CL:AIRE

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NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin provides a guide to different types of nanoparticles used within the NanoRem project.

A Guide to Nanoparticles for the Remediation of Contaminated Sites

1. INTRODUCTION

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) was a research project, funded through the European Union Seventh Framework Programme. The NanoRem project focused on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions. The NanoRem Toolbox, available at www.nanorem.eu, provides outputs which address all these issues.

NPs are typically defined as particles with one or more dimension of less than 100nm. As a result of their smaller size and relatively larger surface area, NPs can be more chemically reactive than their larger counterparts, enabling them to be utilised for novel purposes, including the potential for use in remediation.

This bulletin provides a guide to different types of NPs used within the NanoRem project, looking at their production and properties, and separates them into two broad classes: i) nano zero-valent iron (nZVI) and ii) non-ZVI and composite NPs. The producers/developers of the different NPs are given on page 4.

2. NANO ZVI

The use of ZVI at the micro to millimetre scale is commonplace in remediation, but the application of ZVI at the nanoscale, although reported since 2000, is less common, with only approximately 70 field scale projects identified from a wide range of information sources.

The high chemical reactivity of nZVI particles means that their specific activity and ability to move through the subsurface can be limited by a number of processes within the subsurface, namely, agglomeration, passivation and sorption onto material within the aquifer. To help overcome these problems, and thus increase the usefulness of nZVI in remediation, a number of modifications to the NPs have been developed, including: stabilisation, emulsification, anchoring the particles to a supporting matrix and development of bimetallic nanoparticles. Four nZVI particles were used in the NanoRem Project and are described in the following sections. Three of these are well-established commercially available nanoremediation products, and one is at the laboratory development stage (see also Table 1).

Figure 1. Photograph showing nanoremediation products and equipment prior to departure to the NanoRem Spolchemie I site. On the left are plastic barrels containing NANOFER 25S slurry, in the middle are boxes of NANOFER STAR, together with bags of the stabiliser carboxymethyl cellulose, and on the right is the dispersing unit (© NANO IRON s.r.o.)

2.1 NANOFER 25S

This product is manufactured by NANO IRON s.r.o. It is an aqueous dispersion of nZVI particles with special surface modification which is based on the combination of a biodegradable organic and inorganic stabiliser. Due to the narrow particle size distribution and sophisticated stabilisation process, the product exhibits a high reactivity with a large range of pollutants and a very low degree of agglomeration, which gives NANOFER 25S excellent migration and sedimentation properties.

2.2 NANOFER STAR

This product is manufactured by NANO IRON s.r.o. The product is Surface stabilised, Transportable, Air-stable and Reactive (i.e. STAR), meaning it is much easier to store and process compared to non-air-stable NANOFER 25S. It is a powder and stabilisation by a thin organic surface layer protects the nZVI against rapid oxidation if in contact with air.

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment.
This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517.

2.3 FerMEG12

UVR-FIA GmbH has developed a two-step method to produce a nZVI slurry by a simple mechanical approach (milling). The slurry consists of 15-30% iron and 70-85% monoethylene glycol and is called FerMEG12. The first step involves dry grinding to a particle size of <40 µm, with inhibitors to provide corrosion protection. Wet grinding then takes place, with monoethylene glycol as the grinding liquid and the addition of a surfactant, to produce nano-structured, flake-shaped particles with thicknesses less than 100 nm, called "nanoflakes" (Figure 2a).

2.4 Abrasive Milling nZVI

Abrasive Milling nZVI has been developed by the Centre Tecnològic de Manresa and is a suspension of nZVI particles in pure monoethylene glycol with alumina particles. This product has been obtained through the abrasion of the grinding medium (iron beads) utilising microscale alumina (Figure 2b). The product has been tested at laboratory-scale with PCE, TCE and Cr(VI) and reactivity, stability and mobility have demonstrated positive results.

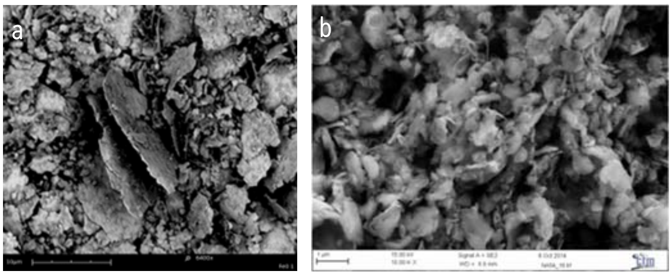

Figure 2. (a) Milled nZVI particles (© UVR-FIA GmbH); (b) Abrasive milling nZVI particles (© CTM)

3. NON-ZVI AND COMPOSITE NANOPARTICLES

NanoRem has also developed non-ZVI and composite NPs, progressing with particle design and the optimisation of self-manufactured and/or purchased particles. Some of these particles can treat a wider spectrum of contaminants than their nZVI counterparts. Two of these are field tested and commercially available nanoremediation products, and the rest are at other various stages of development from premarket to laboratory (see Table 1).

3.1 Nano-Goethite

Nano-Goethite is an iron oxide modified by humic substances, developed at Helmholtz Zentrum Muenchen and the University of Duisburg-Essen. Nano-Goethite is supplied as an aqueous suspension (Figure 3), can be easily injected into aquifers, and thus can overcome the limitation of bulk iron oxides in remediation, which cannot be injected into soils. The iron content of the Nano-Goethite stock suspension is 100 g L^{-1}. This can be diluted on-site to the requirements of the specific site. Due to electrosteric stabilisation, caused by the organic polymer, the stock remains in suspension for at least 5 days, and stirring can be applied to maintain colloidal suspension stability or for resuspension after storage. Nano-Goethite has been field tested and is commercially available from the University of Duisburg-Essen.

Figure 3. Nano-Goethite during handling on-site, prior to injection.

3.2 Carbo-Iron®

Carbo-Iron® is an air-stable *in situ* reagent developed at The Helmholtz Centre for Environmental Research - UFZ (Figure 4) targeting halogenated organic contaminants or heavy metals in groundwater. Carbo-Iron® consists of activated carbon colloids which are doped inside with nanoiron structures (mean cluster size around 50 nm, ZVI content 20-30 wt%). Both materials contribute to the particle properties. The porous composite has an effective density in water of approximately 1.7 g cm^{-3} which in combination with its optimised size and surface properties ensures an effective subsurface transport of the reagent particles. Carbo-Iron® has been field tested and is commercially available from ScIDre GmbH.

Figure 4. Carbo-Iron® is an air-stable powder.

3.3 Trap-Ox Fe-zeolites

Trap-Ox Fe-zeolites are microporous alumosilicates which are loaded with FeII/III ions by ion exchange. Due to their high specific surface area they act as adsorbents for small organic molecules. The iron in the zeolite pores (i.e. close to the adsorbed contaminants) is able to produce reactive species (e.g. hydroxyl radicals) from hydrogen peroxide, which degrade the contaminants. Fe-zeolites have been intensively studied as adsorbents and heterogeneous Fenton-like catalysts for removal of typical groundwater contaminants. Their application in colloidal form for subsurface injection and *in situ* barrier formation which has been investigated by UFZ within NanoRem is a novel approach.

Trap-Ox Fe-BEA35 was developed within NanoRem for *in situ* trap&treat of a variety of typical groundwater contaminants such as MTBE, ETBE, chlorinated ethanes and ethenes and BTEX. Trap-Ox Fe-BEA35 is available in sufficient amounts for field testing from UFZ.

Trap-Ox Fe-zeolites are a developing nanotechnology which would be expected to be market ready in 1 to 5 years.

3.4 Bionanomagnetite

Bionanomagnetite is formed from the bacterially-mediated reduction of ferrihydrite, a low-crystallinity, nano-sized (approx. 2 nm) Fe(III)-oxide by *Geobacter sulfurreducens* (Figure 5).

Fully scalable microbial synthesis routes have been developed at the University of Manchester for the production of bionanomagnetite at ambient temperature, serving as a "green" alternative to chemical synthesis routes, and resulting in magnetite NPs with tunable properties (particle size, magnetic properties and surface reactivity) which can be used in the remediation of heavy metals such as Cr(VI).

The bionanomagnetite can also be functionalised with palladium to form catalysts which show promising results for rapid reduction of redox active heavy metals and organic contaminants in groundwater.

Bionanomagnetites are a developing nanotechnology which would be expected to be market ready in 1 to 5 years.

Figure 5. Ferrihydrite (left), large bottle is control without bacteria and the three small bottles are replicates containing *Geobacter sulfurreducens*, which is reducing ferrihydrite to form bionanomagnetite.

3.5 Magnesium and Aluminium

Magnesium and aluminium have been selected as non-ZVI metals with iron-like reduction potential, but a lower material density showing promise for subsurface transport. Commercially available particles (e.g. Aluminiumgrieß AK 6WA 23 (aluminium spray grit from ECKART GmbH, $d_{10} \leq 0.7\ \mu m$, $d_{50} = 1.0 - 1.9\ \mu m$, $d_{90} = 2.0 - 4.0\ \mu m$)) have been used in order to investigate the reaction behaviour of Mg^0 and Al^0 towards commonly detected groundwater pollutants such as for example PCE. In this context aluminium and magnesium also offer a better stoichiometry relative to mass compared to iron. This is a bench-scale research concept being tested by VEGAS, University of Stuttgart, which has not yet seen field deployment.

3.6 Barium Ferrate

Ferrate(VI) salts are very strong oxidants and could hence be a promising agent for water and wastewater treatment processes. Barium ferrates ($BaFeO_4$) offers slow-release properties and could hence be utilised to create a depot effect in the aquifer. Ferrate(VI) is synthesised electrochemically; barium ferrate is obtained by subsequent precipitation (Figure 6). In order to investigate the reactivity of barium ferrate towards BTEX contaminants batch tests have been conducted using toluene as a model contaminant. This is a bench-scale research concept being tested by VEGAS, University of Stuttgart, which has not yet seen field deployment.

Figure 6. $BaFeO_4$ sample (© VEGAS, University of Stuttgart).

3.7 NanoFerAl

NanoFerAl is a composite of Fe and Al, developed by UVR-FIA GmbH / VEGAS, University of Stuttgart, with the aim of improving degradation of halogenated hydrocarbons by combining iron with a small amount of aluminium (milling approach). This is a bench-scale research concept being tested by NanoRem, which has not yet seen field deployment.

4. ENVIRONMENTAL IMPACT OF REACTIVE NANOPARTICLES

A protocol has been developed for the assessment of the ecotoxicity of NanoRem's NPs. With regard to ecotoxicological aspects it was found that no significant toxic effects were observed on soil and water organisms when ecotoxicological tests were undertaken for a range of NPs available for remediation (including with respect to the particles' interaction with contaminants and the resulting products).

Furthermore, effects on selected soil and water organisms were monitored for up to nine months after NP treatments of the pilot sites. In three out of four sites investigated, no toxic effects were observed at concentrations applied in the field studies. A transient increase in toxicity was observed right after NP injection at the Solvay site. However, a positive effect of NP injection on indigenous microbial communities and more specifically, the apparition of organohalide-respiring bacteria after NP injection, was observed both at the Solvay and Balassagyarmat sites. More information can be found at www.nanorem.eu.

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Table 1: Summary of the properties of NPs used in the NanoRem Project (listed by development status).

Particle name	Type of particle	Manufacturer and website	Process of contaminant removal	Target contaminants	Development status as of January 2017
Carbo-Iron®	Composite of Fe^0 and activated carbon	ScIDre GmbH, Germany www.carboiron.de/	Adsorption + Reduction	Halogenated organics (contaminant spectrum as for nZVI)	Field tested and commercially available
FerMEG12	Mechanically ground nZVI particles	UVR-FIA GmbH, Germany www.uvr-fia.de/	Reduction	Halogenated hydrocarbons	Field tested and commercially available
NANOFER 25S	Aqueous dispersion of nZVI	NANO IRON s.r.o., Czech Republic www.nanoiron.cz/en/nanofer-25s	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
NANOFER STAR	Air stable powder, nZVI	NANO IRON s.r.o., Czech Republic www.nanoiron.cz/en/nanofer-star	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
Nano-Goethite	Pristine iron oxides stabilised with humic acid	University of Duisburg-Essen, Germany www.uni-due.de/biofilm-centre	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals	Field tested and commercially available
Trap-Ox Fe-zeolites	Nanoporous alumosilicate loaded with Fe(III)	UFZ Leipzig, Germany www.ufz.de/index.php?en=2529	Adsorbent + Oxidation (catalyst)	Small molecules (depending on pore size of zeolite) - e.g. BTEX, MTBE, dichloroethane, chloroform, dichlormethane	Premarket
Bionanomagnetite	Produced from nano-Fe(III) minerals	University of Manchester, UK www.geomicrobiology.co.uk/	Reducing agent and adsorption of heavy metals	Heavy metals, e.g. Cr(VI)	Lab to premarket
Palladized bionanomagnetite	Biomagnetite doped with palladium	University of Manchester, UK www.geomicrobiology.co.uk/	Reduction (catalyst)	E.g. Halogenated substances (contaminant spectrum broader than for nZVI)	Lab and premarket
Abrasive Milling nZVI	Milled iron	Centre Tecnològic de Manresa, Spain www.ctm.com.es/en/index.php	Reduction	Halogenated aliphatics and Cr(VI)	Lab
Barium Ferrate	Fe(VI)	VEGAS, University of Stuttgart, Germany www.vegasinfo.de/	Oxidation	BTEX, nitroaromatic compounds (under investigation)	Lab
Mg/Al particles	Zero valent metals	Adaption of commercially available particles by VEGAS, University of Stuttgart, Germany www.vegasinfo.de/	Reduction (reagent)	Halogenated hydrocarbons	Lab
NanoFerAl	Composite of Fe and Al	UVR-FIA GmbH / VEGAS, University of Stuttgart, Germany http://www.vegasinfo.de/	Reduction (reagent)	Halogenated hydrocarbons	Lab

5. CONCLUSIONS

This bulletin has provided a guide to different types of NPs used within the NanoRem project, nano zero-valent iron (nZVI), non-ZVI and composite NPs. It summarised different treatment approaches using nZVI, non-ZVI and composites covering reduction, oxidation and adsorption strategies. This expands the toolbox for the design of nanoremediation operations and extends the spectrum of chemically treatable groundwater pollutants from those treated by conventional nanoiron-based options to non-halogenated substances and non-reducible metal ions.

For further information on NanoRem's NPs and contact details of manufacturers/producers please visit: http://nanorem.eu/safety-data-sheet.aspx

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