



ObservatoryNANO focus report 2010

Nano zero valent iron – THE solution for water and soil remediation?

This report was written in a two step process. In a first phase information from literature and internet was compiled in a draft report. The second phase focused on expert involvement. On November 24th 2009 a workshop was held in Zurich (Switzerland), which brought together different experts from commercial companies, the scientific community and government. Based on the results of the workshop, the draft report was amended and completed.

We would like to thank the following experts for their valuable contribution:

- Dr Jürgen Braun (University of Stuttgart, Germany)
- Dr Johannes Bruns (Golder Associates, Germany)
- Dr Miroslav Černík (University of Liberec, Czech Republic; AQUATEST, Czech Republic)
- Dr Barbara Karn (U.S. EPA, USA)
- Dr Peter Rissing (Alenco, Germany)
- Dr David Rickerby (JRC Ispra, Italy)

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1 Executive Summary

Nano Zero Valent Iron (nZVI) is emerging as new option for the treatment of contaminated soil and groundwater. Due to their small size, the particles are very reactive (more reactive than granular iron which is conventionally applied in reactive barriers) and can be used for in situ treatment. nZVI effectively reduces chlorinated organic contaminants (e.g. PCB, TCE, PCE, TCA, pesticides, solvents) and also inorganic anions (perchlorate). It can even be used to recover/remove dissolved metals from solution (e.g. Cr(VI), U(VI)).

The mobility and the lifetime of nZVI particles are limited. Therefore several modifications of nZVI are studied, tested and commercialized. The most important are: surface-modified nZVI, emulsified nZVI (better miscibility with DNAPL), bimetallic nZVI (higher reactivity) and nZVI on carbon support (better distribution within the soil). In the few remediations conducted in Europe until now only surface-modified nZVI (e.g. with surfactants) was applied.

The injection technology and the density of the injection wells depend among other factors on the site conditions, the concentration of Fe(0) in the slurry and on the nZVI-particle type used. So far mostly low-pressure injection has been applied. The costs for the treatment are estimated at around €300 per kg of contaminant depending on the site conditions.

There are at least three companies in Europe working with nZVI for site remediation and one company producing nZVI. Several case studies highlight the technical challenges to be solved. Major concerns are the limited mobility and lifetime of nZVI. Further hurdles regarding the commercialisation of nZVI are the material handling, the costs, the fear of a public backlash and the fact that the technology is unknown to consultants, governments and site owners.

This report gives an overview over the characteristics and application of nano zero valent iron (nZVI) in general (Chapters 3 to 5) and summarizes the experiences on groundwater remediation with nZVI in Europe (Chapters 6 to 8).

Chapter 3 shortly introduces the developments in the area of groundwater remediation. Different methods are put together and the advantages of nZVI compared to granular iron are highlighted. Chapter 4 lists some institutes investigating the use of nZVI for groundwater treatment in Europe. It also summarizes the production methods and particle characteristics of nZVI and presents some nZVI-modifications which should improve the remedial performance. Chapter 5 introduces the basic mechanism of the reactions and gives an overview over the target contaminants.

Chapter 6 shows experiences from field applications. This includes some information on regulations and acceptance by governments, on the requirements regarding site characteristics as well as on the injection technology. Chapter 7 lists the European pilot projects and presents the three full scale applications that were carried out in Europe until now. Chapter 8 describes the technical and economical challenges and shortly mentions the issue of potential toxicity.

2 Introduction

In the U.S. there are between 235'000 and 355'000 sites that require cleanup at an estimated cost of between €115 and 168 billion (U.S.EPA, 2005). In Europe an estimated 20'000 sites need to be remediated, and another 350'000 potentially contaminated sites have been identified by the European Environment Agency (PROKOP et al., 2000).

There are a number of remediation technologies for groundwater available. But depending on the target contaminant and the hydrogeological conditions not all methods are equally effective. The U.S. National Research Council put out a table describing the relationship between the hydrogeologic conditions and the relative difficulty in addressing various contaminants (available at <http://dels.nas.edu/dels/viewreport.cgi?id=1697>). It was shown that there are several technologies on the market to address volatile organics in homogeneous sands but very few effective ones to address DNAPL contamination in fractured bedrock. Sites contaminated with chlorinated hydrocarbons are difficult to address because chlorinated hydrocarbons are hydrophobic and very persistent. They migrate in the subsurface and slowly dissolve into the groundwater. Due to the diffusion controlled process, this dissolution may persist for several decades.

Until 1992, the predominant treatment technology to address groundwater contamination was pump and treat (KARN et al., in press; U.S.EPA, 2005). As this ex situ treatment is very expensive and slow (The average pump and treat system operates for about 18 years (U.S. EPA, 2001)), public sites in the U.S. remediated by pump and treat have decreased to less than 20% in 2005 (KARN et al., in press). Karn et al. (KARN et al., in press) expect ex situ remediation techniques to be phased out over the coming decade.

As a first in situ treatment method, permeable reactive barriers (PRB) using granular zero valent iron (Fe(0)) were introduced. To date, granular ZVI has been used for many years at numerous sites in the form of PRBs (MÜLLER et al., 2006; NOWACK, 2008) and PRB are still the state-of-the-art method. Their major drawback is that they can only address contaminants that flow through the barrier (see table 1).

Recently a number of new in situ technologies are beginning to be applied (KARN et al., in press; PARBS and BIRKE, 2005; U.S.EPA, 2005):

- thermal treatment (steam enhanced extraction, electrical resistive heating, or thermal conductive heating)
- chemical oxidation
- chemical reduction (e.g. nZVI)
- surfactant co-solvent flushing
- bioremediation

Experts agree that none of the technologies is universally applicable. Depending on the site characteristics and the target contaminants, the most effective method has to be chosen. The following table compares the injection of nZVI with a conventional PRB and two other in situ methods (thermal and chemical oxidation):

Table 1: Comparison of four in situ methods: nZVI, conventional PRB, thermal treatment and chemical oxidation.

	NZVI	PRB	Thermal	Chemical oxidation
<i>Material</i>	nanoscale iron	granular iron	steam, (heat)	oxidizing agents (e.g. permanganate)
<i>Material reactivity</i>	high	low	-	very high
<i>Material mobility belowground</i>	limited (max. a few meters)	not mobile (passive treatment)	limited – depending on thermal conductivity	fairly mobile
<i>Material longevity (treatment time)</i>	up to a few months	years	restricted to the duration of the application	hours (Fenton's reagent) to months (permanganate)
<i>Material costs</i>	high	low	high energy costs for steam/heat production	moderate
<i>Material toxicity</i>	uncertainty about environmental impact of nanoparticles	low	non-toxic	significant
<i>Installation costs</i>	moderate	expensive (especially if contaminant at greater depth)	moderate (high technical expertise and sophisticated equipment necessary)	inexpensive
<i>Operation and maintenance costs</i>	low to moderate	inexpensive	expensive	moderate
<i>Requirements regarding site access</i>	possible underneath buildings	open access for machinery necessary	possible underneath buildings	possible underneath buildings
<i>Plume vs. source treatment</i>	source and plume treatment; rebound possible if source is not completely eliminated	plume treatment only	source treatment; rebound possible if source is not completely eliminated	source and plume treatment; rebound possible if source is not completely eliminated
<i>Formation of by-products</i>	possible (e.g. NH ₃ , H ₂)	possible (e.g. H ₂ , OH ⁻)	possible (hydrolysis-products of chlorinated compounds, uncontrolled condensation of contaminants)	possible (reactive oxygen species, solubilization of heavy metals (e.g. Cr))
<i>Environmental effects</i>	more reducing conditions → temporal change in microbiology	more reducing conditions → temporal change in microbiology	increase in temperature → temporal change in microbiology	oxidation of reducing environment → temporal change in microbiology

PARS Environmental Inc. made a case specific cost comparison of pump and treat, PRB and nZVI on a manufacturing site in New Jersey where the primary contaminants of concern were TCE and PCE (PARS ENVIRONMENTAL, Dec 2009 (last visit)). According to their estimate the costs for a remediation with nZVI were far lower than the other two methods for the specific site analysed (table 2).

Table 2: Cost-comparison between pump and treat, PRB and nZVI based for a specific contaminated site in New Jersey (PARS ENVIRONMENTAL, Dec 2009 (last visit))

Pump and treat	€2'760'000
PRB	€1'460'000
nZVI	€ 300'000

The U.S. EPA supports a website which provides information about innovative treatment and site characterisation technology, which also acts as a forum for all waste remediation stakeholders: <http://www.cluin.org>

Several nanoparticles have been tested for remediation purposes. A list of those materials and their target compounds are found in (KARN et al., in press; THERON et al., 2008; ZHANG, 2003). Of all nanomaterials, nZVI is the most commonly used for soil and groundwater remediation at the time (KARN et al., in press). In the U.S. site remediations with nZVI are increasing rapidly and replacing many ex-situ remediation technologies, while in Europe only a few full scale applications have been carried out yet (see chapter 7).

Nanoscale Zero Valent Iron (nZVI) promises to be significantly more effective than granular iron: The reaction rates are 25-30 times faster and the sorption capacity is much higher compared with granular iron (LI et al., 2006). This is due to the large reactive surface area with 2-5 nm particles giving approximately 142 m²/g (U.S.EPA, 2005). According to the U.S. Navy, nZVI-particles have surface areas up to 30 times greater than larger size powders or granular iron. Thus nZVI is 10^{-1'000} times more reactive (MÜLLER et al., 2006; U.S. NAVY WEBSITE ON NZVI, Aug. 2009 (last visit)).

nZVI promises to be a new method to treat source zones of contaminants that react with ZVI, such as chlorinated solvents or DNAPL. Paul Tratnyek from Oregon Health and Science University (U.S.EPA, 2005) states:

“nZVI reactivity can be looked at in two ways. The first involves reactions that are unique to nanoparticles and are not observed in construction-grade ZVI, such as the degradation of PCBs. The second is the improvement of a reaction seen in construction-grade ZVI. Improvements include faster reaction rates, such as those found with TCE and more favorable degradation products. For example, in the case of carbon tetrachloride (CCl₄), the construction-grade ZVI is more likely to produce chloroform than other less toxic degradation products. If nZVI shifts the reaction more to the less toxic degradation forms, then it will make iron a more desirable remediation option.”

The advantages of nZVI may be summarized as follows (U.S. NAVY WEBSITE ON NZVI, Aug. 2009 (last visit)):

- Fast reaction
 - short treatment time → less costs
 - less exposure for workers, fauna and flora
- Complete reduction pathway to non-toxic end products is possible
 - less exposure for workers, fauna and flora
- In situ treatment
 - less equipment and above-ground structures required → less costs

3 ST Aspects

3.1 Nanoscale Iron for in-situ Treatment

In Europe there are several research institutes working with nZVI and investigating its applicability for soil and groundwater remediation.

Belgium research institute VITO: A group led by Leen Bastiaens is working on soil and groundwater remediation including nZVI.

German Federal Institute for Geosciences and Natural Resources (BGR): The BGR has carried out laboratory tests showing the effectiveness of nZVI for dechlorination of TCE and immobilisation of chromate and arsenate (HOUBEN and KRINGEL, 2007). The BGR has dropped its research activities on nZVI in 2009.

Politecnico di Torino: Rajandrea Sethi's group is modeling nZVI in contaminated aquifers (DALLA VECCHIA et al., 2009).

Technical University of Liberec: A group is working on nZVI for groundwater and soil remediation in collaboration with the Palacky University Olomouc, AQUATEST consultancy and Nano iron.

Umweltforschungszentrum Leipzig (UFZ): At the UFZ nZVI for the immobilization of uranium and arsenic is studied (BURGHARDT et al., 2007).

University of Reading: In the UK an NERC funded project had been started at the Department of Soil Science, University of Reading. The aim of the research is to advance understanding of the impacts of nZVI-particles on microbial communities important for bioremediation, stabilisation and improvement of solids contaminated with highly chlorinated aromatic compounds.

More information at:

http://www.oecd.org/document/27/0,3343,en_2649_37015404_43278299_1_1_1_1,00.html#deployment_of_nZVI

University of Stuttgart: At the Institute for Hydraulic Engineering the mobility of nZVI is studied in a specialized research facility for subsurface remediation (VEGAS) (DE BOER et al., 2009).

3.1.1 Nano Zero Valent Iron (nZVI)

Particle Production Methods

There are several possibilities to make nano zero valent iron (nZVI) particles (MÜLLER et al., 2006; PARBS and BIRKE, 2005; U.S.EPA, 2005).

- One method is to react ferric chloride in water with sodium borohydride. The general properties of this amorphous nZVI are 10-100 nm with a mean size of 50 ± 15 nm and a specific surface area of 10-50 m²/g. The particles produced by this method are referred to as Fe(B).
- It is also possible to heat iron pentacarbonyl to 200-250 °C. At this temperature it will disassociate into nZVI and carbon monoxide. The nanoparticles formed in this reaction are approximately 5 nm.
- A further option is reacting iron oxides with hydrogen which will yield nZVI particles in the size range of 200-300 nm.

- Toda RNIP (reactive nano-scale iron particle) is a crystalline type of nanoiron made from gas phase reduction of FeOOH. It has an average size of 70 nm with a surface area of 29 m²/g. The nanoparticles are coated by polymaleic or polyacrylic acid.
- Lately, a new company produces nZVI from nanosized ferrihydrite (NANOFER). Nanoparticles are stored in an inert atmosphere before surface coating by different chemicals.
- nZVI can also be produced by milling of aggregates or microscale particles.

Iron particles produced by the different methods differ in their structural configurations, size distribution and surface area (U.S.EPA, 2005). They have thus also different reactivities and aggregation properties. Fe(B), NANOFER and RNIP are the most commonly used. Impurities like heavy metals are negligible for remediation purposes.

At the University of Liberec, different nZVI-particles were compared in reactions with chlorinated hydrocarbons. In a pilot project carried out in Pisečna (Czech Republic) it was found that RNIP were significantly less effective in reducing chlorinated ethanes and ethenes than NANOFER (figure 1).

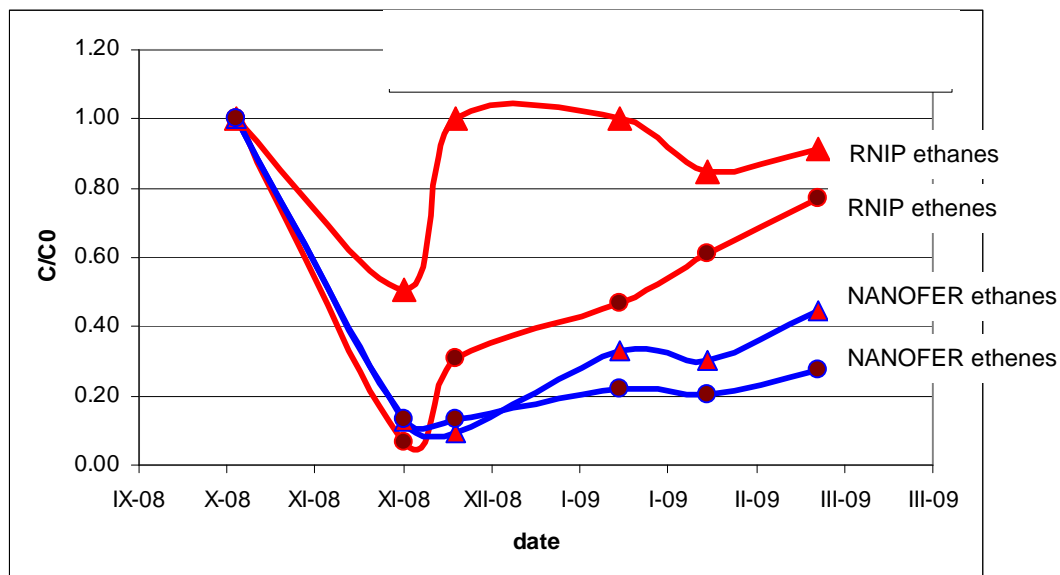


Fig 1: Comparison of RNIP and NANOFER regarding the effective degradation of chlorinated ethenes and ethanes. © Aquatest, Czech Republic

Particle Characteristics

At the University of Stuttgart, different batch experiments are conducted to study the longevity of iron suspensions, the influence of pre-treatment (e.g. dispersion) and the influence of Fe concentrations on the degradation of contaminants. These batch experiments serve as basis for column experiments and further investigations. Based on the batch tests, column experiments are carried out to study the particle behavior (mobility, stability, efficiency of contaminant degradation) under field conditions.

Stability

nZVI is not particularly stable. In dry form, the powder ignites immediately when in contact with air. Storage in dry form is only possible in an inert atmosphere. For safety reasons, nZVI is thus in most cases provided as slurry. However, in suspension it also oxidizes fairly rapidly to iron oxides. Possible oxidants – besides the target contaminants - are oxygen, sulphate, nitrate or water. This fact has implications not only for the application in the soil, but also for its transport and storage. As described in chapter 7.1 nZVI-suspensions may have to be

transported in air-conditioned containers to minimize oxidation reactions and thus H₂-production. For these reasons, the transport and storage time should be kept minimal.

Lowry (U.S.EPA, 2005) showed that the lifetime of the particles depends on the pH of the suspension, and also on the particle type. For instance at pH 8-9 it took about two weeks to oxidize nearly all of the ZVI in the Fe(B), whereas in the RNIP material it took about a year. However, when the pH was reduced to 6.5, the RNIP iron particles were also oxidized after about 2 weeks. He concludes that the hydro- and geochemistry also play a major role in the lifetime of the particles.

Mobility

For the effectiveness of the remediation with nZVI also the particle mobility is crucial. Unfortunately, nZVI particles tend to agglomerate and adhere to soil surfaces resulting in a limited dispersion below ground and thus in a less effective treatment of the contaminated ground water (ZHANG, 2003). According to Lowry (U.S.EPA, 2005) and the AAV (http://www.aav-nrw.de/aav/dokumente/projektinformation/bornheim_ferster.pdf) the transport of unmodified nanoiron in porous media is limited to a few meters. Experiments at the University of Stuttgart have also shown that the mobility of untreated, pure nZVI was even limited to a few centimeters. Particles treated with magnetite and coated with a surfactant moved around 10 cm. Harch Gill (U.S.EPA, 2005) considers about 3-30 m to be a realistic radius of influence.

In a large-scale controlled laboratory experiment at the University of Stuttgart Fe(0) concentrations were measured against time and particle movement. Induction coils were used to measure the amount of magnetic iron (Fe(0)) in the container. In total, 900 L of suspension (with 10 g nZVI/L) were injected at a flow rate of 1000 L/h. It was found that after about 1 h (Fig. 2), the iron concentration at 0.2 m from the injection had reached 18 g/kg, at 0.4 m it was 9 g/kg, at 0.8 m it was 3 g/kg and at 1.5 m the iron content was less than 1 g/kg. (The geogenic iron oxide content is about 55 mg/g.)

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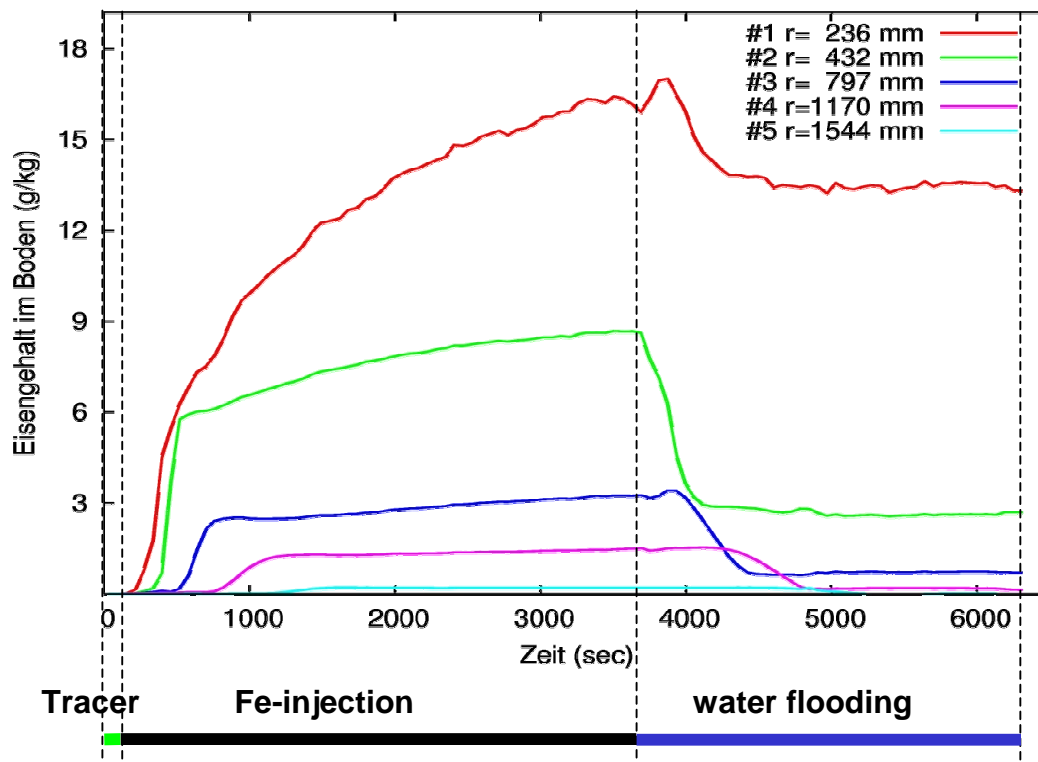


Fig 2: The graph displays the iron content (y-axis) dependency on the time (x-axis) at five different distances (236mm = red line, 432mm = green line, 797mm = blue line, 1170mm = pink line, 1544mm = turquoise line) from the injection point (DE BOER et al., 2009).

The particle inherent mobility depends mainly on two factors: size (degree of aggregation) and pretreatment (dispersion, surfactants). It is not yet clear if a primary particle and an aggregate of the same size behave differently.

According to Wei-Xian Zhang from Lehigh University single particles that are around 100-150 nm have the highest mobility (U.S.EPA, 2005). Jürgen Braun (from the VEGAS research facility at the University of Stuttgart) concluded from their experiments that the transport behaviour of particles in the lower nano-range will not necessarily be optimum. He estimates that – depending on the permeability of the soil – particles between 0.1-5 μm have the highest mobility. A similar optimum size range was stated by Johannes Bruns from Golder Associates (optimum particle mobility at 1-2 μm). Large-scale field tests are planned at the VEGAS research facility to find out whether the optimum size is in the upper nano or in the lower micron-size. If the ideal particle size is greater than 0.5 μm , the particles could be handled as powder (rather than as slurry) which would significantly reduce the material volume and thus facilitate the material handling.

Phenrat et al. (PHENRAT et al., 2007) studied the aggregation of nZVI particles at different concentrations by dynamic light scattering. They found that at very low concentrations (about 2 mg/L) the particle size increased from 20 nm to a final size of about 125-1200 nm after 10min. At high concentrations (about 60 mg/L), most of the particles reached their final size at about 20-70 μm after 30 minutes. Lowry presented similar results at the U.S. EPA Workshop in 2005 (U.S.EPA, 2005). Because of the tendency to aggregate, Lowry concludes that the individual particles should thus optimally be between 20 and 50 nm (U.S.EPA, 2005).

One possibility to increase the mobility of nZVI is by surface coating the particles with e.g. polyelectrolyte, surfactants, and cellulose/polysaccharides (U.S.EPA, 2005). Černík compiled the following surface modifications: inihcor-T, starch, carboxymethylene cellulose, polyacrylic

acid, cellulose, tween60 and 80. Matching surface modifications to site geochemistry offers the potential for well controlled placement. Lowry (U.S.EPA, 2005) states that it is possible to select the distance one would like the particles to move based on the surface coating. However, it is important to note that the design of particles is always a trade off between high reactivity and stability/mobility.

Other possibilities to increase the stability, reactivity and/or the mobility of nZVI-particles are to combine them with other metals (→ bimetallic nZVI), carbonaceous material (→ nZVI on carbon support) or embed the particles in organic membranes (→ emulsified nZVI).

3.1.2 Emulsified nZVI (EZVI)

nZVI is efficient in the destruction of chlorinated organic compounds. But it has a limited mobility and needs to be in the presence of water to promote reductive dehalogenation. The injection of ZVI into a source zone of dense non-aqueous phase liquid (DNAPL) thus only treats the dissolved phase at the edges of the DNAPL (U.S.EPA, 2005).

Researchers at the NASA Kennedy Space Center and the University of Central Florida have thus developed a new method for the delivery of nZVI which has been successfully commercialized (see paragraph: 6.1 companies). Emulsified Zero-Valent Iron (EZVI) was designed for the in-situ treatment of dense non-aqueous phase liquids (DNAPLs) and is one of the few methods that can treat the DNAPL source. Details on EZVI can be found in <http://nasaksc.rti.org/ezvi.cfm>.

EZVI is composed of an iron core (micro or nanoparticles) surrounded by water and packed in a droplet surrounded by food-grade surfactants and biodegradable vegetable oil which form a oil-liquid membrane (see figs. 3 and 4). The droplet is about 15 µm in diameter when using a nZVI-core. Laboratory studies indicated that a more stable and reactive emulsion can be produced with smaller iron particles.

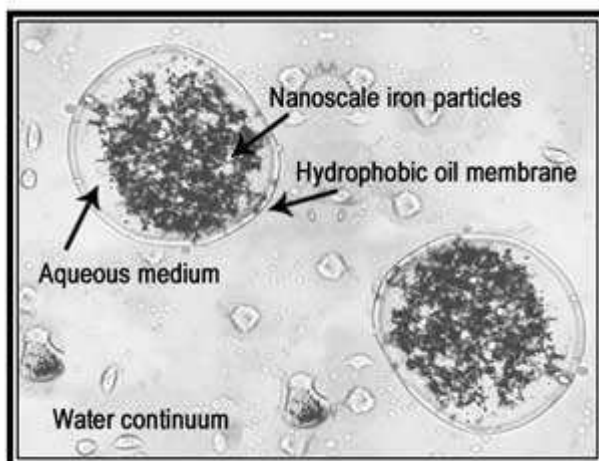


Figure 3: Structure of an EZVI particle (source: <http://nasaksc.rti.org/ezvi.cfm>)

The hydrophobic membrane allows the DNAPL to diffuse through the membrane where it undergoes reductive dechlorination by the ZVI in the aqueous phase. As EZVI is also a DNAPL, it will move in the subsurface in the same way as the target DNAPL which increases the contact between the EZVI and the target DNAPL. According to the NASA, EZVI is thus quick and very cost-effective. Unlike other reductive technologies, EZVI is capable of working in sites with high dissolved oxygen or under saline conditions. The oil membrane around the iron particles protects them from corrosion.

Based on the success of the field tests, NASA licensed EZVI to seven companies (see chapter 6.1) that are producing their own versions of the technology and is now used at commercial and government sites to treat trichloroethylene (TCE) and perchloroethylene (PCE). About 11% of the remedial actions with nZVI are carried out with EZVI. In Europe there is no company working with EZVI. The reason is concerns about the injectability of an emulsified suspension. Some experiments with EZVI were carried out at the Technical University of Liberec with ambiguous results.

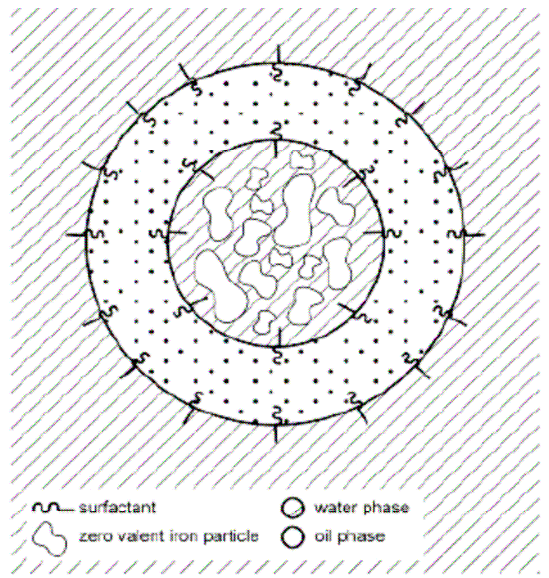


Figure 4: Schematic picture of an EZVI droplet showing the oil-liquid membrane surrounding the ZVI particles in water (QUINN et al., 2005)

3.1.3 Bimetallic Particles (BNZVI)

nZVI can be doped with a catalyst such as Pd, Pt, Cu, Ni, Ag to improve the performance (KARN et al., in press; NOWACK, 2008; U.S.EPA, 2005). Palladized Fe particles are prepared by soaking the freshly prepared nanoscale iron particles with an ethanol solution containing 1wt% of palladium acetate ($[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$). This causes the reduction and subsequent deposition of Pd on the Fe surface (WANG and ZHANG, 1997). Similar methods were used to obtain other bimetallic particles such as Fe/Ag and Fe/Ni (HOUBEN and KRINGEL, 2007; SCHRICK et al., 2002; XU and ZHANG, 2000).

BNZVI have a higher reaction rate but consequently a shorter lifetime. In Europe no field application of BNZVI has taken place - mainly due to concerns regarding the toxicity of the catalysts (e.g. Ni is considered to be a priority hazardous substance under the EU Water Framework Directive.) In the U.S. about 40% of the nZVI-remediations use BNZVI (and 50% standard nZVI). Miroslav Černík from the University of Liberec states that the reaction with BNZVI is too fast and due to the short lifetime of the particles in an aquifer not sustainable for remediation. Experts in Europe agree that the possible advantage of BNZVI (higher reactivity) does not outweigh its disadvantages (possible toxicity, higher costs). They further found that BNZVI-particles are oxidized before they reach the target area.

3.1.4 nZVI on Carbon Support (c-nZVI)

As mentioned in previous paragraphs, nZVI particles tend to agglomerate and adhere to soil surfaces resulting in a loss of effectiveness in remediation (ZHANG, 2003). To enhance the nZVI distribution in contaminated aquifers, nZVI particles can also be linked to colloidal active carbon nanoparticles which are used as a support for iron or bimetallic compositions (<http://www.ufz.de/index.php?de=7038>). c-nZVI was developed at the Helmholtz Centre for Environmental Research in Germany. The carbon platelets are 50–200 nm in diameter and thus smaller than the silt size in essentially all soils (PARBS and BIRKE, 2005).

These sorption/reaction-systems are promising for the degradation of chlorinated hydrocarbons. The combination of activated carbon as a sorbent and ZVI as reductive enhanced the remediation rate through improved distribution in the media (figs.5 and 6). An additional argument is that carbon and iron are both nontoxic and relatively inexpensive.

Unfortunately there are no pilot tests with c-nZVI particles yet. It is thus unclear whether they represent a valuable alternative to nZVI treated with surfactants. Additionally it must be expected that the costs for these functionalized nZVI-particles would be significantly higher than for “conventional” nZVI particles.

A joint research project (NANOSIT) with the partners Helmholtz Zentrum für Umweltforschung UFZ and Golder Associates is expected to start in May 2010. The aim is to assess the effectivity of c-nZVI in lab investigations and field applications. The project is financed by the German Government (Ministry for Education and Research).

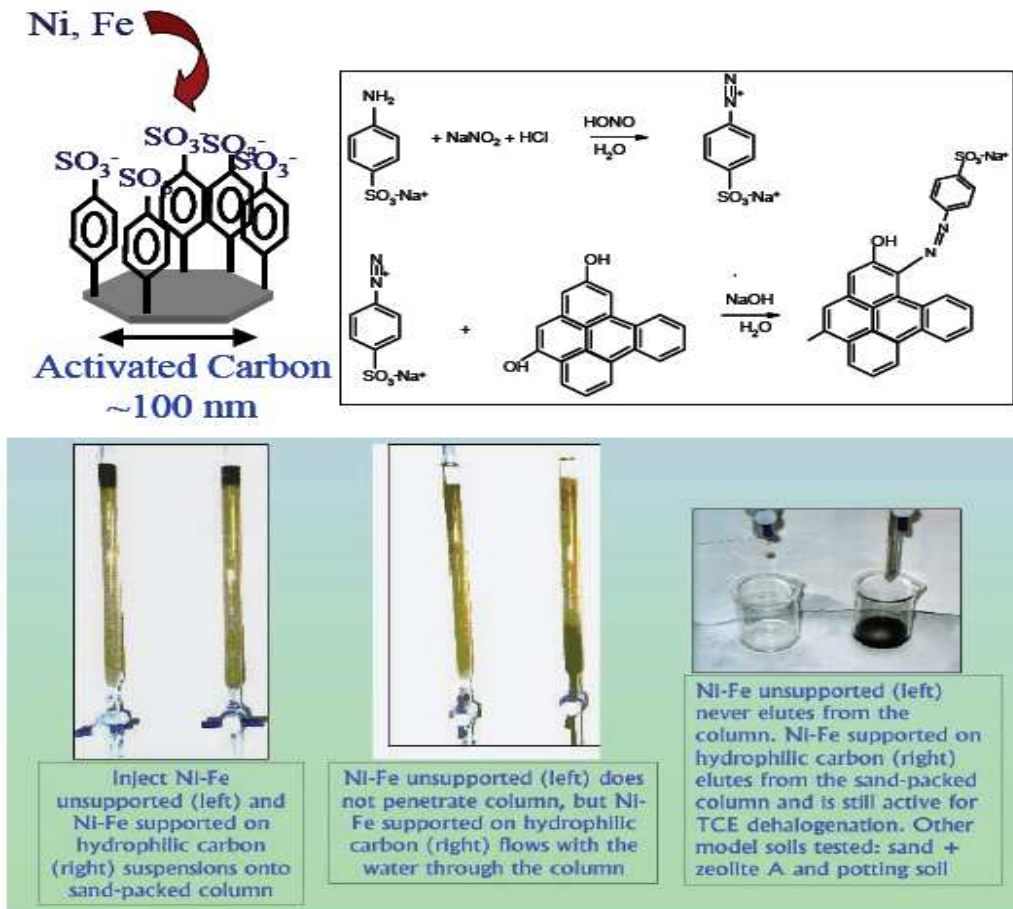


Figure 5 : Carbon support for ZVI. Ni-Fe-particles on carbon support were shown to penetrate the sand-packed column whereas unsupported Ni-Fe-particles were unable to elute from the column (SCHRICK et al., 2002).

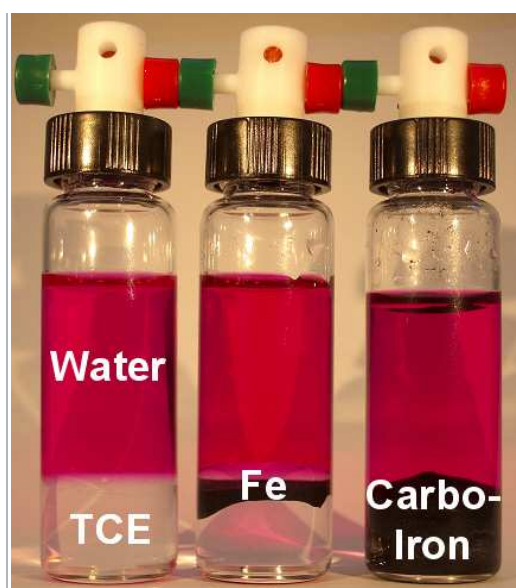


Figure 6: Solubility and distribution of Fe and Carbo-iron in TCE (<http://www.ufz.de/index.php?de=7038>)

In a similar manner as active carbon, water-soluble polyelectrolytes such as polyacrylic acid (PAA) have been used as nanoparticle supports (PARBS and BIRKE, 2005). PAA-supported nanoparticles showed a dramatic enhancement in permeability both towards pure sand and natural soils (PONDER et al., 2001; PONDER et al., 2000; SCHRICK et al., 2002).

3.2 Reactions of nZVI with Contaminants

3.2.1 nZVI as Reductant

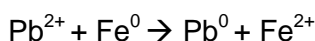
Zero valent iron is a moderate reducing agent. In an aqueous media, ZVI will react with dissolved oxygen, water and if present with other oxidants such as nitrate and possible contaminants (see chapter 4.2). Due to the redox reactions taking place, the application of nZVI results in an increase of the pH and a decrease of the oxidation-reduction potential (ORP). The consumption of oxygen further leads to an anaerobic environment while the reduction of water yields hydrogen.

If chlorinated hydrocarbons are present, the following reaction takes place:



There are two pathways for the degradation of chlorinated hydrocarbons by nZVI (KARN et al., in press). The first is hydrogenolysis through sequential dehalogenation (PCE to TCE to DCE to VC to ethene). The second is beta elimination (TCE to chloroacetylene to acetylene to ethene). The latter occurs in 70-90% of the reactions with nZVI – primarily when the contaminant comes in direct contact with the nZVI (KARN et al., in press).

If nZVI reacts with ionic heavy metals such as Pb^{2+} , the following reaction takes place:



In this case the ionic heavy metals react into their elementary form or into insoluble salts (MÜLLER et al., 2006).

More information on reactions with nZVI are summarized in (MÜLLER et al., 2006). That article also gives an overview over the reaction kinetics of different contaminants with nZVI.

3.2.2 Target Compounds

The range of possible applications is wide as nZVI can not only effectively degrade or immobilize organic contaminants but also inorganic anions such as perchlorate (MÜLLER et al., 2006; NOWACK, 2008; PARBS and BIRKE, 2005; RICKERBY and MORRISON, 2007) and it can even be used to recover/remove dissolved metals from solution (MÜLLER et al., 2006; NOWACK, 2008; PARBS and BIRKE, 2005). Zhang et al. found nZVI to be effective also against PCB and organochlorine pesticides (ZHANG, 2003). According to David Sedlak (U.S.EPA, 2005) nZVI acting as an oxidizing agent, might also be used to treat low concentrations of recalcitrant, miscible, volatile organics such as MTBE, MTBA, and 1,4-dioxane. Other experts doubt that nZVI could be used as oxidizing agent.

Walter Kovalick from EPA (U.S.EPA, 2005) reports that from 15 field scale applications, nZVI was in most cases used to treat a source zone of TCE, TCA, and daughter products and some of the sites were contaminated with Cr(VI). The U.S. Navy promotes nZVI for the treatment of source zones contaminated with chlorinated organic compounds and dense non-aqueous phase liquid (DNAPL) especially chlorinated alkenes such as perchloroethene (PCE) and trichloroethene (TCE) (U.S. NAVY WEBSITE ON NZVI, Aug. 2009 (last visit)). Golder Associates suggests nZVI for the treatment of chlorinated solvents, Cr^{6+} and perchlorate.

According to the EuroDemo report (PARBS and BIRKE, 2005), iron particles are not suitable for creosote or coal tar DNAPLs, because the reductive power of Fe(0) is too small for reductions of aromatic ring systems (as in e.g. PAHs).

The following list summarizes possible target compounds:

- chlorinated methanes (e.g. Chloroform)
- chlorinated ethenes
- chlorinated benzenes
- Pesticides (DDT, chlorinated cyclohexanes, Lindane)
- Other polychlorinated hydrocarbons (e.g. organic dyes, PCB, Dioxins)
- Inorganic anions (e.g. dichromate ($\text{Cr}_2\text{O}_7^{2-}$), arsenate (AsO_4^{3-}), perchlorate (ClO_4^-), nitrate (NO_3^-))
- Heavy metals: Zn, Cd, Be, Ni, U

Nanoiron – a Czech company which produces nZVI-particles – has also a list of contaminants on their website: <http://www.nanoiron.cz/en/?f=contaminants>.

Realistic degradation efficiencies of those contaminants in the field are between 60-80% within one year. But reductions of up to 99% could be achieved in some projects and batch experiments.

3.3 Technical Challenges

The following issues were compiled which need further attention by researchers (U.S. NAVY WEBSITE ON nZVI, Aug. 2009 (last visit); U.S.EPA, 2005):

- Iron passivation (non-target reactions)
- Particle agglomeration
- Incomplete knowledge of mechanism — abiotic versus biotic degradation
- Difficulty to predict particle movement
- Production of hydrogen may reduce permeability
- Possible intermediate (DCE) accumulation
- Transfer from lab (excellent results) to field: difficulty to predict reactivity, particle distribution, hydro and geochemistry, hydrology, geology and microbiology and thus the design of the injection technology, monitoring, upscaling regarding mixing, well conditioning, pretreatment of aquifer with additives etc to facilitate nZVI distribution
- Specialized equipment for mixing and injection
- Potential rebound of contaminants after in situ injection of nZVI

3.4 Toxicity

According to Lowry (U.S.EPA, 2005) ZVI can indirectly cause oxidative stress which indicates a potential toxicity. The radicals and charged particles formed in the Fenton's reaction may penetrate brain cells. When mammalian brain macrophages (microglia) were exposed to iron particles, they took up the iron, which appeared to affect the mitochondria. Both ZVI and magnetite appear to cause oxidative stress at high iron concentrations (U.S.EPA, 2005).

Peter Rissing from Alenco GmbH states that long-term adverse effects on the environment are unlikely, because the longevity of the reactive particles is very limited. After the reaction with the contaminants or other reducible compounds, the iron particles will stay in the soil and form iron sediment which also occur naturally.

Golder Associates (U.S.EPA, 2005) reports on a pilot scale case study where they injected 6,050 liters of slurry containing 11.2 kg of bimetallic nanoparticles (BNP) into fractured interbeds of sandstone and siltstone. They found no significant trends when sampling

microbes before and after the injection. It was also found that less reactive nanoparticles (containing less palladium) will be active in the aquifer for a longer period and will thus travel farther.

On other sites Golder Associates found that nZVI injections render the microorganismic community less diverse for 6 months. But on the other hand nZVI can also be used for enhanced bioremediation. After TOC drops to 20mg/l the remediation of CAH changes from abiotic to enhanced bioremediation (within several months). These effects can be observed for up to 2 years. It is assumed that the reductive, anaerobic environments resulting from nZVI remediation may enhance the growth of bacteria that can further reduce the contaminant (ELLIOTT and ZHANG, 2001).

A study by Gilbert et al. (GILBERT et al., 2007) posts that oxidized nZVI could sorb contaminants and serve as carrier. Contaminants could in this case spread in the groundwater.

Karn has assessed different (governmental) position papers (e.g. from Royal Society, EC, Quebec commission, EPA) and found that in general nZVI for remediation is looked on as more beneficial than harmful but that it is the biggest source of environmental exposure and thus needs more research on its effects.

4 Economic aspects

Based on its relatively broad applicability Miroslav Černík from the University of Liberec estimates that around 100 sites in the Czech Republic and at least 1'000 sites (about 5% of all contaminated sites) in the EU could be remediated with nZVI. European experts estimate that the total market share of nZVI will not exceed 5-15%.

4.1 Companies

In the USA numerous companies are working with nZVI for environmental remediation (e.g. Pars Environmental (www.parsenviro.com)). The Emulsified Zero-Valent Iron (EZVI) technology - patented by NASA - is currently licensed to the following companies:

- GeoSyntec Consultants <http://www.geosyntec.com>
- Huff & Huff, Inc. <http://www.huffnhuff.com>
- RNAS, Inc. <http://www.rnasinc.com>
- Starlight Environmental Group, Inc. <http://www.starlightenvironmental.com>
- Terra Systems, Inc. <http://www.terrasystems.net>
- Toxicological & Environmental Associates (TEA), Inc. <http://www.teainconline.com>
- Weston Solutions, Inc. <http://www.westonsolutions.com>

Among them, Weston Solutions is the only one working outside the U.S. It has office locations in Korea, Japan, UAE, Afghanistan, Canada and India. In Asia GeoNano Environmental Technology, Inc. is marketing nZVI for remediation of soil and groundwater: <http://gnet.myweb.hinet.net/>. In South America a company named Nanoteksa produces nanoscale iron: <http://www.nanoteksa.com/>

The following companies are working with nZVI for environmental remediation in Europe.

4.1.1 Alenco Environmental Consult GmbH

A German company (former Alstom Power Environment Consult) offering laboratory studies, field test and full-scale remediation. The website offers a lot of detailed information on nZVI; injection technology and costs. Alenco has performed three field tests and one full scale application of nZVI. All projects were in Germany.

→ www.fe4u.com (site in German)

4.1.2 Golder Associates

Golder Associates – an originally Canadian company - is now working worldwide. The company has 34 offices in Europe in 15 different countries. Golder has performed more than 40 projects with nZVI worldwide since 2002 - most of them in the U.S. Projects in Europe have been carried out in the Czech Republic, Italy and Germany since 2004. In 2006 a pilot scale remediation of a CHC/chromate/nickel impact (in combination with pump & treat) was run in Thuringia (Germany). Worldwide Golder Associates has implemented nZVI treatments at 20 sites, achieving up to 99 percent reduction in source concentration.

→ www.golder.com

Golder has established a Nanomaterials Risk Group to assess the potential risk from the nZVI injection in soil. The contact person is Larry Kapustka (lkapustka@golder.com).

4.1.3 Aquatest

Aquatest is a Czech consultancy company working in the field of water management and environmental protection. It has projects in 10 countries. So far 2 full scale remediations with nZVI and about 10 pilot projects have been carried out in the Czech Republic and Slovakia.

→ www.aquatest.cz/

4.1.4 Nanoiron

This company was founded in 2008 in the Czech Republic. It produces nZVI particles (NANOFER) for environmental remediation. NANOFER is delivered in different forms (surface modified, unmodified, dry, as slurry).

→ www.nanoiron.cz

4.2 Costs

4.2.1 nZVI

In 2004 the prices for nZVI or bimetallic iron varied between €30 and €102 per kg. Micro-scale iron and granular iron were available for less than €1 per kg (Nancy Ruiz (U.S.EPA, 2005)). Compared to the cost for nZVI and EZVI, the cost for micro-scale ZVI is significantly lower and for BNZVI significantly higher.

Depending on the amount ordered and the modifications, nZVI today (2009) costs around €100-125/kg of pure iron. Prices for slurries are difficult to compare because they contain different amounts of nZVI (e.g. TODA offers between 30-70% of zero-valent iron (rest is mixture of oxides) compared to NANOFER (80-90% of zero-valent iron)). One expert mentioned a price of €10/kg pure iron.

4.2.2 Costs for Treatment/Remediation

The Navy Website on nZVI (U.S. NAVY WEBSITE ON nZVI, Aug. 2009 (last visit)) indicates the cost for a site remediation to be about €120-200 per m³ of contaminated soil in the identified source zone. The major cost items are:

- Size of area to be treated
- Number of monitoring and injection wells
- Injection method
- Amount of nZVI required
- Sampling and analysis for performance and compliance monitoring

Alenco GmbH estimates the costs for a field study around €35'000 +/- 15'000 depending on the site conditions and the extent of the contamination. Actual costs for a full-scale project were found to be about €290 per kg of contaminant or €366/m³. As it is difficult to estimate the amount of contaminants, it is usually appropriate to calculate the remedial cost based on the volume of treated aquifer. After a field study, the costs can be estimated more precisely.

4.3 Practical Experience

4.3.1 Regulations and Acceptance by Governmental Bodies in Europe

There is no European country which has - to our knowledge - specific regulations on the use of nanomaterials for environmental remediation. Concretely, there is no country which explicitly prohibits the use/application of nZVI. This means that the use of nZVI has to be evaluated by the governmental agencies by means of the current laws and regulations on chemical substances. In contrast to the U.S., most agencies are – based on the precautionary principle – rather cautious; especially since there have been only a few full scale remediations carried out in Europe so far.

The following list summarizes the situation in different European countries:

Table 3: Overview over nZVI-acceptance in some European countries

Germany	<ul style="list-style-type: none"> - Authorization by regional environmental agencies / State agencies - At least one full scale remediation has been carried out
UK	<ul style="list-style-type: none"> - Potential authorization by national Environmental Agency - No field implementation so far - Unclear whether a nZVI-remediation project would/could be stopped - Waiting for more information on toxicity and environmental fate
Finland	<ul style="list-style-type: none"> - Potential authorization by regional environmental agencies (after consultation of municipal and national agencies) - Situation comparable to UK
Italy	<ul style="list-style-type: none"> - National Environmental Agency is rather open-minded towards nZVI - Pilot tests carried out
Czech Republic	<ul style="list-style-type: none"> - National Environmental Agency is open-minded towards nZVI application - Several projects completed

For all other countries it is not known whether a remediation project with nZVI would be accepted.

4.3.2 Requirements regarding Site Characteristics

Site Characteristics and Evaluation

Before injecting nZVI, a precise site model is needed that includes the site hydrogeology as well as the geochemistry (KARN et al., in press). The hydrogeology influences the transportability and the lifetime of the particles (see previous chapters) while the geochemistry shows potential substances that nZVI could react with (other than the target compounds). In a case study at a Navy site, the amount of nZVI chosen was based on a straight stoichiometric calculation (how much would be needed to treat about 60 kg of TCE). The monitoring showed that this was by far not enough. Nancy Ruiz (Navy) concludes that it would have been better if the geochemical conditions in the subsurface were also considered in the calculation to ensure a sufficient amount of nZVI to accommodate non-target reactions.

Before a remediation starts a three step evaluation process must be carried out.

First step: Geology, hydrogeology, geochemistry and microbiology of the site are assessed and the contaminant(s) are determined.

Second step: In laboratory tests, it is investigated whether the remediation with nZVI promises to be successful.

Third step: If the lab tests are ok, a pilot test is carried out in a small area of the site. This test provides further information on the amount of nZVI needed and possible unexpected challenges. It further allows a vernier adjustment of the injection parameters (pumping, concentration, velocity etc.)

Field applications have been conducted in porous aquifers, fractured rocks and unconsolidated sediments. It is generally agreed that remediation in dense geological formations is less efficient.

Media treated

In the U.S. nearly three quarter of the site remediations targeted groundwater. About one fifth involved the treatment of groundwater and soil simultaneously and only a few sites treated sands, clayey silts or soils (fig.7).

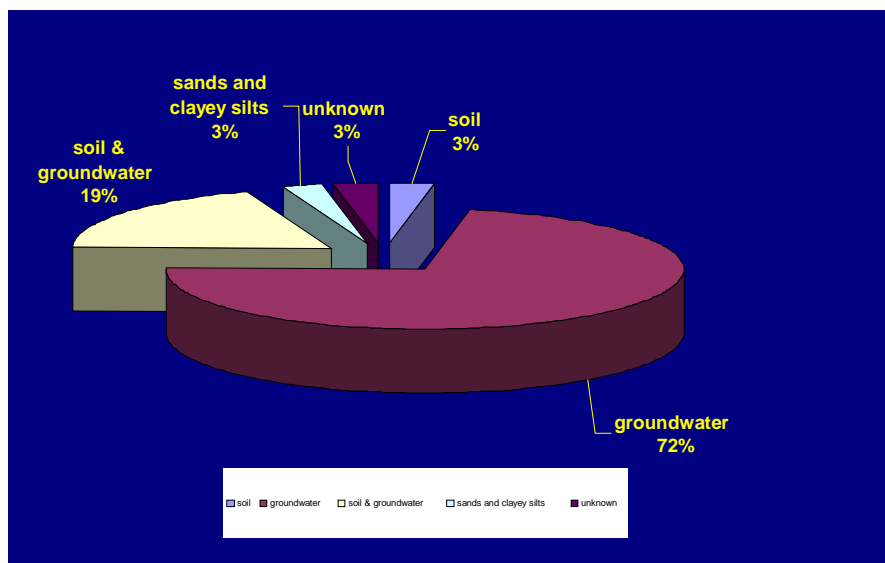


Fig 7: Application of nZVI to different media. 37 site remediations were analyzed. Almost three quarter of them targeted groundwater and another fifth groundwater and soil. Source: Barbara Karn, U.S. EPA

Experts agree that unsaturated media are difficult to target. One possibility is to flood the contaminated site before the treatment.

There is no agreement whether nZVI should be used for plume remediation only or whether source remediation is also feasible. It is clear though that source remediation would require a very high amount of reactive particles. In some cases this may still be economically viable.

4.3.3 Injection Process and Technology

nZVI (particle size, total mass, concentration)

nZVI-particles used for remediation are usually about 50-300 nm in diameter (U.S.EPA, 2005). Due to the fast aggregation process, it is difficult to get aggregates smaller than 1 μ m in the field despite mixing.

Aquatest identified an injected concentration of 1-2 g/L to be sufficient for plume treatment and to ensure particle mobility. They found that the particle mobility decreases with increasing concentration (for concentration in range of grams/L). Other experts found higher concentrations (10-30g /L) to be more mobile. It was agreed though that there is a trade off between injection velocity and injected concentration.

A slurry of nZVI can be introduced into the subsurface using a variety of carrying fluids such as water, nitrogen gas or vegetable oil (U.S. NAVY WEBSITE ON NZVI, Aug. 2009 (last visit)). This helps dispersing the nZVI-particles in the target area.

nZVI has a relatively short lifetime which typically requires more than one treatment to remediate a site. The required total mass of nZVI and the injection interval (number of reinjections) depends on:

- Volume of contaminated soil and groundwater
- Contaminant concentration, phase (separate or dissolved) and total mass
- Aquifer characteristics including permeability and anisotropy
- Groundwater chemistry
- Incidental biodegradation rates

Golder Associates injected between 10k g and 4.5 t per site. For pilot tests 10-100 kg are used. In Europe 1.3 t was the largest amount applied on a site.

Wells

The well density depends on the radius of influence from each injection point and thus on the particle movement. In chapter 3 the particle inherent factors (size, functionalizations) were described. Other important determinants are: The geology (permeability, pore size, heterogeneity of the aquifer)

- The injection technology (nZVI concentration in the slurry, injection velocity)

Studies at the University of Stuttgart have shown that within 20 min the particles moved between 100-900 mm at an injection velocity of 0.6 m/h to 3.2 m/h respectively (at a constant concentration of 30 g/l). In a radial flow from the injection point, the velocity decreases exponentially with an increasing distance from the injection point. The significance of this space dependency in flow velocity of the mobility of the particles is currently being investigated at the VEGAS research facility (DE BOER et al., 2009).

The distance from well to well should be in a similar range as the projected particle movement – thus a few meters (e.g. in the remediation project in Bornheim (see chapter 7.1), the radius of injection was around 2 m).

Hydraulic bedrock fracturing conducted by Golder Associates in the U.S. in Triassic Basin sediments achieved a radius of influence of >20 m (>70 feet) based on visual observation of particles in observation wells.

In Jacksonville (U.S.EPA, 2005) a recirculation system was set up with four injection wells and three extraction wells. Extracted water was pumped to a holding tank where it was mixed with nZVI and reinjected. The purpose of the recirculation system was to keep the iron in the source zone and facilitate mixing. The problem encountered was that oxygen was introduced during recirculation which passivated the nZVI. Nancy Ruiz highlighted that in future designs of these systems, care should be taken that no oxidizing agents are introduced during storage or mixing.

Injection Technology and above-ground Equipment

According to Florin Gheorghiu from Golder Associates (U.S.EPA, 2005) generally only little infrastructure is needed for the injection of nZVI compared to conventional methods and the system allows for modification over time. Peter Rissing from Alenco GmbH reported that quite some infrastructure is needed to store and handle the large volumes of nZVI suspensions such as air-conditioned containers, deagglomeration equipment, mixing tanks and a ventilation system (see figure 9).

Typically, nZVI injection is accomplished with the following four methods (U.S. NAVY WEBSITE ON NZVI, Aug. 2009 (last visit)):

- *Direct push techniques* involve a direct push rig or stationary injection point to introduce nZVI into the treatment zone.
- *Pneumatic fracturing* uses air to create a fracture network of preferential flow paths around the injection point and enhance nZVI distribution.
- *Pressure pulse technology* uses regular pulses of pressure while injecting the nZVI slurry, which forces the slurry forward through the subsurface.
- *Liquid atomization injection* combines an nZVI-fluid mixture with a carrier gas (e.g. nitrogen) to create an aerosol that can be dispersed into the treatment zone.

The injection pressure used in porous media is less than 1-2 bar.

The U.S. EPA (U.S.EPA, 2005) has analysed 15 field scale applications of nanoiron or bimetallic nano-scale iron. In a majority of these studies, nanoiron was applied by gravity-feed or low pressure injection. Alenco GmbH conducted three pilot tests in Europe with push-infiltration and sleeve pipe injections.

At the Kennedy space centre EZVI was applied by pressure pulse technology with pulsing applied every $\frac{3}{4}$ of a second. The pulsing causes a dilation of the pore structure in the subsurface, which allows the pulsed fluid to enter more of the formation. Nevertheless, at Kennedy space centre it was difficult to get the emulsion to the desired depths.

Injection pressure should not exceed the overburden pressure; otherwise the suspension will not distribute horizontally but instead the suspension (and contaminants) may be pushed to the surface. Special attention has to be paid to this fact when contaminants are at a low depth.



Fig. 8: Slurry feeding during treatment. © Aquatest, Czech Republic

Monitoring

Continuous site monitoring is crucial to assure longterm effects. If rebound effects are observed, reinjection might be necessary. Nancy Ruiz (Navy) states that Oxidation-Reduction-Potential (ORP) levels are a good long-term monitoring performance parameter.

At a site in northern New York State, Golder Associates measured 51%-99.9% reductions in TCE (from 1,900 $\mu\text{g/L}$ to 2 $\mu\text{g/L}$ and from 750 $\mu\text{g/L}$ to 370 $\mu\text{g/L}$, respectively). Reductions are continuing after 3 years of the initial nZVI treatment using geoprobe injections. However, in several other studies a significant rebound occurred, which asks for careful long-term monitoring and adaptation of the project if necessary.

4.4 Case Studies in Europe

Karn et al. (U.S.EPA, 2005) have compiled a nice overview of some of the sites treated with nZVI. Some details about these sites can be viewed at the website: http://www.nanotechproject.org/inventories/remediation_map. Other detailed descriptions of case studies in the U.S. are found in (U.S.EPA, 2005), on <http://nasaksc.rti.org/ezvi.cfm> and on <http://www.parsenviro.com/reference/klockner-ngt-III-2005.pdf>.

4.4.1 Pilot projects

In Europe a couple of pilot studies and a few full scale remediations have been conducted (e.g. in the Czech Republic, Italy and Germany). Subchapters 7.1-7.4 present the full-scale remediations carried out in Europe so far. The following table summarizes the European pilot projects with nZVI.

Table 4: Pilot tests in Europe: Overview

Site	Date	Contaminant	Amount of nZVI	Particle type	Injection technique	Media	Source
Spolchemie, CZ	2004, 2009	Cl-Ethenes	20 kg	Fe(B)	Infiltration wells	Porous aquifer	a), b)
Kurivody, CZ	2005, 2006	Cl-Ethenes	50 kg	Fe(B), RNIP	Infiltration wells	Fractured bedrock	a), b)
Piestany, CZ	2005	Cl-Ethenes	20 kg	Fe(B)	Infiltration wells	High permeable aquifer	a)
Permon, CZ	2006	Cr(VI)	7 kg	RNIP	Infiltration wells	Fractured bedrock	a)
Rozmítal, CZ	2007-2009	PCB	150 kg	RNIP, Nanofer	Infiltration wells	Fractured bedrock	a)
Hluk, CZ	2007, 2008	Cl-Ethenes	150 kg	RNIP, Nanofer	Infiltration wells	PRB filter	a)
Uherský Brod, CZ	2008	Cl-Ethenes	50 kg	Nanofer	Infiltration wells	Porous aquifer	a)
Uzin, CZ	2009	Cl-Ethenes	150 kg	Nanofer	Infiltration drain	Low permeable aquifer	a)
Brownfield, SK	n.a.	TCE, DCE	n.a.	n.a.	n.a.	Unconsolidated sediments	e)
Biella, I	2005	TCE, DCE	10 kg	nZVI	Gravity infiltration	Porous aquifer	b)
Thuringia, D	2006	CAH, Ni, Cr, NO ₃ ⁻	120 kg	nZVI	Injection wells	Porous aquifer	b)
Hannover, D	2007	CHC, BTEX, HC	1 kg	n.a.	Aqueous slurry	Chemicals storage facility	c)
Schönebeck, D	2005	VC	70 kg	RNIP	Push-Infiltration	Porous aquifer	d)
Asperg, D	2006	Cl-Ethenes	44 kg	RNIP	Sleeve pipe	Fractured rock	d)
Gaggenau, D	2006	PCE	47 kg	RNIP	Sleeve pipe	Porous aquifer	d)

n.a. information not available, a) Aquatest, Czech Republic, b) Golder Associates, Germany, c) Bundesamt für Geowissenschaften und Rohstoffe, Germany (HOUBEN and KRINGEL, 2007), d) Alenco GmbH, Germany, e) http://www.nanotechproject.org/inventories/remediation_map

The results of the pilot applications differ largely. At one site in the Czech Republic contaminant concentrations remained low for 6 months; but increased thereafter to the original concentration. At another site (also in the Czech Republic) the contaminant concentrations were reduced permanently by 75-95% (PCE decreased from 2'500 µg/L to 500 µg/L, TCE from 1'500 µg/L to 100 µg/L and DCE from 1'000 µg/L to 250 µg/L). The remediation in Biella led to a reduction of the total chlorinated solvent concentrations (20'000 – 50'000 µg/L) by about 20-50% within one month. The pilot test in Thuringia conducted by Golder Associates also showed significant reductions in contaminants.

4.4.2 Full scale remediations

Bornheim, Germany

Bornheim (Rhein-Sieg-Kreis, Germany) was the first contaminated site in Europe where nZVI was used for a full-scale remediation (FRIEDL, 2006). The site was originally contaminated with several tons of perchlorethylene (PCE) from an industrial laundry/dry cleaner which had spread over several km² and up to 20 m depth. For 14 years the groundwater had been treated by “pump and treat”-technology and the air from soil pores had been extracted and treated. These measures could degrade around 5 tons of perchlorethylene at a cost of more

than one million Euro. It was estimated that the remediation with this methods would need to continue for another 50 years to completely remove all contaminants.

The 1-2 tons of perchlorethylene left in the ground (sandy gravel) were then addressed with nZVI (70 nm – stabilized by polycarboxylic acid). 1 t of nZVI and 2 t of microsize ZVI were pumped into the ground within one month (August 2007). The Fe-suspension (about 90g /l) was introduced by plastic tubes, which had small holes at 18 regular intervals and led the particles to 16-22 m depth (sleeve-pipe injection). 10 wells were placed on the area with an injection radius of 2 m each.

The nanoiron had to be imported from Japan (Toda RNIP) in air-conditioned containers to minimize oxidation (and thus the production of H_2 → danger of explosion) during the transport.

The remediation was conducted by Alenco Environmental Consult GmbH and cost about €290'000 (about €366/m³ or €290/kg PCE). The costs were distributed as follows:

Injection wells €80'000

Material and injection €195'000

Monitoring and documentation €15'000

→ These costs did not include the costs for site investigation as well as the costs for the regular monitoring programme.



Fig. 9: Set up at the site (indoor). Stirring tanks for nZVI resuspension. © Alenco GmbH, Germany

The results of the project are an approximately 90% reduction of the PCE concentration. Two years after the injection no rebound has been observed but there is still a trend for declining contaminant concentration (Fig. 10)

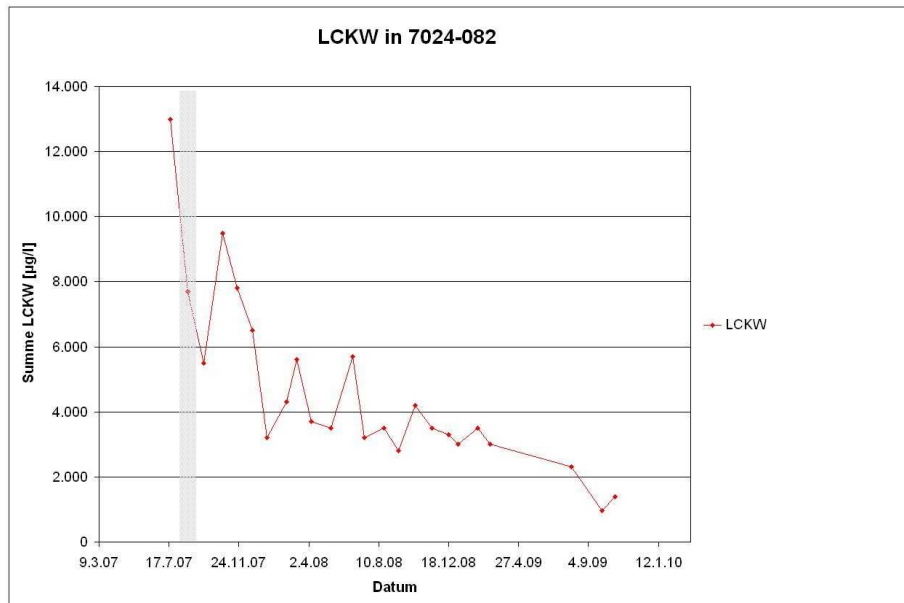


Fig 10: Contaminant concentration on the site in Bornheim. Monitoring results over 2 years. Source: Alenco GmbH, Germany

Horice, Czech Republic

The full scale application in Horice (Czech Republic) targeted an area of 120 x 60 m contaminated with PCE (TCE, DCE). The contamination was at a depth of 3-10 m. Contaminant concentrations were up to 70 mg/l. The hydraulic conductivity was low ($\sim 10^{-6}$ m/s).

In the first stage (11/2008), 82 injection wells were set up. 300 kg of nZVI (RNIP and NANOFER) were injected by a direct push method with a pressure of 0.8 MPa. Reduction to 25-40% (> 90 % (in the diffuse part)) of the original contaminant concentration were achieved (figure 11). In the second stage (11/2009) another 300 kg of nZVI were injected. The final results are not yet evaluated.

The costs can be summarized as follows:

Direct push well network: 80 wells x 10 m x 40€ = 32'000€

NanoFe: 300 kg x 5 x 23€ = 35'000€

Other (water, electricity, management): 30'000€

Monitoring: 100'000€

TOTAL (including monitoring) = 200'000€

The second stage cost another 100'000€ (shared monitoring).

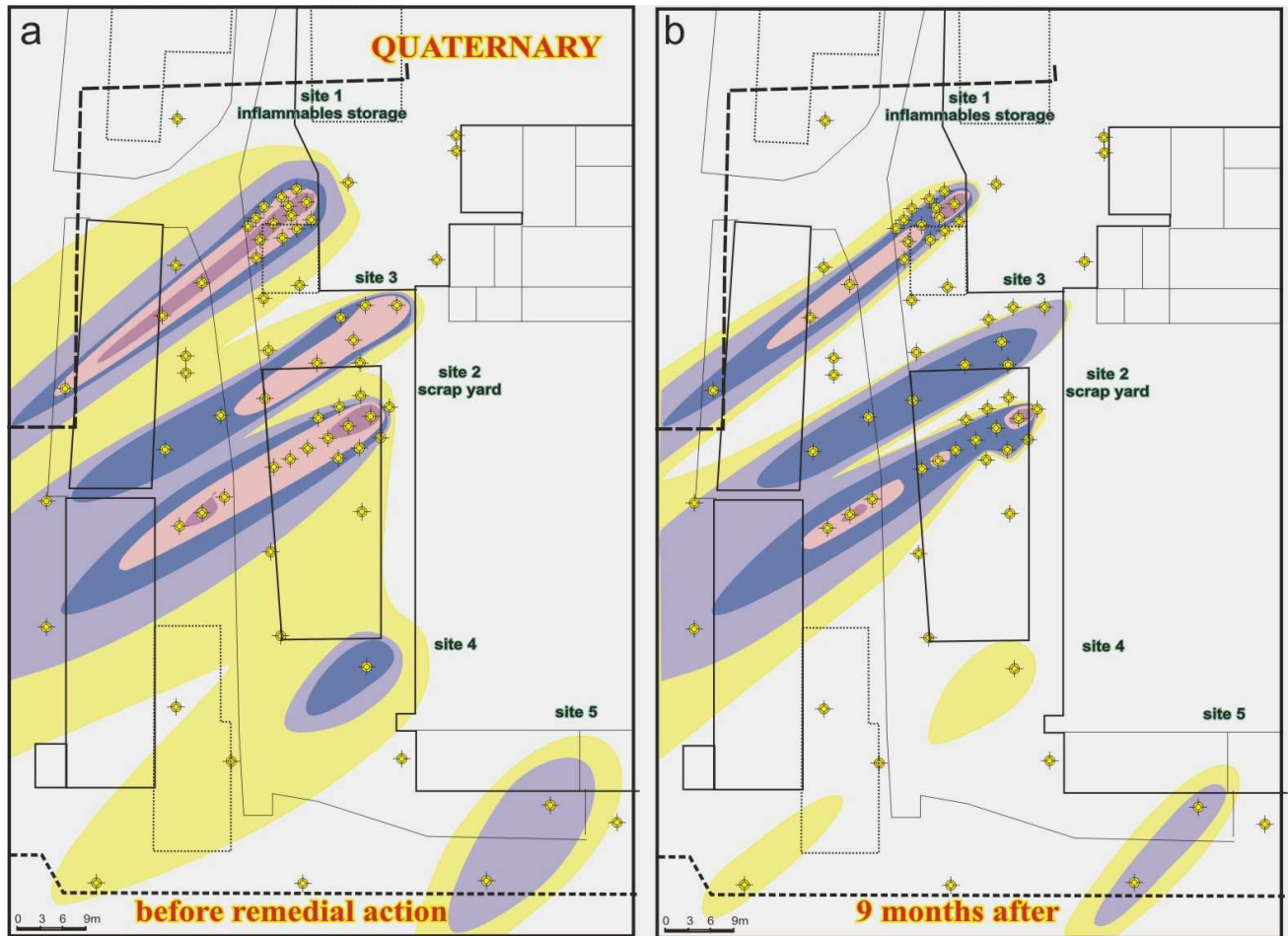


Fig.11: Monitoring of the full scale remediation in Horice. Left: before remedial action. Right: after 9 months. © Aquatest, Czech Republic

Pisecna, Czech Republic

In Pisecna the contaminated area was around 2000 m³. 30 wells were set up to treat about 1ton of chlorinated ethenes at a depth of 20-35 m bellow surface (figure 12). 1.3 tons of RNIP and Nanofer were introduced in three steps (2 tests with RNIP and NANOFER, 1 full scale application (NANOFER only)).

The total costs were around 360'000€ (nZVI: 140'000€, Wells: 60'000€, Other: 40'000€, Monitoring: 120'000€).

The results of the pilot test showed a significant decrease of CHC concentration of 40-80%. The full scale remediation started at the end of 2009 and results are not yet available.



Fig. 12: Remediation in Pisečna ©Aquatest, Czech Republic

4.5 Challenges

At first there is a general problem in environmental science which is not specific for nZVI, but all the same applies to this new technology and its commercialisation. While laboratory studies are unable to precisely simulate the environmental conditions, field work can rarely yield reproducible results. Mitch Lasat from the EPA (U.S.EPA, 2005) describes it as follows: "Research proposals for field work get bad grades because in field work it is hard to control the many variables. Therefore, universities usually have a preference for applied research than for field work."

Even though several companies are working with nZVI for the remediation of contaminated soils and groundwater, there are still questions to be answered by researchers but also by governments. The German Federal Institute for Geoscience and Resources for example has dropped its activities in the field of remediation with nZVI. According to Robert Kringel, the technical difficulty of disseminating the iron belowground and a cost-benefit analysis show that nZVI-technology is not yet ready for large scale applications.

Peter Rissing from Alenco GmbH agrees that the competitiveness of nZVI for source treatment is in general very limited in comparison with i.e. ISCO (in situ chemical oxidation). The reasons are that the handling, mixing and injection of the suspension are more expensive than the handling of a solution, the limited radius of injection and the more sophisticated injection equipment needed for nZVI. He concludes that the price of nZVI must be <10 €/kg to make it a feasible option. However, there is a general agreement that site characteristics determine the optimum method. The best opportunities to apply nZVI may be in cases where PCE is the sole contaminant, at low concentrations of reducible species (sulphate, nitrate etc.) and in highly permeable aquifers.

There was also a discussion on hurdles for the commercialisation of nZVI and for the implementation of projects/field tests (U.S.EPA, 2005).

- Expense (nZVI is possibly not cost-effective for large dispersed plumes)
- All costs arise within one or two years (which can ruin the budget) while the costs of pump and treat spread over 10-20 years (which may be more favourable also because of tax reductions).
- Authority acceptance (The environmental marketplace is driven and constrained by regulations and laws (U.S.EPA, 2005). These regulations may largely differ from country to country or even from state to state.)
- Difficulty in getting approval for field tests by state agencies

- Difficulty to find funding for pilot projects
- Existing patents on nZVI and groundwater remediation
- Lack of information about nano-remediation by consultants and potential clients. Consumers are not anxiously awaiting the newest innovation for environmental remediation (U.S.EPA, 2005) and they are reluctant to use new technologies because of their inherent risk.
- Lack of longterm experience with the technology (e.g. How ready is the technology? What kind of risks are there? How great is its effectiveness? Will there be hurdles posed by governments?)
- Fear of a large public backlash (e.g. Gill (U.S.EPA, 2005): “The public's concern is that injecting nano-iron into site could lead to transport far downstream while my concern is usually that it will travel far enough to reach the contaminants.”)

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6 Glossary

BGR	German Federal Institute for Geosciences and Natural Resources
BNZVI	Bimetallic nano zero valent iron
CAH	Chlorinated aliphatic hydrocarbons
c-NZVI	Carbon-based nZVI
DNAPL	Dense non-aqueous phase liquid
DCE	Dichloroethylene
EC	European Commission
EPA	U.S. Environmental Protection Agency
EZVI	Emulsified zero valent iron
MTBA	Methyl tertiary butyl <i>alcohol</i>
MTBE	Methyl tertiary butyl ether
NANOFER	Name for nZVI particles produced by the Czech company Nanoiron
nZVI	Nano zero valent iron
ORP	Oxidation-reduction potential
PCB	Polychlorinated biphenyls
PCE	Tetrachloroethenes/Perchloroethenes
RNIP	Reactive nanoscale iron particle (Name for nZVI particles produced by the Japanese company TODA Kogyo Inc.)
PRB	Permeable reactive barrier
TCA	Trichloroacetic acid
TCE	Trichloroethylenes
TODA	Japanese company producing nZVI
TOC	Total organic carbon
VC	Vinyl chloride
VEGAS	Research facility for subsurface remediation at the University of Stuttgart