Injectable reducing iron particles technology

Technology description:
General information & application area

Target Audience: Authorities, site owners, consultants, contractors

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Project website address: aquarehab.vito.be

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1 INTRODUCTION

Reactive zones with injectable reducing iron particles (iZVI technology) are an innovative in-situ remediation technology for contaminated aquifers and groundwater. This document intends to provide general information about this technology, its application area and boundary conditions for authorities, consultants, contractors and site owners.

For more details, the reader is referred to the generic guideline that was composed within AQUAREHAB for supporting consultants, authorities and scientists to evaluate the feasibility and the impact of the iZVI technology for remediating 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 GENERAL EXPLANATION OF THE IZVI TECHNOLOGY

2.1 CONCEPT

Zerovalent iron (ZVI) is known for its capacity to degrade abiotically a number of compounds like chlorinated ethenes, via abiotic reducing processes (Gillham and O'Hannesin, 1994; Mathenson and Traynek, 1994). The general idea of the iZVI technology is to inject small sized ZVI particles as a suspension into the subsurface to spread the ZVI over a certain distance before sedimenting or adsorbing to the aquifer matrix. 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.

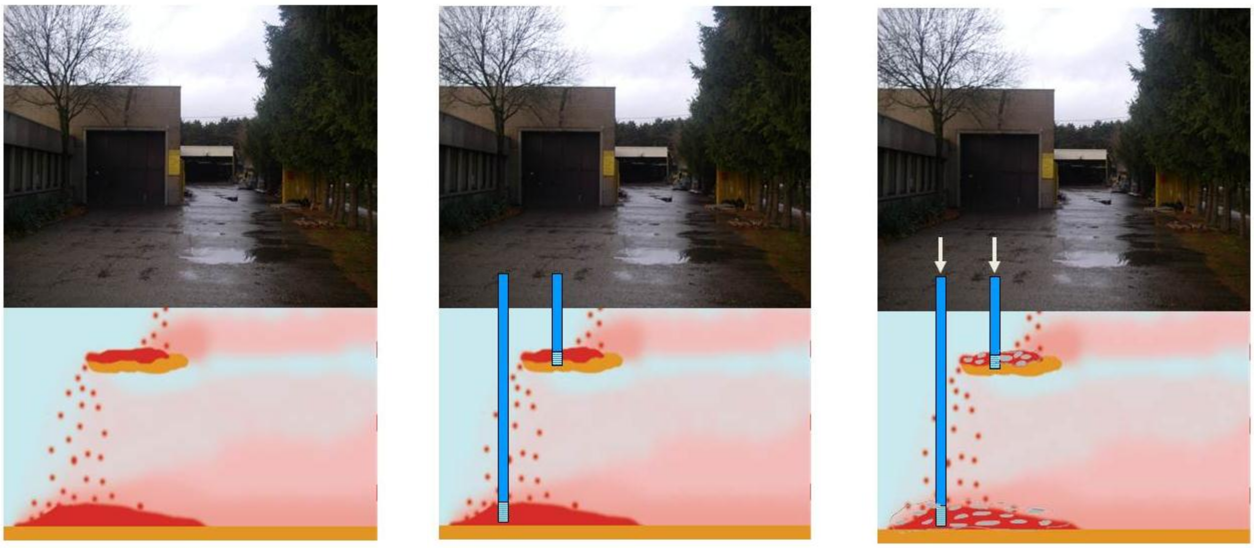

Figure 1 Contamination underneath buildings - Drilling of injection wells – Injection of iZVI particles (pollutants are represented by the red colour; the darkest red colour represents small droplets of residual phase).

To be injectable, the ZVI-particles need to be nano- or lower micro-scale to prepare a suspension and facilitate its entry into soil pores. As small-sized ZVI-particles are known to have a limited life-time before they are consumed, the injection zone remains reactive for a finite time period (months – maximum a few years) and re-injections may be needed to remediate a site. The life-time of ZVI particles depends on the size (Velimirovic et al., 2014a) and particle type, as well as on a number of site-specific parameters, like concentration of contaminant, type and concentration of dissolved species which can give rise to side reactions with undesired iron consumption, etc.

The iZVi technology is related to the more established permeable reactive iron barrier technology, where mm-sized ZVI is installed in the subsurface by digging trenches that are refilled with the ZVI. Compared to ZVI barriers, the more innovative iZVI technology is less invasive during the implementation as injectable iron particles are applied as aqueous suspensions. This reduces the efforts for implementation drastically and allows for application (nearly) independent of existing infrastructures. 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. On the other hand, the life-time of fine sized particles is lower and the price increases significantly with reduced size (Figure 2).

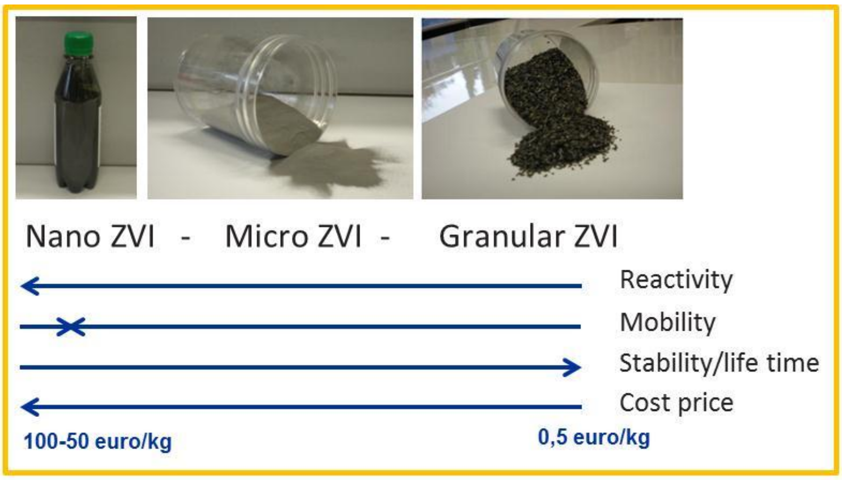

Figure 2 Comparison of different sized ZVIs.

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). Part of the mentioned compounds 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 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)

Substance	Substance
Pentachlorobenzene (C6HCl5)	*cis*-Dichloroethene (C2H2Cl2)
Tetrachlorobenzenes (C6H2Cl4)	*trans*-Dichloroethene (C2H2Cl2)
Trichlorobenzenes (C6H3Cl3)	1,1-Dichloroethene (C2H2Cl2)
Dichlorobenzenes (C6H4Cl2)	Vinyl chloride (C2H3Cl)
Chlorobenzene (C6H5Cl)	**Chlorinated ethanes**
Pesticides	1,1,1-Trichloroethane
DDT (C14H9Cl5*)*	1,1-Dichloroethane
Lindane (C6H6Cl6*)*	**Other polychlorinated hydrocarbons**
Organic dyes	PCBs
Orange II (C16H11N2NaO4S)	Dioxins
Chrysoidine (C12H13ClN4)	Pentachlorophenol (C6HCl5O)
Tropaeolin O (C12H9N2NaO5S)	**Other organic contaminants**
Acid Orange	N-nitrosodimethylamine (NDMA) (C4H10N2O)
Acid Red	TNT (C7H5N3O6)
Heavy metal ions	**Inorganic anions**
Mercury (Hg^{2+})	Dichromate (Cr2O^{2-}7)
Nickel (Ni^{2+})	Arsenic (AsO^{3-}4)
Silver (Ag^{+})	Perchlorate (ClO^{-}4)
Cadmium (Cd^{2+})	Nitrate (NO^{-}3)

2.3 REACTION MECHANISM

The use of ZVI as a nontoxic material has been shown as one of the most promising remediation techniques for in situ passive removal of CAHs via abiotic reductive dehalogenation. Since early 1990s zero-valent iron has been used for site remediation in permeable reactive barriers because of its low cost, availability, and high ability to dehalogenate chlorinated organic compounds over a wide concentration range (EPA, 1999).
Three possible reaction mechanisms are described for reduction of chlorinated solvents by ZVI (Matheson and Tratnyek 1994; Figure 3).

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

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

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

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

The third abiotic mechanism involves hydrogen produced as a product of iron corrosion with water:

$H_2 + RCl$ ----> $RH + H^{+} + Cl^{-}$ (3)

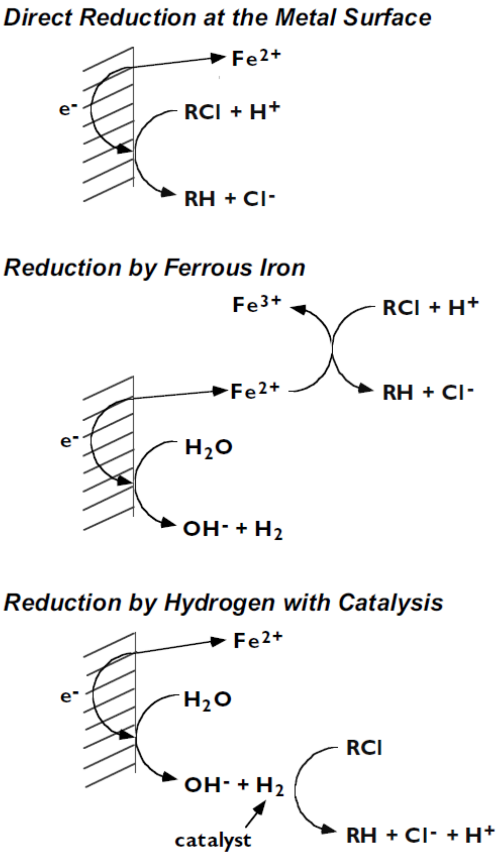

Figure 3 Possible mechanisms for reduction of CAHs by ZVI (Matheson and Tratnyek, 1994).

In the presence of zerovalent iron, reductive dechlorination of chloroethenes occurs through different pathways involving *β*-elimination, hydrogenolysis, *α*-elimination, and/or hydrogenation (Arnold and Roberts 2000). The main degradation pathways of chlorinated ethenes are presented in Figure 4**.**

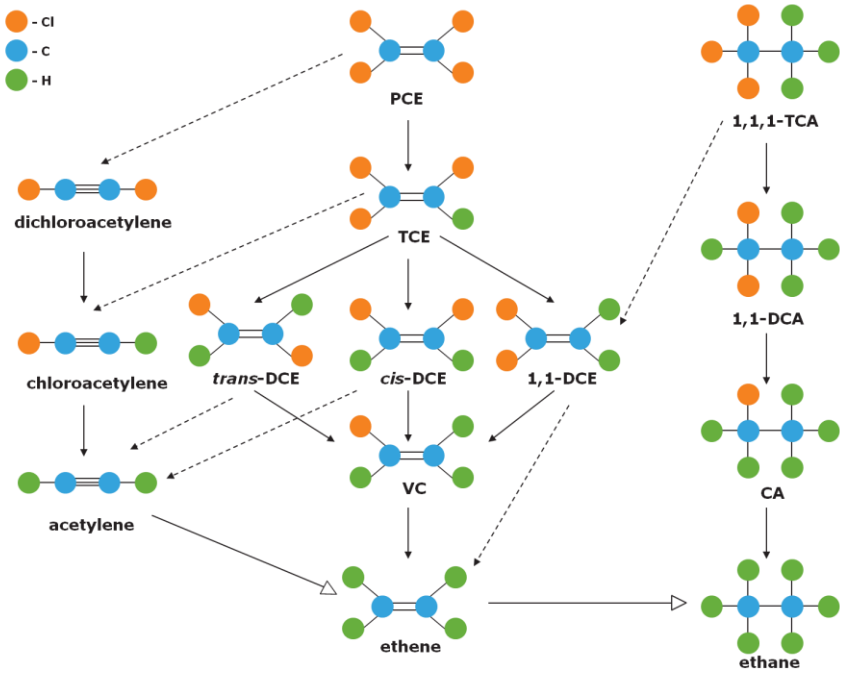

Figure 4 Hypothesized transformation pathways of selected chlorinated ethenes and ethanes by ZVI (adapted from Arnold and Roberts 2000; Tobiszewski and Namieśnik, 2012). Solid arrows represent hydrogenolysis reactions, while dashed arrows indicate reductive *β*-elimination reactions. Open arrowheads indicate reductions not involving dehalogenation

2.4 DEVELOPMENT STAGE OF THE TECHNOLOGY

The use of granular zero-valent iron in permeable reactive barriers for in-situ remediation of groundwater contaminated with chlorinated solvents is an available technology (Matheson & Tratnyek, 1994; Gillham, 1996; Gavaskar, 2000). Micro and nano scale ZVI show similar chemical properties, however due to their size they have a much bigger relative surface area and, hence, a much higher reactivity. Also the emplacement process (injection) is scientifically more challenging than the trenching method applied for PRB.

Although quite a number of field applications have been conducted worldwide, the iZVI technology still lacks a sound scientific proof. The majority of the applications have been conducted in North America and reliable data on success or failure are only publically available to some degree (Karn et al., 2009). Therefore, the technology can be categorized **"becoming transferable"** until additional field data are made available and further proof of success has been shown. In some EU countries the injection of nano-scale ZVI particles is currently prohibited pending positive proof of their environmental safety.

For very small, potentially injectable ZVI particles discussed in this document questions were raised regarding their fate after injection into the subsurface and about environmental safety in general. Within AQUAREHAB environmental risks were assessed and a positive benefit/risk was found, especially for micro-scale particles.

For more details the reader is referred to the generic guideline.

3 APPLICABILITY AND BOUNDARY CONDITIONS OF THE TECHNOLOGY

Table 2 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 2 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	+++	
	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.

4 PERFORMANCE OF THE IZVI-ZONE TECHNOLOGY

The **abatement rate** can be defined as the substance concentration after the technology implementation divided by the substance concentration before implementation of the technology. The 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%.

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) of and contact with ZVI particles, (3) the type of ZVI particle used and (4) the composition of the suspension and groundwater/aquifer.

Longevity of the technology is influenced by (1) the type, size and specific surface area of the ZVI used, (2) the composition of the groundwater, and (3) the groundwater velocity through the injected zone. The time period the technology can be operational before reinjection is strongly dependent on ZVI particles size, hydro geochemistry, contaminants to be treated. Generally, for nano-sized ZVI it will be in the order of weeks to a few months, while for micro-scale ZVI rather months to a few years (Velimirovic et al., 2014a).

5 COST OF THE TECHNOLOGY

Cost drivers for iZVI-zone technology include (1) detailed site assessment, (2) preliminary lab tests to match ZVI particles and the injection technology to the hydrogeology and chemistry of the site (eg decision particle size, required dose), (3) geometry of the injected zone (depth, length, width, height) and necessary spacing of injection wells, (4) price of the injectable ZVI particles and suspension, (5) loss of usable 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 cost for the creation of a reactive zone is strongly dependent on the price of the particles that is determined by its size/shape (Figure 2), composition, performance and required loading. Some indicative costs are:

- 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 costs: The iZVI-zone technology is an emerging technology. Currently there are no sites which offer both a conclusive proof of achieved remediation goal and sufficient information with respect to cost incurred. Hence, no cost estimation supported by sustainable data can be offered to date.

6 GENERIC APPROACH TO DETERMINE APPLICABILITY OF AN IZVI-ZONE FOR A SPECIFIC SITE OR AREA

For a successful application of the iZVI-zone technologies, the following steps, illustrated in Figure 6, 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 5). 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.

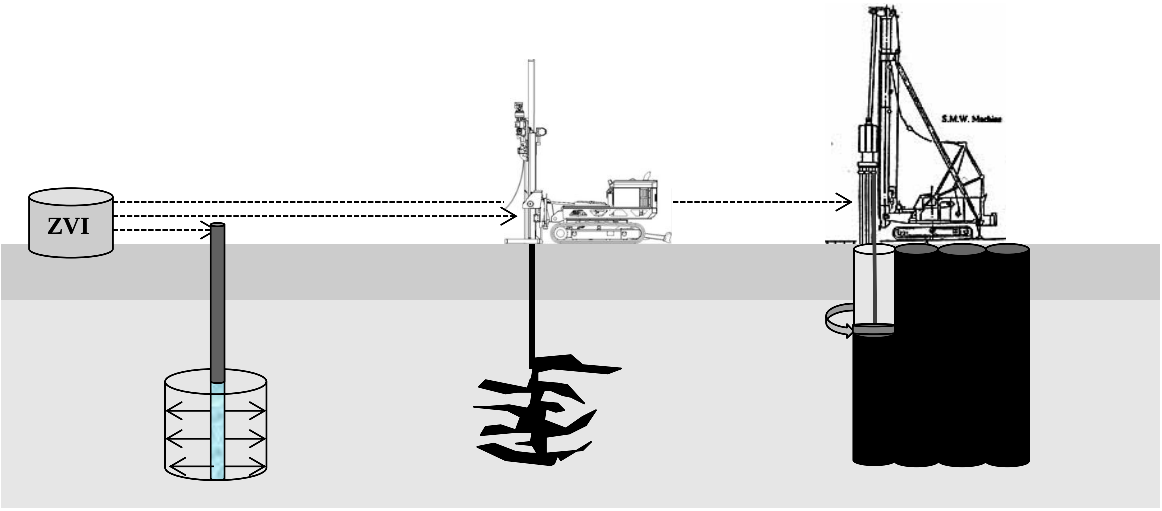

Figure 5 Simplified schematic representation of ZVI-injection via permeation (left), injection via fracturing (middle) and soil mixing (right).

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 (eg required minimal dosing) needed as input parameters for the design of the iZVI-zone.

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.

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., submitted).

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 cleanup. 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 site

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

For more detailed information the reader is referred to the associated generic guideline.

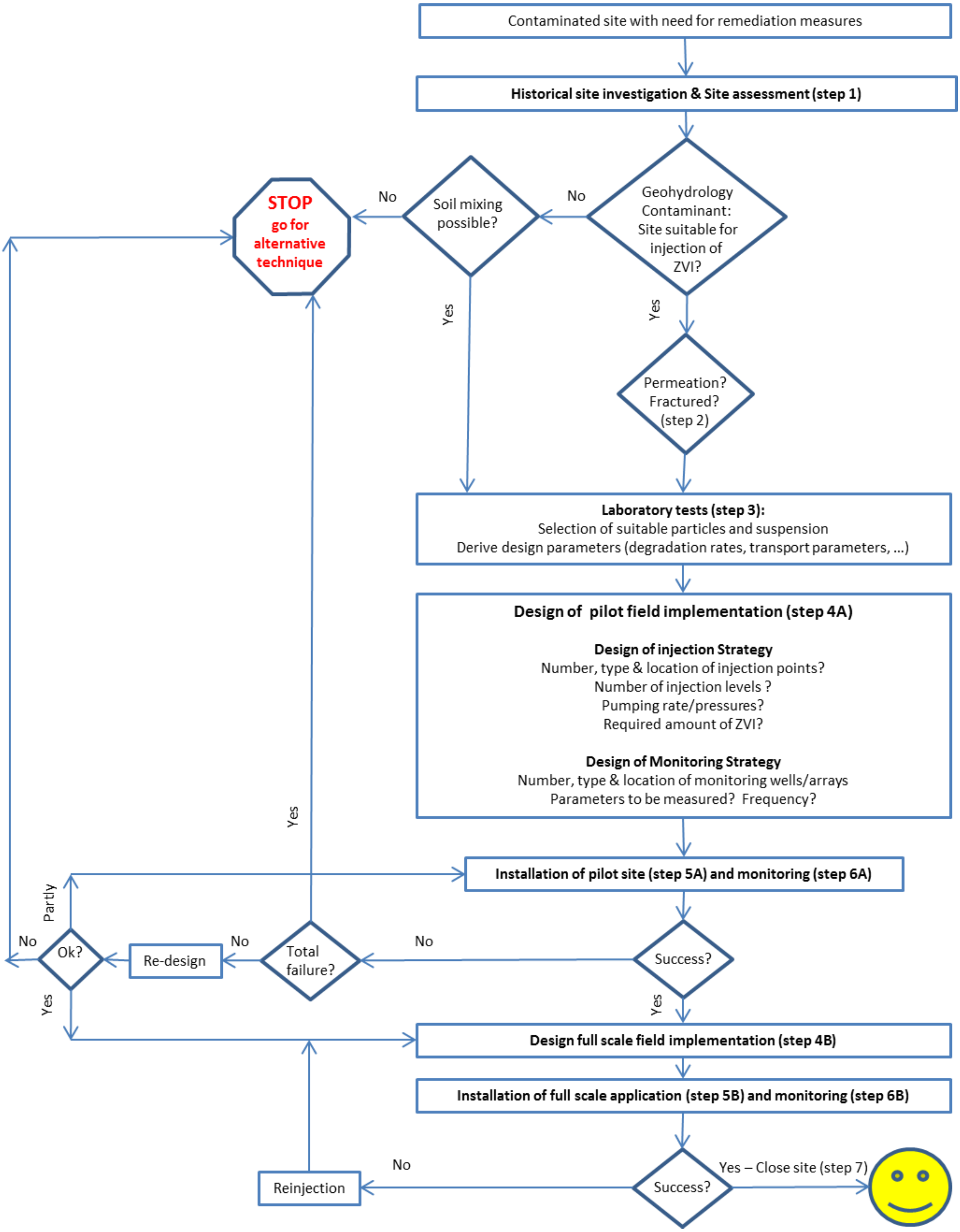

Figure 6 Flowchart for application of the iZVI technology application.

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8 REFERENCES

Arnolds, W.A., A.L. Roberts. 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acethylene reaction with Fe(0) particles. Environ. Sci. Technol. 34: 1794-1805.

Comba, S. AND J. Braun. 2012. A new physical model based on cascading column experiments to reproduce the radial flow and transport of micro-iron particles. J. Cont. Hydrol. 140-141:1-11.

Dalla Vecchia, E., Luna, M., and Sethi, R. 2009. Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum. Environmental Science & Technology 43(23), 8942-8947.

EPA, EPA 542-R-99-002, April 1999, Field Applications of *In Situ* Remediation Technologies: Permeable Reactive Barriers.

Gastone F., Tosco T., and Sethi R. 2014. Green stabilization of microscale iron particles using guar gum: bulk rheology, sedimentation rate and enzymatic degradation. Journal of Colloid and Interface Science, 421, 33-43.

Gavaskar, A., N. Gupta, B. Sass, R. Janosy, J.Hicks. 2000. Design guidance for application of permeable reactive barriers for groundwater remediation. Battelle Press, Columbus, Ohio.

Gillham, R.W. 1996. In situ treatment of groundwater: metal-enhanced degradation of chlorinated organic contaminants. In Advances in Groundwater Pollution Control and Remediation. Ed. M.M. Aral, Kluwer Academic Publishers, Nederland, p249-274.

Gillham, R.W., S.F. O'Hannesin. 1994. Enhanced degradation of halogenated aliphtics by zerovalent iron. Ground Water, 32, 958-967.

Karn B, Kuiken T, Otto M. Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environmental Health Perspectives. 2009;117:1832–1831

Matherson, L.J. P.G. Tratnyek. 1994. Reductive dehalogenation of chlorinated methanes by iron metal. Environ. Sci. Technol. 28, 2045-2053.

Tobiszewski, M., Namieśnik, J. 2012. Abiotic degradation of chlorinated ethanes and ethenes in water. Environ. Sci. Pollut. Res. Int. 19(6), 1994–2006.

Tosco, T., Sethi, R., 2010. Transport of non-Newtonian suspensions of highly concentrated micro- and nanoscale iron particles in porous media: a modeling approach. Environmental Science & Technology, 44:9062-9068.

Tosco T., Gastone F., Sethi R. (submitted), Guar gum solutions for improved delivery of iron particles in porous media (Part 2): iron transport tests and modelling in radial geometry, Journal of Contaminant Hydrology, under review.

Velimirovic M., P-O L, Q. Simons, L. Bastiaens. 2013. Reactivity screening of microscale zerovalent irons and iron sulphides towards different CAHs under standardized experimental conditions. J ournal of Hazardous materials 252-253, 204-212.

Velimirovic M., Carniato L., Simons Q., Schoups G., Seuntjens P., Bastiaens L. 2014a. Corrosion rate estimations of microscale zerovalent iron particles via direct hydrogen production measurements. Journal of Hazardous Materials 270, 18-26.

Velimirovic M., Q. Simons, Bastiaens, L. 2014b. Guar gum coupled mZVI for in-situ treatment of CAHs: continuous-flow column study. Journal of Hazardous Materials, 265, 20-29.

Xue, D., R. Sethi. 2012. Viscoelastic gels of guar and xanthan gum mixtures provide long-term stabilization of iron micro- and nanoparticles. J. Nanopart. Res. 14:1239-1253.

Zhang, W. 2003. Nanoscale iron particles for environmental remediation: An overview. J. Nanoparticle Res. 5, 323 – 332.