fracture propagation. A granular material, called proppant, is often added to the fracturing fluid. The proppants will remain inside the fracture and keep it open at the end of the process. Usually, the average thickness of the fractures ranges from 0.5 to 1 cm. After the whole process is completed, the casing can be driven deeper to generate other fractures. It is recommended to create fractures with vertical spacing varying from 1.5-3.5 m, because with shorter vertical distance two fractures will most likely merge.

The fluid used for hydraulic fracturing must have a low leak off rate, the capacity to carry a proppant, if used, and a low pumping friction loss. In other words the fluid must be a viscous fluid (0,15-0,2 Pa s), able to transport coarse grained material into the fracture, and food grade if it is to be applied for groundwater remediation.

Guar gum gel is an example of injection fluid suitable for fracturing environmental applications (Frank, U. and N. Barkley, 1995; Suthersan, S.S., 1999). Silica sand is commonly used as propping agent and is useful to avoid fracture collapse after relaxation of injection pressure, and later when the guar gum gel is decomposed by enzymes added during injection.

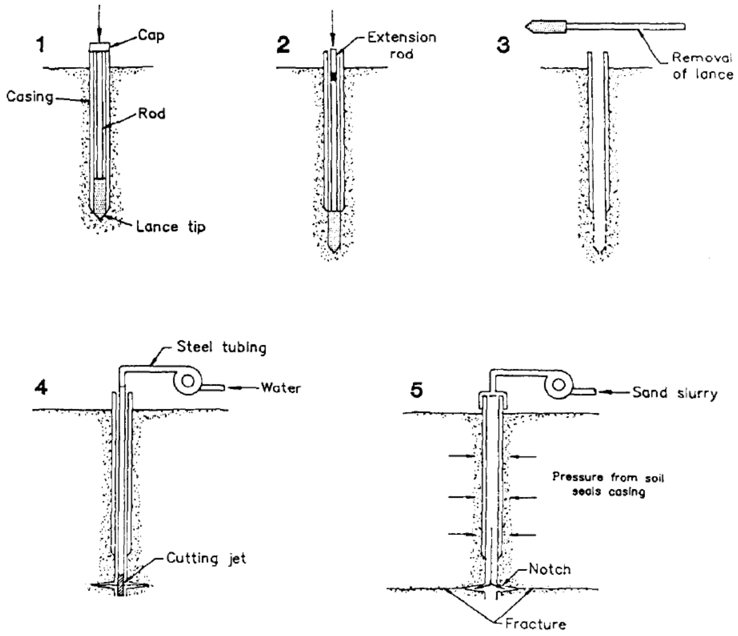


Figure 27 Hydraulic fracturing, from (Frank, U. and N. Barkley, 1995)

8.2.2.2 Direct Push

Direct Push Technology (DPT, also known as “direct drive,” “drive point,” or “push technology”) is a drilling method often used for hydraulic fracturing applications. DPT drives small-diameter (usually not larger than 4 inches) hollow steel rods into the subsoil using vibrating or hydraulic technology. DPT can be used for direct installation of piezometers. Also, the bottom end of the rods can be equipped with a variety of sampling tools to collect soil, soil-gas, and groundwater samples, with probes for continuous in-situ measurement of subsurface properties (e.g., geotechnical characteristics and contaminant distribution), and tools for the injection in subsurface of grout or reactive materials, which can then be performed without requiring a predrilled borehole (Direct Push Injection, DPI).

DPI is particularly suitable for permeation injection in relatively homogeneous deposits, with a medium to high permeability. In low permeability deposits permeation can be extremely slow, or even not possible: increasing injection rates implies increasing injection pressures, thus often resulting in a fracturing of the formation. The pressure which can be applied for fracturing with DPI is extremely high, up to hundreds of bars.

DPI injection can be performed bottom-up or top-down. Today the majority of injection interventions take place using the bottom-up method (Figure 28). According to this procedure rods are driven directly to the bottom of the injection interval, and the material is injected through the probe during retrieval. Injection can be performed either slowly withdrawing the tool string with continuous injection or injecting with the tool stationary at a fixed depth and then pulling in the tool up to the following depth.

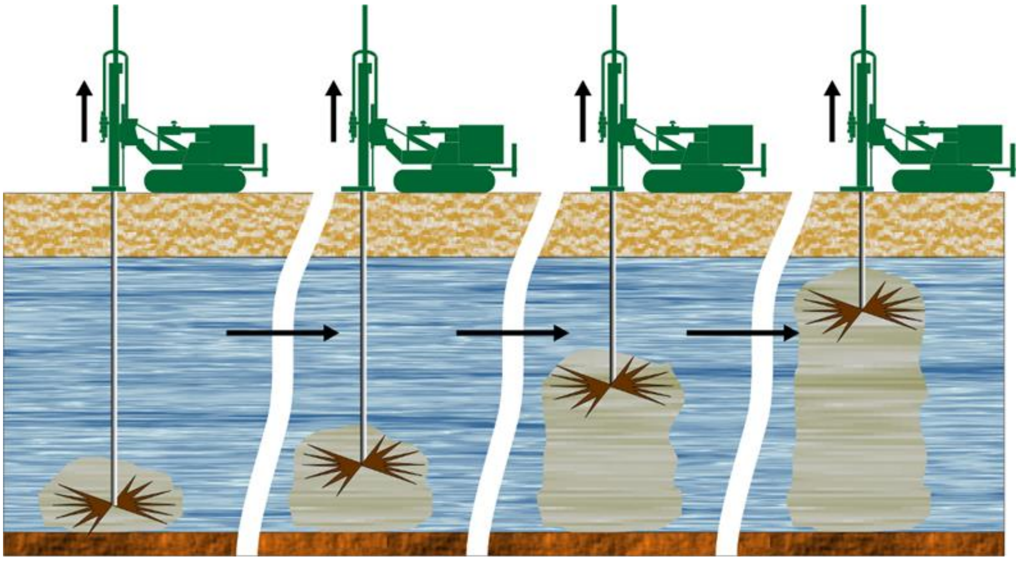


Figure 28 Bottom-top method for Direct Push Injection

The top-down injection procedure is gaining increasing interest in the last years. In this case, the tool string is first hydraulically advanced down to the top of the injection interval. The material is then injected with the tool string stationary, and when the proper amount of reagents has been delivered, pumping is stopped and rods driven to the following desired depth. It is worth mentioning that top-down injection is more at risk of bypass or daylighting during the first injection steps, which can prevent further injection at higher depths. However, also bottom-top approach is not completely exempt from such risks.

Several factors affecting the efficiency of direct push injection must be taken into account in the choice of the most proper injection machine, pumps and tools: viscosity of the fluid, volume to be injected, geological properties of the formation, chemical properties of the reagents.

Concerning injection devices, piston pumps are specifically designed for high pressure injection of highly viscous fluids. They (Figure 29) use hydraulic power to actuate a piston in a hydraulic cylinder, coupled with another grout piston via piston rod. The reciprocal action of the two pistons generates the pumping effects in the grout cylinder.

Figure 29 Pumping system of Direct- Push machines (from www.geoprobe.com)

A proper Injection Probe (Figure 30) allows for either top-down or bottom-up injection when using any grout or injection machine, allowing materials to be injected laterally into the subsurface. Unlike conventional injection methods, this probe ensures accurate placement of the material into the intended injection interval. A key feature of this probe is that it acts as a backflow preventer.

Table 8 Specifications of different piston pumps commercially available for Direct Push injection

	A	B
PUMP TYPE	Dual piston hydraulic pump	Dual piston hydraulic pump
PRESSURE (bar)	69	127
FLOW RATE (l/min)	3.4-8.7	3.4-13.6

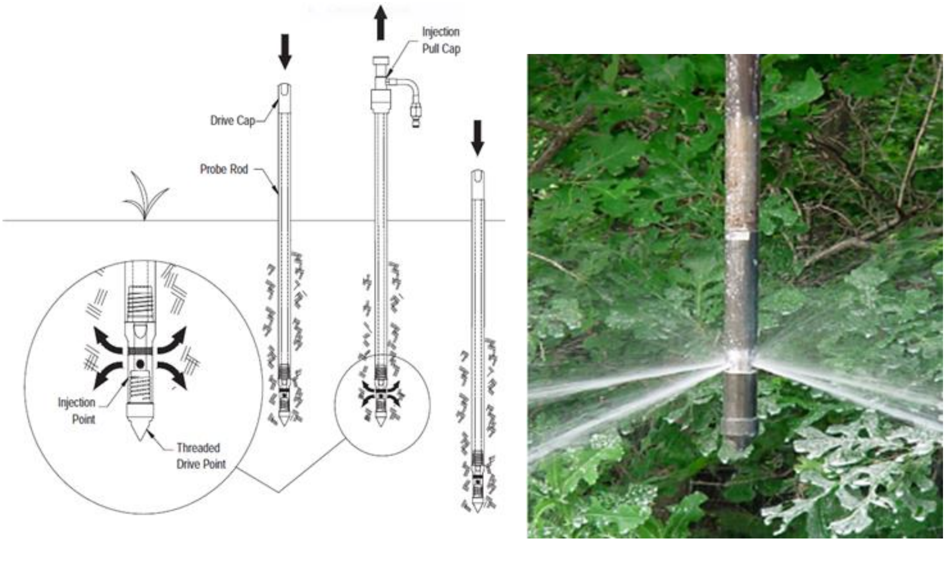


Figure 30 Pressure-activated probe (from www.geoprobe.com)

8.2.2.3 Pneumatic fracturing

In pneumatic fracturing, fractures are generated by injecting air or nitrogen gas, without the use of any proppant. Also in this case the fracture propagation is predominantly horizontal, although some upward inclination of the fractures has been observed. Also, the number and size of the fractures can significantly differ from those generated hydraulically, which are usually longer and thicker (Christiansen, C.M., et al., 2008; Venkatraman, S.N., et al., 1998).

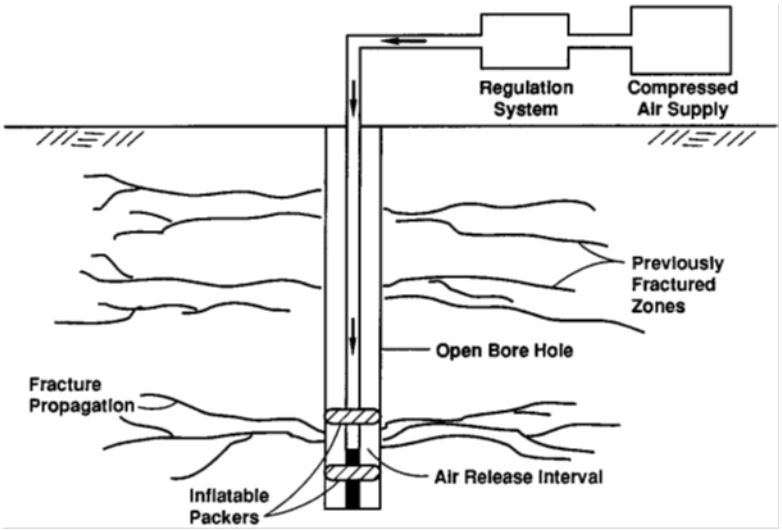


Figure 31 Pneumatic fracturing (Suthersan, S.S., 1999)

The pressure required for the fracture opening is proportional to the cohesive strength of the formation as well as the overburden pressure. Typical values of initial pressure able to open fractures vary in the range of 7-15 bar.

Field observations show that, when open, pneumatically induced fractures quickly reach their maximum dimension. Once the forming fractures intersect a sufficient number of pores or existing discontinuities, the leak off into the formation will equal to injection flow rate. As a consequence, injection after this phase simply maintains fracture in a dilated state. Generally injection flow rate of 0.5 m^3/s is sufficient to generate a fracture network, and enhance formation permeability (Zhang, D.W., et al., 2009).

An individual pneumatic fracture is accomplished by positioning the injector at the desired depth in an open borehole, inflating the flexible packers on the injector with nitrogen gas, and applying pressurized air for 30 s. A typical fracture cycle lasts about 15 minutes (Mizell, D.E. and D.P. Hunt, 1996).

8.2.3 Soil mixing Technologies

8.2.3.1 Jet grouting

Jet grouting was developed for geo-technical applications both for the improvement of soil mechanical properties through injection of cement slurries and for the construction of impermeable barriers (Spence, R.D., J.L. Kauschinger, and B.E. Lewis, 2000; Kauschinger, J.L., 1987; Modoni, G., P. Croce, and L. Mongiovi, 2006). For these applications, a fluid is injected into the subsoil at high pressure and high discharge to erode and mix the soil to form the so called “soilcrete”. More in

detail, a borehole is first drilled and held open by grout or drilling mud, which consist of a pre-mixed slurry of cement and water. In some cases, depending on treatment depth, it can be stabilized by installing a steel or plastic casing. After that a drill bit with the jet grouting tool is advanced to the bottom of the treatment zone and a fluid (air or water and grout) is ejected from the rotating nozzle at high pressure and velocity in order to erode the surrounding soil in an almost cylindrical area of influence (Spence, R.D., J.L. Kauschinger, and B.E. Lewis, 2000). Compared to other injection technologies, the pressures needed for jet grouting are very high (ranging from 200 to 600 bar), so as the fluid velocity.
The three main injection approaches are:

- Single fluid: the cement slurry is injected at high pressure, as described.
- Double fluid: the grout is injected with air to enhance soil erosion.
- Triple fluid: grout is injected both with air and water through three different lines. This configuration proved to be the most effective for cohesive soils.

8.2.3.2 Mechanical soil mixing

Soil mixing is a technique developed for in situ remediation in order to contain, stabilize and otherwise treat contaminated soils. This technique normally involves mechanically mixing of soils with a drilling fluid (Figure 32). The mixing is carried out by a crane-mounted, high-torque turntable that turns one or more special mixing augers, with a diameter ranging between 0.4 and 4 m, into the soil without excavation (Al-Tabba, A., M.J. Ayotamuno, and R.J. Martin, 2000).
Two methods are currently adopted (Day, S.R. and C. Ryan. Containment, 1995):

- Shallow Soil Mixing (SSM): for treatment depth down to 10 m, one single, large auger is preferred. The auger is continuously turned and moved up and down while the fluid (reactant, air or any other kind of slurry) in injected through the stem down to the tip, and ejected at high pressure. A cylinder of mixed soil is obtained for each treatment position.
- Deep Soil mixing (DSM): for higher depth (down to 35 m), a set of mixing augers with smaller diameters are simultaneously counter-rotated, and panels of treated soil are obtained.

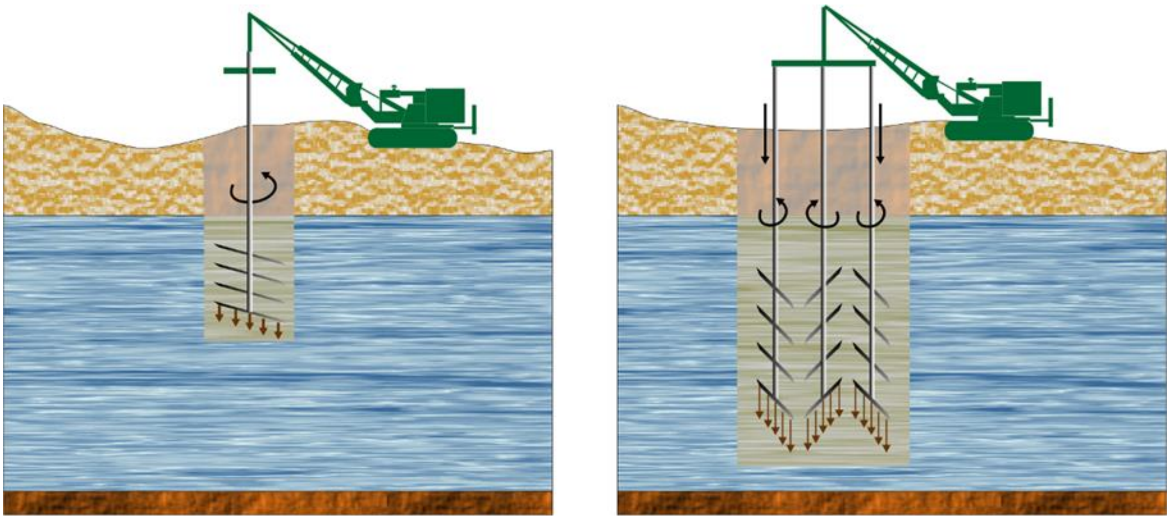


Figure 32 Shallow (a) and Deep (b) Soil Mixing

8.2.4 Conclusions for Injection Technologies

Injection technologies available to delivery reagents in the subsurface for in situ remediation can be classified into three main groups: permeation, fracturing and soil mixing technologies. Permeation injection is suitable for aquifers characterized by medium-high permeability, and requires large volumes of reagents, because all pore water within the influence radius is to be replaced by the reactant. In low permeability formations fracturing technology is needed in order to enhance hydraulic conductivity and assure reagents delivery. Also, fracturing is required when injecting reactants containing suspended particles which are too large if compared to the pores of the aquifer: in permeation injections, large particles would be filtered by the porous medium, thus dramatically reducing their radius of influence.

Using soil mixing, the size of the particles would not be relevant; however this technology is not suitable underneath buildings. Also, on areas remediated with soil mixing foundation of new buildings may be challenging since the soil structure has been altered and compaction is to be expected.

When using fracturing technology, contrary to permeation difficulties arise in understanding fracture geometry and propagation. This may result in a different remediation time frame since the contaminants need to travel diffusion controlled a greater distance to the remediation agent. Another problem might occur in monitor fracture generations and remediation efficiency.

8.3 Preparation of iZVI-suspension

The preparation of a good quality ZVI suspension is crucial for a successful injection. Criteria for a good ZVI suspension refer to (1) stability of the iZVI-suspension for at least 2 hours, which may require the use of stabilisers, (2) minimal exposure to oxygen during preparation and storage, and (3) a homogeneous iZVI-suspension without flocks of for instance stabiliser (especially important for permeation injections).

Within the AQUAREHAB project guar gum stabilised iZVI-suspensions have been prepared at different scales. Where in the laboratory actions like heating, mixing sieving are relatively simple to perform, in the field a more practical approach is needed. The preparation procedure that was used within AQUAREHAB to prepare a 1.5 m³ volume of guar gum stabilised is depictured in Figure 33. A hand mixer was used suspend sieved guar gum in tap water. Batches of 50 L were prepared and stored in 1 m³ vessels. In order to avoid bacterial growth and loss of viscosity, it is recommended to store the guar gum suspension not longer than 1 day.

Figure 33 Guar gum preparation as was performed within AQUAREHAB for a small pilot test (1.6 m³ ZVI suspension).

Just before the injection, the ZVI-powder (mZVI) was mixed with the guar gum (Figure 34). Recirulation of the suspension by a simple submerged pump was found to perform very well. A disperser unit (Ultra-Turrax for huge volumes) may be required to prepare iZVI-suspensions for permeation injections

100 kg ZVI (H20-) | Mixing of guar gum & ZVI | Injection vessel & pump ! | Geoprobe injection

Figure 34 Preparation and immediate use of the ZVI-suspension as performed within AQUAREHAB for a small pilot test (injection of 100 kg mZVI, 1.6 m^3 ZVI suspension).

For the preparation of 10 m^3 guar gum stabilised mZVI-suspension different equipment was used. A larger scale dispersing unit (Ytron ZC-0, also used to prepare ice-cream) was found very effective to prepare a high quality (fine) guar gum suspension in a relatively short time (> 1 m^3/h). Again the prepared slurry was stored in 1 m^3 vessels with addition of the mZVI just before the injection (Figure 35).

Figure 35 Dispersing unit (Ytron ZC-0) used within AQUAREHAB during pilot test 2 &3 to prepare 10 m^3 of guar gum suspension in the field.

For full scale applications flexible and fast preparation methods need to be available. A possibility may be the use of bentonite mixing equipment, which was shown to be suitable to inject 3500 kg mZVI as guar gum stabilised slurry via soil mixing in the subsurface (Figure 36). For permeation applications an additional dispersing unit may be required to remove remaining guar gum flocs.

Figure 36 Large scale preparation of mZVI-slurry for a soil mixing application using an existing device designed for bentonite mixing.

8.4 Day lightening

During iZVI-injections, day lightening of the ZVI-suspension can not be excluded, especially for more shallow injections, at higher pressure, and when the spacing between 2 subsequent injection points is low.

9 MONITORING OF THE IZVI-ZONE (STEP 6)

9.1 General considerations

Any remediation measure used for a specific site needs some kind of verification or an evaluation of the success. Therefore, appropriate measurements need to be made and corresponding data has to be collected and evaluated. In the case of the application of reducing iron particles, this verification has two parts:

- the proof of the distribution of the particles in the subsurface during (and after) the injection and
- the proof of the reactivity of the iron with the contaminants.

The first part comprises mainly the detection of the movement of the particles or the containing suspension during the injection. This requires the direct or indirect detection of the particles during or immediately after the injection (short time monitoring).

The second part requires measurement systems for both the presence of iron as well as contaminants and reaction products. In addition, this instrumentation has to allow for measurements over a longer period of time (long term monitoring).

9.2 Assessment of the distribution of the ZVI particles

The main focus of this short-time monitoring is finding proof that the particles could be distributed during the injection as predicted or intended. This information should ideally be available directly on site, for instance via in-situ on-line measurements, since the injection procedure could be adapted to the findings if the distribution does not match the expectations. Another approach may be to take undisturbed core samples after the injection.

The detection of the iron can be done by quantifying the ZVI mass, e.g. using the magnetic susceptibility or chemical measurement, or indirectly by measuring effects caused by the suspension such as a change in the temperature, redox potential or electrical conductivity. For a detection of the suspension a tracer dye can be added which can be visualized by pumping ground water or by in-situ measurements with fibre optic systems. If an indirect measurement is chosen, there is the problem of deducing the radius of influence of the particles from the distribution of the liquid part of the suspension. Although retention factors can be determined in laboratory studies before the field application, the deduction of the travel distance of the particles is much more uncertain compared to direct measurements. On the other hand, indirect measurements usually require less effort.

In each case heterogeneities in the subsurface will strongly affect the distribution of the particles and will make the interpretation of the measurements difficult. This is especially a problem, when a fractured flow is chosen for the injection.

9.2.1 In-situ measurements during the injection

Within the AQUAREHAB project special combined sensor systems have been developed, which allow for the direct detection of the liquid phase of the suspension and the zerovalent iron during

the injection as well as for taking samples with a high spatial resolution for the long term monitoring. These sensor systems have been designed as sensor arrays which can be installed via direct push and will permanently remain in the subsurface. The corresponding measurement strategy is based on placing several of these arrays in a test area each array containing several sensors and sampling ports (see Figure 37).
The arrays are designed such that distinct iron sensors, which will finally be placed in different depth, are connected with 1” teflon rods. Along these rods the cables of the sensors together with the cables of the temperature sensors (designed to detect the liquid phase of the suspension during the injection) and the lines of the sampling sysems are taped and guided to the top of the arrays. For each measuring sensor a reference sensor is placed in the unsaturated zone, since the electronic measurement is based upon the measurement of a difference of two sensors in order to improve the sensitivity. The sampling ports consist of mini pressure pumps (or small filters connected to a peristaltic pump) which are small enough to fit in the required diameter for direct push (65 mm) and provide spatially highly resolved samples. The working principle is shown inFigure 38. The pumps consist of three connected lines, two of which end at the surface, one is located at the desired position in the aquifer. The lower line and one of the surface lines have a ball valve, which lets water through in the upward direction. In the third line repeated pulses of gas pressure are applied such that the water has to move up in the other surface line.

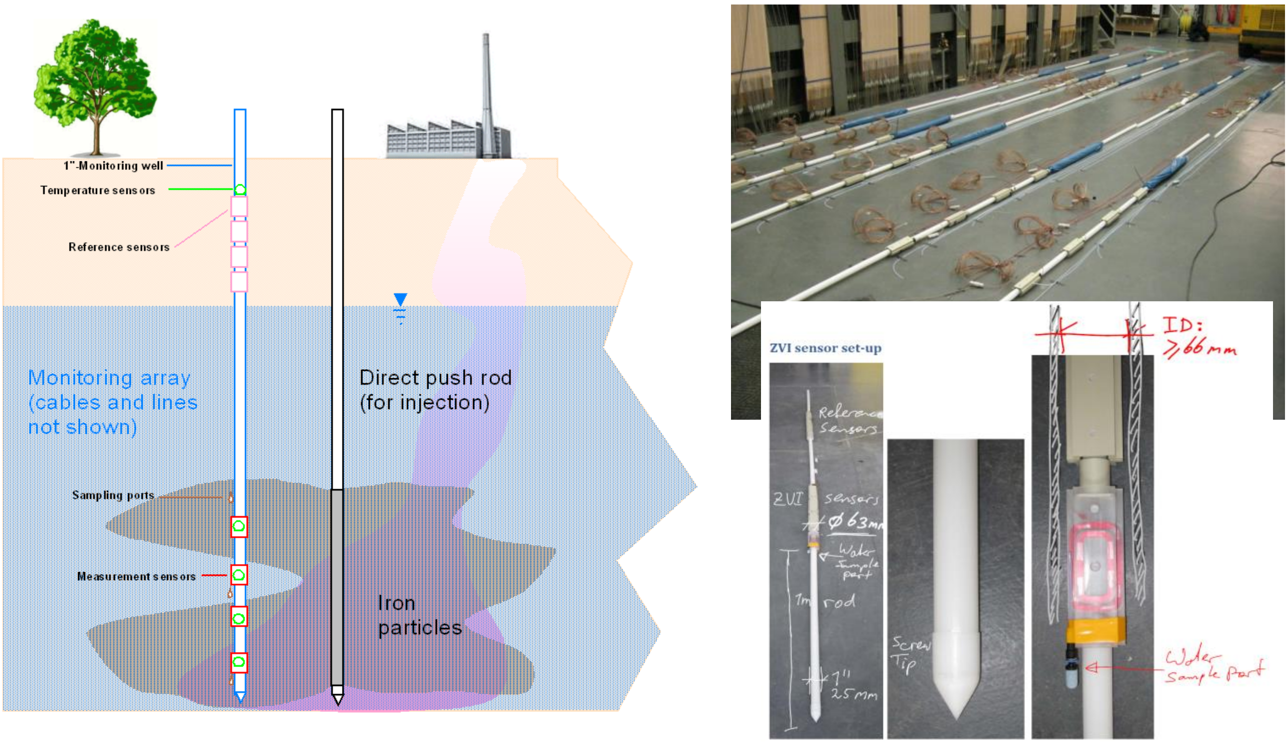


Figure 37 Installation of a sensor array (left), Sensor arrays during assembly (right)

For the installation of monitoring systems the use of direct push techniques could be favourable. This technique has some limitations concerning the geology and the depth where it can be applied, but if applicable it can save cost and efforts and the installation of the sensors and sampling ports can be accomplished in a relatively short period of time and with a high flexibility concerning the location of the sampling and measurement probes.

In general, a pre-period is advisable where measurements and samples are taken to determine the condition before the particle injection. I.e., the monitoring systems should be installed some time (> 1 month) before the particles are injected and several sampling and measurement campaigns should be conducted during this time.

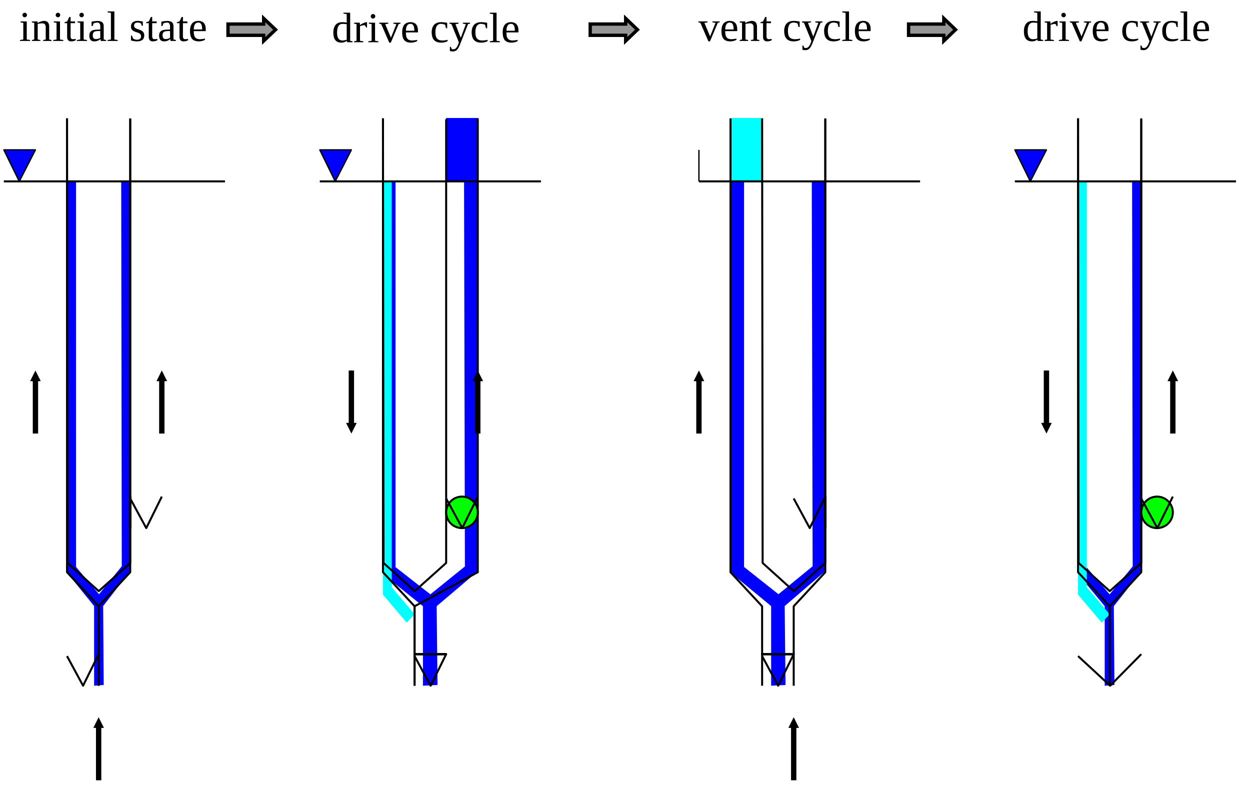


Figure 38 Working principle of mini-pressure pumps

Figure 39. Installation of the multilevel monitoring systems at the Field for a AQUAREHAB pilot test (installation up to 7 m bgs).

An exemple of the layout of a test field is shown in Figure 40 representing a direct push application of nZVI. The idea is to have different measurement arrays located in different distances between the injection locations. With this layout and the combined iron and temperature sensors the distribution of the suspension and the particles can be assessed. If the time of the injection together with the exact injection position is recorded, a 3D-distribution of the particles can be deduced. This data is aimed to be available online during the injection, allowing an adjustment of the injection conditions (locations, volumes injected at each depth, concentration of the suspension…).

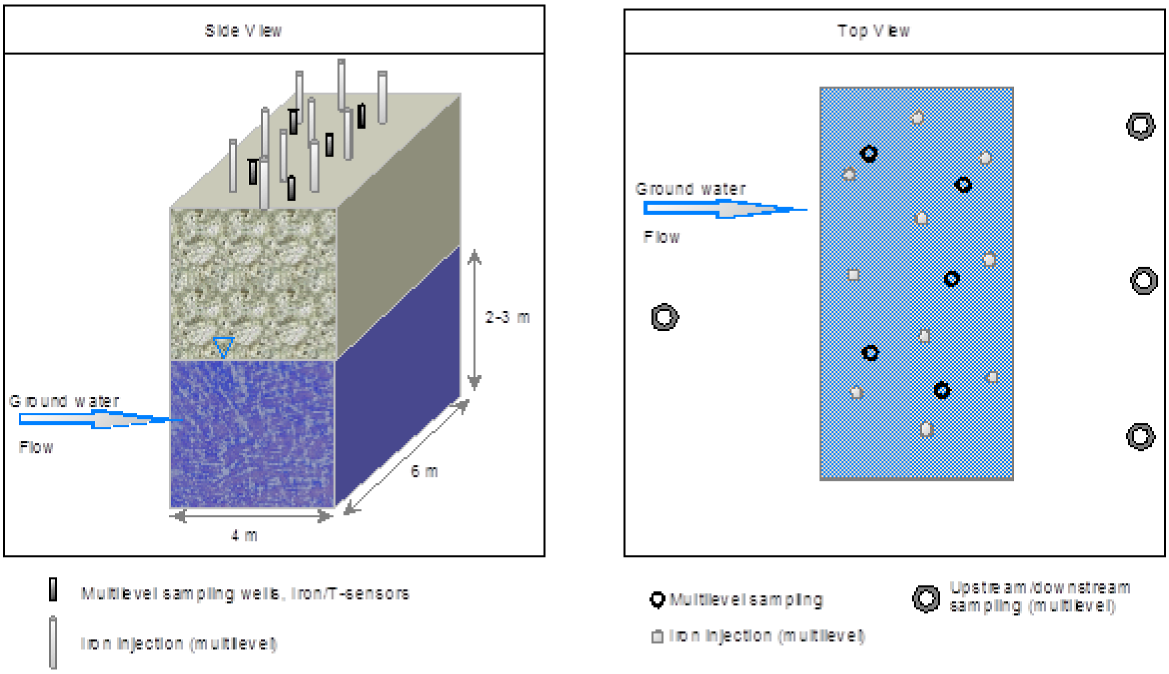


Figure 40 Layout of a test field with injection positions and measurement arrays

Figure 18 and Figure 41 show how to combine susceptibility measurements and sampling system can be used in a pilot test configuration. Both iron spatial distribution and concentration over time can be monitored with this multilevel detection system (MLDS).

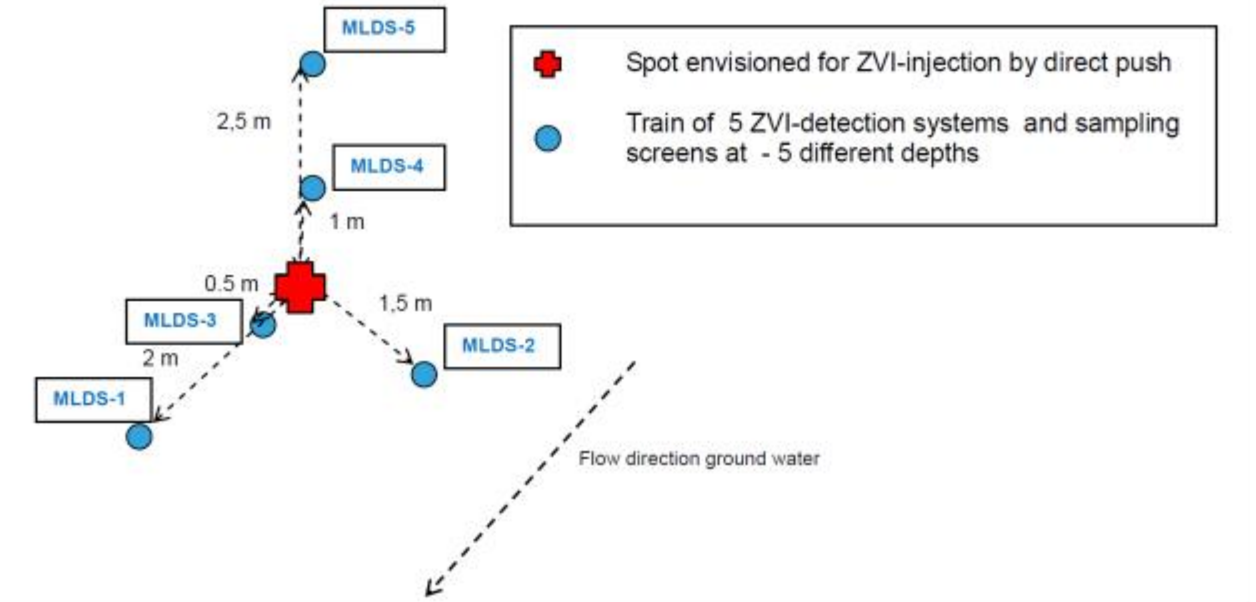


Figure 41 Conceptual representation of the pilot test

Figure 42 shows the results of the calculation of the concentration at the two sensors which showed distinct signals. For the calculation the difference between the background signal and the signal caused by the presence is considered.

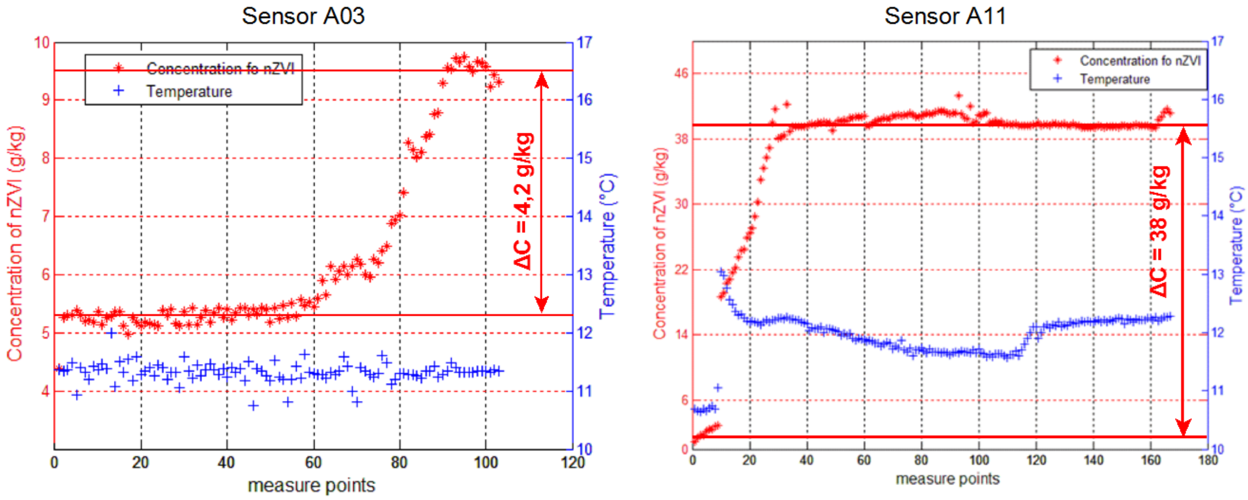


Figure 42: Calculation of the iron concentration (time between measure points: 1 minute) via in-situ susceptibility measurements.

9.2.2 Measurements on undisturbed aquifer core samples (liners)

Spatial distribution may also be monitored through the extraction of liners (Figure 43). Different approaches exist to determine in a next step the iron concentration profile in the liners: (1) magnetic susceptibility measurements (Dalla Vecchia et al. 2009, Gastone et al. 2014b, Tosco et al. 2014), (2) direct chemical analyses or (3) indirect chemical analyses via acidification and measurement of hydrogen produced (Velimirovic and al., 2014b).

Figure 43. Liners extraction and collection.

The number of core samples and the configuration depends on the purpose of the test and test scale. The most intense monitoring is needed during the pilot trial to derive the injection parameters. Figure 18 displays the monitoring configuration that was used during an AQUAREHAB pilot test in the field. Core samples were taken in different directions and at different distances from the injection point. While the sensors described earlier give a distribution as a function of time, liners will give a very accurate spatial distribution at one point in time.

As an example, within AQUAREHAB, 10 days after injection, 8 core samples from 1-6 m bgs were taken to evaluate the distribution of injected mZVI in the subsurface. The presence of mZVI in core samples determined via magnetic susceptibility measurements is presented in Figure 44. According to the data non-homogenous distribution of the particles at several different depths was observed. mZVI was clearly present in the core samples taken in the close vicinity (approximately 0.5 m) of the injection spots. mZVI was also detected close to the upstream well (at approximately 1.5 m from closest injection point) indicating that preferential flow paths were created. ZVI-concentrations obtained via the H_2 analysis were in agreement with susceptibility measurements.

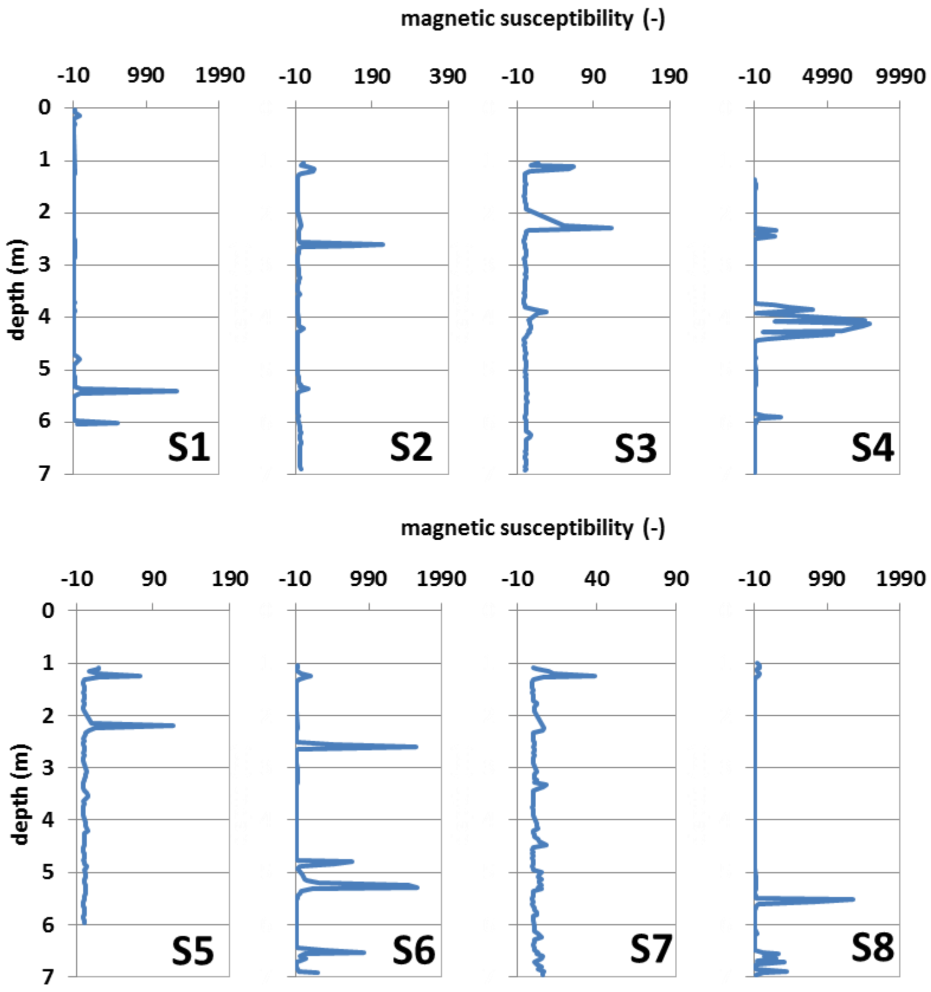


Figure 44. Magnetic susceptibility profiles of 8 core samples extracted close to the injection points.

9.3 Monitoring of the impact of the injected ZVI particles in the subsurface

While the focus of the short-time measurements is on the distribution of the particles, the main purpose of the long-time measurements is to follow the reaction and to make sure that the particles are still active in the subsurface.

Usually, monitoring wells placed upstream, in and downstream of the injection area are used to evaluate the pollutant situation in the groundwater at site level.

The measurement systems described in 9.2.1 can also be used as they allow groundwater sampling besides ZVI-detection. During the monitoring, the presence of elemental iron is insufficient to evaluate the activity of the particles. Water samples have to be taken in order to verify the reaction. By evaluating the water samples which are taken from time to time a verification of the temporal development of the efficiency of the reaction can be done. The right moment for a potential reinjection can be determined either by detection of the consumption of the particles, i.e. loss of the signal for elemental iron in the sensors, or by a decrease of the reaction rate between the contaminants and the iron.

A decrease of the reaction rate, deduced e.g. by the decrease of the chlorinated compound concentration in the ground water, does not necessarily mean that the iron is really consumed. A ceasing in the reaction could also be produced by a clogging of the surface of the iron particles due to precipitations (e.g. iron carbonate, $FeCO_3$) or by the formation of hydrogen gas which clogs the aquifer and hinders the contact between the colloids and the contaminants.

Thus, it would be desirable to have both options: the verification of the success of the colloid application by water samples and the information about the presence of elemental iron by sensor measurements. For an evaluation of the efficiency of the reaction with the contaminants a variety of parameters might be considered with different significance, which also depends on the specific site conditions and contaminants.

As an example, analytical parameters to consider for a PCE-contaminated site are listed in Table 9.

Table 9 Analytical parameters with indication and significance

Parameter	Indicator for	Remarks
Chloride	Degradation product	Essential for assessment of remediation success, but a higher background will make it difficult to evaluate
PCE	Main contaminant	Important to detect changes in emission
TCE	Contaminant, possible intermediate product	Possibly difficult to evaluate
DCE	Intermediate product	Indicators for incomplete degradation, difficult to sample!
VC	Intermediate product	
Ethene	Final product	THE parameter for assessment, difficult to sample!
H_2	Corrosion	Assessment of ratio corrosion/reaction, difficult to sample!
E_h	Redox milieu	Important parameter for lifetime of particles
pH	Corrosion+reaction	
O_2	Redox milieu	Indicator for changing flow regime
EC		Nice to have
Dissolved organic and inorganic carbon		DOC – nice to have (indicator for surfactants, additives…) DIC – microbial activity
NH_4^+	Redox sensitive cation	Indicator for Nitrate reduction by iron (can be dropped, if constantly absent)
NO3-, NO2-, SO42-, PO43-	Redox sensitive anions	
Acid/base capacity	Change in pH-milieu	Indicator for stability of pH-milieu
$Fe_{dissolved}$	Degradation product	Degradation product (corrosion+reaction), concentration not directly transferable due to precipitates

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Politecnico di Torino (Italy)	Rajandrea Sethi rajandrea.sethi@polito.it Tiziana Tosco tiziana.tosco@polito.it Francesca Gastone Michela Luna	Mobility aspect – modelling Pilot test design/implementation Lab & in-situ ZVI detection systems General aspects
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12 APPENDIX A: DETAILS REACTIVITY FEASIBILITY TESTS

12.1 Standardized lab scale reactivity test

The described test procedure was used within AQUAREHAB to screen and compare the reactivity of ZVI (Velimirovic et al., 2012).

Artificial groundwater consists of anaerobic autoclaved MilliQ water supplemented with $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $NaHCO_3$ and $KHCO_3$ to a final concentration of 0.5mM each. Under anaerobic conditions, the pH is adjusted to neutral by adding 1M HCl and the artificial groundwater is spiked aiming at a final concentration of approximately 5 mg $L^{-1}$of PCE, TCE, cDCE and 1,1,1-TCA each.

Lab scale test procedure to study degradation of a mixture of CAHs by ZVI. The proposed iron concentration for nZVI particles is 5 g/L, for granular ZVI and mZVI 50 g/L. More precisely, 160 ml glass vials with butyl/PFTE grey septum were used containing ZVI, 100 ml of anaerobic simulated groundwater and 60 ml of headspace. A test condition without reactive materials, to be included in each experiment, serves as a reference to determine sorption percentages, as well as potential biodegradation. The vials should be then placed for continuously gently mixing at a temperature relevant for the groundwater at the examined site. Monitoring comprises of:

- Measurement of CAHs and by- and end-products can be performed via headspace analysis, at start up and different time intervals (for instance after 3, 6, 8 and 22 days for nZVI particles; for instance after 14, 28, 49 and 105 days form mZVI and granular ZVI) using for instance a GC-FID.
- In addition to CAHs and by- and end-products, at each sampling point the redox potential and pH can be measured using a redox/pH meter.

Mass balances are to be made on molar basis (PCE +TCE + cDCE + VC + 1,1,1-TCA + 1,1-DCA) + acetylene + ethene + ethane) to determine if sorption occurred.

12.2 ZVI dose test

The following test procedure was used within AQUAREHAB for ZVI dose tests, aiming at providing information related to the minimal required doses of ZVI for CAHs removal.

Dose tests are actually screening tests (see 12.1) performed with different doses of ZVI. The lab-scale experiment is to be set-up with aquifer material and groundwater sampled at a relevant spot on the site where the iZVI technology is envisioned. The following different concentrations of ZVI particles can be used being: for instance 0.1; 0.5; 1; 2.5 and 5g per kg of aquifer material for nZVI particles and higher doses for mZVI, for instance 1, 5, 10, 25 and 50 g ZVI per kg aquifer. In time (for instance at the beginning, and after 6, 8, 15 and 22 days for nZVI material and after 14, 28, 49 and 105 days for mZVI), the evolution of the contaminant concentration as well as redox potential and ORP (hydrogen) can be followed using the same procedures as described in 4.3.1.1. It is important to include in this assay also a poisoned control (0.4 % of formaldehyde) to distinguish biodegradation from abiotic remediation if it is present at selected site.

As an example, results obtained within AQUAREHAB with 5 different ZVIs and aquifer/groundwater ratio (w/w) of 3:2 is given in Table 10. The legend describes the criteria that were used (1) to categorize the iron based on efficiency in degrading the pollutants as well as (2) to determine the minimal iron concentration needed for remediation taking into account different legislations. It was concluded that mZVI particles can be efficient in pollutants removal at a concentration comparable to that of nZVI particles. This is an encouraging observation for further examination and exploitation of mZVIs, which are significantly cheaper than nZVI.

Table 10 Summary of the efficiency of different ZVI particles towards removal of pollutants for a specific site studied within AQUAREHAB site and their minimum required doses

pollutant	mZVI1	mZVI2	mZVI3	HQ	Nanofer25s
TCE	+++	++++	++++	++++	++++
cDCE	++	++	+++	++++	++++
1,1DCE	++	++	++++	++++	++++
1,1 DCA	-	±	+	+	±
Minimum concentration needed for TCE remediation (70 µg/l)*					
slurry	1 g/kg	1 g/kg	5 g/kg	5 g/kg	2.5 g/kg
aquifer	0.5 g/kg	0.5 g/kg	2.5 g/kg	2.5 g/kg	1.25 g/kg
groundwater	1.5 g/L	1.5 g/L	7.5 g/L	7.5 g/L	3.75 g/L
Minimum concentration needed for cDCE remediation (50 µg/l)*					
slurry	> 50 g/kg	> 50 g/kg	10 g/kg	10 g/kg	5 g/kg
aquifer	> 25 g/kg	> 25 g/kg	5 g/kg	5 g/kg	2.5 g/kg
groundwater	> 75 g/L	> 75 g/L	15 g/L	15 g/L	7.5 g/L
Minimum concentration needed for 11DCE remediation (7 µg/l)**					
slurry	50 g/kg	25 g/kg	5 g/kg	5 g/kg	2.5 g/kg
aquifer	25 g/kg	12.5 g/kg	2.5 g/kg	2.5 g/kg	1.25 g/kg
groundwater	75 g/L	37.5 g/L	7.5 g/L	7.5 g/L	3.75 g/L
Minimum concentration needed for 11DCE remediation (50 µg/l)***					
slurry	25 g/kg	5 g/kg	5 g/kg	5 g/kg	2.5 g/kg
aquifer	12.5 g/kg	2.5 g/kg	2.5 g/kg	2.5 g/kg	1.25 g/kg
groundwater	37.5 g/L	7.5 g/L	7.5 g/L	7.5 g/L	3.75 g/L
Minimum concentration needed for 11 DCA remediation (330 µg/l)*					
slurry	/	> 50 g/kg	> 50 g/kg	50 g/kg	> 5 g/kg
aquifer	/	> 25 g/kg	> 25 g/kg	25 g/kg	> 2,5 g/kg
groundwater	/	> 75 g/L	> 75 g/L	75 g/L	> 7,5 g/L

Legend

++++	100% degraded within 1 month
+++	100% degraded within 3.5 months
++	>70% degraded within 3.5 months
+	50-70% degraded within 3.5 months
±	10-50% degraded within 3.5 months
-	Less than 10% degraded within 3.5 months

* Maximum contaminant level (Flanders Groundwater Legislation)
** Maximum contaminant level (US EPA Drinking Water Regulations)
*** Maximum contaminant level for cDCE (Flanders Groundwater Legislation)
The iron requiring the lowest dose are indicated (coloured cells)

12.3 ZVI column test

Within the AQUAREHAB project, the following test procedure was elaborated and used to evaluate the reactivity of bare and guar gum stabilized mZVI (50 µm) under subsurface conditions (Velimirovic et al., 2014a). Experiments were carried out at 12°C (relevant groundwater temperature) in Plexiglas columns (diam. = 4 cm; length 50 cm) containing collected aquifer material, iron and/or stabilizer (guar gum).

The following test conditions were set-up to simulate different situations: A first column system (C-1) was completely filled with a mixture of aquifer material and filter sand (1-2 mm). A second system (C-2) contained the same filling material amended with 25 g/kg of mZVI, while a third (C-3) was amended with 25 g/kg of mZVI as well as 2 g/kg of guar gum. Two dead control (DC) columns were included. One filled with only aquifer/filer sand material (C-4) and the other (C-5) contained in addition ZVI (25g/kg) stabilized by the guar gum (2g/kg).

The groundwater was pumped into the column in an up flow direction at 17 ml/day/column, with an envisioned hydraulic retention time of the water in the column of 8-17 days. For monitoring purposes, liquid samples were collected from the effluent and along the column (different sampling ports; Figure 12). To minimise disturbance of the column and uncontrolled volatisilation of the pollutants, the sampling was performed by connecting 12 mL vials (previously capped and flushed with nitrogen, at overpressure) to a sampling port allowing the samples to spontaneously flow into the vials. The effluents were sampled every 2 weeks (CAHs, their breakdown products, pH, ORP, H_2 evolution) while more extended monitoring campaigns (samples taken along the columns) were made only at specific moments – about every month (CAHs, pH, ORP, H_2 evolution). CAHs and their breakdown products, as well as H_2 production are analysed using different GC techniques. While pH and ORP measurements can be obtained using HI1330 electrode (Hanna instruments) and PT5900A electrode (Schott Instruments), respectively.

The duration of such tests is typically 3-6 months, and may be longer when interested in longer-term effects. The pollutant removal capacity of the column systems can be quantified by calculating degradation rate constants and half-lives.

As an illustration, some results are given in Figure 45.

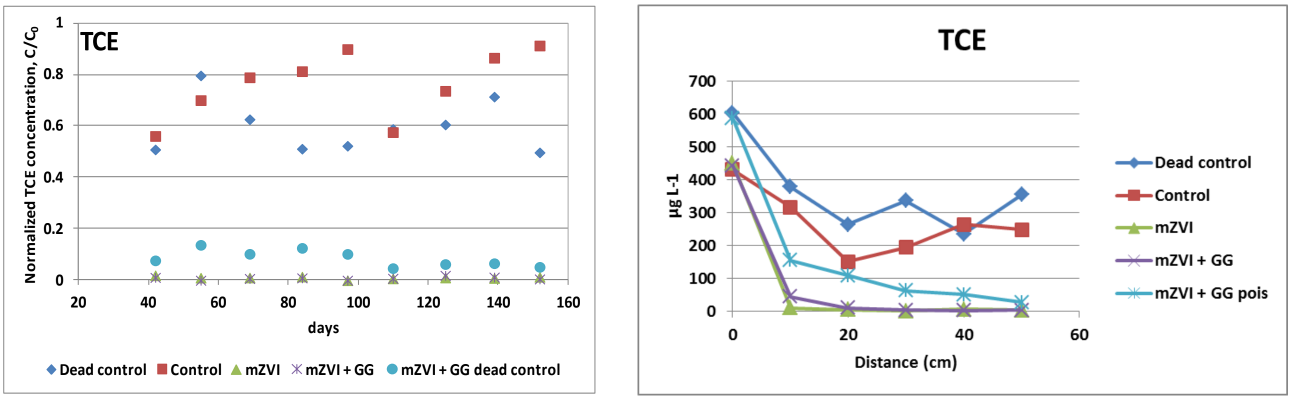


Figure 45 (a) TCE removal in the column systems based on effluent concentrations over time; (b) TCE concentration profiles along the columns visualising the situation at a specific moment (after 110 days).

13 APPENDIX B: MODELLING ZVI TRANSPORT

13.1 One-dimensional transport modelling

One-dimensional models are required for the analysis of laboratory column tests. A transport model for the prediction of iron particles transport through porous media must take into account advection-dispersion phenomena, as well as particles interaction with the porous medium, and the rheological properties of the carrier fluid, if any polymer is added to the suspension to improve colloidal stability.

The numerical model E-MNM1D was developed in the framework of the Aquarehab research project to include all these phenomena (Tosco and Sethi, 2010, Tosco et al. 2009) and is now included in the user interface MNMs (www.polito.it/groundwater/software). The model includes the following aspects:

- Modified advective-dispersive transport equations. The transport equations for the iron particles should include the mass balance for the liquid phase and the mass balance for the solid phase, modelled with one or more interaction kinetics:

$$\begin{cases} \frac{\partial}{\partial t}(\varepsilon_m c) + \sum_i \frac{\partial(\rho_b s_i)}{\partial t} = -\frac{\partial}{\partial x}(q_m c) + \frac{\partial}{\partial x}\left(\varepsilon_m D \frac{\partial c}{\partial x}\right) \\ \frac{\partial(\rho_b s_i)}{\partial t} = f(c, s_i) \end{cases} \qquad \textbf{(14)}$$

- where ε_m is the porosity, D is the hydrodynamic dispersion, q_m is the Darcian velocity, c is the concentration of suspended particles, s_i is the concentration of deposited particles for the i-th interaction site (expressed as mass of deposited particles per unit mass of the porous medium). Interaction kinetics can include physical interactions (filtration, straining, etc.) and physical-chemical interactions (linear deposition, blocking, ripening dynamics). All phenomena can be modelled as reversible (i.e. particles can be retained by the porous matrix and then eventually released) or irreversible. As an example, a general formulation for attachment/detachment dynamics, which can be adapted to all commonly used interaction kinetics, is (Tosco and Sethi, 2014).

$$\frac{\partial(\rho_b s_i)}{\partial t} = \varepsilon_m k_{a,i}\left(1 + A_i s^{\beta_i}\right)c - \rho_b k_{d,i} s_i \qquad (15)$$

- where $k_{a,i}$ is the deposition rate, $k_{d,i}$ is the release rate, β_i and A_1 are the kinetic parameters controlling the kinetic process of deposition.
- Darcy's law for Newtonian and non-Newtonian fluids. The "usual" form of Darcy's law was applied also for the case of non-Newtonian fluid, provided that the true pore fluid viscosity is replaced by the apparent viscosity, that includes all non-Newtonian effects.
- Porosity available for fluid flow. The pore space available for the fluid flow can be related to the concentration of deposed particles: increasing concentration of deposed particles, the medium porosity decreases.
- Viscosity of the pore fluid. Dynamic viscosity of polymeric solutions is known to be a function of shear rate, polymer concentration and particles concentration. As an example, for guar gum solutions viscosity is in the order of a few g/l, the dependence of viscosity on shear rate can be described by a modified Cross model.

- Permeability coefficient. When colloids depose on the soil grains, the pore space available for the fluid flow decreases, and the specific surface area increases. Both phenomena contribute to the reduction of the permeability coefficient.

Coupling of flow and transport was solved in E-MNM1D under the hypothesis that clogging of the porous medium is not a repent process, thus handling the problem as a quasi-stationary phenomenon. The proposed formulation relies on the hypotheses of 1D horizontal quasi-stationary flow, constant discharge, negligible compressibility of particles, porous matrix, pore fluid and particles deposits. The structure of the coupling among the model equations is summarized in Figure 46.
The system is solved iteratively using a Picard's iteration scheme. An example of the model results is provided in Figure 47 and shows a breakthrough curve of iron concentration for an injection of iron particles dispersed in a shear-thinning fluid, followed by a flushing with particle- and polymer-free water. Clogging of the porous medium is simulated by the linear increase of pressure during injection.

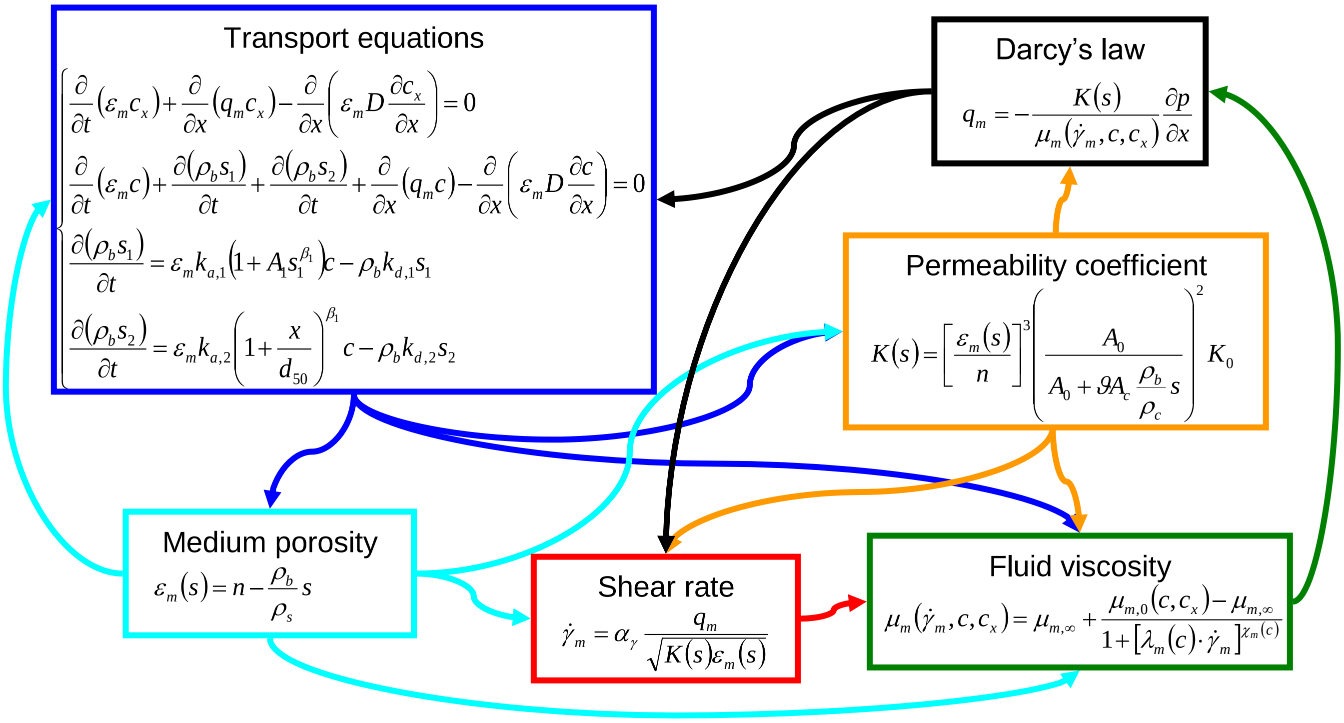
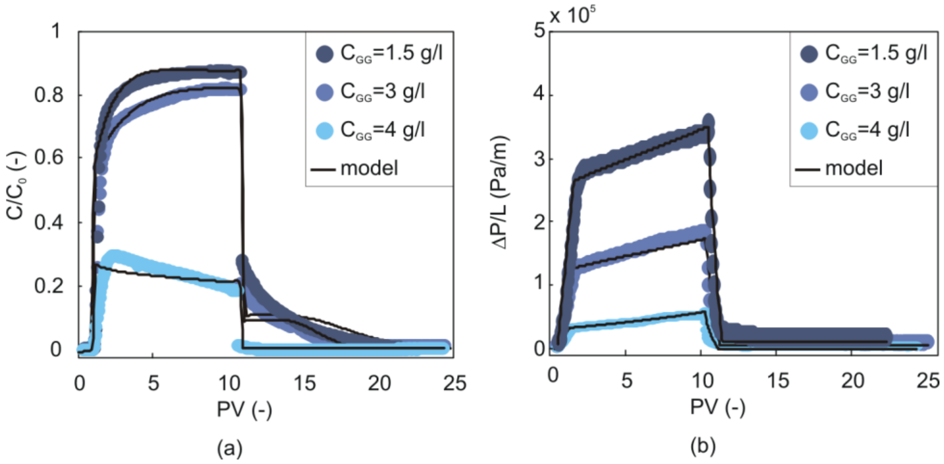


Figure 46 Scheme of the coupled model equations for iron particles transport (Tosco T. et al. 2014).



(a) (b)

Figure 47 Example of breakthrough and pressure curves calculated with the macroscale 1D transport model for iron particles (injection of particles dispersed in polymeric solution, followed by flushing of particle-free water). Modified from Tosco et al. (2014)

13.2 Multi-dimensional transport modelling

When considering radial transport of iron particles suspensions, unlike in 1D transport, the flow rate is not constant over the model domain, but decreases hyperbolically with increasing distance from the injection point. For this reason, a space-variable flow velocity is considered in the model, affected both by reductions in porosity and by increasing distance from the injection point. As all model equations are strictly coupled, changes in flow rate affect the non-Newtonian viscosity of the carrier fluid, and consequently the pressure drop, as well as the deposition and release kinetics.

The expression of deposition/release kinetics as a function of flow rate and suspension viscosity is a key point for a correct simulation of radial injection of iron suspensions (Tosco et al., 2014). It is known from the literature that attachment/detachment rates do depend on a number of parameters, and in particular on flow rate. Equations expressing the dependence of such coefficients on flow rate and rheological properties of the particles dispersions are to be implemented in a radial transport model. The relationships expressing the dependence of deposition and release kinetics on flow rate and fluid viscosity can be derived from the literature, or developed starting from the analysis of column transport tests. If the second approach is adopted, column tests performed at different flow rates can be inverse modelled using software implementing the one-dimensional transport solution (for example E-MNM1D), and the fitted parameters can be modelled using relationships like (Tosco et al., 2014):

$$k_a = \lambda (v_e \mu)^{\beta} \qquad (16)$$

$$k_d = \lambda' (v_e \mu)^{\beta'} \qquad (17)$$

where v_e is the pore velocity, λ and λ’, β and β’ are empirical coefficients, which depend in turn on a number of parameters (porosity, specific surface area, average grain size of porous medium and particles, etc.) and are empirically derived from the analysis of the interaction kinetics of one-dimensional tests.

The final output of a transport model for the simulation of iron particles injection should include the following results:

- Spatial distribution of iron $C_{TOT}(x,y,z)$
- Spatial distribution of permeability
- Spatial distribution of porosity

- Surface area of liquid/solid (to be used for calculations involving chemical reactions at the iron-water interface).

An example of the output of a radial transport model (E-MNM1R) is provided in Figure 48. E-MNM1R is also implemented in the user interface MNMs (www.polito.it/groundwater/software).

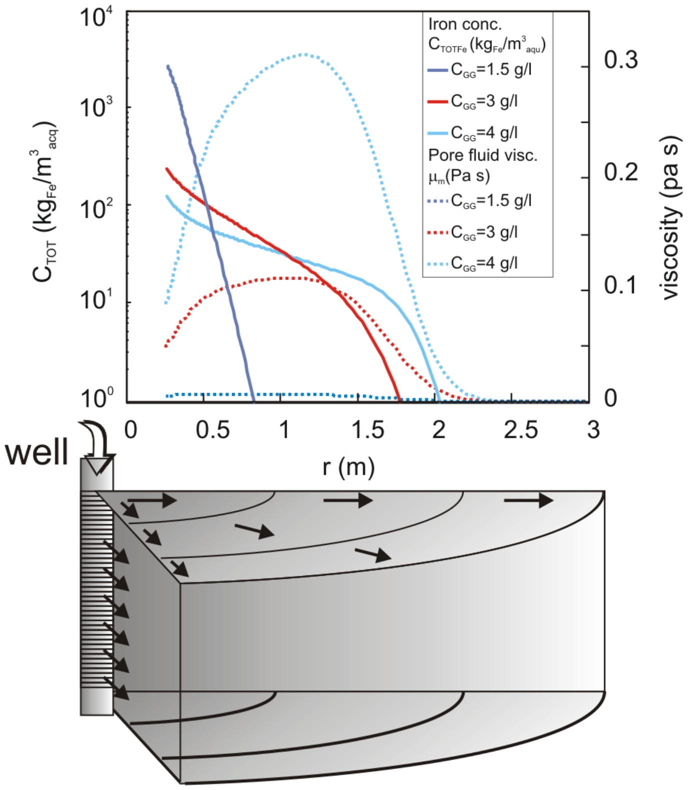


Figure 48 Simulation of radial injection of 5 m^3 of MZVI slurry (20 g/l of iron, 1.5, 3 and 4 g/l of guar gum) at a discharge rate of 1 m^3/h: final concentration of total iron (suspended + retained) per aquifer volume (left axis) and pore fluid viscosity (right axis) as a function of radial distance.

14 APPENDIX C: MODELLING ZVI REACTIVITY

The reactivity of iron particles towards the target contaminants must be carefully assessed, for example performing batch experiments. These experiments can be performed filling 160 ml glass bottles with 100 ml of contaminated groundwater and injectable iron at the expected field concentration. The analysis of the headspace gas can be used to determine the contaminant concentration in the water phase at different times. VITO has performed this type of experiment for several types of injectable iron. TUD has developed a customized geochemical module in PHREEQC to describe the main degradation reactions and the geochemical processes expected to occur in the subsurface after the injection. The geochemical model is here briefly reported.

The anaerobic iron corrosion of the iron particles was described as in Mayer et al. 2001:

$$R_{IrC} = -\max\left\{\left[k_{IrC} \cdot M_{Fe^0}\left(1 - \frac{IAP_{IrC}}{K_{IrC}}\right)\right], 0\right\} \qquad (18)$$

Where R_{IrC} is the actual corrosion rate (mol L^{-1} s^{-1}), k_{IrC} is the calculated corrosion rate (mol g_{Fe0}^{-1} s^{-1}) and M_{Fe0} is the amount of iron present in the bottle (g_{Fe0} L^{-1}). As the iron corrosion proceeds the mass of iron M_{Fe0} is updated. The initial value of the constant k_{IrC} was estimated from the amount of hydrogen produced in the bottle.

The specific reactive surface S_s was estimated by BET analysis (mol g_{Fe0}^{-1}). The actual amount of reactive surface S (mol L^{-1}) was computed by:

$$S = S_s M_{Fe^0} \qquad (19)$$

The contaminant degradation by iron particles is assumed to mainly occur by b-elimination with negligible formation of toxic intermediates reaction products (Arnold and Roberts 2000). The kinetic rate for VOC degradation was described by a mixed-order rate law.

$$\frac{d[VOC]}{dt} = -k_{VOC} \cdot S \frac{[VOC]}{K_{1/2} + [VOC]} \qquad (20)$$

wherek_{VOC} is the contaminant degradation rate (s^{-1}). The contaminants considered in the model were: PCE, TCE, cis-DCE, VC, 1,1,1-TCA and 1,1-DCA. To reproduce the observed pH values aragonite and iron hydroxy carbonate precipitation reactions were also included in the model.

In preliminary PHREEQC runs, aragonite and iron hydroxy carbonate saturation indices were strongly positive, suggesting that the precipitation of these minerals is very likely to occur.

The precipitation rates of aragonite and iron hydroxy carbonate were modelled using the following reaction rate model:

$$R_i^m = \max\left\{\left[k_{eff,i}\left(\frac{IAP_i^m}{K_i^m} - 1\right)\right], 0\right\} \qquad (21)$$

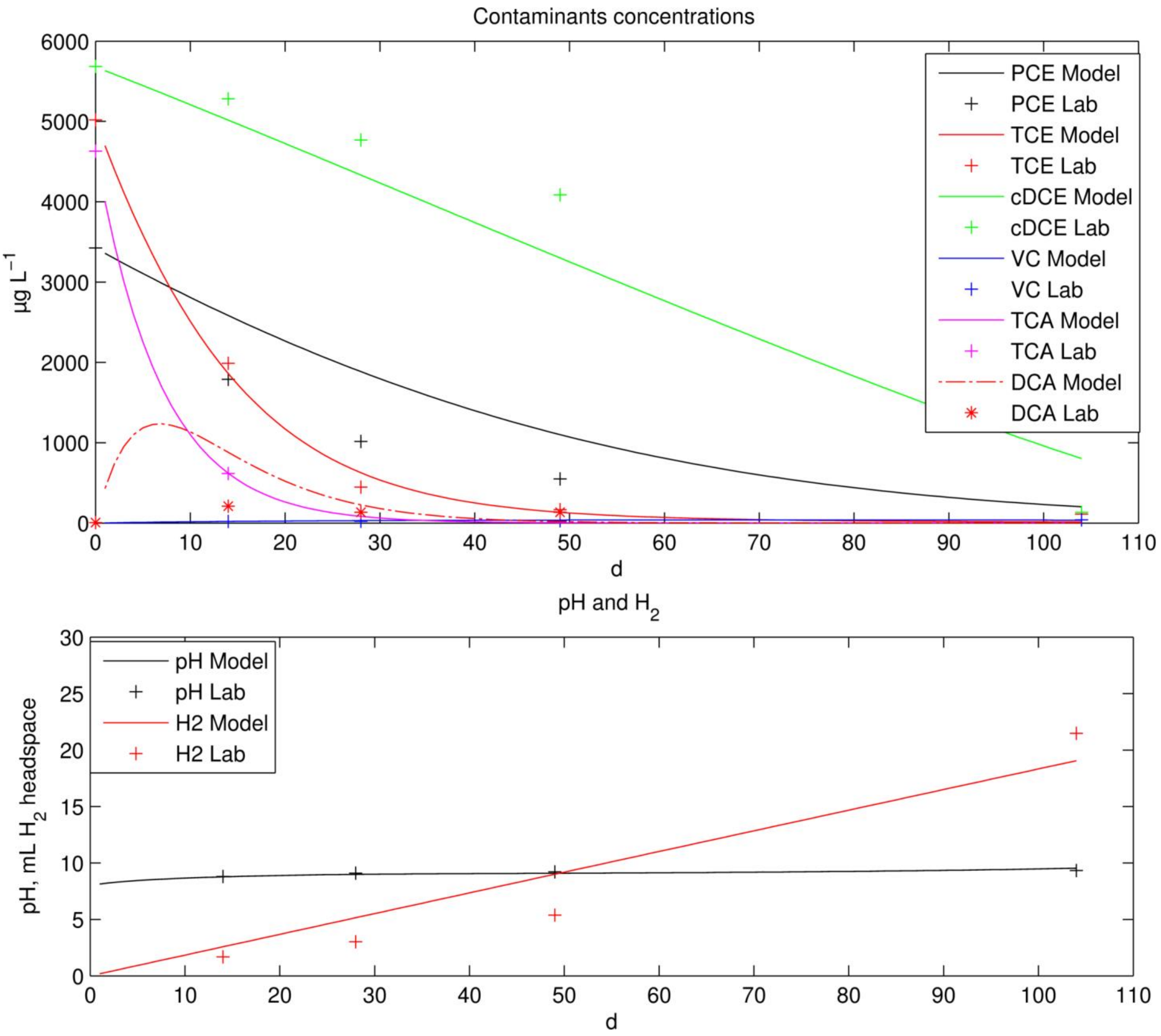


Figure 49 Comparison between observed (symbols) and simulated (solid lines) values in the injectable iron batch experiment. Top: contaminant concentrations. Bottom: pH and amount of hydrogen produced in the headspace.

The corrosion rate k_{IrC} and the mineral precipitation rates $k_{eff,I}$ were calibrated on the measured pH and on the observed amount of hydrogen produced in the bottle headspace. Subsequently, the k_{VOC}degradation rates were calibrated on the measured PCE, TCE, cis-DCE, VC, 1,1,1-TCA and 1,1-DCA concentrations. The fitting to the experimental data is shown in Figure 49. The observed PCE concentrations and the initial 1,1-DCA concentrations were overestimated while the cis-DCE concentrations were underestimated. This suggests that some adjustment of the molar conversion model can be made to improve the ability of the model to reproduce the measurements, also considering that the stoichiometric coefficients can be iron-specific.

A good agreement of the simulated results with the measured values was obtained for pH and hydrogen. These two species are mainly affected by the corrosion process, which determine the longevity of the iron particles (resistance to corrosion). However, under site condition the geochemical composition of the groundwater can play a determinant role on the particle life time. For example, high carbonate concentrations can promote iron corrosion by buffering the pH. Additional batch experiments confirmed this hypothesis, showing a remarkable difference between the estimated lifetimes using artificial and real groundwater.

After calibration on the batch experiment, the reactive model was coupled to a 1D transport model to simulate iron injection and subsequent transport process, where the iron (g_{Fe0} L^{-1}) is distributed along a short distance from the injection point. The iron concentrations in the soil matrix were simulated by the MNM1D model, which was used as input for the reactive transport model (equation 18 & 19). The 1D flow was simulated along a 1m long column using a specified flux on the left boundary and a specified head on the right boundary. Simulated groundwater velocity was 10 m year^{-1}. The initial contaminant and inorganic concentrations of the batch experiment were used as influent concentrations for the 1D transport experiment. The results are shown in Figure 50.

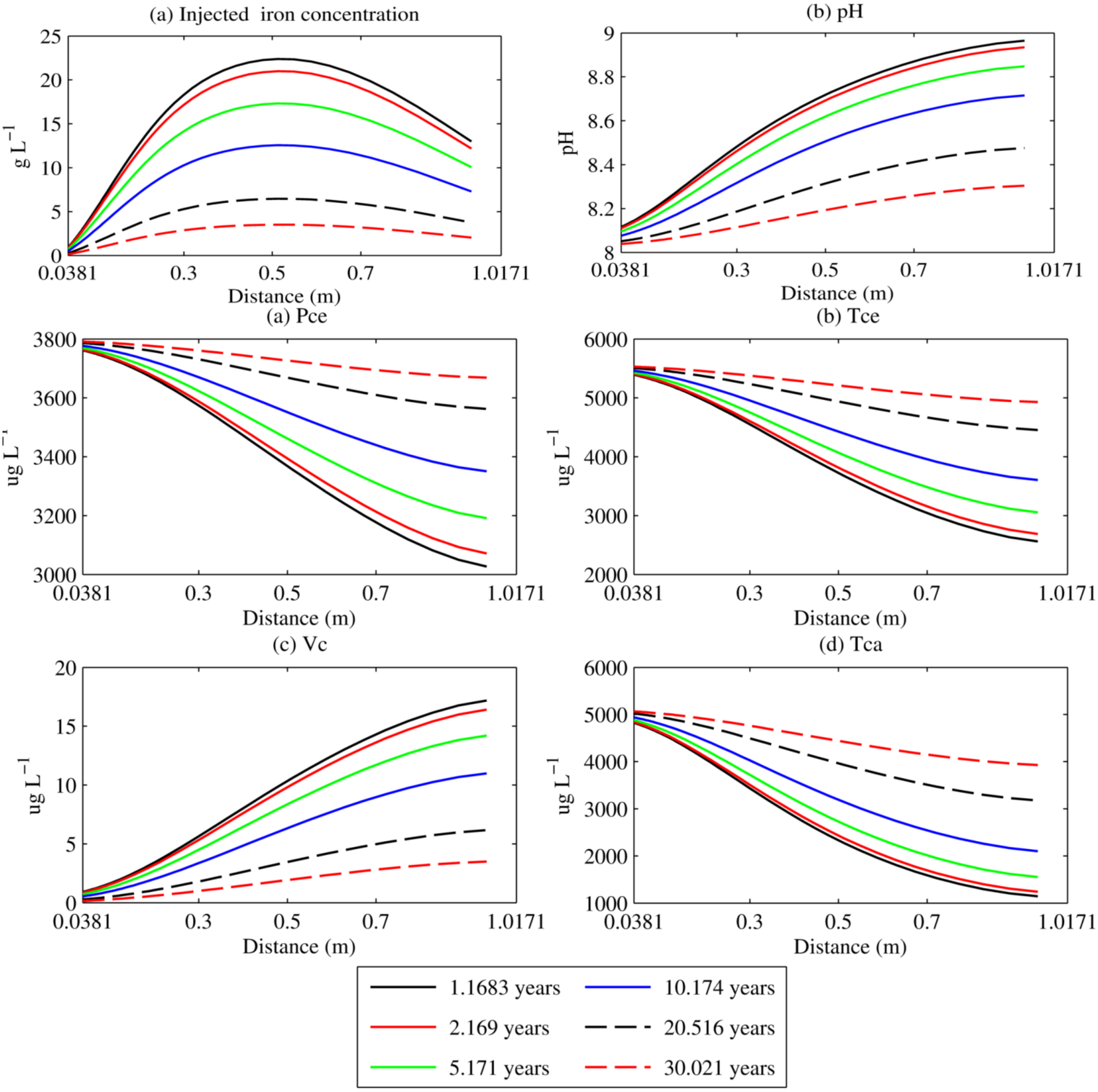


Figure 50 Simulated profiles along 1 m from the injection point. (a) injected iron concentration, (b) pH, (c) PCE, (d) TCE, (e) VC and (f) 1,1,1 TCA.

As expected the results show that the contaminant degradation rates are directly proportional to the zero valent iron concentration injected into the soil (Figure 50a). However, as the corrosion reaction proceeds, the injected iron is consumed and the contaminants are less efficiently removed (Figure 50c-f).

The reactive transport model described here was applied in a **hypothetical injection scenario** to quantify the mass of NAPL which can be removed with a single injection.
In this scenario, a pool of NAPL phase is present between 3 and 4 m below the groundwater table (Figure 51a). The horizontal dimension of the pool is 3 m by 4 m. The pool consist of 88 kg of PCE and 532 kg of 1,1,1-TCA (0.8 % of PCE and 5.9 % of 1,1,1-TCA in the void space). The groundwater velocity was 2.5 m y^{-1} from the left to the right part of the domain.
The NAPL release from the pool was described by the following equation:

$$\frac{dC}{dt} = \max\left[k_{LA}(C^* - C), 0\right] \tag{22}$$

where$C$ is the dissolved contaminant concentration (mol L^{-1}), k_{LA} is a mass transfer coefficient (s^{-1}) and C^* is the solubility of the contaminant in the groundwater.

During the first 10 years of simulation the contaminant is only dissolving from the pool and no degradation reaction is occurring. This produces a long 1,1,1-TCA plume extending downstream of the source (Figure 51b). After 10 years, 30.4 kg iron is injected into the NAPL pool. Resulting iron concentrations are assumed to be distributed as shown in Figure 15c. In Figure 15d, the 1,1,1-TCA concentrations after iron injection are shown. As can be seen, the dissolved concentrations close to the injection area are strongly reduced compared to Figure 13b.

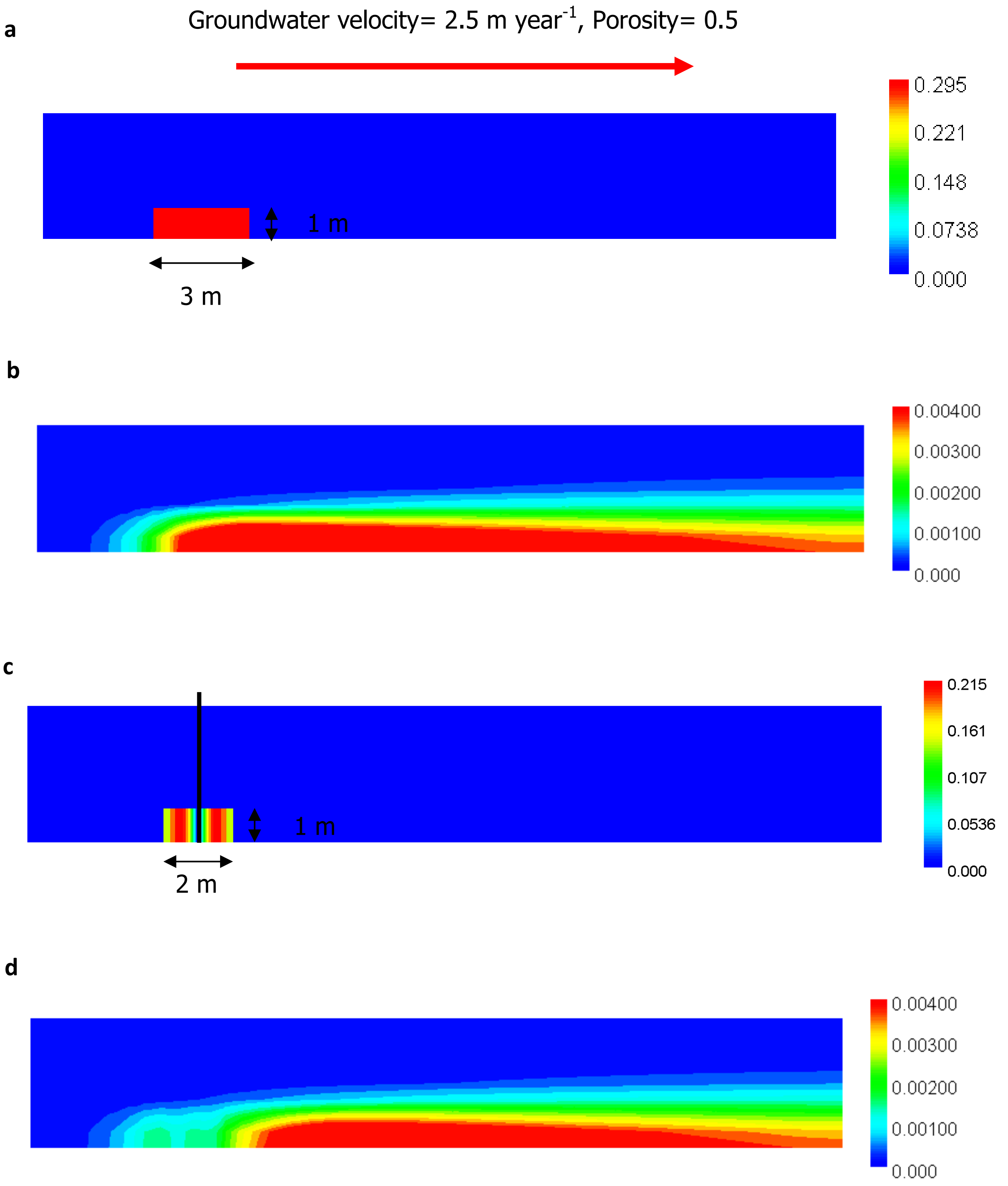


Figure 51 Hypothetical injection scenario. (a) initial 1,1,1-TCA NAPL concentration (mol L_{bulk}^{-1}), (b) dissolved 1,1,1-TCA after ten years (mol L^{-1}), (c) hypothetical iron distribution around the injection point (mol L_{bulk}^{-1}) and (d) dissolved 1,1,1-TCA three months after the injection (mol L^{-1}).

In Figure 52a, total 1,1,1-TCA NAPL mass in the injection volume (1 meter radius by 1 meter depth) is shown as a function of time. In the first 10 years, the 1,1,1-TCA NAPL phase is removed only by dissolution. After the injection (year 10) the contaminant is removed by dissolution and degradation. This effect can be seen from the changed slope of the function. From the figure it can be concluded that a single injection is not sufficient to degrade the NAPL pool in a reasonable time frame. In this scenario, the iron to contaminant mass ratio was 0.375, much lower than the suggested minimum ratio of 1kg of iron for 1 kg of contaminant (see 2.2.6). In field applications, more injections may be required to increase the iron content in the source area and promote contaminant degradation.

In Figure 52b, total mass of iron as function of time is also shown (the injected iron is consumed by anaerobic iron corrosion).

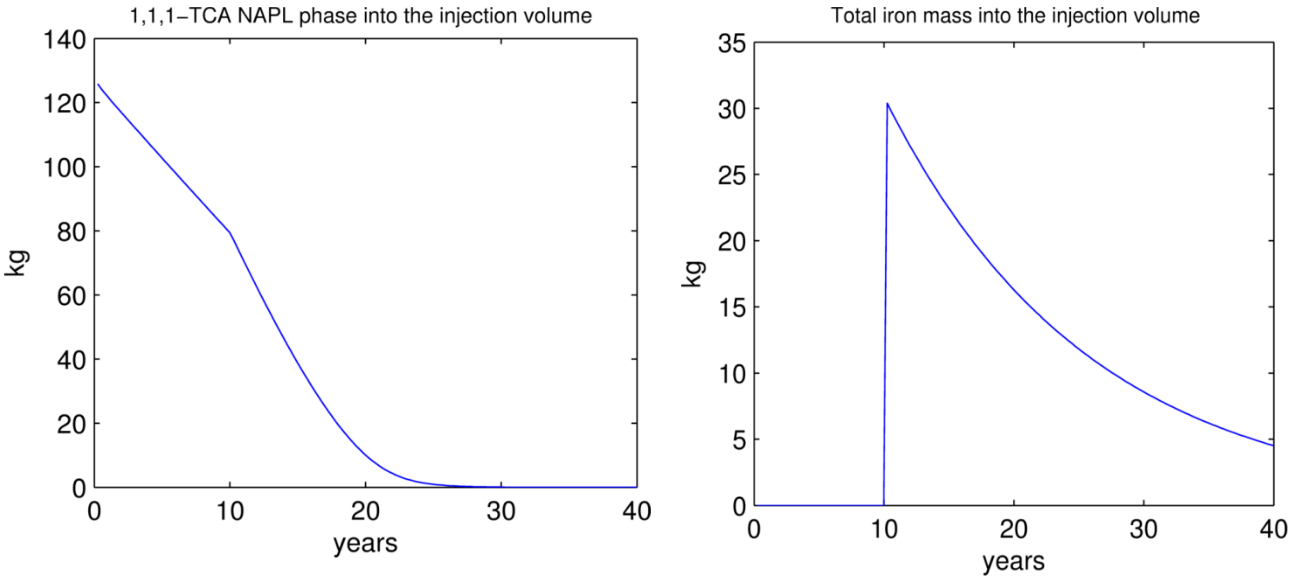


Figure 52 (a) Total 1,1,1-TCA NAPL mass into the injection volume (ca 3 m^3) and (b) total mass of iron injected as function of time.

15 APPENDIX D: DETAILED DESIGN DATA FOR PILOT TESTS PERFORMED WITHIN AQUAREHAB

15.1 Design of an iZVI Zone Using Darcian Flow (Permeation)

15.1.1 Geometry

Geometry of wells must suffice the following requirements (Luna et al., submitted):

- The well must be drilled via continuous core drilling with water as drilling fluid. The borehole must larger in the upper part, in order to improve sealing. At the bottom, below the screen, there must be a blind tubing 0.5m long.
- In order to improve well productivity, the gravel pack grain size distribution can range from 2 and 3 mm and the slot size 0.5 mm.
- It is very important to perform purging after well installation. Purging must be performed after well installation, pumping water for at least one hour or, in any case, until clear water is pumped.
- Moreover a grain size distribution analysis must be performed in the material extracted during drilling operation as well as the analysis for background iron concentration.
- Moreover a flange must be designed in order to seal the well during injection. The flange must have an air valve to allow the air to come out of the well and assure complete saturation with fluid.

In summary requirements for the injection well are:

- Continuous core drilling shown in the following example Figure 53 and Table 11;
- Purging (at least one hour or clear water);
- Grain Size Distribution Analysis;
- Chemical Analysis for back ground iron concentration;
- A flange must be designed with air valve.

The following is an example scenario to meet the requirements for the injection well are reported in Table 11 and Figure 53.

For this scenario the injection has to be performed in a 4” well, drilled at least three weeks before injection and far from other wells. The construction of an injection well is not significantly different from the installation of a monitoring well, however it is pivotal the sealing in order to prevent daylighting during injection.

Table 11 Injection well specifications.

Injection well	
Diameter (cm)	10.16 (4”)
Material	PVC
Total Length (m)	6 or 7
Length of the screen Ls (m)	3 or 4
L (m-bgl)	3
Drain diameter D_d (mm)	178
Sealing diameter $D_{sealing}$ (mm)	220
Gravel Pack Grain Size (mm)	2-3
Slot size of the tubing (mm)	0.5

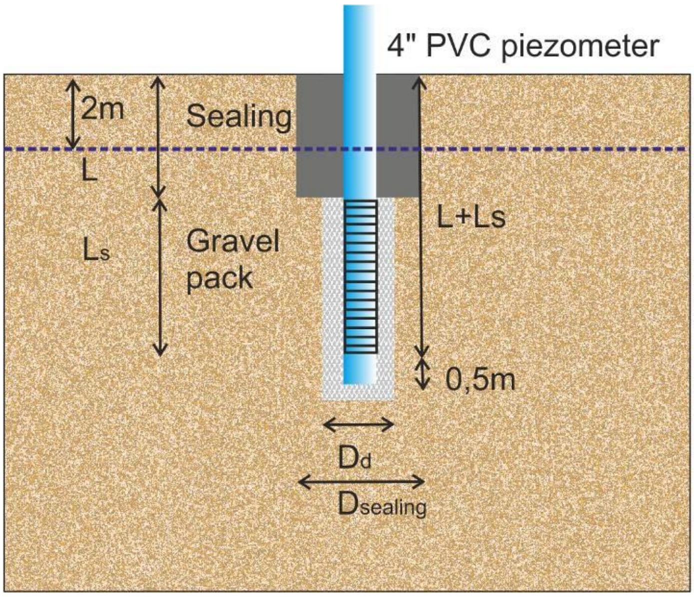


Figure 53 Injection well

15.1.2 Injection Test

The injection test is pivotal in order to determine both the well properties and the ideal injection flow rate. The test consists in injecting water into the well at different discharges continuously measuring the piezometric level into the well until it is stable (at least 1 h each step).In Figure 54 is shown how an injection test works.

A Woltmann meter is necessary to measure water flow rate in order to have a precise discharge value, as well as a transducer to measure continuously the water level.

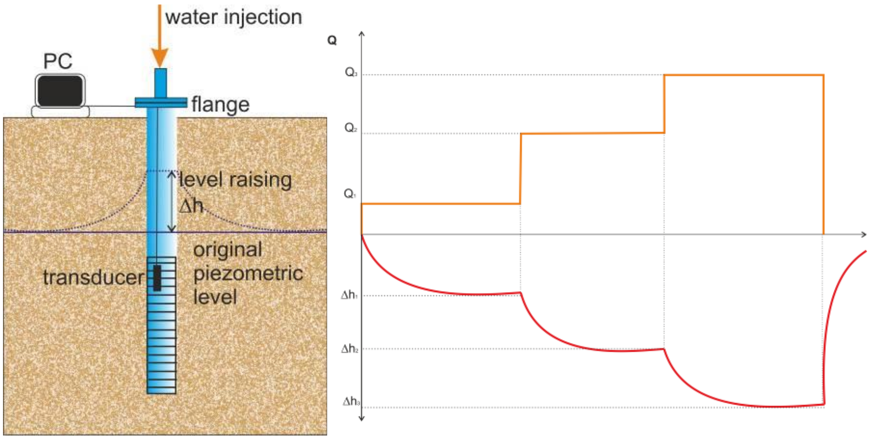


Figure 54 Injection test.

In summary in order to perform the test the following devices are needed:

- Pump (external centrifuge pump and able to provide a discharge of 1e-3 with pump head equal to 10 m);
- Woltmann meter to measure discharge;
- Transducer for water level measurement (such as Levelogger- Solinst)

15.1.3 Design of the slurry injection

The pilot test design has been performed taking into account both the use of nanoscale (NANOFER) and micrometric (BASF HQ) iron particles, using E-MNM model in radial geometry.

For both particles different scenarios has been implemented starting from the data provided by reactivity test: the iron concentration for kg of aquifer necessary for contaminants degradation, which are respectively 5 $g/kg_{aquifer}$ for BASF HQ and 2,5 $g/kg_{aquifer}$ for NANOFER.

Thanks to E-MNM it is possible to determine which is the radial distance from injection point where the concentration is higher than a certain concentration. The Radius of Influence, as well as the flow rate and the maximum pressure reached have been determined running the model. In this document we distinguish between ROI_{iron} and $ROI_{guar\ gum}$ (Figure 55).

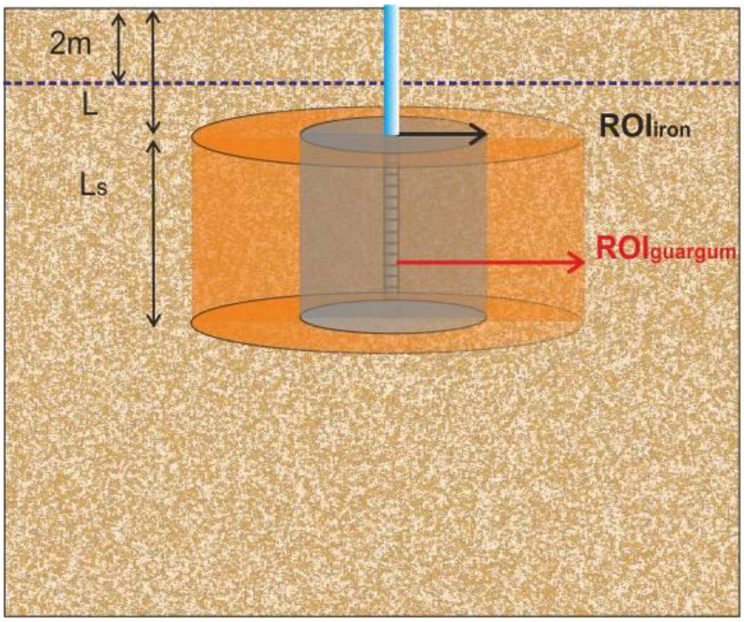


Figure 55 Radius of influence of iron and guar gum

The influence radius of iron is defined as the radial distance where the iron concentration is one half of the target concentration:

$$ROI_{iron} = R(C = 0.5 * \text{Target concentration}) \quad (23)$$

On the other hand the influence radius of guar gum can be defined as the radial distance of the advective front of guar gum at the end of injection:

$$ROI_{\text{guargum}} = R(C_{gg} = 0.5 * Cgg \text{ initial concentration}) \quad (24)$$

Simulation were performed for different volumes (5 m^3, 10 m^3 and 15 m^3), three different hypothesised reasonable injection time (2 h, 3 h and 4 h) and three different screen length (3 m, 4 m, and 5 m). Results are shown in the following paragraphs. It must be taken into account that the simulated results are based on coefficients that are not site specific, but are obtained by column test in a coarser medium (See Deliverable 5.2). Moreover since for nanoiron and guar gum column test are missing, coefficient has been hypothesised and so are more affected by errors than results obtained for micro-iron.

Iron concentration in the slurry is assumed constant equal to 10 g/l and the guar gum concentration is equal to 2 g/l.

BASF HQ (PSD=0.7-1.2-1.8 μm)

In Table 12, Table 13 and Table 14 are reported modelling results for BASF HQ. In order to perform successful permeation injection the pressure must be lower than 5 atm and ROIiron higher than 0.5 m. According with the table below the more realistic hypothesis is to inject 10 m^3 in 2 hours (length of the screen 3 or 4 m) or in 3 hours (Ls=3), since the injection of 15 m^3 will be probably more difficult.

Table 12 Injection of 5 m^3

Injection Volume=5 m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.4\cdot10^{-4}$
	P_{max} (atm)	1.7	1.3	1
	ROI_{iron} (m)	0.55	0.48	0.43
	$ROI_{guargum}$ (m)	1.4	1.2	0.7
t_{inj} =3 h	Q (m^3/s)	$1.5\cdot10^{-4}$	$1.2\cdot10^{-4}$	$9.2\cdot10^{-5}$
	P_{max} (atm)	1.3	0.9	0.7
	ROI_{iron} (m)	0.48	0.42	0.37
	$ROI_{guargum}$ (m)	0.7	1.2	1.1
t_{inj} =4 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$8.7\cdot10^{-5}$	$6.9\cdot10^{-5}$
	Pmax (atm)	2.2	0.8	0.6
	ROI_{iron} (m)	0.63	0.38	0.34
	$ROI_{guargum}$ (m)	2	1.2	1

Table 13 Injection of 10 m^3

Injection Volume=10m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$4.6\cdot10^{-4}$	$3.4\cdot10^{-4}$	$2.7\cdot10^{-4}$
	P_{max} (atm)	3.6	2.6	2
	ROI_{iron} (m)	0.8	0.69	0.61
	$ROI_{guargum}$ (m)	1.9	1.7	1.5
t_{inj} =3 h	Q (m^3/s)	$3.1\cdot10^{-4}$	$2.3\cdot10^{-4}$	$1.9\cdot10^{-4}$
	P_{max} (atm)	2.7	2	1.6
	ROI_{iron} (m)	0.69	0.6	0.53
	$ROI_{guargum}$ (m)	1.9	1.7	1.5
t_{inj} =4 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.4\cdot10^{-4}$
	P_{max} (atm)	2.2	1.6	1.3
	ROI_{iron} (m)	0.62	0.5	0.5
	$ROI_{guargum}$ (m)	2	1.7	1.5

Table 14 Injection of 15 m^3

Injection Volume=15m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$6.9\cdot10^{-4}$	$5.2\cdot10^{-4}$	$4.2\cdot10^{-4}$
	P_{max} (atm)	5.3	4	3.2
	ROI_{iron} (m)	0.99	0.85	0.76
	$ROI_{guargum}$ (m)	2.4	2.1	1.9
t_{inj} =3 h	Q (m^3/s)	$4.6\cdot10^{-4}$	$3.5\cdot10^{-4}$	$2.8\cdot10^{-4}$
	P_{max} (atm)	4.1	3	2.4
	ROI_{iron} (m)	0.86	0.74	0.65
	$ROI_{guargum}$ (m)	2.4	2.1	1.9
t_{inj} =4 h	Q (m^3/s)	$3.5\cdot10^{-4}$	$2.6\cdot10^{-4}$	$2.1\cdot10^{-4}$
	P_{max} (atm)	3.4	2.5	2
	ROI_{iron} (m)	0.78	0.67	0.6
	$ROI_{guargum}$ (m)	2.4	2.1	1.9

NANOFER (d_{50} about 60 nm)

In the case of NANOFER, Table 15, Table 16 and Table 17 show a smaller influence radius and an higher porous medium clogging. In this case the only feasible option is to inject 10 m^3 of slurry in 2 hours and a screen length of 3 m.

Table 15 Injection of 5 m^3

Injection Volume=5m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.4\cdot10^{-4}$
	P_{max} (atm)	2	1.5	1.2
	ROI_{iron} (m)	0.5	0.42	0.4
	$ROI_{guargum}$ (m)	1.4	1.2	1.1
t_{inj} =3 h	Q (m^3/s)	$1.5\cdot10^{-4}$	$1.2\cdot10^{-4}$	$9.3\cdot10^{-5}$
	P_{max} (atm)	1.6	1.2	0.9
	ROI_{iron} (m)	0.42	0.36	0.3
	$ROI_{guargum}$ (m)	1.4	1.2	1.1
t_{inj} =4 h	Q (m^3/s)	$1.2\cdot10^{-4}$	$8.7\cdot10^{-4}$	$6.9\cdot10^{-5}$
	P_{max} (atm)	1.4	1	0.8
	ROI_{iron} (m)	0.38	0.3	0.3
	$ROI_{guargum}$ (m)	1.4	1.2	1.1

Table 16 Injection of 10m^3

Injection Volume=10m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$4.6\cdot10^{-4}$	$3.5\cdot10^{-4}$	$2.8\cdot10^{-4}$
	P_{max} (atm)	4.1	3.1	2.4
	ROI_{iron} (m)	0.7	0.62	0.55
	$ROI_{guargum}$ (m)	1.9	1.7	1.5
t_{inj} =3 h	Q (m^3/s)	$3.1\cdot10^{-4}$	$2.3\cdot10^{-4}$	$1.9\cdot10^{-4}$
	P_{max} (atm)	3.3	2.4	1.9
	ROI_{iron} (m)	0.62	0.53	0.47
	$ROI_{guargum}$ (m)	1.9	1.71	1.5
t_{inj} =4 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.4\cdot10^{-4}$
	P_{max} (atm)	2.8	2.1	1.7
	ROI_{iron} (m)	0.56	0.47	0.42
	$ROI_{guargum}$ (m)	1.97	1.7	1.5

Table 17 Injection of 15m^3

Injection Volume=15m^3				
		Ls=3 m	**Ls=4 m**	**Ls=5 m**
t_{inj} =2 h	Q (m^3/s)	$4.6\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.4\cdot10^{-4}$
	P_{max} (atm)	4.8	1.5	1.2
	ROI_{iron} (m)	0.8	0.42	0.37
	$ROI_{guargum}$ (m)	2.4	1.2	1.1
t_{inj} =3 h	Q (m^3/s)	$2.3\cdot10^{-4}$	$3.5\cdot10^{-4}$	$2.8\cdot10^{-4}$
	P_{max} (atm)	2	3.6	2.9
	ROI_{iron} (m)	0.49	0.67	0.6
	$ROI_{guargum}$ (m)	1.4	2.1	1.9
t_{inj} =4 h	Q (m^3/s)	$3.5\cdot10^{-4}$	$2.6\cdot10^{-4}$	$2.1\cdot10^{-4}$
	P_{max} (atm)	4.2	3.2	2.5
	ROI_{iron} (m)	0.71	0.6	0.53
	$ROI_{guargum}$ (m)	2.4	2.1	1.9

15.1.4 Slurry injection design: Volume, Discharge and Iron Mass needed

On the basis of modelling results the most feasible scenarios is the injection of 10 m^3 of iron slurry, The total iron mass needed is 100 kg. Since, as already mentioned model do not precisely reproduce the field conditions, we expected a ROIiron lower than the calculated one. However, reasonably a radius of influence ranging from the one resulting from 5 m^3injection and the one from 10 m^3 injection is expected. In this case ROIiron will range from 0.55 m and 0.8 m for HQ and from 0.7 and 0.5 for NANOFER. In the table below (Table 18) are summarised results and cost are estimated. Since the cost is significantly higher in the case of NANOFER, the best option is probably BasfHQ.

Table 18 Comparison between BASF HQ and NANOFER injection

	HQ	**NANOFER**
Slurry Volume (m^3)	10	10
Iron Concentration (g/l)	10	10
Iron Mass (kg)	100	100
Guar Gum concentration (g/l)	2	2
Guar Gum Mass (kg)	20	20
Q	$4.6 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$
L_s (m)	3	3
ROI_{iron} (m)	0.55-0.8	0.5-0.7
Iron unit cost (€/kg)	34.70	120
Total Cost (€)	3470	12000

15.1.5 Field activities

Concerning field activities, guar gum slurry must be prepared the day before the injection, since the maximum viscosity is developed after about 20 hours, and stored in a clean vessel (if it has been already used it is necessary disinfect the vessel, the recirculation and the pumping system with hot water and if possible hypochlorite).

The injection must be performed injecting the whole volume without interruptions in pumping at constant discharge. In Figure 56the field injection set-up is shown.

While there are no requirements for pump P2, since it is needed only to recirculate the slurry avoiding sedimentation, the pump for injection P1 must be an external centrifuge pump able to provide a flow rate of 1·10-3 m^3/s, with a pressure head of 10 m.

In order to perform the injection are needed:

- Access to Tap Water;
- Electric Supply;
- Two pumping systems (P1 and P2);
- Dispersing unit (something like Ultra-Turrax for huge volumes);
- m^3 Vessel.

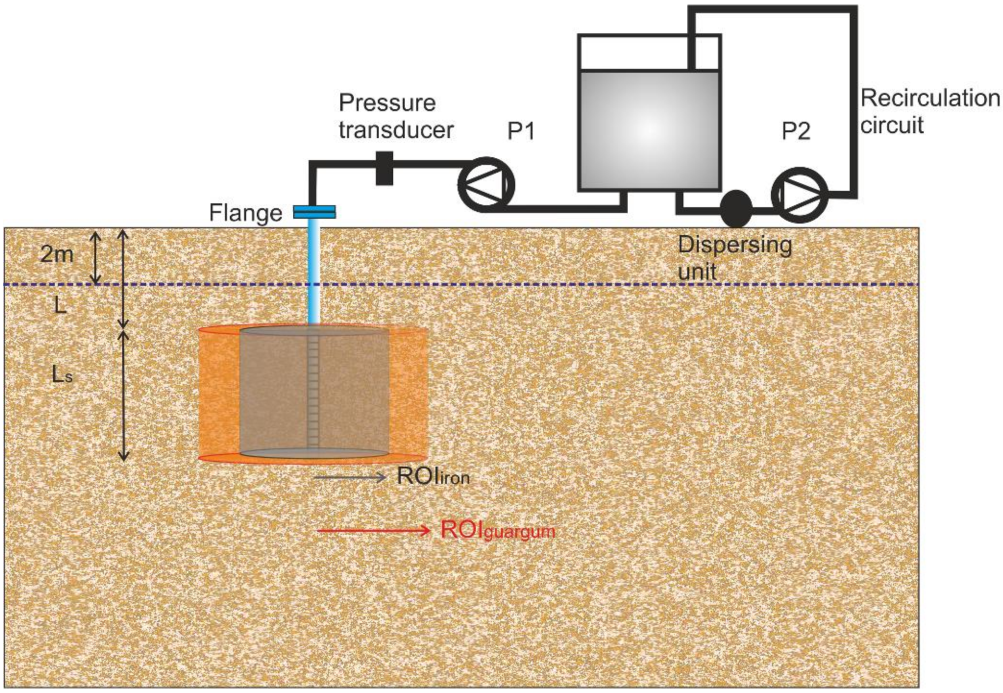


Figure 56 Pilot test set-up

15.2 Design of an iZVI zone Using Preferential Flow from Direct Push Point

Aiming to select the best injection technology, it is first necessary to identify whether permeation or fracturing injection is more appropriate. Two main topics are to be considered:

- the size of iron particles compared to the grain size distribution of the aquifer (8 & 9) in order to verify whether permeation is possible;
- the volume of iron slurry to be injected in the case of permeation and of fracturing, and consequently the discharge and injection pressure required for the field-scale delivery.

Table 19reports the particle size distribution of the iron samples taken into consideration in the AQUAREHAB project and their comparison with grain size distribution of the aquifer. From size data it is evident that most of micro-sized particles are too big to be transported through the sandy aquifer of Layer 3.

An estimation of the injection pressure required for the delivery of iron slurries in can be obtained from the non-linear Darcy equation (Darcy-Forchheimer equation). Pressure build-up during permeation process is the sum of two phenomena: laminar flow and a turbulent flow in proximity of the well. To avoid fracturing, the injection pressure *p* must be lower than the critical value p_{cr}:

$$p \approx \left(\frac{\mu}{K} Q + \beta \rho Q^2 \right) \cdot ROI < p_{cr} \qquad (25)$$

Table 19 Comparison of iron particle size distribution and aquifer grain size distribution (Layer 3).

(Green boxes indicate a ratio $d_{50,part}/d_{50,soil}$ or $d_{90,part}/d_{10,soil}$<0.5%, yellow boxes correspond to ratios ranging between 0.5% and 2%, red boxes correspond to ratios exceeding the limits for permeation injection (>1-2%))

Iron	Size			Straining	
	d10	d50	d90	$d_{50,part}/d_{50,soil}$	$d_{90,part}/d_{10,soil}$
	[µm]	[µm]	[µm]	[-]	[-]
H1	8	26	50	0.12	0.53
H2	29	82	172	0.39	1.83
H3	36	84	168	0.40	1.78
H4	22	41	62	0.19	0.66
H5	50	112	178	0.53	1.89
H6	41	98	162	0.47	1.72
H7	44	96	158	0.46	1.68
H8	34	63	97	0.30	1.03
H9	3	7	16	0.03	0.17
H10	9	22	42	0.10	0.45
H11	6	19	38	0.09	0.40
H12	6	17	32	0.08	0.34
H13	7	18	34	0.09	0.36
H14	21	79	162	0.38	1.72
H16	1	5	12	0.02	0.13
H19	3	6	9	0.03	0.10
Basf-MS200	-	4.7	-	0.02	-
Basf-MS200 +	-	4.8	-	0.02	-
Basf-HQ	0.7	1.2	1.8	0.01	0.02
Nanofer 25-S	0.03	0.1	0.3	0.0005	0.0032

Where µ is the viscosity of the injected fluid (Pa s), *K* is the hydraulic conductivity (m/s), *Q* is the injection flow rate (m^3/s) $\beta$is the turbulence factor (m^{-1}) ρ is the fluid density (kg/m^3) and *ROI* is the radius of influence (m).

The turbulence factor β can be determined from well tests. If β is unknown it is impossible to make any consideration about the injection flow rate needed.

The volume of slurry to be injected via permeation, $V_{inj,perm}$, depends both on injection radius and injection thickness, and can be calculated with the following formula:

$$V_{inj,perm} = \pi \cdot b_i \cdot ROI^2 \cdot n \tag{26}$$

whereb_i is the injection thickness (m), and *n* is the porosity of the aquifer (-).

If iron microparticles are used, it is necessary to recall that such particles, when dispersed in water, undergo very fast sedimentation. Consequently, when injected, they are to be dispersed in viscous fluids (guar gum solutions are used in AQUAREHAB project), which retard sedimentation for a limited time. The t_{50}, i.e. the time in which half the particles sediment, depends on the particle size, and can be used as an indicator of the stability of the iron slurry. For an efficient placement of particles it is evident that that the time of injection, $t_{inj,perm}$, must be lower than the t_{50}:

$$t_{inj,perm} = \frac{V_{inj,perm}}{Q} < t_{50} \tag{27}$$

Following this approach, it is possible to calculate the flow rate *Q* needed to sufficiently reduce sedimentation of the iron particles during the injection:

$$Q = \frac{V_{inj,perm}}{t_{50}} \tag{28}$$

If the corresponding pressure (calculated from equation (23)) exceeds the critical pressure of the soil, then injection via permeation is not possible and fracturing is to be considered. As a consequence, the mechanical properties of the aquifer systemdo not limit injection pressure and flow rates, which then depend only on the properties of the injection devices.

In case of fracturing, the volume of slurry required to fill each fracture can be estimated as:

$$V_{inj,frac1} = \pi \cdot b_f \cdot ROI^2 \tag{29}$$

whereb_f is the estimated thickness of the fracture (m) and the assumption is made that fractures form like discs in the treatment zone.In this case the total volume to fill all fractures shown below in equation

$$V_{f,TOT} = V_{f,\sin gle} \cdot N \tag{30}$$

where$N$ is the number of fractures.

Below, shown in Table 20, typical volumes for a general site are given

Table 20 Estimation of injection volume needed for a single fracture ($V_{f,\,single}$) and for all fractures ($V_{f,\,TOT}$), for different ROIs, and for a number of fracture N = 5 with fracture opening b_f=0.01 m.

ROI (m)	**Injection volume**	
	$V_{f,\,single}$ (m^3)	**$V_{f,\,TOT}$** (m^3)
1	0.03	0.16
1.5	0.07	0.35
2	0.13	0.63
2.5	0.20	0.98
3	0.28	1.41

Again there are limitations in the time it takes for the particles to reach t_{50}, this must be realized in the calculation of the time needed to generate a fracture. The time needed to generate a fracture must be lower than the sedimentation time of the iron particles (which depends in turn on particles size and concentration and on guar gum concentration). It can be calculated for two different injection devices, namely Geoprobe GS500 and GP300, and ranges between 0.35 and 1.4 hours, depending on the flow rate (Table 21):

$$T_f = \frac{V_{f,\sin gle}}{Q} < t_{50}$$

Table 21 Time needed for fracture generation, basing on the discharge rate (minimum, average and maximum) provided by different injection devices.

Pump	**Q (m^3/s)**	**T_f**(hours)
GP300/GS500 (min)	$5.67 \cdot 10^{-5}$	1.39
GP300 (average)	$1.08 \cdot 10^{-4}$	0.72
GS500 (max)	$1.45 \cdot 10^{-4}$	0.54
GP300 (max)	$2.22 \cdot 10^{-4}$	0.35

The required iron concentration and iron mass can be determined following different approaches. Studies performed in VITO highlighted that the required mass of iron to be injected, which would guarantee a satisfactory degradation of the contaminants within the radius of influence. Consequently the iron concentration in the slurry can be determined as

$$C_{iron} = \frac{Mass_{iron}}{V_{f,TOT}} \tag{31}$$

The volume of slurry to be injected along an aquifer thickness b_i is much lower than in the case of permeation, and is calculated multiplying the volume injected for each fracture by the expected number of fractures:

$$V_{inj,frac} = \pi \cdot b_f \cdot ROI^2 \cdot \frac{b_i}{f} \tag{32}$$

where f is the distance between two nearby fractures.

Since the flow rate is given by the injection apparatus, once injection volumes have been calculated, the injection time can be easily determined and compared with the sedimentation time of the iron slurries:

$$t_{inj,frac1} = \frac{V_{inj,frac1}}{Q} < t_{50} \tag{33}$$

The t_{50} values can be obtained from laboratory sedimentation tests performed over iron slurries prepared using different iron samples. The corresponding discharges to be used in the field are calculated using equations (28) and (29), are reported in Table 22.

Table 22 Injection volumes and flow rate required for permeation injection.

ROI (m)=		1,5			2			1,5			2		
porosity=		0,3			0,3			**0,19**			**0,19**		
bi(m)=		2	5	10	2	5	10	2	5	10	2	5	10
Total Injected volumes (m^3)=		**4,24**	**10,60**	**21,21**	**7,54**	**18,85**	**37,70**	**2,69**	**6,72**	**13,43**	**4,78**	**11,94**	**23,88**
Iron	t_{inj} (h)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)	**Q** (l/min)
MS200	4,57	15,5	38,7	77,3	27,5	68,7	137,5	9,6	24,1	48,1	17,1	42,8	85,6
HQ	5,92	11,9	29,9	59,7	21,2	53,1	106,1	14,3	35,9	71,7	25,5	63,8	127,5
MS200+	1,78	39,7	99,3	198,6	70,6	176,5	353,0	24,2	60,5	121,0	43,0	107,6	215,1
H4	0,67	105,5	263,8	527,5	187,6	468,9	937,8	66,8	167,0	334,1	118,8	297,0	593,9
H16	24	2,9	7,4	14,7	5,2	13,1	26,2	1,9	4,7	9,3	3,3	8,3	16,6
H19	1,75	40,4	101,0	202,0	71,8	179,5	359,0	25,6	64,0	127,9	45,5	113,7	227,4

The results indicate that the flow rates needed to avoid particle sedimentation during injection are very high, since the injection volumes are huge. Injecting these flow rates the pressure required will be far above permeation pressure and will fracture the porous medium. A suitable injection technology would then be direct push injection. As an example, a Geoprobe injection machine (GS1000) can inject fluids with a flow rate ranging from 3.4 to 8.7 l/m, and very high pressures (about 70 bar). The volume to be injected for each injection point can be estimated using equation (24)

Assuming a fracture thickness of 1 cm and a distance between to nearby fractures equal to 0.5 m and a discharge rate Q is given by the injection apparatus, then, once volumes have been calculated, the injection time for each point can be easily determined and compared with the sedimentation time of the iron slurries using equation (28).

In some cases the sedimentation time has a trivial influence on the injection time, since it is for all considered values of influence radii and discharge rates, much lower than t_{50}.

Table 23 Required injection volume as a function of injection thickness and influence radii in the case of fracturing injection performed with Geoprobe GS1000

$Q_{Geoprobe}$(l/min)=		3,4						8,7					
$Q_{Geoprobe}$(m^3/s)=		**5,70E-05**						**1,45E-04**					
ROI (m)=		1,5			2			1,5			2		
$b_{fracture}$(m)=		0,01			0,01			0,01			0,01		
porosity=		1			1			1			1		
b(m)=		2	5	10	2,5	5	10	2	5	10	2	5	10
N°injection points over depth=		4	10	20	5	10	20	4	10	20	4	10	20
Injected volumes each fract (m^3)=		0,07			0,13			0,07			0,13		
Total Injected volumes (m^3)=		**0,28**	**0,71**	**1,41**	**0,63**	**1,26**	**2,51**	**0,28**	**0,71**	**1,41**	**0,50**	**1,26**	**2,51**
Total Injection time (h)=		**1,4**	**3,4**	**6,9**	**3,1**	**6,1**	**12,2**	**0,5**	**1,4**	**2,7**	**1,0**	**2,4**	**4,8**
Injection time single fracture (h)=		**0,34**			**0,61**			**0,135**			**0,24**		
Iron	**t_{50}** (h) (iron 20 g/l+GG3g/l)	**t_{50}<$t_{inj\ single\ fracture}$?**						**t_{50}<$t_{inj\ single\ fracture}$?**					
MS200	4,57	🟩			🟩			🟩			🟩		
HQ	5,92	🟩			🟩			🟩			🟩		
MS200+	1,78	🟩			🟩			🟩			🟩		
H4	0,67	🟩			🟨			🟩			🟩		
H16	24	🟩			🟩			🟩			🟩		
H19	1,75	🟩			🟩			🟩			🟩		

The following is an explanation of a specific site, Aarschot site is a CAHs polluted site in Belgium, where ZVI is to be injected in the framework of the AQUAREHAB project. The hydrogeological structure of the site includes:

- Layer 1 (0 to 3 m b.g.l.): shallow sandy aquifer, water table at approximately 2 m-bgl (unless seasonal variation);
- Layer 2 (3 to 8 m b.g.l.): fine clayey-sandy aquitard;
- Layer 3 (8 to 20 m b.g.l.): deep sandy aquifer (grain size distribution: d_{50} = 211 µm, d_{10} = 94 µm). This layer is the target of the injection test of iron particles.

The results of field tests (aquifer pumping tests and slug tests), performed in order to assess the hydraulic conductivity of the two lower layers, are shown in Table 24.

Table 24 Hydraulic conductivity

LAYER	***HYDRAULIC CONDUCTIVITY (m/s)***
1	n.d.
2	$1.5 \cdot 10^{-6}$
3	$4.4 \cdot 10^{-5}$

Studies performed in VITO highlighted that the required mass of iron to be injected, which would guarantee a satisfactory degradation of the contaminants within the radius of influence, is in the range 80-100 kg for a radius of influence equal to 3 m. Consequently the iron concentration in the slurry can be determined using equation (27) and is equal to approximately 57 g/l.
The injection volume was calculated, and the flow rate derived, considering different scenarios:

- two radii of influence (1.5 m and 2 m);
- three different heights for the zone to be treated (2 m, 5 m and 10 m);
- two porosity values (0.3 and a more realistic value of to 0.19).

The *t_{50}* values were obtained from laboratory sedimentation tests performed over iron slurries prepared using different iron samples, at a particle concentration of 20 g/l, and a guar gum concentration of 3g/l. The corresponding discharges to be used in the field, calculated using equations

$$V_{inj,frac} = \pi \cdot b_f \cdot ROI^2 \cdot \frac{b_i}{f} \qquad (32)$$

and

$$t_{inj,frac1} = \frac{V_{inj,frac1}}{Q} < t_{50} \qquad (33),$$

are reported in Table 22.

For this site a fracture thickness of 1 cm was assumed with and a distance between to nearby fractures equal to 0.5 m and a discharge rate *Q* is given by the injection apparatus, then, once volumes have been calculated, the injection time for each point can be easily determined and compared with the sedimentation time of the iron slurries using equation (33).
In this case the sedimentation time has a trivial influence on the injection time, since it is for all considered values of influence radii and discharge rates, much lower than *t_{50}*.