CL:AIRE

NanoRem 2
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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 summarises the appropriate use of nanoremediation technologies for treating contaminated soil and groundwater.

Appropriate Use of Nanoremediation in Contaminated Land Management

Foreword

In the past there has been significant public and regulatory concern over the use of nanoremediation owing to perceived hazards from the introduction of nanoparticles in the subsurface. NanoRem has recognised these challenges and produced guidance and tools to support appropriate use which is briefly summarised in this paper. In most EU countries there are no explicit regulatory barriers to nanoremediation technologies use and recognising the objectives of the Water Framework Directive and daughter Directives the COMMON FORUM welcomes NanoRem's contribution to this debate.

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Common Forum

Introduction and Aim

This short guidance paper provides a concise overview about the appropriate use and application of nanoremediation technologies for treating contaminated soil and groundwater and clarifies how they are currently regulated in comparison with other forms of *in situ* reduction and oxidation remediation technologies. It has been produced by a major European project on nanoremediation called NanoRem. The NanoRem Project has held a number of workshops and focus group meetings with different types of stakeholders from around Europe. These have expressed a need for clear messages about nanoremediation provided in simple language for the different stakeholders involved in contaminated land decision making. This paper is aimed at remediation practitioners and regulators, with the goal of providing the necessary information to encourage greater uptake on nanoremediation techniques within the industry. This overview is broad ranging but provides links to other NanoRem outputs where more detail can be found.

Nanoremediation and NanoRem

Nanoremediation describes the use of nanoparticles (NPs) in the treatment of contaminated groundwater and soil. Depending on the properties of different particles, nanoremediation processes generally involve reduction, oxidation, sorption or their combination. NPs are usually defined as particles with one or more dimensions of less than 100 nm (1×10^{-7} m). In practice, nanoremediation may apply to particles which are larger, for example composites, but which include activities at nanoscale dimensions. NPs used in remediation are mostly metals or metal oxides, most frequently nano-scale zerovalent iron (nZVI). They may be modified in various ways to improve their performance, for example inclusion of a catalyst (often palladium), use of coatings or modifiers, or emplacement on other materials such as activated carbon or zeolites (for iron oxides). They are generally applied *in situ* via various injection methods, which may include the use of viscosity control agents or other materials to facilitate targeted emplacement of NPs in the subsurface.

Figure 1. Air-stable Carbo-Iron® contains iron NPs sorbed to activated carbon (Photo: A. Kuenzelmann, UFZ).

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's 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 risks and benefits of NPs, market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and to support both the

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.

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Figure 2. The NanoRem consortium.

appropriate use of nanotechnology in restoring land and water resources and the development of the knowledge based economy at a world leading level for the benefit of a wide range of users in the European Union environmental sector.

Regulatory Position

Nanoremediation must comply with the same regulatory requirements that apply to any other substance being injected into the subsurface as part of a remediation process; and the same health and safety requirements for materials handling and use:

1. Materials and substances used in remediation must fully comply with prevailing health and safety legislation, and public domain material safety data sheets (or their equivalents) are a prerequisite;
2. Adequate demonstration that the remediation being deployed will achieve the necessary risk management goals for which it is being used. As for all contaminated land management activities, effective use of conceptual site models underpins reliable and robust decision making;
3. Adequate identification and understanding of potential risks, and application of appropriate risk management for any substance release, unreacted fractions and potential by-products in the ground (including delivery, transport and change over time) with respect to human health, ecological and environmental risks/toxicity; and
4. Compliance with REACH regulations and other relevant product stewardship rules with respect to production and marketing of (new) substances.

At a European level nanoremediation is not seen as being a special case from a regulatory standpoint. However, given that there have been stakeholder concerns over nanotechnologies, NanoRem carried out comprehensive ecological testing of a range of NPs, sustainability assessments and risk-benefit analyses. Additionally, NanoRem developed a protocol for risk assessment of the *in situ* deployment of NPs for its own field pilot testing[1]. Other key outputs include in-depth reporting of field studies (described below) and field based monitoring protocols. All of these outputs are included in the NanoRem Toolbox (see page 4).

There are no specific generic sustainability advantages or disadvantages to the use of nanoremediation. As for all *in situ* remediation work, sustainability is highly dependent on site specific factors, and all technologies should be considered on their particular merits for any particular site. With regard to eco-toxicological aspects it was found that no significant toxicological nanoparticle related effects were observed on soil and water organisms when ecotoxicological tests were undertaken using the NanoRem NPs (including with respect to the particles' interaction with contaminants and the resulting products)[2]. However, toxicity was detected from a process additive for one of the milled nZVI products, but this may have been an anomaly. Field scale observations detected transient perturbations in aquifers, attributed to (intentional) pH and redox shifts resulting from NP introduction. Of course, NP injections were taking place into already highly disturbed subsurface environments.

Figure 3. Preparation of nZVI suspension for the Spolchemie I site. © Palacký University in Olomouc, J. Filip.

Appropriate Use

There are a number of nanoremediation variants. To date nanoremediation has mostly been deployed as an *in situ* chemical reduction or oxidation technology (ISCR/ISCO). However, it can also act as an *in situ* stabilisation technology, and there is also good evidence that some approaches can act to enhance processes of *in situ* anaerobic bioremediation. The type of effect depends on the type of NP deployed. Table 1 lists the NP types investigated by NanoRem in the laboratory and in the field, which are commercially available and are **ready for adoption** for a range of applications.

Although the first deployment of nanoremediation in the field took place as early as 2000, its rate of adoption has been slow compared for example with other ISCR/ISCO technologies over the subsequent 17 years. Over 100 field deployments have taken place worldwide, the majority of these have been field tests rather than practical commercial technology deployments. The work of NanoRem has included multiple, well documented, European field trial applications of various particles (see Table 2, page 3 and NanoRem Toolbox, page 4).

Figure 4. Preparation of the monitoring equipment at the Spolchemie I site. © VEGAS, University of Stuttgart, Germany.

[1] Nathanail, C. P., Gillett, A., McCaffrey, C., Nathanail, J. and Ogden, R. (2016), A Preliminary Risk Assessment Protocol for Renegade Nanoparticles Deployed During Nanoremediation. Remediation, 26: 95–108. doi:10.1002/rem.21471

[2] http://www.nanorem.eu/Displaynews.aspx?ID=824

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Table 1: Summary of NPs investigated by NanoRem which are now commercially available.

Name	NANOFER 25S	NANOFER STAR	FerMEG12	Carbo-Iron®	Nano-Goethite
Type of particle	Aqueous dispersion of nZVI	Air stable powder, nZVI	Mechanically ground nZVI particles	Composite of Fe^0 and activated carbon	Pristine iron oxides stabilised with humic acid
Process of contaminant removal	Reduction	Reduction	Reduction	Adsorption + Reduction	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals
Target contaminant	Halogenated hydrocarbons and heavy metals	Halogenated hydrocarbons and heavy metals	Halogenated hydrocarbons	Halogenated organics (contaminant spectrum as for nZVI)	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals
Manufacturer	NANO IRON s.r.o., Czech Republic	NANO IRON s.r.o., Czech Republic	UVR-FIA GmbH, Germany	ScIDre GmbH, Germany	University of Duisburg-Essen, Germany

Table 2: Listing of NanoRem field sites.

NanoRem Site Name	Spolchemie I	Spolchemie II	Solvay	Balassagyarmat	Neot Hovav	Nitrastur
Site Primary Investigator	AQUATEST	AQUATEST	Solvay	Golder	Ben Gurion University of the Negev	Tecnalia
Country	Czech Republic	Czech Republic	Switzerland	Hungary	Israel	Spain
Current use	Industry	Industry	Industrial brownfield, some subletting	Brownfield	Industry	Brownfield
Specification of contamination (source/plume)	dissolved plume	residual phase and dissolved plume	pooled phase and dissolved plume	dissolved plume	phase and plume in fractures	anthropogenic backfill containing heavy metals
Main contaminant(s)	chlorinated hydrocarbons	BTEX (mainly toluene and xylenes), styrene	chlorinated hydrocarbons	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
Type of Aquifer	porous, unconfined	porous, unconfined	porous, unconfined	porous, unconfined	fractured	porous, unconfined
Hydraulic conductivity	10^{-4} to 10^{-6} m/s	10^{-4} to 10^{-6} m/s	8 10^{-3} to 2 10^{-5} m/s	5 10^{-3} to 2 10^{-8} m/s	n/a	2 10^{-4} to 10^{-5} m/s
Seepage velocity	0.2 m/d	0.9 m/d	5-20 m/d	0.3 m/d	not available	1 m/d
NP used	NANOFER 25S/ NANOFER STAR	Nano-Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
NP provided by	NANO IRON s.r.o.	University Duisburg Essen	UVR-FIA GmbH	ScIDre GmbH	UFZ	NANO IRON s.r.o.
Mass of NP injected	200 kg / 300 kg	300 kg	500 kg	176.8 kg	5 kg	250 kg
Injection System	Direct Push	Direct Push	Wells (with packers)	Direct Push	Wells (with packers)	Wells (with packers)
Remediation outcome[3]	See NanoRem Bulletin #7	See NanoRem Bulletin #8	See NanoRem Bulletin #9	See NanoRem Bulletin #10	See NanoRem Bulletin #11	See NanoRem Bulletin #12

[3] The NanoRem Bulletins are freely available from www.nanorem.eu.

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Figure 5. Left: Preparation of the NP suspension for injection into the large scale flume (LSF) at VEGAS. Right: Taking samples during the LSF experiment at VEGAS © VEGAS, University of Stuttgart, Germany.

As for any ISCR/ISCO technology, the *appropriate* use of nanoremediation requires:

- Sound technical evidence for effectiveness of the nanoremediation solution being offered for the particular problems being considered;
- A sound rationale for the specific risk management functionality required, linked to a robust site conceptual model and suitable verification procedures;
- A clear option appraisal case, including consideration of sustainability aspects, for example as described by ISO[4]; and
- That all materials used must fully comply with all relevant safety, health and environmental information requirements and must be suitably documented as doing so.

Applications

Nanoremediation technologies have predominantly been applied to remediate chlorinated solvents, but have also been applied in the mitigation of heavy metals and BTEX. Most field applications so far have focused on plume (dissolved phase hydrocarbon in groundwater) management. While there have been few applications for treatment of large contaminant source terms, there is potentially a good opportunity for source management using nanoremediation in dealing with secondary or diffuse sources. Examples include free phase NAPL from smaller spills or residual sources remaining after an extraction treatment, such as dual-phase extraction. In addition, there is growing evidence that nanoremediation techniques can work well in tandem with biological treatments, facilitating a more rapid change in subsurface redox conditions and hydrogen availability, facilitating microbial processes such as dehalorespiration.

Detailed application information is available in the NanoRem Toolbox (Figure 6) including a "Generalised Guideline for Application", a series of short bulletins providing condensed information and an exhaustive publications catalogue of supporting information and external publications. The NanoRem Toolbox will enable all users to include, when suitable, nanoremediation in option appraisals and practical applications.

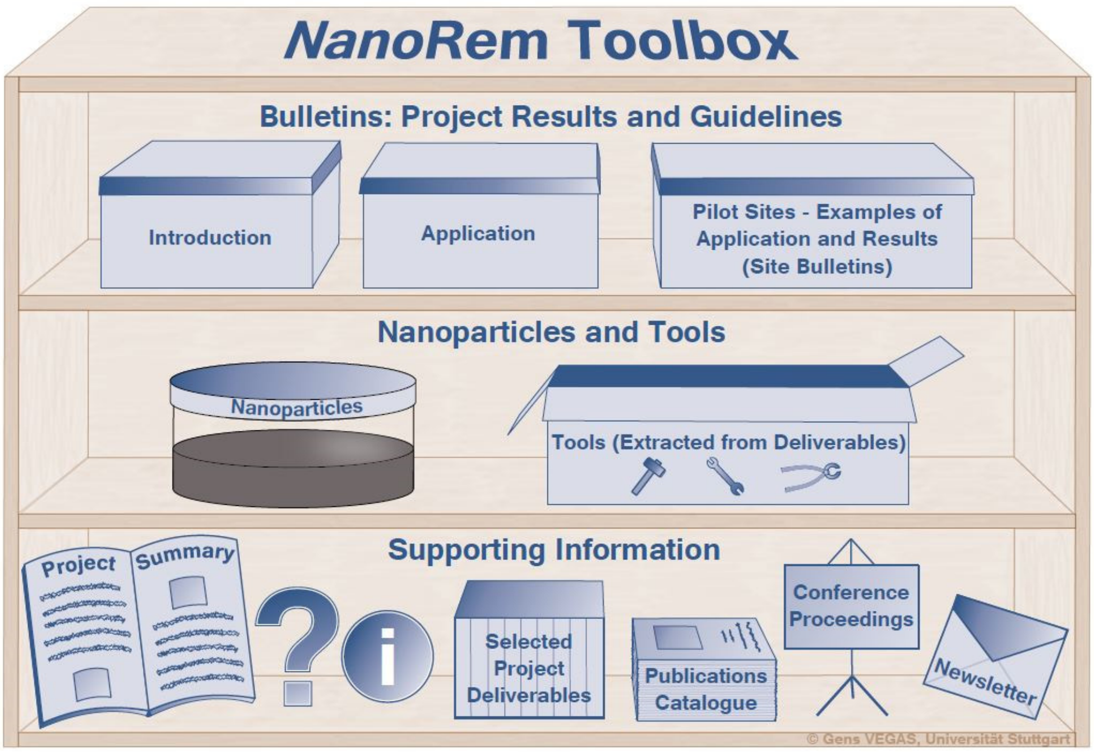

Figure 6. The NanoRem Toolbox, freely available from www.nanorem.eu

For further information on NanoRem please visit www.nanorem.eu

The lead editor of this bulletin was Paul Bardos - r3 with contributions from all NanoRem Work Packages and the Project Advisory Group.

If you would like further information about other CL:AIRE publications please contact us at the Help Desk at www.claire.co.uk

[4] International Standards Organization – ISO (2015) ISO/DIS 18504 Soil quality -- Guidance on sustainable remediation http://www.iso.org/iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=62688 Accessed November 2015