Injectable iron-oxides

Generic guideline

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

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1 INTRODUCTION

The injectable Iron oxides technology aims at stimulating biodegradation processes by supplying electron acceptors for biodegradation of organic contaminants in anoxic aquifers. The bioavailability of natural ferric oxide minerals is extremely low, resulting in very low reaction rates. This document intends to provide general information about this technology, and its application area and boundary conditions for authorities, consultants and site owners. Further, information is enclosed for supporting consultants, authorities and scientists to evaluate the feasibility and the impact of the technology to rehabilitate degraded waters, as well as for designing, implementing and monitoring the injectable iron oxide technology.

This document was composed in the frame of the FP7 project AQUAREHAB (GA 226565), and comprises outcomes and lessons learned during this project. The pollutants that were focussed on, are mono-aromatic compounds (BTEX) that are frequently detected in groundwater at gasoline station and industrial sites.

2 GENERAL PRINCIPLES OF THE INJECTABLE IRON-OXIDES TECHNOLOGY

2.1 CONCEPT

Iron oxides have the potential to be major electron acceptors for biodegradation in contaminated aquifers. However, the bioavailability of natural ferric oxide minerals is extremely low resulting in very small reaction rates in aquifers. Besides, natural iron oxides are often depleted in contaminants plumes. In preliminary laboratory experiments it was found that the injection of colloidal ferric oxides can overcome this limitation. It adds a highly reactive iron oxide phase to the aquifer functioning as electron acceptor and, furthermore, activating the already present ferric minerals by making them more bioreactive (Meckenstock et al., unpublished data).

The novel technology therefore aims at the stimulation of intrinsic natural attenuation properties of the aquifer. The technology is based on the injection of iron oxide nanoparticles into contaminant plumes or contaminant sources, creating a bioreactive zone as depictured inFigure 1.Due to this injection, the intrinsic microbial iron reduction will be greatly stimulated, which will result in turn in an enhancement of the contaminant oxidation rate.

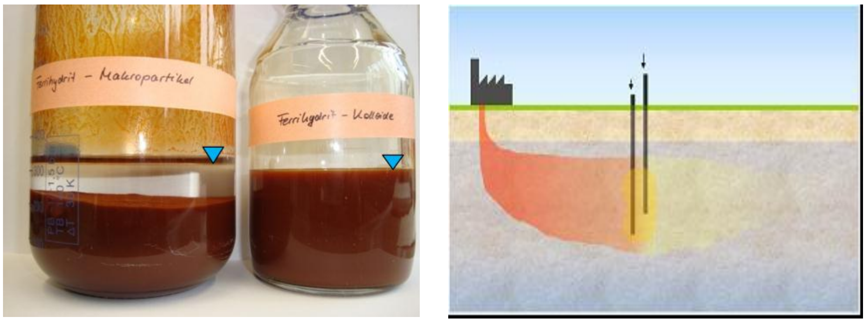

Figure 1: Injectable Fe-oxide particles (left) to create reactive zones for groundwater treatment (right)

2.2 TARGETED SUBSTANCES

An overview of the substances that can be targeted by this technology are summarized in Table 1, along with potential emissions sources of the different substances.

Table 1 Overview of substances that can be tackled by the injectable Fe-oxide technology

Targeted substances		Emission sources
Class	Specific substance	
BTEXs	Benzene, Toluene, Ethylbenzene, Xylene, styrene	Production, storage, accidents
PAHs	Naphthalene	Production, storage, accidents
Oils compounds	C6-C10 C10-C40	Petrochemie

These contaminants represent two of the most common classes of groundwater contaminating substances, and therefore a broad field of applications projected.

2.3 REACTION MECHANISM

For in-situ bioremediation of BTEX and PAHs like naphthalene via the injectable iron-oxide technology, the following requirements need to be fulfilled:

- Bacteria with the capacity to degrade these pollutants under iron-reducing conditions (Table 2)
- Ferric iron that can serve as electron acceptor in this process (like iron-oxides)
- Environmental conditions that do support growth of the iron-reducing bacteria
- Mobility of the injected iron-oxides to a certain extent.

Table 2.Selection of iron-reducing bacteria able to degrade BTEX and PAHs.

Bacteria	Pollutant	Reference
Desulfitobacterium aromaticivorans	Toluene, o-xylene, phenols, cresols	**DOI:** 10.1099/ijs.0.003525-0
Geobacter toluenoxydans	Toluene, Phenols, cresols	**DOI:** 10.1099/ijs.0.003525-0
Strain N49	Naphthalene	**DOI:** 10.1111/j.1574-6941.2011.01193.x
enrichment cultures	BTEX	**DOI:** 10.1128/AEM.71.6.3355-3358.2005
Strain BF	Benzene	**DOI**:10.1038/ismej.2007.73

The reaction proceeds according to the redox equation

(eq. 1) $CH_3COO^- + 8Fe^{3+} + 3H_2O \leftrightarrow 8Fe^{2+} + HCO_3^- + CO_2 + 8H^+$,

where CH_3COO^- is an example of an electron donor, such as mono- or polyaromatic hydrocarbons that can be used as electron donor in microbial iron reduction and therefore biodegradation. The reaction kinetics observed in the lab can reach up to 20 mM/d, but this greatly depends on the microbial strain, microbial colonization status, environmental conditions, type and concentration of contaminants and more. However, in the field, an adaptation of the local microbiota to the supply of iron oxides can be expected, which would then lead to increasing biodegradation rates.

Examples of iron oxides are nanosized colloids of ferrihydrite, hematite, goethite or akaganeite. The stimulation of BTEX-degradation by addition of Fe-oxides is illustrated in Figure 2.Within AQUAREHAB ferrihydrite iron oxide colloids were identified as particles with promising potential for application in groundwater treatment operations for the oxidation of organic compounds (pollutants).

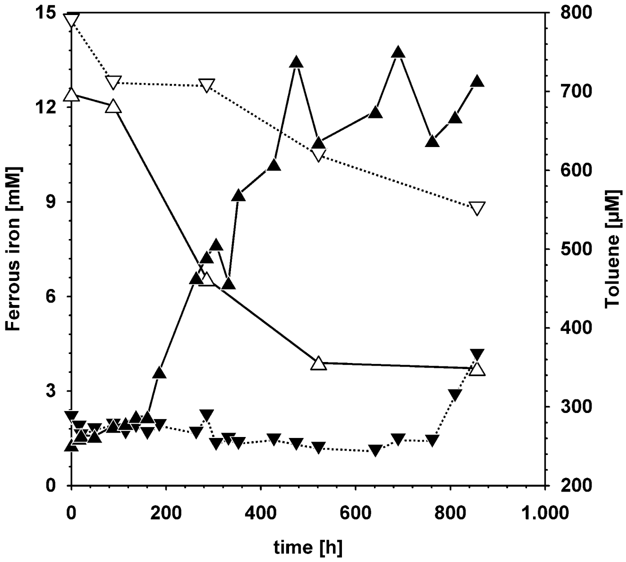

Figure 2: Enhanced oxidation of toluene (open symbols) by the addition of nanoferrihydrite (upward triangles) in comparison to conventional bulk ferrihydrite (downward triangles). Closed symbols: respective ferrous iron increase from microbial iron reduction by strain TMJ1.

2.4 INJECTABILITY & MOBILITY OF IRON-OXIDES

Experimental results (Tosco et al., 2012) suggested that the mobility of iron oxide nanoparticles can be controlled by adjusting the ionic strength of the suspension and the injection rate. If the ferrihydrite suspension is injected in the subsurface via permeation, the flow rate distribution generating around the injection point is likely to ensure a reasonable radius of influence, at least of 3 to 6 meters. Moreover, if the nanoparticles are desired not to travel far from the reactive zone, the colloidal suspension can be prepared adjusting the ionic strength to the value that provides the desired travel distance. However, the injection flow rate, the particles concentration and the required ionic strength of the injected dispersion are strictly site-specific, and therefore column tests are recommended before a field injection, as well as modelling of their results for a preliminary design of the full scale intervention.

2.5 DEVELOPMENT STAGE OF THE TECHNOLOGY

The mechanisms have been studied in lab experiments on small and larger scales (Bosch et al. 2010 a and b). Additionally, a range of experiments has been conducted which demonstrated the enhanced oxidation of BTEX compounds in small scale lab experiments. No field application has

been done so far. Currently, large scale lab experiments und simulated environmental conditions are performed.
The technology still should be classified as “very emerging”.

3 APPLICABILITY AND BOUNDARY CONDITIONS OF THE TECHNOLOGY

The application of colloidal iron oxide nanoparticles requires no specific treatment or storage of the injection solution prior to its injection into the field. Iron oxide nanoparticles are stable and do not react with ambient oxygen.
However, the ionic strength of the groundwater at the injection site will determine the mobility of the nanoparticles. If heavy contamination with high ionic strength is targeted, only an injection as a biobarrier would be feasibly. This would imply a very limited mobility of the particles immediately after injection and marginal mixing with ground water. However, the mobility and a certain radius of influence may be enhanced by using a low-ionic strength injection medium
The technology aims to enhance microbial iron reduction, which is an anaerobic respiration process. Anoxic aquifers are therefore the main field of application. The pH of the sites may range from neutral to slightly acidic. However, strongly sulfidic aquifers would be not suitable, as iron oxides react with sulfides to pyrite minerals which do not support microbial oxidation.

Certain boundary conditions are related to the hydrodynamic properties of the targeted aquifers. High flow velocities would probably cause difficulties for creating a biobarrier. However, this has to be tested in field applications.
An important boundary condition which has not been investigated so far in the field is the microbial response to the injection. It is not known whether the microbial community really makes use of the supplied electron acceptor. However, it is known that microbial iron reducing communities are commonly established within contaminant plumes.

The amount of iron oxide nanoparticles for injection depends on the concentration of contaminant. The oxidation of 1 mole of toluene theoretically requires 36 moles of iron oxide. Additionally, losses by diffusion and inactivation have to be accounted for. On the other side a putative activation of autochthonous iron oxides has been reported (Bosch et al. 2010 b).
On the basis of AQUAREHAB experimental data, it was calculated that for the full remediation of a 5 mg L^{-1} toluene plume via a nanoparticle injection cylinder of 4 m depth and 3 m radius, a groundwater flow velocity of 0.5 m d^{-1}, and an average soil porosity of 30%, this would result in the need for an injection of ~ 100 kg iron oxide nanoparticles per year. Up to 400 kg of iron oxide nanoparticles can be injected during one injection campaign into a single well. To increase the depot effect, several injection cylinders can be injected along the plume.

Positive side-effects: The stimulation of the microbial iron reducing communities will lead to an increase in bacterial biomass at the treated site. This will cause a long-termed sustainability of the enhanced reactivity even after the depletion of the nanoparticulate iron oxide material.

Negative side-effects: Due to the reduction of the injected iron oxide nanoparticles, elevated concentrations of ferrous iron can be expected downstream. This could cause ferric iron flocculation at drinking water wells. This is a well-known phenomenon that can also be encountered with established technologies. Iron(III) has a particularly low electron accepting capacity for its mass, and therefore iron(II) may quickly exceed water quality thresholds in groundwater as it reacts and dissolves.

4 PERFORMANCE OF THE TECHNOLOGY

Based on all lab results, an almost complete oxidation of BTEX within designed reactive biobarriers seems possible. Residual components are expected to amount to ~ 10% of the initial inflow contaminant concentration. However, due to the planned application in diverse soil environments and under all kinds of hydrological and biogeochemical settings, this has still to be investigated. Due to the individual design of each injection to each specific site, a 90% plus elimination of the contaminants will be targeted.

In lab studies, a complete BTEX oxidation within days was observed. In realistic environmental settings, including low nutrients, low temperature and competing biotic and biotic reaction, a 10-fold reduction of this rate can be expected at least. However, this is by far efficient enough to ensure a full oxidation of BTEX compounds within the passage of a reactive biobarrier. The biobarrier needs to be designed to fit the groundwater flow velocity.

As the technology is ‘very emerging’, no field data are available yet.

5 COST OF THE TECHNOLOGY

In comparison to conventional large scale technologies, which easily cost 5 Million € for source treatment, the injectable iron oxide technology is low-cost.

According to the stoichiometry outlined above, a typical BTEX contaminant plume for one year would result in a cost of ~ 5000 € for the nanoparticles. The injection technology will cause costs depending on the sites and putative pre-instalments of wells. For a 10-fold increase which is needed for a source treatment, ~ 50.000 € are calculated. In comparison to conventional large scale technologies, this can be regarded as very cheap. This is a result of the effective utilization of the microbial natural attenuation potential.

6 GENERIC APPROACH TO DETERMINE APPLICABILITY OF THE INJECTABLE IRON-OXIDE TECHNOLOGY AT A SPECIFIC SITE OR AREA

For a successful application of the injectable iron oxides technology, the following stepped approach is recommended:

Step 1: Evaluation of available data

At first, it needs to be evaluated which contaminants or contaminant cocktail are present at the site of concern. This survey of the available data will indicate if the technology is applicable.

Step 2: Detailed assessment of site

This step comprises a more detailed assessment of the site, comprising collecting additional data related to: (1) extent of contaminated area, (2) heterogeneity of subsurface and contaminant distribution, (3) detailed characterization of aquifer and ground water chemistry, (4) assessment of the total mass of contaminants.

The hydrology, soil properties and biogeochemistry of the targeted sites are investigated. The amount of contaminant is assessed, and the specific needs are outlined.

Questions to be resolved by a detailed assessment of the targeted site comprise:

- Is a source or plume treatment desirable?
- Injection in the complete contaminated volume, or is the establishment of a biobarrier needed?

Step 3: Feasibility study

Small scale lab-experiments are conducted using soil core material from the actual site. This will build a bridge between the site assessment and the planning of the injection. The reactivity of the iron oxide nanoparticles can be tested, and also the response of the individual microbial community.

Step 4: Design

Based on the two previous steps, an individual design will be made for the specific scenario. This includes the amount of iron oxide nanoparticles, the ionic strength of the injection medium, the injection volume, the location of injection points and injection rates. Also the design of the nanoparticles will be adapted in an advanced state of the technology.

Step 5: Field implementation

Step 5A: Installation of the injection equipment (pumps, wells, storage tanks) on-site.
Step 5B: The injection with iron-oxides is performed.

Step 6: Monitoring and Success Control

The monitoring of (enhanced) biodegradation will be done (1) indirectly by measuring the increase of the reaction product of iron reduction (Fe^{++}) and (2) directly by measuring the concentrations of residual contaminants and by measuring their isotope signatures ($^{13}C/^{12}C$, $^{2}H/^{1}H$). Biodegradation leads to a significant increase of isotope values and can be quantified by a substance- and process-specific proportionality factor (isotope enrichment factor ε).

Step 7: Reinjection

Depending on the individual injection schemes, repeated injection and monitoring loops can take place.

Step 3 to step 5 are explained more in detail in the following sections.

7 GENERIC APPROACH TO TEST THE FEASIBILITY OF THE INJECTABLE IRON OXIDE TECHNOLOGY (STEP 3)

7.1 INTRODUCTION

The benefit of a lab feasibility study for the injectable iron-oxide technology is to be evaluated for each case. However, as it concerns a 'very emerging' technology, it is strongly advised to perform some lab scale tests prior to field testing.Different types of feasibility tests exist.

- Degradation tests (batch) to evaluate the added value of Fe-oxide additions on pollutant degradation rates – selection of most appropriate iron-oxide, evaluating its longevity, …
- Degradation test (batch) to screen the presence at the envisioned site of an iron-reducing biodegradation potential towards the envisioned pollutant.
- Column degradation test: For each field implementation, the performance of a lab scale column test under in-situ conditions is recommended for deriving design parameters (degradation rates, minimal required retention times, ...). Also information on the longevity of filling materials, biofouling, … can be evaluated.
- Column transport test: for evaluating the mobility of the iron-oxide particle in the aquifer – derive design parameters
- Pilot test in the field: especially for evaluating the injection characteristics (pressure, radius of influence, required time, …) , some work in the field can be every useful.

It is recommended to perform the lab scale tests with groundwater (and aquifer material) from the site. For this purpose, undisturbed soil cores are generally used to maintain the in-situ redox conditions.

7.2 BATCH DEGRADATION TESTS WITH PURE IRON REDUCING CULTURES

To evaluate the **added value of specific Fe-oxide additions for stimulating iron reducing bacteria**, and/or to compare the effect of different iron-oxide types, batch degradation experiments with pure iron-reducing bacterial strains can be performed.
The effect can be monitored based on iron reduction rates where for instance, sodium acetate can be added as a model organic electron donor. Within AQUAREHAB, such tests were set-up with *Geobacter sulfurreducens* in 100 ml anoxic batch experiments. The aim was to compare nanosized colloids of ferrihydrite, hematite, goethite, and akaganeite with their respective macroaggregate, bulk phases in their reactivity in microbial iron reduction. In dense cell suspension, the reduction of the applied iron oxides to ferrous iron was monitored via photometric assays, X-ray diffraction, BET-surface measurements, Dynamic Light Scattering techniques and flow cytometry. The aim of these experiments was to select the iron oxide nanoparticle with the highest "reactivity" as electron acceptor and therefore potentially also the highest activity in contaminant degradation. The results in Figure 3 clearly show the high reactivity. Ferrihydrite colloids of 330 nm in diameter turned out to have the highest potential among the particles under investigation to reduce the iron. They also showed the highest stability against coagulation and also a catalytic effect on larger iron oxide particles (Bosch et al. 2010a).

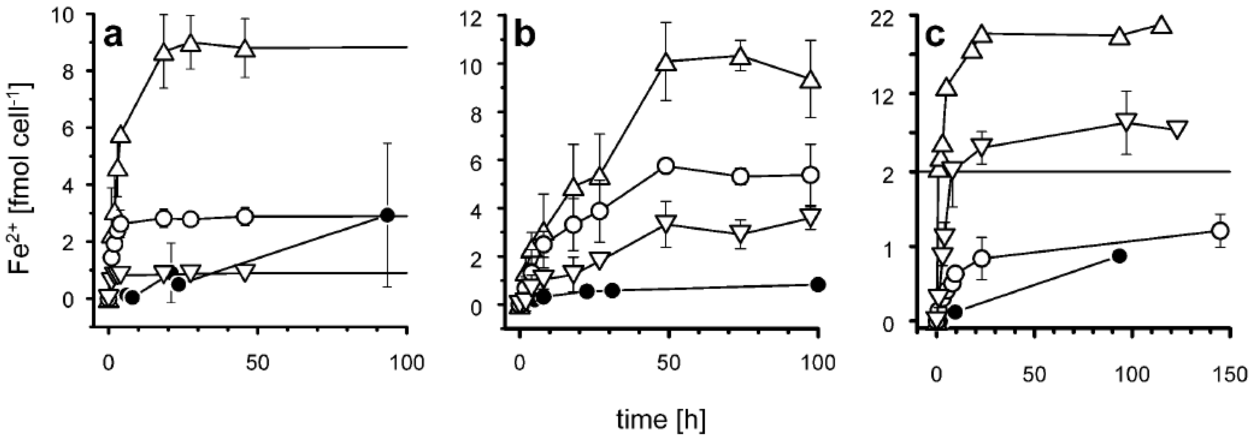

Figure 3.Fe(III) reduction of colloidal and bulk iron oxide aggregates by *Geobacter sulfurreducens* at different initial Fe(III) concentrations. (a) *ferrihydrite*: 336-nm-ferrihydrite colloids 0.29 mM (0.9 fmol cell^{-1}, n=3, -▽-), 0.86 mM (2.9 fmol cell^{-1}, n=3, -○-) and 1.71 mM (9.2 fmol cell^{-1}, n=3, -△-), and bulk ferrihydrite 3.52-19.36 mM (87 fmol cell^{-1}, n=3, -●-). (b) *hematite*: 123 nm hematite colloids 0.75 mM (9.3 fmol cell^{-1}, n=3, -▽-), 1.76 mM (22.0 fmol cell^{-1}, n=3, -○-) and 3.26 mM (40.7 fmol cell^{-1}, n=3, -△-), bulk hematite 14.79 mM (69.3 fmol cell^{-1}, n=3, -●-). (c) *goethite/akaganeite*: akaganeite colloids 1.72 mM (12.0 fmol cell^{-1}, n=3, -▽-) and 2.28 mM (21.4 fmol cell^{-1}, n=1, -△-). Bulk goethite 0.73 mM (3.7 fmol cell^{-1}, n=1, -●-). Colloidal goethite 0.34 mM (1.49 fmol cell^{-1}, n=5, -○-). Due to the large difference in initial concentrations, the y-axis is divided.

Similar tests can be performed with BTEX-degrading iron-reducing bacteria to **evaluate the impact of the iron-oxides on the pollutant removal**. Here pollutants need to be added in the test vials and the impact of the iron oxides can be followed via quantification of the pollutants over time, as illustrated in Figure 2.

7.3 BATCH DEGRADATION TESTS WITH AQUIFER MATERIAL FROM THE SITE

To evaluate the feasibility of a specific Fe-oxide for stimulation of BTEX or PAH-removal at a specific site, a batch degradation tests can be performed with aquifer material and groundwater from the site. By comparing BTEX removal over time in test conditions with and without Fe-oxide amendments the impact of the Fe-oxide can be evaluated. Poisoned controls need to be included to distinguish between abiotic (sorption, volatilisation) and biological removal mechanisms.

7.4 COLUMN DEGRADATION TESTS

For deriving design parameters (degradation rates, minimal required retention times, ...) a column degradation tests is preferred rather than batch degradation experiments, as the set-up is closer to the reality (continuous system, liquid/solid-ratio). The column is filled with a solid material (usually aquifer material) and fed in an upflow mode with water. The Fe-oxide particles can be injected after filling of the column, simulating the real process.

Such experiments can be set-up for **research purposes in a controlled way**, using for instance artificial sediment (quartz) with iron-reducing bacteria and simulated groundwater with acetate as model organic compound (Bosch et al. 2010b). Bosch et al. used stainless steel columns with an inner diameter of 35 mm and a height of 250 mm (volume = 240 cm^3). They proved that ferrihydrite colloids sustained their high reactivity and served as a superior electron acceptor and acetate oxidizer. This suggests that ferrihydrite iron oxide colloids may be a suitable particle for application in groundwater treatment operations for the oxidation of organic compounds (pollutants).

Similar experiments can be performed with pollutants as electron donor, which allows to derive pollutant degradation rates.

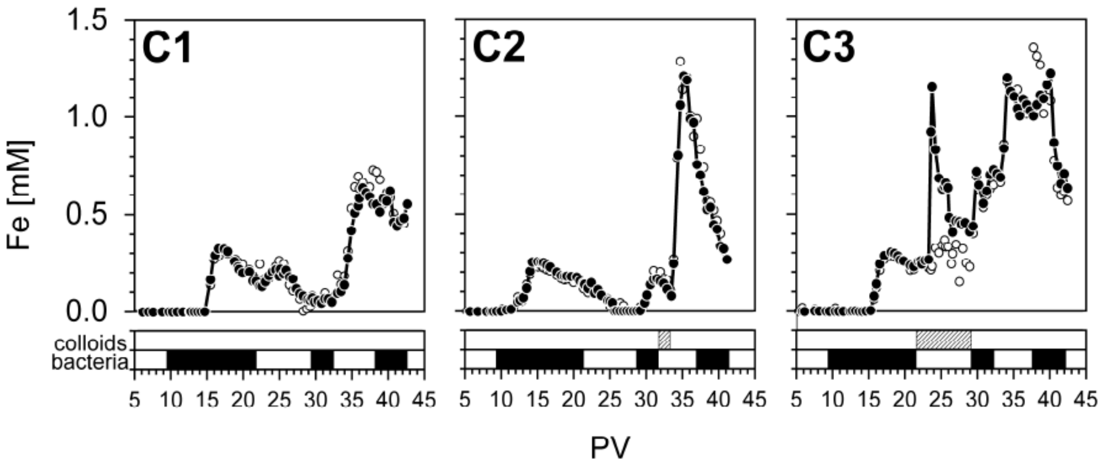

Figure 4Fe^{2+} (○) and total Fe (●) discharge from continuous-flow sand columns inoculated with *Geobacter sulfurreducens*. Different forms of ferric iron were applied in the columns. C1: goethite-coated quartz sand. C2: ferrihydrite colloids introduced via the influent, no goethite-coatings. C3: goethite-coated quartz sand and introduced ferrihydrite colloids. Black bars: periods of microorganism inoculation. Hatched bars: periods of colloidal ferrihydrite input. PV = pore volume.

However, to **derive design parameters for a specific site**, it is advised to fill the column with relevant aquifer material from the site and to use real groundwater from the site as influent.

7.5 COLUMN TRANSPORT TESTS

Column transport tests simulating the injection of iron oxide particles in the soil columns under well controlled laboratory conditions are useful to assess the mobility of these particles when injected in the contaminated aquifer (and consequently the radius of influence of an injection point) and, in a second stage, to predict the long-term fate when they are subjected to natural flow conditions. Numerical modelling of the column tests results is required to gather information for the preliminary design of the full-scale application (discharge rate, expected radius of influence, expected clogging, etc.).

Column tests can be performed under constant or transient ionic strength, including injection of ferrihydrite colloidal dispersions, followed by flushing with particle-free electrolyte solutions. The suspension of ferrihydrite colloids should be carefully prepared before injection, ensuring a good dispersion of the particle (for eg. by sonicating the suspension prior to inject in into the column). pH and electrical conductivity of the suspension should also be measured periodically.

The column test protocol can be as follow:

- pre-equilibration of the column filled by the porous medium by flushing with DI water
- pre- equilibration of the column by flushing with water at the same I.S. which will be used for iron oxide particles
- injection of the colloidal dispersion at constant ionic strength

- flushing of the column in one or more steps for the release of deposited particles: the first step of flushing should always be performed at the same ionic strength applied during iron oxide injection. Eventual subsequent flushing steps can be performed injecting particles with progressively decreasing ionic strength. Tests with flushing at progressively decreasing ionic strength are suggested, since experimental studies evidenced a strong influence of ionic strength on particles mobility (Tosco et al., 2012).

It is suggested to inject, for each step, at least 3 pore volumes. In case of relevant interactions among particles and porous medium, the injection of 5 to 10 pore volumes is suggested. During the test, the concentration of iron oxide particles is to be monitored both at the inlet and at the outlet of the column. It is suggested to adopt in-line measurements, for example using a spectrophotometer equipped with flow-through cells, in order to better follow the evolution of the concentration in real time. At the end of the test, it is also suggested to measure the concentration of retained particles. To this aim, the column can be extruded and dissected in several parts. An example of such an experimental procedure is proposed by Tosco et al. (2012).
In case of the injection of concentrated suspensions of iron oxide nanoparticles (i.e. in the order of few grams per liter or higher) which show a partial aggregation of the particles, clogging phenomena (i.e. reduction of porosity and permeability due to particles deposition) may occur, and consequently it is suggested to monitor also the pressure drop at the column ends using pressure transducers.

An example of experimental results of column transport tests performed for injection of iron oxide nanoparticles in a sand-packed column is provided in Figure 5.

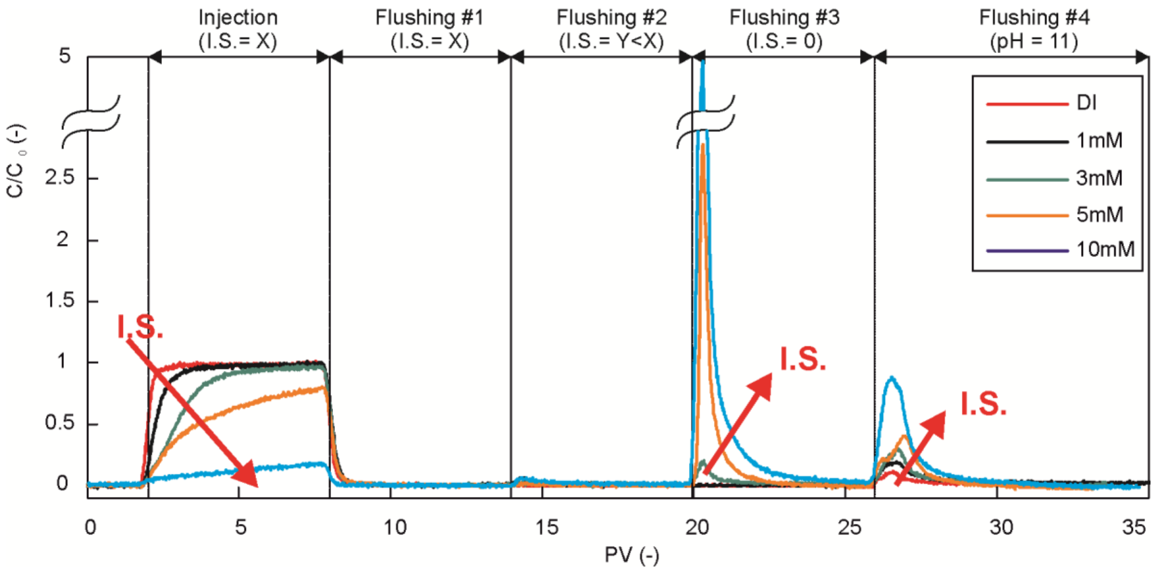

Figure 5. Breakthrough curves for column transport tests performed at a Darcy flow velocity of 7.76·10^{-5} m/s for ferrihydrite particles dispersed in D.I. water (red), and dispersed in water at a ionic strength of 1 mM (black), 3 mM (green), 5 mM (orange) and 10 mM (blue). The tests are performed injecting particles at contant ionic strength, and then flushing with a stepwise decrease in ionic strength. Each release peak corresponds to a step decrease in ionic strenth. Modified from Tosco et al. (2012)..

In order to gain knowledge on the mechanisms controlling the interaction among iron oxide particles and the porous medium, and consequently to infer the expected mobility of the particles when injected at the field scale, numerical models are suggested for the simulation of the particles transport. Porous media transport models for colloids are usually based on advection-dispersion equations, modified on purpose to include deposition and release phenomena, clogging, and other specific processes. The experimental results of column transport tests (i.e. breakthrough curves and concentration profiles along the column) can be fitted by numerical models to determine the mechanisms of interaction between particles and porous medium (i.e. retention due to physical-chemical interactions, mechanical filtration, straining, etc.) and to quantitatively determine the interaction parameters. A tool for the simulation of the injection of colloidal suspensions in porous medium columns is E-MNM1D, which was developed in the framework of Aquarehab (Tosco et al., 2014), and is implemented in the user interface MNMs (www.polito.it/groundwater/software). A detailed description of a possible modelling approach is provided by Tosco et al. (2014).

8 GENERIC APPROACH FOR DESIGN OF THE INJECTABLE IRON OXIDE TECHNOLOGY (STEP 4)

8.1 INTRODUCTION

During the design stage of this technology, scientific and economic issues are of vital importance. Scientifically, the designing aims at achieving a high reactivity in contaminant degradation, while maintaining a high level of reliability in different settings. Each individual contaminated site differs in terms of soil, contaminant plume and groundwater properties, and a reproducible clean-up effect cannot be assumed beforehand. Secondly, the designing aims at keeping costs at a minimum, in terms of a minimum of injection effort and volume

8.2 APPROACH

Based on field data collected in step 1 and step 2, the area to be treated can be derived. Technology design is guided by experimental data. The laboratory tests performed in step 3, should provide information on the feasibility of the injectable iron-oxide particles technology for reducing the pollution that was found at the site. A decision needs to be made (1) on the iron-oxide particle type to be used in the field test and (2) the minimal required dose of this particle to reduce the pollutant mass present at the site. Further the type, dimensions, number and position of the injection points need to be determined. Here, the mobility properties of the selected Fe-oxide particle in the envisioned site are crucial. Numerical modelling may be important in this phase.

8.3 DATA INTERPRETATION

Numerical modelling of experimental laboratory-scale tests is necessary to derive transport and reactivity parameters applicable to the field scale. With the help of modelling experts, the experimental data will be transferred to the individual field, so that a custom-made injection campaign can be established for each individual site. By this effort, both scientific and economic success can be achieved. Simultaneously, local and distant toxicity effects can be unveiled.

The modelling of laboratory column tests can be done using advection-dispersion equations, modified to include deposition and release phenomena, clogging, dependence of particles deposition and release on ionic strength, and other specific processes.

In summary, the following modelling approaches developed within AQUAREHAB should be taken into consideration for the implementation of iron oxide nanoparticles in a contaminated site:

- *Laboratory-scale modelling*: laboratory tests can be interpreted for the up-scaling via numerical modelling, or applying constitutive relationships, in order to derive transport parameters applicable to the field scale. In particular, the following freeware software can be applied:
    - MNM1D (Tosco et al., 2009; Tosco and Sethi, 2009), for the simulation of colloid transport in porous media in the presence of transients in ionic strength;
    - E-MNM1D (Tosco and Sethi, 2010), for the simulation of colloid transport in the presence of porous medium clogging due to deposition of particles around the injection point;
    - MNMs, a software with graphical interface which couples MNM1D and E-MNM1D as well as other features useful for column transport tests analysis.
- *Up-scaling of laboratory tests modelling*: The results of the modelling of laboratory-scale tests can be can be used to estimate the dependence of transport parameters on flow properties (flow rate) and fluid properties (ionic strength). These relationships are implemented in larger-scale models.

  Field-scale modelling: For a correct design of a field injection of iron oxide nanoparticles in porous media, it is necessary to predict the final spatial distribution of the particles around the injection point. Consequently, the modelling at this stage should include transport modelling in radial and/or spherical geometry, to simulate the injection of the particles into the subsoil. Transport mechanisms and kinetics to be implemented in the multi-dimensional model are derived from the analysis of laboratory-scale tests (Tosco et al, 2014). A numerical solution to the transport of colloidal particles in a radial domain is provided by E-MNM1D (Tosco et al., 2014) and is implemented in the user interface MNMs.

The cited software is available for download from Polito's website: www.polito.it/groundwater/software.

8.4 CONCLUSIONS

In order to achieve a custom-made approach, which is probably vital for the economic success of the technology, a certain experimental and modelling effort has to be performed. Compared with conventional engineering approaches, this effort does not appear unrealistic.

9 GENERIC APPROACH TO IMPLEMENT THE INJECTABLE IRON-OXIDE TECHNOLOGY (STEP 5)

9.1 INTRODUCTION

Once the experimental pre-tests (step 3) were successful and an injection campaign has been designed (step 4), the technology can be easily implemented using current standard injection technology. The iron oxide nanoparticle solutions can be easily injected, and the subsurface travel distance can be adjusted by tuning the ionic strength of the inflow solution (Tosco et al., submitted).

9.2 EXPERIMENTAL APPROACH

As this technology is “very emerging”, no pilot tests have been done so far. So every field test can be regarded to be experimental. The generated data in terms of particle mobility, reactivity and contaminant degradation will help in establishing a data base, which will in turn serve as guideline for future application.

Potential injection methods comprise (1) injection via permanent injections wells, and direct push injections. Both methods are explained more in detail in the generic guideline on biobarriers.

9.3 CONCLUSIONS

So far, no specific problems can be seen in the implementation of this technology. Still, the technology is only very emerging, which has undergone no field application so far.

10 GENERAL CONCLUSIONS

The novel approach of injecting iron oxide nanoparticles to enhance the microbial biodegradation potential is a promising new approach for the remediation of BTEX contaminated groundwater aquifers. It combines the use of nanoparticles with the power of microbiological mass and electron turnover capacities. By this approach, low costs and a minimal injection effort can be achieved while reaching a broad remediation success.
Yet this technology is only in an experimental stage and in development. The step from small scale lab experiments to large scale experiments has been done recently, but a field pilot application requires more research and development.

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