Injectable iron-oxides

Technology description:
General information & application area

Target Audience: Authorities, site owners, consultants, contractors

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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 the injectable iron oxide technology and its application area and boundary conditions for authorities, consultants and site owners. More detailed information 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 oxides technology is described in the associated generic guideline.

This document was composed in the frame of the FP7 project AQUAREHAB (GA 226565). 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 colloidial ferric oxides can overcome this limitation. It adds a highly reactive iron oxide phase to the aquifer (1) functioning as electron acceptor and (2) activating the already present ferric minerals by making them more bioreactive (Meckenstock et al., unpulished 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 in **Error! Reference source not found.**. 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.

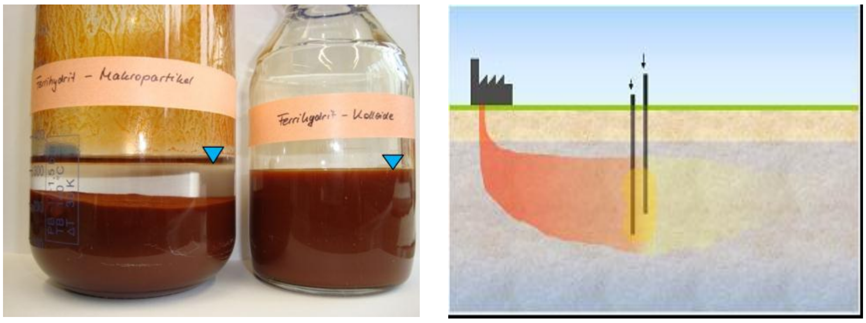

Figure 1: Injectable Fe-based particles (left) to create reactive zones for groundwater treatment (right)

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 nano technology

Targeted substances		Emission sources
Class	Specific substance	
BTEXs	Benzene, Toluene, Ethylbenzene, Xylene, Styrene	Production, storage, accidents
PAHs	Naphthalene	Production, storage, accidents
Oil compounds	C6-C10 C10-C40	Petrochemical industry

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

2.3 DEVELOPMENT STAGE OF THE TECHNOLOGY

The mechanisms of stimulating iron reduction by Fe-oxides have been studied in lab experiments on small and larger scales (Bosch et al. 2010 a and b) using acetate as electron donor. 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 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 (Fe(II)) can be expected downstream. This could cause ferric iron (Fe(III)) flocculation at drinking water wells. This is a well-known phenomenon that can also be encountered with established technologies.

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 aimed for.

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 reactions, 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.

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 to three years, depending on the plume and aquifer characteristics, would result in a cost of ~ 15000 € for the nanoparticles. The injection technology will cause costs depending on the sites and putative pre-instalments of wells. For a source treatment, a 10-fold increases of the costs should be counted on. 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. The technology is suited for instance BTEX or PAHs contaminations.

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 can be 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. Furthermore, the expected mobility of the particles when injected into the subsoil can be inferred based on column transport tests, and numerical modelling of the column tests results can provide information for the preliminary design of the full-scale application (namely, discharge rate, expected radius of influence, expected clogging, etc.).

Step 4: Design

Based on the two previous steps, an individual design needs to be made for the specific scenario. This includes the amount of iron oxide nanoparticles, the ionic strength of the injection medium, the injection volume, 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: The injection equipment (pumps, wells, storage tanks) are installed on-site.
Step 5B: The injection of iron oxide particles is performed.

Step 7: 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 8: Reinjection

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

7 Contacts

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8 References

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