Permeable Reactive zerovalent iron barriers (ZVI-barrier)

Technology description:
General information & application area

Target Audience: Authorities, site owners, consultants, contractors

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1 INTRODUCTION

Permeable reactive zerovalent iron barriers (ZVI-barriers) are an innovative in-situ remediation technology for contaminated groundwater. This document intends to provide general information about this technology, and its application area and boundary conditions for authorities, consultants, contractors and site owners. More detailed information for supporting consultants, authorities and scientists in evaluating the feasibility, designing, implementing and monitoring ZVI-barriers is given in the associated generic guideline.
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2 GENERAL PRINCIPLES OF THE ZVI-BARRIER TECHNOLOGY

2.1 CONCEPT

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

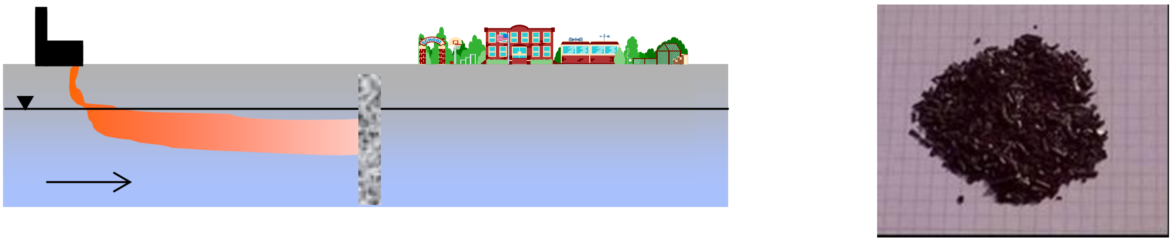

Figure 1 Schematic representation of the ZVI-barrier technology.

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

2.2 TARGETED SUBSTANCES

An overview of substances that can be targeted by the ZVI-barrier technology is given in Table 1, along with their potential emissions sources.
For compounds like PCE and TCE the ZVI can realise a full dechlorination. For other compounds the dehalogenation is only partial. Halogenated compounds (and break down products) that are hardly degradable by ZVI comprise: dichloromethane (DCM), chloromethane (MCM), 1.2-dichloroethane (12DCA), chloroethane (MCA) and 1,4-dichlorobenzene.

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

Targeted substances		Emission sources
Class	Specific substance	
Chlorinated ethenes & ethanes	Tetrachloroethylene (PCE) Trichloroethylene (TCE) Cis-dichloroethylene (cDCE) Trans-dichloroehtylene (tDCE) 1,1-dichloroethylene (1,1DCE) Vinylchloride (VC) Hexachloroethane 1,1,2,2-tetrachloroethane 1,1,1,2-tetrachloroethane 1,1,1-trichloroethane (111TCA) 1,1,2-trichloroethane (112TCA) 1,1-Dichloroethane (11DCA)	*Drycleaner activities, degreasing activities, ...*
Chlorinated methanes & propanes	Tetrachloromethane (PCM) Trichloromethane 1,2,3-trichloropropane 1,2-dichloropropane	*Chemical industry* *Agricultural activities*
Other chlorinated aliphatics	Hexachlorobutadiene	*Chemical industry*
Pesticides & herbicides	Hexaclorocyclohexanes (HCHs) Dichlorodiphenyltrichloroethane (DDT) Lindane	*Agricultural activities* *Gardening*
Nitrobenzenes	nitrobenzene	*Chemical industry*
nutrients	nitrate	*Agricultural practices, cattle*
Dyes	Azo dyes	*Textile industry*
explosives	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) 1,4,6-tronitrotoluene (TNT) Octahydro-1,3,5,7-tetranitor-1.3.5.7-tetrazocine (HMX)	*military activities*
Metals (via immobilisation)	Cathionic metals (Cu, Ni, Zn) Selenium Uranium Chromium Arsenic	*Mining* *Industrial activities*
Brominated & fluorinated compounds	Tribromomethane (TBrM) 1,2 dibromomethane Trichlorotrifluoroethane (Freon 113) Trichlorofluoromethane (Freon 11)	*Chemical industry*

2.3 REACTION MECHANISM

The pollutants are degraded by ZVI via a chemical reduction process where, in case of chlorinated compounds, dechlorination is realised. The reduction of contaminants into less toxic or less mobile compounds is mainly driven by the oxidation (corrosion) of Fe^0 (reaction 1) or surface-bound Fe^{2+} (reaction 2), and to a lesser extent by hydrogen generated as a product of anaerobic corrosion as given in reaction 3 (Figure 3). The relative importance of the different reactions is function of the Fe^0 material and potentially also the composition of the groundwater.

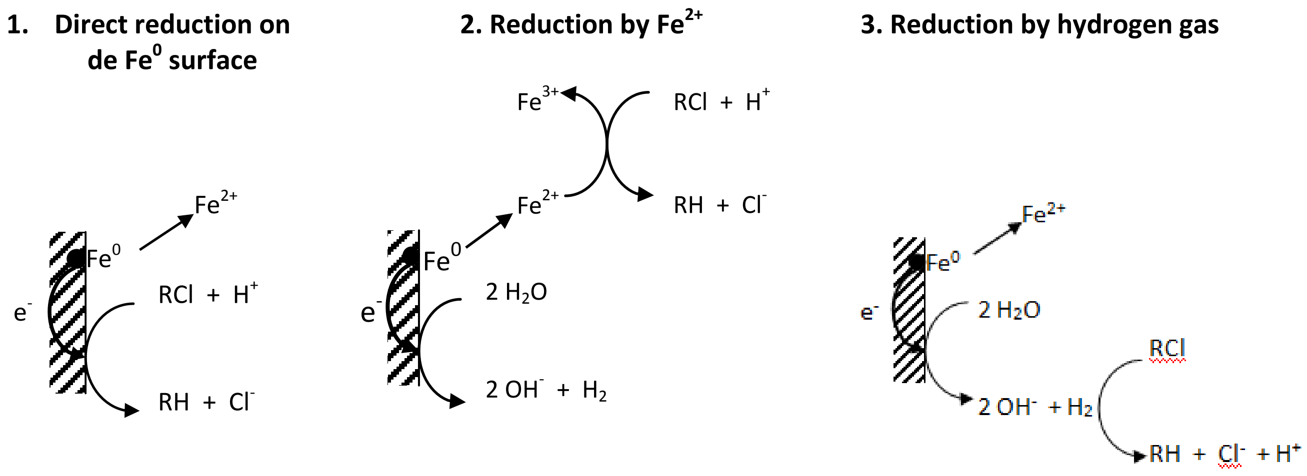

Figure 2. Possible reaction mechanisms for reductive dechlorination of CAHs by zerovalent iron (based on Matherson & Tratnyek, 1994).

Reaction of water with ZVI under anaerobic conditions, called anaerobic corrosion, is responsible for the pH-increase that is often associated with zerovalent iron applications. This is also the process that generates hydrogen.

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

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

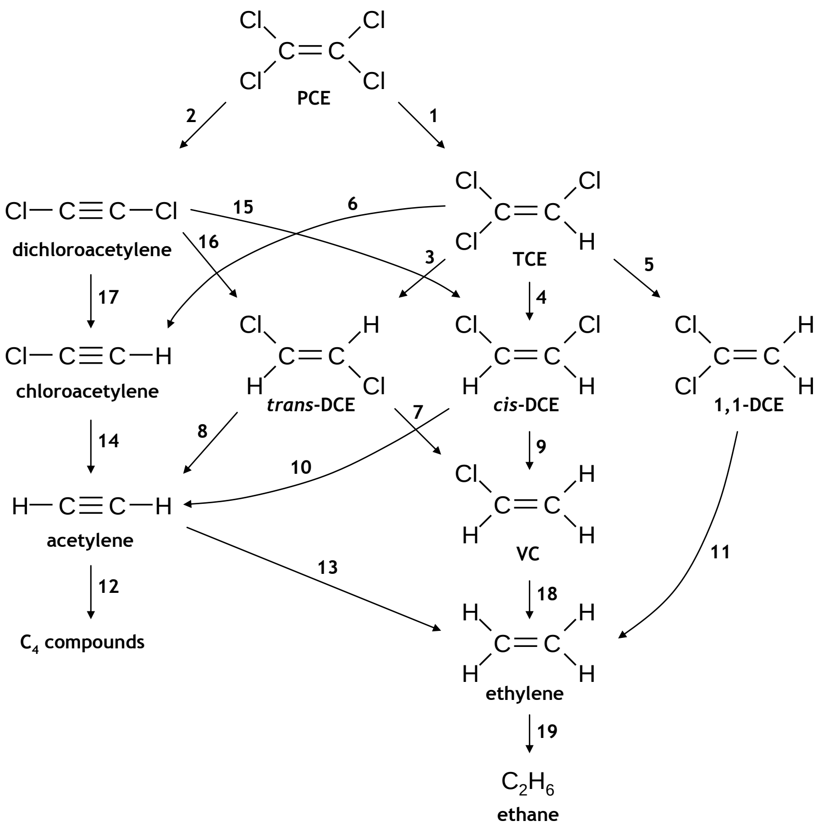

Figure 3. Hypothesized reaction pathways for the degradation of chlorinated ethylenes during reduction by Fe^0. Reactions 1, 3, 4, 5, 7, 9, 14, 17 and 18 correspond to hydrogenolysis reactions, while reactions 2, 6, 8 and 10 are reductive *β*-elimination reactions. Reaction 11 proceeds via reductive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

2.4 Development stage of the technology

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

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

3 Applicability and Boundary Conditions of the Technology

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

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

The use of ZVI-barriers is not recommended:

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

Positive secondary effects linked to the ZVI-barrier technology:

- During anaerobic corrosion of ZVI, hydrogen is generated as shown in Figure 2. This hydrogen can stimulate micro-organisms, like anaerobic CAH-degrading species and sulphate reducing species.
- In addition, the reduced redox potential (ORP) that is created by the ZVI, also stimulates anaerobic bacteria like CAH-degrading or sulphate reducing species.
- The reduced ORP and stimulation by hydrogen of sulphate reducing bacteria, creates conditions where pollutants like metals can be removed from the groundwater by in-situ bioprecipitation, besides via direct immobilisation on the ZVI surface.

Negative secondary effects linked to the ZVI-barrier technology:

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

4 Performance of the ZVI-technology

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

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

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

The **longevity of the technology** is influenced by (1) the composition of the groundwater, (2) the groundwater velocity through the barrier and (3) the mass, type and grain size of the ZVI used. Generally, the time period during which the technology can be operational without making significant additional investments is at least 10 to 20 years. The need for regeneration of the ZVI-barrier is advised to be taken into account for every 15 to 20 years (O'Hannesin, 2003). This regeneration process may for instance imply the replacement of a part of the ZVI.

5 COST OF THE TECHNOLOGY

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

The investment cost of ZVI-barriers are relatively high, while the maintenance costs is nearly non-existing with exception of regeneration of the barrier system and monitoring. Total costs (site investigation, design, implementation, maintenance & monitoring) for ZVI-barriers, considering a 30 years operational time, have been calculated to range between 642 and 2397 keuro (EPA/600/R-02/034 and calculations made within AQUAREHAB). This comprises the cost for 1 renewal of the ZVI-material after 15 years of operation, which may not be needed for each site. The associated relative cost structure is given in Figure 4.

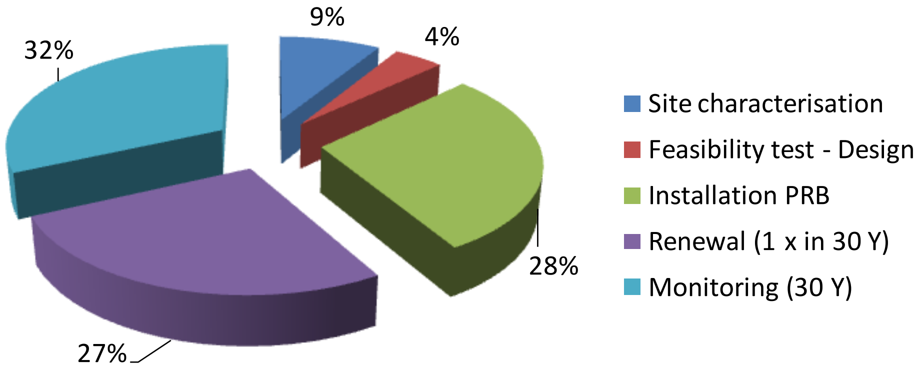

Figure 4 relative cost structure (%) of ZVI-barriers comprising on operational time period of 30 years. Note, except renewal of the ZVI-material after 15 years and monitoring, no maintenance costs are involved.

Pump and treat technologies do have a lower initial investment cost, but are associated with higher maintenance costs (maintenance of equipment, electricity, discharge of iron sludge, activated carbon, ...). When the operational time is more than 8-10 years, ZVI-barriers are economically favourable (ITRC report, 2005). For some sites, the reactive barriers were already within 1 year economically more interesting than pump & treat systems (O'Hannesin).

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

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

Step 1: site characterisation

A site characterisation is required for checking the application and boundary conditions associated with the technology (see section 3). The site characterisation comprises:

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

Step 2: Feasibility test at lab scale

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

Within the AQUAREHAB project, an improved test procedure has been elaborated which allows to deduce parameters related to the de-activation of the ZVI over time, enabling to estimate the life-time of the barrier for specific sites (see part A.2).

Step 3: Design & dimensioning of pilot/full scale

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

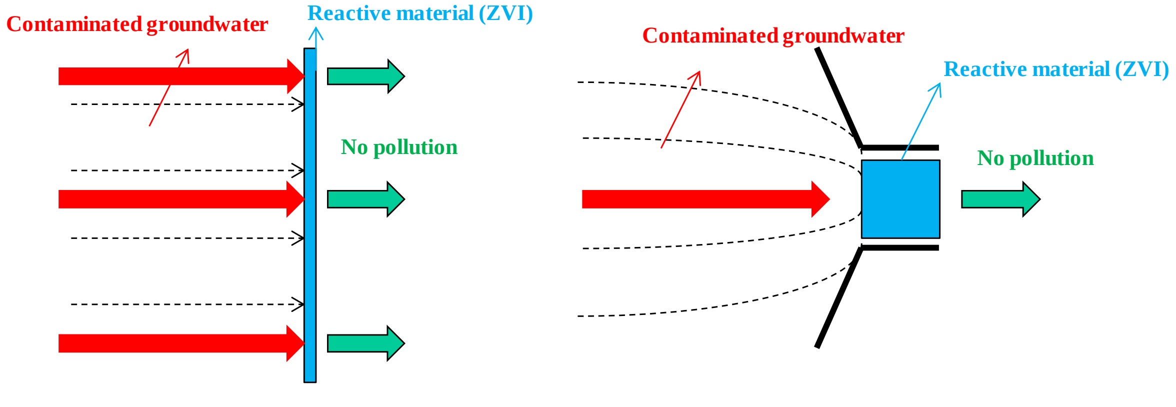

Figure 5 Schematic representation of a continuous (left) and funnel & gate (right) PRB concept

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

Step 4: Implementation of the ZVI-barrier

This step comprises the installation of the ZVI-barrier conform to the design parameters. Barriers are installed by excavating the soil, and refilling the trench with the ZVI-containing barrier material (Figure 6). Different implementation methods have been described and used, comprising continuous trenching and refilling of a stabilised (sheet piles, or guar gum) trench.

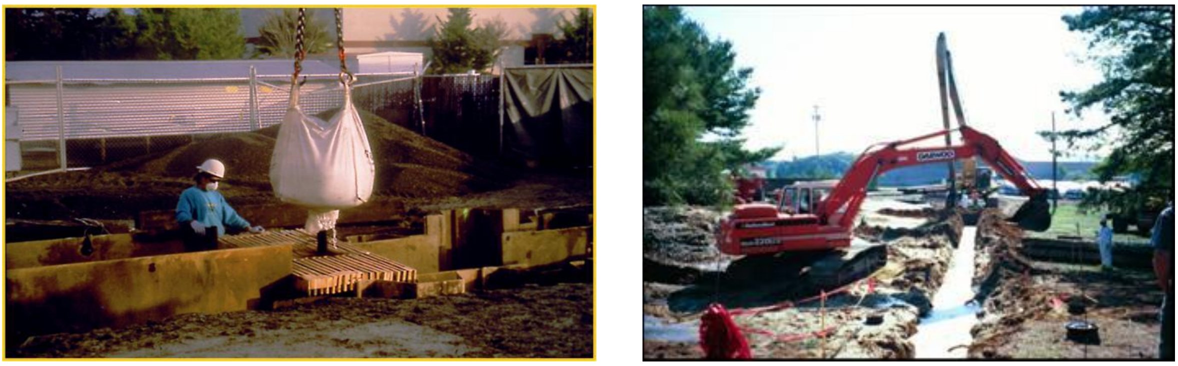

Figure 6: Implementation of ZVI-barriers (SOURCE: ETI)

Step 5: Monitoring of the ZVI-barrier

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

Step 6: Site closure

Generally, ZVI-barriers are expected to remain in the subsurface once the site is closed.

For more detailed information the reader is referred to part A.2 of this document or to specialised literature.

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