



**Taking Nanotechnological Remediation Processes  
from Lab Scale to End User Applications  
for the Restoration of a Clean Environment**

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**WP1: Scientific Project Management and Coordination**

**DL1.1: European advances in nanoremediation  
technology: NanoRem sessions and presentations  
at the AquaConSoil 2015**

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[Downloaded from www.nanorem.eu/toolbox](http://www.nanorem.eu/toolbox)

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Contributions of many NanoRem researchers have been put together for this deliverable. The authors are separately noted in the included papers.

**Reviewed and agreed by PMG**

## Executive Summary

NanoRem had a major presence at the International AquaConSoil Conference 2015 held in Copenhagen in June. The conference is the major European event for contaminated land and water management practitioners dealing with remediation technologies, and focuses on sustainable use and management of soil, sediment and water resources. NanoRem partners presented a broad range of their work through two special sessions, ten platform presentations, and about twenty posters.

NanoRem project's profile was raised on day three of the conference where the first of three nanoremediation sessions was held which provided an opportunity for the audience to find out about nanoremediation - "All they wanted to know (a practical guide to nanoremediation)". This session set the scene for a hugely successful event by giving the audience the opportunity to understand more about nanoremediation, what it is, its effectiveness as a technology to date and concerns that people have had in using it. After the introduction presentation on nanoremediation, an introduction to the NanoRem project was provided and showed how the project is aiming to address nanoremediation's effectiveness in the field, how it is looking to provide more certainty for implementation costs and looking at addressing potential risks of use. The session was extremely well attended and there was discussion about what NanoRem needs to do and to develop the market for nanoremediation to be a credible alternative remediation technology.

The second session "Nanoremediation - your future business opportunities (strategic and market intelligence)" was interactive. It provided the audience with presentations on market intelligence that the NanoRem project had gathered from key stakeholder workshops that have previously been organised in Berlin and Oslo. The session was organised as a World Café™ format where groups of people from different backgrounds were asked to openly discuss what they perceived were the technical and commercial hurdles currently existing and need to be overcome to develop credible market opportunities for nanoremediation. Although less participants attended this session in comparison to the first session, the workshop was fruitful and again gave the NanoRem project many ideas to move forward with and develop.

Later in the afternoon a whole NanoRem technical session "European Advances in nanoremediation technology: novel catalysts, targeted delivery, and scaling up to field" occurred where five presentations were given. This session was chaired by Hans-Peter Koschitzky the NanoRem project coordinator. This session gave the audience an opportunity to hear from some of the NanoRem partners on different aspects of their research, including laboratory and field based experiments and information about the pilot site applications that NanoRem are using.

In addition to the special NanoRem focussed sessions, a further five platform presentations and about twenty posters were given at the conference by NanoRem partners drawing from the extensive research work undertaken within the project.

We surveyed experiences from our team after the meeting, and found that they had received really positive feedback about what the NanoRem project has achieved so far and people were keen to see further field results. People felt that the main hurdles to overcome were:

- To demonstrate the use of nanotechnology in large scale remediation - as it was felt that there is still uncertainty as to its effectiveness in the field,
- Implementation costs - as these are not known with enough certainty,
- Potential exposures to unintended receptors – as these are still not fully understood.

All these elements need to be addressed and will help build confidence in the use of nanotechnology as a credible remediation option. If NanoRem could help address some or all of these issues then the project will be seen as a success. The challenge is set !!

For further information on the papers and posters presented at AquaConsoil, please visit the Quick Links area of the NanoRem website <http://www.nanorem.eu>

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# 1 The NanoRem Project at the AquaConSoil Conference

The AquaConSoil conference is the major European event for contaminated land and water management practitioners. At the 2015 edition of the Conference, NanoRem had a major presence. NanoRem partners gave 15 talks about their work in Thematic Session 1C.28S: *European advances in nanoremediation technology* and two special sessions, Session 1C.23S: *Nanoremediation all you wanted to know – a practical guide to nanoremediation* and Session 1C.24S: *Nanoremediation – your future business opportunities*. These sessions and their position in the overall conference program are marked in Figure 1.

Moreover, the ACS Programme Committee placed some of the presentations and posters submitted by the NanoRem consortium in other sessions, e.g. Thematic Session 1C.15: *Combined treatment technologies 2* or Thematic Session 1C.17: *In Situ Chemical Oxidation (ISCO) 2*.

More information on the scope of the sessions and the presentations given in the sessions is given in chapter 2.

| Time/ Room                 | Auditorium (10/11/12)  | Auditorium 10   | Auditorium 11  | Auditorium 12   | Meeting Room 18  | Meeting Room 19  | Meeting Room 20  | Special locations       |
|----------------------------|--|---|--|---|--|--|--|-------------------------|
| <b>MONDAY • 8 June</b>     |  |   |  |   |  |  |  | <b>MONDAY • 8 June</b>  |
| 14:00-18:00                |  |   |  |   |  |  |  | Courses                 |
| 18:30-20:00                |  |   |  |   |  |  |  | Get Together            |
| <b>TUESDAY • 9 June</b>    |  |   |  |   |  |  |  | <b>TUESDAY • 9 June</b> |
| 09:00-10:30                | <b>Opening session</b>   |   |  |   |  |  |  |                         |
| 10:30-11:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 11:00-12:30                |  | 1C.9: Bioremediation of chlorinated solvents in groundwater 1       | 1C.18: Uncertainty in remediation                              | 2.25: Towards Urban Land Management 2065 – Brownf.          | 1A.1: Passive sampling                                       | 1D.4S: Holistic water planning: protect groundwater, DK?   |  |                         |
| 12:30-14:00                | Lunch  | Lunch   | Lunch  | Lunch   | Lunch  | Lunch  | Lunch  |                         |
| 14:00-15:30                |  | 1B.15: Implementation EU Water Framework Directive                  | 1C.10: Bioremediation of chlorinated solvents in groundwater 2 | 1C.14: Combined treatment technologies                      | 2.3: Redevelopment of brownfields part 1                     | 1B.25A: Wt gr -w. contam. from pesticide point sources     | 1C.1: Comparison sustainable rem. approaches               |                         |
| 15:30-16:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 16:00-17:30                |  | 1A.2: Molecular monitoring  | 1C.20: New remediation technologies 1                          |   | 2.4: Redevelopment of brownfields part 2                     | 1B.25B: Wt gr -w. contam. fr. pesticide point sources      | 1C.2: Integr. sustainable rem. into other policies         |                         |
| 17:30-18:30                |  |   |  |   |  |  |  | Poster Social           |
| <b>WEDNESDAY • 10 June</b> |  |   |  |   |  |  |  | <b>WED • 10 June</b>    |
| 09:00-10:30                |  | 1B.6: Env. Risk Assessment – soil & groundw. 1                      | 1C.16: In situ Chem. Oxidation (ISCO) 1                        | 1D.15: Contam. sites – evolution from the fumbling          | 2.5: Reuse of contaminated soil & sediments 1                | 1A.3: Novel monitoring approaches 1                        | 1C.3: Decentralization and harmonization                   |                         |
| 10:30-11:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 11:00-12:30                |  | 1B.7: Env. Risk Assessment – soil & groundw. 2                      | 1C.11: Bioremediation of coal tar and fuels                    | 1C.15: Combined treatment technologies 2                    | 2.6: Reuse of contaminated soil & sediments 2                | 1A.4: Novel monitoring approaches 2                        | 1C.5S: Contaminated site rem. – practical decision making  |                         |
| 12:30-14:00                | Lunch  | Lunch   | Lunch  | Lunch   | Lunch  | Lunch  | Lunch  |                         |
| 14:00-15:30                |  | 1B.5S: Vapor intrusion – state of the art                           | 1C.17: In situ Chem. Oxidation (ISCO) 2                        | 1D.5S: From source tracing to rem. & dealing with con. risk | 2.7: Reusing materials from mining activities and landfills  | 1A.7S: US EPA 1: Best Practices Site Characterization      | 1C.4S: Practices achieving sust. rem. – avoiding greenwash |                         |
| 15:30-16:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 16:00-17:30                |  | 1B.8: Indoor air pollution from soil and groundwater                | 1C.22: Zero valent iron  | 1C.19: Miscellaneous remediation topics 2                   | 3.5: Ecosystems services and combined approaches             | 1A.6: Adaptive monitoring based on real time data          | 1D.3: Risk mitigation and intervention measures            |                         |
| <b>THURSDAY • 11 June</b>  |  |   |  |   |  |  |  | <b>THUR • 11 June</b>   |
| 09:00-10:30                |  | 1B.3S: After 25 years of land-related human exp. in the Netherlands | 1C.23S: Practical guide to nanoremediation                     |   | 3.1S: Application of Aquifer Therm. Energy Storage in Europe | 4.1: Adaptive water quant. & qual. management urban areas  | 1C.6S: Sust. in contam. site management – case Finland     |                         |
| 10:30-11:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 11:00-12:30                |  | 1B.4S: TRIAD investigations of soil & groundwater Contam.           |  | 1C.12: In situ remediation technologies 1                   | 3.3S: Unforeseen events in management of the subsurface      | 4.2S: Artificial Recharge of coastal Aquifers              | 1C.7: Strategies for remed. and brownfield regeneration    |                         |
| 12:30-14:00                | Lunch  | Lunch   | Lunch  | Lunch   | Lunch  | Lunch  | Lunch  |                         |
| 14:00-15:30                |  | 1C.28S: Europ. advances in nanoremediation technology               | 1C.26: Thermal remediation 1                                   | 1C.29S: A countries' approach contam. site issue            | 3.4: Subsurface planning and management                      | 1A.5: Persistence historical & emerging subsurface contam. | 1C.8: Uncertainty in remediation                           |                         |
| 15:30-16:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 16:00-17:30                |  | 1C.27: Risk modelling   | 1C.27: Thermal remediation 2                                   | 1C.13: In situ remediation technologies 2                   | 3.2S: European strategic res. agenda soil & land use         | 4.3S: climate robust water availability managem. Int. &    | 1C.30S: US EPA 2: Evol. optimization cleanup/R&D           |                         |
| 17:30-18:00                |  |   |  |   |  |  |  | Conference Dinner       |
| <b>FRIDAY • 12 June</b>    |  |   |  |   |  |  |  | <b>FRIDAY • 12 June</b> |
| 09:00-10:30                |  | 1B.10: Risk management and practice                                 | 1C.25: Phytoremediation  | 1C.21: New remediation technologies 2                       | 2.1S: Biomass for bio-based economy or for soil fertility?   | 1C.31S: US EPA 3: Remedies, greener cleanups               | 1D.2: Large scale inventories, strategies                  |                         |
| 10:30-11:00                | Coffee break   | Coffee break  | Coffee break   | Coffee break  | Coffee break   | Coffee break   | Coffee break   |                         |
| 11:00-12:00                | <b>Closing session</b>   |   |  |   |  |  |  |                         |
| 12:30-17:00                | In parallel • 10 € • start: 12:30 h • end: approx. 16–17:00 h • busses start & end at Bella Center |   |  |   |  |  |  | 6 Technical tours       |

Figure 1: AquaConSoil 2015 Programme with 3 NanoRem Special Sessions (Source: [www.aquaconsoil.org](http://www.aquaconsoil.org))

During the conference, NanoRem project members exhibited about 20 posters, which can be found in Chapter 4.

After the conference, NanoRem work package 9: Dissemination, Dialogue with Stakeholders and Exploitation surveyed experiences from the NanoRem team after the meeting. First results showed that the feedback was really positive. People were keen to see further field results

and were interested in the applicability for large scale remediation and the implementation costs. Similar to the WP9 survey, but focusing on the conference as a whole, the conference organisers have also conducted a survey. The results of this survey were announced by email after the conference.

*“All the common efforts resulted in a great conference which is nicely reflected by the results from 146 delegate evaluation forms. The scientific level, the overall judgement and many other indicators have been boosted significantly, compared to the previous two AquaConSoil editions in Salzburg and Barcelona.”* – Conference organiser Suzanne van der Meulen.

Although the boost in indicators for the scientific level can not only be attributed to the NanoRem presentations and posters at the conference, they have surely contributed to the increase.

## 2 NanoRem Sessions

The special sessions were very well prepared by WP9 together with WP1 before the ACS and were submitted to the ACS Committee. The sessions were accepted as proposed and integrated into the Conference Programme. The special sessions consisted of two parts:

*Part I of the Nanoremediation session focused on providing a practical grounding in nanoremediation theory and practice with particular reference to applied examples in the field.*

*Part II of the session focused on providing business and strategic intelligence for delegates with interests in utilizing or developing nanoremediation activities within their organisations or at client sites.*

### 2.1 Special Session 1C.23S Nanoremediation 1 – all you wanted to know (a practical guide to nanoremediation)

#### **Organizers:**

Paul Bardos (r3 environmental technology ltd, GB),  
Juergen Braun (University of Stuttgart, DE),  
Miroslav Černík (Technical University of Liberec, CZ),  
Dan Elliott (Geosyntec Consultants, US),  
Elsa Limasset (BRGM, FR),  
Hans-Peter Koschitzky (University of Stuttgart, DE)

#### **Moderator:**

Paul Bardos (r3 environmental technology ltd, UK)



**Figure 2:** View of the Auditorium of session 1C.23S (courtesy of VEGAS, 2015)

Nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants which have limited remediation alternatives. In 2007 in Europe it was forecast that the 2010 world market for environmental nanotechnologies would be around \$6 billion (JRC Ispra 2007). In fact, adoption of nanoremediation has been much slower. However, the recent emergence of nanoremediation as a commercially-deployed remediation technology in several EU countries indicates that it is timely to reconsider its potential applications and the consequent implications for their business activities.

Since early 2014, the EU FP7 NanoRem project ([www.nanorem.eu](http://www.nanorem.eu)) has been carrying out an intensive development and optimisation programme for different nanoparticles (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact. NanoRem is a €14 million international collaborative project with 28 Partners from 12 EU countries, and linkages to the USA and Asia. It is a major initiative, which will support the effective deployment of nanoremediation technologies in Europe. This session was attended by approximately 150 people.

The session was chaired by Paul Bardos and contained the following presentations:

- What nano-remediation is and what it can and cannot do,  
*Miroslav Černík (Technical University Liberec, Czech Republic)*
- Practical experience in nanoremediation,  
*Dan Elliott (Geosyntec Consultants, USA)*
- Regulatory perspective on nanoremediation use,  
*Elsa Limasset (BRGM, France)*
- The NanoRem experience: large scale and case study testing,  
*Jürgen Braun (University of Stuttgart, Germany)*

The content of the sessions can be found in more detail in the following chapters.

### 2.1.1 What nano-remediation is and what it can and cannot do

*Miroslav Černík (Technical University Liberec, Czech Republic)*

This presentation provided a practical foundation into the application of nanotechnology to environmental remediation. It provided a survey of the major drivers underpinning the development of the nanoscale zero-valent iron (nZVI) technology, other related nanotechnologies under development, as well as the key identified applications of the technology and implications associated with its use. Perspectives on the last two decades of development were covered including key upsides/downsides, technology advances, regulatory issues, and apparent limitations.

NPs are typically defined as particles with one or more dimension of less than 100nm. As a result of their size, NPs can have markedly different physical and chemical properties compared to their micro-sized counterparts, potentially enabling them to be utilised for novel purposes, including remediation. To date the most widely used NP in remediation has been nZVI. As produced, most nZVI tested falls into the 10-100 nm size range (O'Carroll et al. 2013, Karn et al. 2009), although it tends to agglomerate to form larger particles.

nZVI is used in two broad contaminant risk management configurations: elimination of source terms and/or pathway (plume) management. A range of deployment techniques may be used, and the nZVI may be modified in different ways to improve its remediation effectiveness (in particular its ability to be transported through zones of contamination, its resistance to deactivation, and its ability to bring about contaminant degradation). All of these interventions have a bearing on the relative balance of deployment risks and benefits from the nZVI use. O'Carroll *et al.* (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI.

Wiesner *et al.* (2006) describe two general nZVI synthesis methods that are used commercially: bot-

tom-up and top-down approaches. The bottom-up approach begins with dissolved iron in solution and uses a reductant to convert dissolved metal to nZVI. The top-down approach begins with micro-metre to millimetre-sized iron filings, which are ball-milled to fine, nano-sized particles. Top-down methods may also include condensation and attrition processes. In addition, a number of modifications have been developed to improve the effectiveness of nZVI by reducing the scale of agglomeration and the immediacy of passivation. Other modifications include doping with other metals to improve reactivity and suspension in emulsions to better access free-phase non-aqueous phase liquid NAPL (reviewed in Bardos *et al.* 2014).

### 2.1.2 Practical experience in nanoremediation

*Dan Elliott (Geosyntec Consultants, USA)*

This presentation traced the field experience using nanotechnology in remedial applications starting with the pioneering initial nZVI field demonstration in 2000 and progressing into the present day. Key aspects including the evolving thought on the role of nZVI in remedial design, dosage and delivery systems, stabilisation methods, and utilisation with complementary technologies were covered.

The first documented field trial of nZVI, in 2000, involved treatment of trichloroethylene in groundwater at a manufacturing site in Trenton, New Jersey, USA (Elliott and Zhang, 2001). Several commentators anticipated that nZVI technology would take off rapidly because of its perceived benefits such as rapid and complete contaminant degradation. However, subsequent uptake of the technology has been relatively slow compared to other contemporary process based technologies. Lee *et al.* (2014) have reviewed 60 field applications worldwide. Bardos *et al.* (2014) identified around 70 projects documented worldwide at pilot or full scale. Most such deployments of nZVI have focussed on the degradation of chlorinated solvents for plume (i.e. pathway interruption) management although pilot studies have also demonstrated successful treatment of BTEX, perchlorates, hexavalent chromium, diesel fuel, PCBs and pesticides. O'Carroll *et al.* (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI. Several approaches can be taken to NP deployment for contaminant remediation, including direct injection.

To date, the use of nZVI in remediation in practice is largely a niche application for chlorinated solvents in aquifers, competing with more established techniques such as in situ bioremediation, chemical reduction and granular ZVI (e.g. in permeable reactive barriers). Bardos *et al.* (2011) identified just 58 examples of field scale applications of nZVI, which was expanded to 70 examples by Bardos *et al.* (2014). Of the identified examples, 17 were in Europe (Czech Republic, Germany and Italy).

nZVI is anticipated as having two major benefits for process based remediation: possible extension of the range of treatable contaminant types, and increasing the efficacy of treatment (speed and degree of completion), and several additional or consequential benefits. To date, the use of nZVI in remediation in practice has largely been for chlorinated solvents in aquifers, competing with more established techniques such as in situ bioremediation, chemical reduction and granular ZVI (e.g. permeable reactive barriers). The majority of nZVI applications have taken place in North America, with a small number of applications in the field in mainland Europe (e.g. in the Czech Republic, Germany and Italy).

At present nano-remediation may offer advantages in some applications, compared with other in situ

remediation tools, but this will be highly dependent on site specific circumstances. In the medium to longer term nanoremediation could substantially expand the range of treatable land contamination problems.

The available evidence supports, but does not irrevocably confirm, a view that the risks of nZVI deployment should be considered in the same way as other potentially hazardous treatment reagents, such as persulphates (commonly used in situ remediation reagents (Nathanail et al. 2007, US EPA 2006) which are potentially harmful to the biological functioning of soil and can be transported over significant distances in groundwater plumes).

A substantial impediment to the use of nZVI in remediation is the uncertain basis for understanding the risks of its deployment to the wider environment, in particular to groundwater and surface water receptors. Although most laboratory studies and practitioner experience would suggest that adverse effects would be minor, localised and short-lived, there is a lack of effective particle monitoring technologies and peer reviewed and validated data from applications in the field that corroborates this view. This presents a significant challenge to regulatory acceptance which the NanoRem project seeks to address.

### 2.1.3 Regulatory perspective on nanoremediation use

*Elsa Limasset (BRGM, France)*

NanoRem is a research project, funded through the European Commission's 7<sup>th</sup> Framework Programme, on facilitating practical, safe, economic and exploitable nanotechnology for in situ remediation. The project is focusing on a whole range of particles, including the use of nano-scale zero valent iron (nZVI), which is the dominant nanoparticle used in remediation to date.

One of the activities of the project is to support a dialogue and engagement with various stakeholders in Europe in order to develop consensus about appropriate use of nanoremediation. This presentation provided NanoRem's understanding of the current regulatory perspective on nanoremediation use, including perception from key stakeholder's networks (COMMON FORUM and NICOLE).

During the NanoRem Workshop that took place in Oslo in December 2014, regulators confirmed that no major evolution in regulations specific to nanoremediation is anticipated. For the other stakeholders, nanoremediation does not appear hugely different to any other emerging and relatively unused in situ technology, except for specific issues related to nanoparticles (NP). But, as an emerging technology there are some uncertainties about its deployments risks, making some of the industry still reluctant yet. These are being addressed by NanoRem and discussed in this paper.

#### *Concerns about nanoparticle release in several countries regarding the use of nanoparticles (NP) for remediation*

Nanoremediation can be seen as a relatively recent technology with gaps in knowledge of both the technology and in the fate and transport of nanoparticles in the environment. In general, great promise is foreseen in the uptake of the technology, but there is concern that there are no clear guidelines for how health, safety and environment, nor material sustainability, concerns should be integrated into product design. It is therefore viewed as a potentially risky technology by some members of the

general public and problem holders. This cautious approach has also been adopted by some major private sector corporations, perhaps reflecting a desire to avoid any adverse reputational impact, and not seeing yet the benefits of this new technology.

At EU level, regulators do not raise any fundamental concerns regarding nano-remediation, although they are still in demand for more information to prove the applicability of NP at acceptable risks. There is however the case of a precautionary approach the UK, which has led to a voluntary moratorium on the release of engineered NPs.

This project therefore seeks to address the gap in knowledge by providing information from both laboratory and field trials. It is important to remember that risk depends on the likely fate, transport and toxicity to receptors of the substance added. NanoRem considers source-receptor-pathway linkages, possible degradation products, for the contaminants being considered in the trials, but also considers nanoparticles as a possible “source” that should not pose any danger to receptors (humans, etc.). Initial NanoRem results are showing that no significant toxicological effects are occurring on the soil or groundwater organisms for a range of nZVI nanoparticles. NanoRem’s findings also confirm an anticipated trend, i.e. as nanoparticles interact within the soil matrices they become less reactive, and therefore less toxic with time (very similar to how chemicals in general react in soil).

#### *What affects regulatory acceptance for nanoremediation- is it a special case?*

Each EU Member State has a legal and regulatory framework for dealing with remediation that may be driven by European Directives or national legislation. A nanoremediation project may involve engagement with a number of regulators. These may be to address chemical classification, labelling and packaging, health and safety, achieving remediation objectives, control of emissions (to air, land and water) from the remediation process, etc. The regulatory framework should be sufficiently developed in all or most Member States to accommodate the use of nanoparticles in remediation. However, similar to any new technology, there may be some additional barriers or perceived barriers to deployment to address with the regulators. These may include stringent, precautionary approaches or policy (e.g. moratorium in the UK) or perception of low benefits and high risks (compared to other remediation technologies), leading to doubts expressed on the usefulness or effectiveness of nanoremediation

Although there is a perception by some stakeholders on potential risks from NPs in the environment, as well as limited published evidence from nZVI use in the field for the time being- particularly for modified forms - it is unlikely that a higher burden of proof will be required by regulators prior to licensing nZVI based in situ remediation techniques, compared with other in situ remediation techniques. However, it is anticipated that on a more local level, the burden proof will be linked to the factor of safety deemed necessary by the local regulator

#### *Likely future direction of travel*

No major evolution in the regulations is anticipated that will be specific to nanoremediation. However, perceived risks on the use of nanoremediation need to be acknowledged and addressed if the benefits of nanotechnology are to be fully realised.

Field trials and research into potential toxicological effects will help address the dread of the environmental impact associated with the technology and the slow market adoption. NanoRem will aim at strengthening the evidence base for nZVI effectiveness and address public concern associated with deployment safety. This will also be reinforced by the number of projects taking place across Europe in particular, some further addressing nanoremediation testing and some others looking into developing novel NPs (e.g. development of new coatings to improve persistence and mobility).

Therefore, it is likely that over time the use of NPs within the natural environment will be viewed as less risky and improvements of the technology will occur. NanoRem's activities are a key component in achieving these improvements.

### *Sources of information*

Paul Bardos, Brian Bone, Pdraig Daly, Dan Elliott, Sarah Jones, Gregory Lowry, Corinne Merly, Stephan Bartke, Jürgen Braun, Nicola Harries, Niels Hartog, Thilo Hofmann, Stephan Wagner, Paul Nathaniel (2014) A Risk/Benefit Appraisal for the Application of Nano-Scale Zero Valent Iron (nZVI) for the Remediation of Contaminated Sites, NanoRem Taking Nanotechnological Remediation Processes from Lab Scale to End User Application for the Restoration of a Clean Environment Project Nr.: 309517, EU, 7th FP, NMP.2012.1.2. Supporting MS3 - NanoRem information for decision makers [www.nanorem.eu](http://www.nanorem.eu).

Paul Bardos, Sarah Jones, Stephan Bartke, Elsa Limasset, and Brian Bone (2015) IDL 9.4 Broad exploitation strategy and risk benefit appraisal NanoRem Taking Nanotechnological Remediation Processes from Lab Scale to End User Application for the Restoration of a Clean Environment Project Nr.: 309517, EU, 7th FP, NMP.2012.1.2. NanoRem Project Internal Deliverable IDL9.4 [www.nanorem.eu](http://www.nanorem.eu). DOI: 10.13140/RG.2.1.3773.0728

Tomkiv, Y., Bardos, P, Bartke, S., Bone, B. And Oughton, D. (in publication). The NanoRem Sustainability and Markets Workshop, Oslo, Norway, December 2014. NanoRem Report. To be available from <http://www.nanorem.eu/displayfaq.aspx?id=12>

## **2.1.4 The NanoRem experience: large scale and case study testing**

*Jürgen Braun (University of Stuttgart, Germany)*

A key part of NanoRem's research agenda is the use of large scale tank experiments and well monitored field based case studies to provide the kind of practical performance data that some regulators and users feel may be missing. This presentation provided an overview of NanoRem's work and findings to date from these activities.

A feature of the NanoRem project, unique in Europe, is the inclusion of the VEGAS containers which allow not only a closed mass balance but also indoor experiments at a field relevant scale with exactly controlled initial and boundary conditions. Moreover these containers allow maximum flexibility with contaminants and a highly disaggregated monitoring grid. Thus direct conclusions regarding the improvement of the real field sites may be drawn.

Three container experiments have been set up:

### *The Large Scale Container*

In a large heterogeneous, unconfined aquifer ( $L \times W \times H = 9 \times 6 \times 4.5\text{m}$ ) steady state groundwater flow was established. Then a BTEX plume was introduced. The goal of the experiment was to inject Goethite nanoparticles to enhance the microbial degradation of this plume.

The container is equipped with 378 groundwater sampling ports, thus a highly defined spatial analysis of the plume was possible. A numerical model (MODFLOW) was set up to model flow and transport in the aquifer. This model was also used to optimize the location of an injection well for the nanoparticles. Requirement for the injection was that the particles are “homogeneously” distributed throughout the pathway of the contaminant. At the same time it had to be insured that the injection flowrate would allow for a maximum particle transport while daylighting was prevented.

Based on these calculations then  $6 \text{ m}^3$  of a slurry containing  $20 \text{ kg/m}^3$  goethite nanoparticles was injected at a rate of  $Q=0.7 \text{ m}^3/\text{h}$ . Water samples were taken to delineate the spreading of the nanoparticles: It had to be shown that the particles reach the target zone and at the same time that they do not migrate beyond this zone. Subsequently the groundwater was sampled at regular time intervals to delineate the effect of the nanoparticle injection on the BTEX degradation.

### *The large Scale Flume I*

The first large scale flume experiment was set up to chemically reduce a chlorinated hydrocarbon (PCE) source using nano zero valent iron (nZVI) produced by Nanoiron (CZ). The artificial aquifer in the flume has dimensions of  $L \times W \times H = 6 \times 1 \times 3\text{m}$ . The unconfined aquifer ( $WT = 1.7 \text{ m}$ ) is homogeneous and a steady state groundwater flow ( $q = 0.2 \text{ m/d}$ ) was established to simulate field conditions. In this aquifer 2 kg of PCE were injected in 20 mL increments to create a residual contaminant source of about  $0.7 \text{ m}^3$ .

At 32 sampling ports water samples were taken at regular intervals to prove that the source was stable in space (no remobilization) and that a steady state plume was established. After establishment of the plume Nanofer 25s particles were injected using a direct push rod. The injected slurry was prepared online using the AQUATEST Vulcanus mixing unit which allows for a continuous addition of concentrated nZVI slurry into the injection stream. A total of  $1 \text{ m}^3$  suspension with a concentration of  $c_{\text{nZVI}} = 10 \text{ kg/m}^3$  was injected at different locations throughout the contaminant source. The spreading of the nanoparticles was monitored using susceptibility probes as well as micro pumps. Again the injection pressure and flowrates were limited to prevent daylighting. First preliminary results indicate that the injection rate thus chosen ( $Q = 0.1 \text{ m}^3/\text{h}$ ) was not sufficient to provide a flow field sufficient to transport the nanoparticles for an appreciable distance. Currently the particle suspension is being improved to obtain better migration results in the next injection.

### *The Large Scale Flume II*

The aquifer in the second large scale flume is identical to the one in the first flume, but the monitoring equipment installed is slightly different. Where the first flume sports a series of susceptibility spoils, these have been omitted in the second flume since here Carbo-Iron® was injected. Carbo-

Iron<sup>®</sup> contains of approx. 60w% activated carbon (AC) and both 25w% nZVI 15wt% iron oxide inside the AC grain. To obtain an injectable suspension, 20kg Carbo-Iron<sup>®</sup> powder and a minimal amount of CMC (5 wt% compared to particle mass) were mixed in tap water. CMC was used to prevent agglomeration of Carbo-Iron<sup>®</sup> particles and, thus, to ensure controlled migration of the reactant in the aquifer. While the flume experiment had been set up and steady state base flow had been obtained the Carbo-Iron<sup>®</sup> suspension was being optimized. NanoRem milestones required an injection in June of 2015. This deadline was held and first initial results were reported in the AQUACONSOIL presentation.

### 2.1.5 Wrap Up and Clinic Offer

*Paul Bardos (r3 environmental technology ltd, GB)*

A NanoRem brochure “Nanoremediation: what’s in it for me?” was provided to participants. This included an enquiry form which could be completed and handed back to the session organisers on the day. The brochure and form were also available as a link on [www.nanorem.eu](http://www.nanorem.eu). The enquiry form offered the chance for delegates to find out more about the NanoRem project, but also to ask specific questions about their own nanoremediation interests which the consortium endeavoured to answer in the weeks following AquaConsoil.

Note: Delegates were provided with a NanoRem web link for take home materials from special session presentations that they can use within their own organisations to support further decision-making

## 2.2 Special Session 1C.24S Nanoremediation part 2 - your future business opportunities (strategic and market intelligence)

### **Organizers:**

Paul Bardos (r3 environmental technology ltd, GB),  
Stephan Bartke (Helmholtz Centre for Environmental Research, DE),  
Nicola Harries (CL:AIRE, GB),  
Hans-Peter Koschitzky (University of Stuttgart, DE)

### **Moderator:**

Nicola Harries (CL:AIRE, GB)

Nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants which have limited remediation alternatives. In 2007 in Europe it was forecast that the 2010 world market for environmental nanotechnologies would be around \$6 billion (JRC Ispra 2007). In fact, adoption of nanoremediation has been much slower. However, the recent emergence of nanoremediation as a commercially-deployed remediation technology in several EU countries indicates that it is timely to reconsider its potential applications and the consequent implications for their business activities.

Since early 2014, the EU FP7 NanoRem project ([www.nanorem.eu](http://www.nanorem.eu)) has been carrying out an intensive development and optimisation programme for different nanoparticles (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact. NanoRem is a €14 million international collaborative project with 28 Partners from 12 EU countries, and linkages to the USA and Asia. It is a major initiative, which will support the effective deployment of nanoremediation technologies in Europe.

### **Programme:**

- Preliminary scenarios for the EU nanoremediation market in 2025 – assessment of market drivers (opportunities and challenges) affecting the take-up of nanoremediation,  
*Stephan Bartke (Helmholtz Centre for Environmental Research - UFZ, DE)*
- Discussion in groups about market prospects and drivers,  
*Nicola Harries (CL:AIRE, UK), Elsa Limasset (BRGM, France), Stephan Bartke (UFZ, Germany), Paul Bardos (r3 environmental technology ltd, UK)*
- Plenary reporting back of discussion groups, wrap up and clinic offer,  
*Paul Bardos (r3 environmental technology ltd, UK)*

### **2.2.1 Preliminary scenarios for the EU nanoremediation market in 2025 – assessment of market drivers (opportunities and challenges) affecting the take-up of nanoremediation**

*Stephan Bartke (Helmholtz Centre for Environmental Research - UFZ, DE)*

This presentation reviewed stakeholder meeting and focus group information collected by NanoRem over 2014/2015 on factors determining market developments. The intention was to provide an informative but not prescriptive talk. Part of the strategic and business intelligence provided was from self-learning as the session delegates interacted with each other in a structured way in small groups.

Various external determinants from economy, technology development, politics and society affect the property market in general and the industry for contaminated land remediation in particular. In order to develop an exploitation strategy that considers the medium to longer term potential market development for nZVI, any analysis has to deal with an uncertain future. The factors (i.e. drivers and uncertainties related to driver development) that foster or inhibit the evolution of the market need to be better understood. It is unclear how the factors likely to influence the nanoremediation market development are linked, and how they are likely to develop in the future. It is challenging, therefore, to make any straightforward predictions regarding the emerging nanoremediation market. As a result, traditional supply and demand modelling is unsuitable. A simple use of neo-classic economics' theory fails to reveal and quantify the role that nano-remediation options could unfold under different future market conditions, because there are severe caveats regarding standard assumptions made in such traditional market assessments. A scenario approach was therefore used to help forecast potential market developments. The outcomes are utilisable for: "real-world" business development, deducing strategies for market activities; informing policy development, identifying governance options for market expansion; and/or informing regulatory authorities, highlighting the potential for nanoremediation.

### *The Scenario Approach*

Scenarios can be defined as "internally consistent stories about ways that a specific system might evolve in the future" (March *et al.* 2012, 127). Scenario analysis builds on both i) a system thinking approach, i.e. it acknowledging that actors are in a complex network of manipulable and uncontrollable drivers, which are connected to each other; and ii) the ability to think in multiple futures, i.e. actors do not reduce strategic thinking to merely one precise anticipated future, instead, they insure alternative futures are generated and applied in strategic management (Gausemeier *et al.* 1998).

In essence, a scenario-based approach to understanding possible market trends uses available evidence and stakeholder participation to develop a number of narratives describing the potential evolutionary outcomes of a specific market system. Hence, this approach has been applied in order to help determine:

- What the factors (drivers and uncertainties) are in the nanoremediation market-system.
- What the extent of the factors' impacts is.
- How the factors interdepend.

Scenario design and analysis differ, but usually a stepwise approach is taken. In NanoRem, the following procedure was selected:

- Conducting a present situation analysis to establish the baseline for scenario development and a framework for factor identification.
- Filtering and systematising factors that drive or inhibit market development. Establishing key determinants.
- Projection of key factors' developments and producing consistent stories about ways the system might evolve in the future. Identification of multiple alternative development trajectories is possible.

- Deciding on planning-oriented exploitation strategies, which may be responsive or proactive. Development of governance recommendations.

Scenarios can be established through participatory or through individual, often analytically based research (van Notten et al., 2003; Alcamo 2008). When accomplished in a stakeholder involving manner, scenario development may serve as an exercise in ‘anticipatory’ or ‘social’ learning. NanoRem applied a participatory approach, as this is said to better being able to capture the high diversity of drivers affecting the evolution of a system into the future (March et al. 2012). Involving experts ensured the relevance of the work for practical stakeholder needs, decision support as well as for recommendations on exploitation strategies.

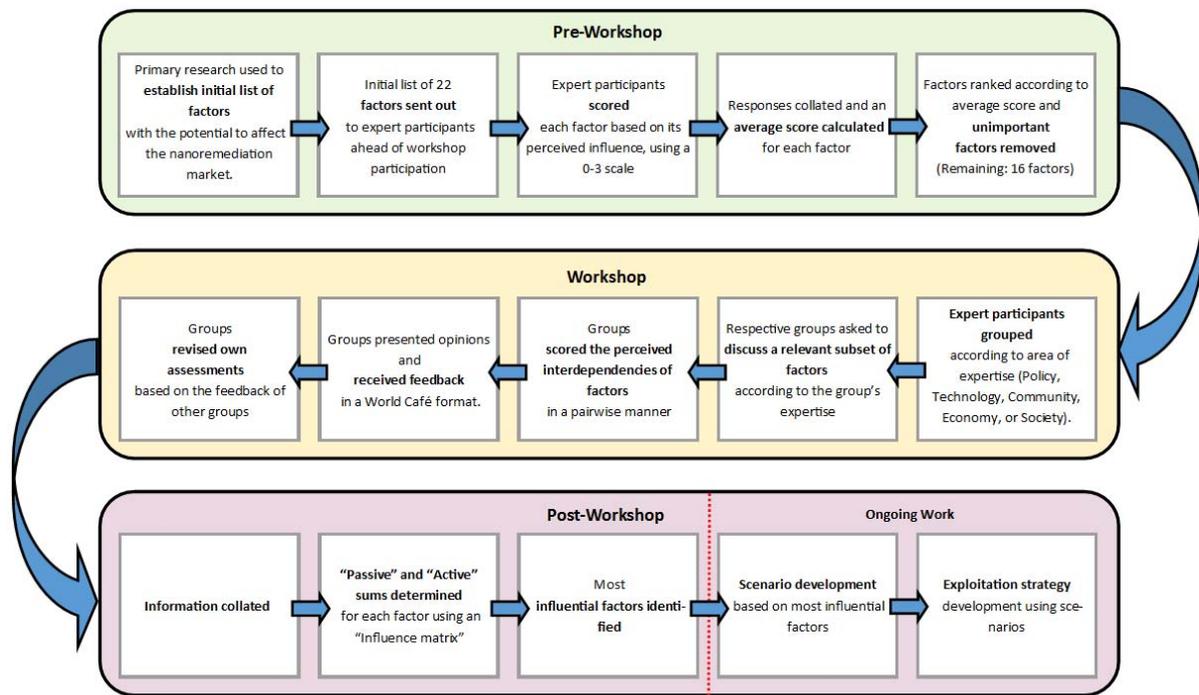
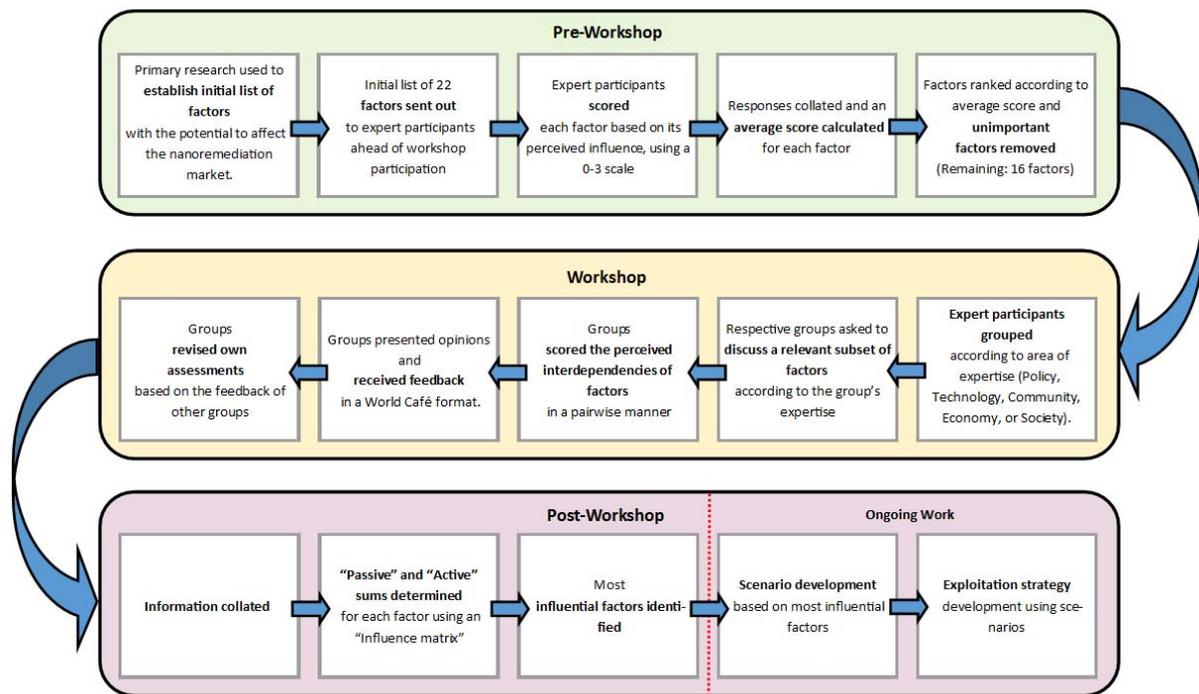


Figure 3 below gives an overview of the the work conducted so far as part of a scenario approach, and ongoing work. The steps are discussed further in the following sections. The overall approach is discussed in more detail in Bardos *et al.* 2015 and the workshop is reported in further detail in Tokiv *et al.* 2015



**Figure 3:** Overview of the scenario approach process (courtesy UFZ, 2015)

### *Establishing the Baseline for Scenario Development*

To fulfill step one of the scenario development approach, a baseline understanding of the nanoremediation market and the set of factors with the potential to influence the future development of the nanoremediation market was established. This was achieved via key-informant interviews and literature analysis, taking into account the market *status quo* and risk-benefit appraisal (cf. Bardos et al. 2014). This preliminary research helped establish a variety of external determinants from economy, technology development, politics and society that may affect:

- The property market in general;
- The industry for contaminated land remediation broadly, and;
- The potential evolution of nanoremediation in particular.

Expert engagement (key informant interviews and expert discussion) was utilised to establish the most worthwhile timeframe for the scenario approach. A consensus was reached that evolution of the market up to 2025 was the most appropriate scope. It was felt that a very long-term assessment would be impossible due to the significance of unknown and uncertain factors. After several iterations with expert involvement, a condensed list of 22 potentially influencing factors was established.

### *Systematising Market Development Factors*

To aid step two of the scenario design process, a “Market Opportunities” session was included in the Sustainability and Markets workshop (cf. Tomkiv et al. 2015). The Oslo event was a participatory approach to conclude on the systematic interdependencies and importance of the factors in order to capture through engagement with the participants with their different backgrounds the high diversi-

ty of drivers and inhibitors affecting the market system.

The 22 factors determined in the preliminary research stage were grouped into different categories (policy, economy, society, communication, technology and megatrends). The use of categories helped to align the factors with appropriate expertise for later discussions. In order to further condense the list of factors and remove less important factors, the list was sent to the workshop participants in advance of the workshop. Participants were asked to provide feedback on how important they perceived each factor to be for the development of the EU nanoremediation market from present to 2025. Participants scored each factor according to the following scale:

- (0) = Negligible relevance – the factor is not an important driver or inhibitor;
- (1) = Minor relevance – the factor might have a limited but not so important effect;
- (2) = Considerable relevance – the factor is likely to have a notable (indirect) effect;
- (3) = Key relevance – this factor is most certainly among those of utmost importance to push or pull the nanoremediation market development.

The responses (20 respondents) were collated and an average score (the arithmetic mean as the sum of the scores collected from all the respondents, divided by the number of the respondents) was calculated for each factor.

The results are shown in **Table 1** below, in descending order of obtained scores.

**Table 1:** Preliminary factors and their perceived importance with regards to influencing nanoremediation market development in the EU up to 2025

| Factor  | Score | Category      |
|---|-------|---------------|
| <b>Most important factors (<math>\geq 2.00</math>):</b>                         |       |               |
| Innovation on treatment of known contaminants with NPs                          | 2.48  | Technology    |
| Regulation of nanoparticles   | 2.45  | Policy        |
| Validated information on NP application potential                               | 2.40  | Communication |
| Costs of competing technologies   | 2.35  | Economy       |
| Standardization for nanoparticles   | 2.20  | Policy        |
| Innovations along NPs production chain  | 2.18  | Technology    |
| Environment (especially soil) protection policies                               | 2.10  | Policy        |
| Synergies with other technologies   | 2.05  | Technology    |
| Public stakeholder dialogue   | 2.00  | Communication |
| <b>Less important factors (<math>&gt;1.50</math> and <math>&lt;2.00</math>)</b> |       |               |
| NP treatment of emerging contaminants   | 1.95  | Technology    |
| Public perception of NPs in general   | 1.93  | Society       |
| Science-Policy-Interface  | 1.93  | Communication |

|  |      |           |
|--|------|-----------|
| Technology and research policies                       | 1.75 | Policy    |
| Growing number of nanoparticles suppliers              | 1.73 | Economy   |
| Real estate market development                         | 1.68 | Economy   |
| Innovation attitude                                    | 1.60 | Society   |
| Environmental awareness                                | 1.55 | Society   |
| <b>Minor relevant factors (<math>\leq 1.50</math>)</b> |      |           |
| EU economic development                                | 1.50 | Economy   |
| Globalisation  | 1.20 | Megatrend |
| Industrial and military land use                       | 1.00 | Society   |
| Climate change   | 0.70 | Megatrend |
| Demographic change                                     | 0.60 | Megatrend |

The scorings indicate that several factors influence the market's development. Some of the scorings, e.g. the ability to treat emerging contaminants with NPs, are surprising and may indicate either bias or epistemic issues in the mind of the responders. As no factor had a scoring  $> 2.50$ , it was concluded that no factor is likely to singlehandedly "push" or "pull" nanoremediation market development.

In order to create scenarios, the interdependencies of the factors determined to be important needed to be better understood. Stakeholders were provided with the factors in **Table 1**.

including short descriptions of each factor. During the workshop, stakeholders were asked to provide opinions, comments and suggestions about the factors and were also asked to identify and discuss the interrelations of the factors. In order to do this, stakeholders were divided into smaller groups based on their field of expertise. The groups formed were Regulators / Policy makers, Technology, Communication, Economy and Society. Participants in the respective groups were asked to discuss the influence of three or four factors of their respective expert domain on the full list of factors identified to be of importance.

For each group a poster with an empty influence matrix was provided showing a short list of factors from the respective field of a group's expertise in the rows on the vertical axis and the full list of factors in the columns on the horizontal axis. Figure 4 illustrates the influence matrix's outline.

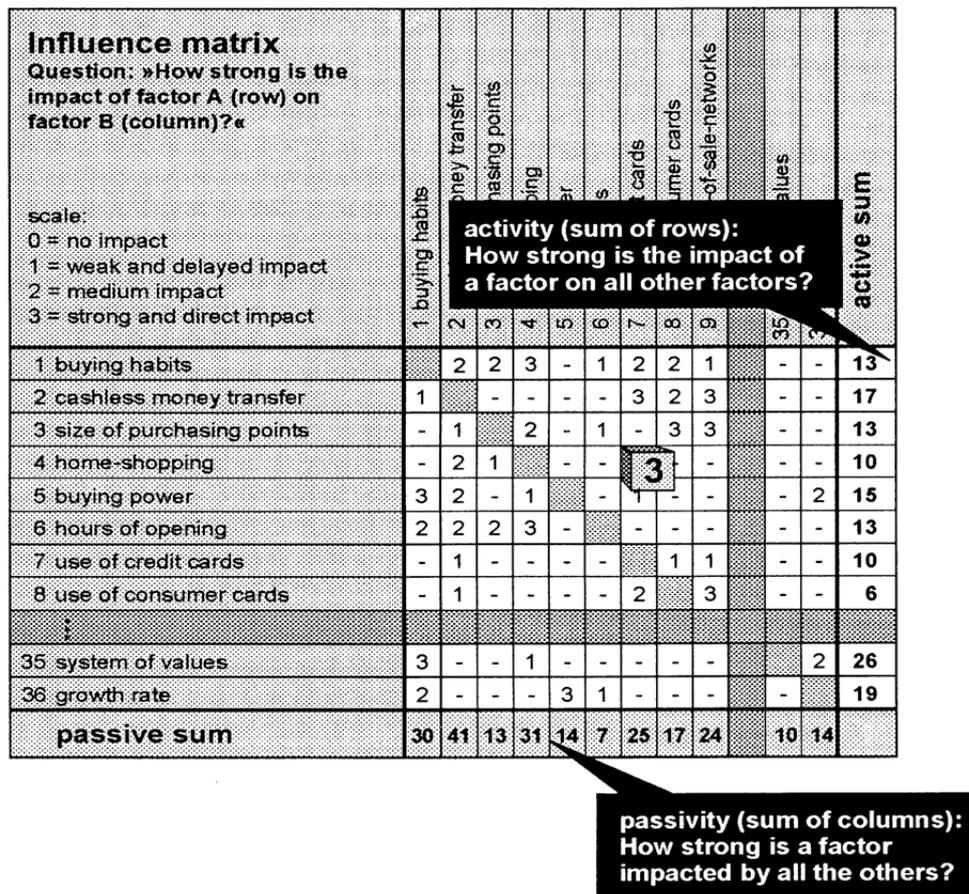


Figure 4: Interaction matrix illustration (Gausemeier et al., 1998, p. 119)

The participants in a first phase were asked to review and provide opinions, comments and suggestions about the collected factors in the rows. Next, they were asked to identify and discuss the interrelations of the development of each of their factors in the lines on the full list of factors, i.e. to discuss pairwise the influence of development of a factor from the vertical axis on the development of a factor from the horizontal axis. For the assessment, again a scoring was re-requested (as indicated in Figure 4, too): Considering the European Union in 2025, the impact of the development of the factor in the row on the development of the factor in each column was gauged using the scale:

- (0) = No impact;
- (1) = Weak / delayed impact;
- (2) = Medium impact;
- (3) = Strong / direct impact.

At the end of this phase, each group had filled in their part of the influence matrix. After the workshop it was possible to add up the rows and to obtain a full matrix containing all factors in the rows and columns – however, this was not done at the Oslo event, as the key objective here was to best substantiate the assessments within the matrix. Therefore, in a subsequent phase of the event, taking up the World Café™ format, the participants were invited to discuss one by one the results of the other groups. Facilitators guided these discussions from the identification to the review of the linkages of factors. At the end of the phase, the participant returned to their “home table” and revisited their assessments based on the feedbacks collected from the other groups. At the end of the Session,

the annotated posters and notes of facilitators were collected and interpreted.

After the workshop, the information collected from the group sessions was analysed and the factors that are more “active” in influencing other factors were identified, as well as those that are more driven by the active ones. These relationships are expressed by the “active sum” and “passive sum” as indicated in Figure 4 above and in Table 2, below. Table 2 lists the five most active factors from those recorded in order of their activity (i.e. how influential a factor is relative to other factors).

**Table 2:** Interrelatedness of factors determining the development of the nanoremediation market

| Factor  | Active sum* | Passive sum* |
|---|-------------|--------------|
| Science-Policy-Interface                          | 38          | 26           |
| Validated information on NP application potential | 36          | 21           |
| Environment (especially soil) protection policies | 25          | 17           |
| Public stakeholder dialogue                       | 25          | 20           |
| Synergies with technologies                       | 24          | 20           |

\*Active and Passive sums had a maximum potential value of 48. The closer the active sum for a factor is to 48, the more influential that factor is. Conversely if the passive sum for a factor is close to 48, it is likely to be highly influenced by changes in other factors.

#### *Projection of Factor Development and Establishing Consistent Scenarios*

As part of ongoing work, a series of expert engagement activities is underway. In March 2015, NanoRem conducted a first focus group meeting and expert workshop in Berlin, Germany, in order to discuss the establishment of consistent scenarios. The participants were provided with an overview of the interim results of the scenario analysis work. They were shown that the two most “active” of the key factors were identified as: “Science-Policy-Interface” and “Validated information on NP application potential” (see Table 2 and hence, these factors are likely to be crucial in determining the development of the nanoremediation market system. These two factors were suggested for the development of framing elements for a conceptual scheme for scenario states. The participants discussed the meaning of these factors and tentatively defined them as follows:

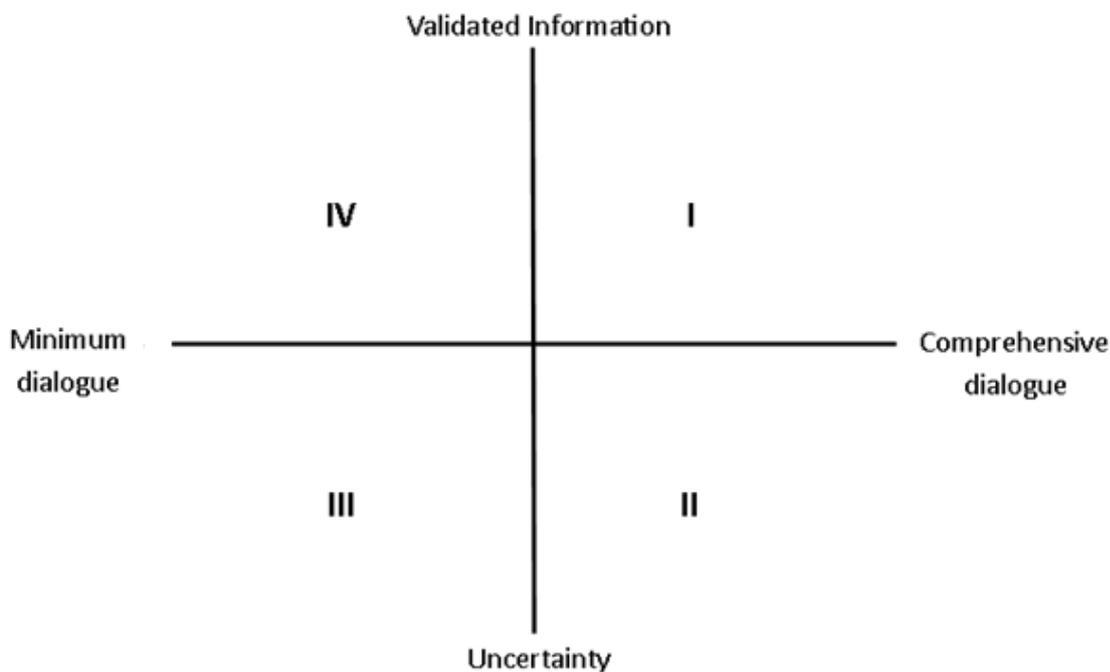
Science-Policy-Interface is part of a broader ‘Dialogue’, which is the process by which stakeholder groups (in particular those from science, policy and regulation) have informal/formal discussions, consultations and other forms of engagement in order to ascertain the potential application of nanoremediation (in general or in specific cases).

Validated information on NP application potential is an ‘Information’ dimension, which describes the quality of available information for decision-making. Information can range from a level of great uncertainty with regards to the potential developments of the market and the set of factors driving the market, to a situation where information about nanoremediation is readily available, well tested, and broadly accepted (i.e. “validated”). “Validated information” gives credence to a decision regarding its applicability.

These dimensions form the conceptual scheme for the scenario states of the nanoremediation market. These scenario states show four potential future states for the market, see

Figure 5 **Fehler! Verweisquelle konnte nicht gefunden werden.** below, (going clock-wise in each quadrant of the matrix):

- I. Validated information is broadly available AND there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.
- II. Validated information is lacking and uncertainty is still significant BUT there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.
- III. Validated information is lacking and uncertainty is still significant AND there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.
- IV. Validated information is broadly available BUT there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.



**Figure 5:** Conceptual Scheme for Scenario States (courtesy of UFZ, 2015)

The final steps of the scenario analysis will be the discussion of the key factors' developments within the different scenario states, and based on these, the deduction of scenario storylines. These discussions will finally inform the conclusion of recommendations for the exploitation strategy.

The Scenario approach will continue to be expanded, with scenario development continuing over Year 3 of the NanoRem project. Further expert engagement in focus groups and workshops has been planned in order to discuss the scenario scheme and future market states that reflect the interactions identified in the Oslo workshop and specify directions of factor development under the potential market states. The scenario storylines concluded from these activities will be used to derive conclusions on the medium to longer term exploitation opportunities and recommendations for entrepreneurs and policymakers.

### 2.2.2 Discussion in groups about market prospects and drivers

*Nicola Harries (CL:AIRE, UK), Elsa Limasset (BRGM, France), Stephan Bartke (UFZ, Germany), Paul Bardos (r3 environmental technology ltd, UK)*

Discussion in groups, each with a NanoRem facilitator provided a chance for active discussion and exchange of ideas about market prospects, drivers and recommendations were concluded on the day. A short report of findings was provided on <http://www.nanorem.eu/news.aspx>.

The discussion addressed the following questions in particular

1. How are things changing / likely to change
2. What is the most critical information to achieve positive shifts in the uptake of nanoremediation
3. How are the factors presented likely to influence the various organisations and people taking part in the Café.

Discussions used the World Cafe™ discussion format and were followed by a plenary session where each group reported back and exchanged ideas.

### 2.2.3 Plenary reporting back of discussion groups, wrap up and clinic offer

*Paul Bardos (r3 environmental technology ltd, UK)*

A NanoRem brochure “Nanoremediation: what’s in it for me?” was provided to participants. This included an enquiry form which could be completed and handed back to the session organisers on the day. The brochure and form were also available as a link on [www.nanorem.eu](http://www.nanorem.eu). The enquiry form offered the chance for delegates to find out more about the NanoRem project, but also to ask specific questions about their own nanoremediation interests which the consortium endeavoured to answer in the weeks following AquaConsoil.

Note: Delegates were provided with a NanoRem web link for take home materials from special session presentations that they could use within their own organisations to support further decision-making.

## 2.3 Session 1C.28S European advances in nanoremediation technology

### Chair:

Hans-Peter Koschitzky (University of Stuttgart, DE)

The ACS Programme Committee and the NanoRem Coordination (WP1) agreed to group five of the submitted presentations in a plenary session. This session was held in one of the conference centre's large Auditoriums and took place on Thursday afternoon, right after the lunch break. The session was chaired by the coordinator of NanoRem, Hans-Peter Koschitzky, approx. 100 interested participants attended the session and discussed the following talks:

- In-situ Groundwater Remediation Using Carbo-Iron®: Large Scale Flume Experiment to Investigate Transport and Reactivity in a source-treatment approach,  
*Kumiko Miyajima (University of Stuttgart, DE)*
- Reactivity tests in columns for simulating source zone and plume remediation of chlorinated hydrocarbons by zero-valent metal particles under subsurface-like conditions,  
*Christine Herrmann (University of Stuttgart, DE)*
- Agar agar stabilized milled zerovalent iron particles for in situ groundwater remediation,  
*Stephan Wagner (University of Vienna, AT)*
- Demonstrating Nanoremediation in the Field - The NanoRem Test Sites  
*Juergen Braun (University of Stuttgart, DE),*
- Performance of Carbo-Iron particles in in-situ groundwater plume and source treatment approaches,  
*Katrin Mackenzie (Helmholtz Centre for Environmental Research, DE)*
- Nanoiron and Carbo-Iron® particle transport in aquifer sediments - Targeted deposition,  
*Steffen Bleyl (Helmholtz Centre for Environmental Research, DE)*

These presentations gave an overview of the research progress made in the NanoRem project and showed impressive first results of the tests. The speakers also highlighted future possibilities for remediation using nanoparticles and clarified issues during the discussion after the talks.

The presentations managed to create more interest in the NanoRem project. After the session, many attendees approached the table with NanoRem project information and picked up a copy of the promotional material about nanoremediation and the project itself.

A summary of the talks given during this session can be found in the following chapters.



**Figure 6:** Impressions of the special session 1C.28S with the speakers K. Miyajima, C. Herrmann, K. Mackenzie, S. Bleyl, S. Wagner and J. Braun (courtesy of VEGAS, 2015)

### 2.3.1 In-situ Groundwater Remediation Using Carbo-Iron®: Large Scale Flume Experiment to Investigate Transport and Reactivity in a source-treatment approach

*Kumiko Miyajima (University of Stuttgart, DE), Katrin Mackenzie (Helmholtz Centre for Environmental Research - UFZ, DE), Juergen Braun (University of Stuttgart, DE)*

This presentation focused on the goal and set-up of the experiments, the injection of NP and presented first results of the investigation of transport and reactivity issues.

NanoRem (Nanotechnology for contaminated land Remediation) is a research consortium (EU, FP7) dedicated to develop in-situ groundwater remediation technologies. Nanoparticles were developed to be injected into the contamination to create a reactive zone in which contaminants degradation or immobilization will take place. Investigations were conducted at various scales including large scale containers with volumes of over 240 m<sup>3</sup>. These large scale upscaling investigations were indoor experiments at a field relevant scale with exactly controlled initial and boundary conditions and a highly disaggregated monitoring grid. They allowed for a closed mass balance, and maximum flexibility with contaminants and conclusions with respect to improving the real field sites.

To test the performance of Carbo-Iron® for the first time in a source-remediation approach, a large scale flume experiment in a container of stainless steel (L x W x H = 6 x 1 x 3m) was set-up at VEGAS, University of Stuttgart. The aquifer was contaminated with a perchloroethene (PCE) source and chemically reduced utilizing an injected Carbo-Iron® suspensions. The accurate description of the aquifers and the contaminant distribution as well as a dense monitoring system allow for the testing of these nanoparticle materials and provide insight in particle transport in porous media and knowledge on degradation products under field-relevant conditions.

Goals of the experiment were

- a. remediation of PCE source (2kg) utilizing the Carbo-Iron®, composite particles containing nZVI in a colloidal activatedcarbon framework
- b. design, set-up and test of Carbo-Iron® injection system; determination of suitable composition of suspension and of necessary flow velocities during injection
- c. transport and targeted deposition of NP in the subsurface
- d. quantification of remediation (degradation) rates and longevity of NP (reinjection intervals).

In the large scale flume an artificial aquifer was set up consisting of a flow domain of 5.6 x 1.0 x 3.0 m (L x W x H) of medium sized homogeneous sand. Inflow and outflow boundaries were established using hydraulically communicating wells, with constant flux and constant head control, respectively. The aquifer was unconfined and its thickness during base flow ( $v = 0.2$  m/d) was at approximately 1.7 m, resulting in an unsaturated zone of approx. 1.3 m. The flume offered a total of 36 sampling ports, distributed in six horizontal planes and six vertical planes to the flow direction.

The PCE source was emplaced by injecting pure PCE into the saturated zone soil. A total mass 2 kg of PCE was injected at six locations placed at equal distances on a circle of  $r = 30$  cm, at 10 different depths (33.3 g each) at 10 cm vertical intervals starting at the groundwater table. By this kind of injection a contaminant source zone of approximately 0.90 m diameter, a depth of 1 m, and hence a volume of 0.64 m<sup>3</sup> was established with residual saturation around 0.6%.

For the remediation of this source, the injection of Carbo-Iron® was designed along the following

criteria:

- a. Place particles in sufficient quantity within the source zone: based on stoichiometry a remediation of 2 kg PCE requires 2.6 kg nZVI (= 13 kg Carbo-Iron®). To account for heterogeneities and competing reactions a total mass of 20 kg Carbo-Iron® was injected.
- b. Minimize injected volume to avoid loss of PCE during injection. Thus 1 m<sup>3</sup> suspension with a high concentration (20 g/L) of Carbo-Iron® and optimized concentration of the stabilizer carboxymethylcellulose was employed.

During and after the injection, the particle transport distance, concentration and sedimentation were monitored. The preliminary remediation result was obtained after the injection.

### **2.3.2 Reactivity tests in columns for simulating source zone and plume remediation of chlorinated hydrocarbons by zero-valent metal particles under subsurface-like conditions**

*Christine Herrmann, Maurice Menadier, Norbert Klaas (University of Stuttgart, DE)*

Chlorinated hydrocarbons are commonly detected groundwater contaminants. Permeable reactive barriers composed of zero-valent iron are well-established for remediation of the contaminant plume. Current studies are aiming at implementing the injection of zero-valent iron (nano)particles into the subsurface, thus allowing for a treatment of source and plume areas. (Cundy et al., 2008)

However, it has been reported that iron particles show a poor transport behaviour (Phenrat et al., 2007). Aluminium and magnesium have a lower density compared to iron which might promise better transport properties. In addition, aluminium and magnesium offer a better stoichiometry relative to mass in comparison with iron. On the other hand aluminium and magnesium particles are more susceptible to corrosion due to their lower redox potential. In order to investigate and compare the efficiency of remediation as well as the long-term behaviour of zero-valent aluminium, magnesium and iron particles under subsurface-like conditions reactivity tests in columns are performed.

For this purpose two set-ups with 12 experimental columns in all were available for simulating source zone and plume remediation of selected contaminants like for example tetrachloroethene (PCE). The set-up allowed for studying the long-term behavior of the particles (several months) under flow-through, thus fieldsimilar conditions. The experimental columns were made of glass and had a length of 100 or 200 cm and an inner diameter of 3.6 cm. Sampling ports were installed before and after each column for analysing contaminant concentration and degradation products in solution. Quantitation of hydrogen formed as a consequence of anaerobic corrosion was enabled by gas traps. pH and redox potential were measured online. Present findings for commercially available magnesium and aluminium microparticles indicated that the dechlorination reaction (simulation of a plume remediation of PCE) was overwhelmed by anaerobic corrosion.

Batch reactivity tests carried out for aluminium have shown an increase in chloride formation under initially alkaline conditions. Therefore, the investigations focused on the possibility of modifying the aquifer properties by increasing pH also considering the relationship between dechlorination and anaerobic corrosion. Amongst the different iron particles tested so far for a source zone remediation of PCE a milled iron particle (provided by UVR-FIA GmbH, Germany) seemed to be promising regarding its longevity and its relationship between dechlorination and anaerobic corrosion.

[1] A. Cundy, L. Hopkinson, R. L. D. Whitby, *Science of the Total Environment* 2008, 400, 42.

[2] T. Phenrat, N. Saleh, K. Sirk, R. D. Tilton, G. V. Lowry, *Environmental Science & Technology* 2007, 41, 284.

### 2.3.3 Agar agar stabilized milled zerovalent iron particles for in situ groundwater remediation

*Milica Velimirovic, Doris Schmid, Stephan Wagner, Vesna Micic Batka, Frank von der Kammer, Thilo Hofmann (University of Vienna, AT)*

The use of nanoscale zerovalent iron (nZVI) particles as a nontoxic material for effective in situ degradation of chlorinated aliphatic hydrocarbons (CAHs) into less harmless products has been inhibited by many factors, including the high production costs. For that reason, submicro-scale milled zerovalent iron particles were recently developed (milled ZVI, UVR-FIA, Freiberg, Germany) by grinding macroscopic raw materials of elementary iron as a cheaper alternative to products produced by solidstate reduction. However, currently milled ZVI particles tend to aggregate and sediment due to the rather large particle size ( $d_{90} = 16.9 \mu\text{m}$ ). To prevent aggregation and consequently sedimentation of milled ZVI suspension (1 g L<sup>-1</sup> of particle concentration) and consequently improve the mobility after in situ application, the use of a stabilizer is necessary. In this study, milled ZVI particles were stabilized by environmentally friendly polymer agar agar (>0.5 g L<sup>-1</sup>), which had a positive impact on the milled ZVI stability significantly decreasing sedimentation rate by increasing the suspension viscosity. Column transport experiments were performed for bare and agar agar stabilized milled ZVI particles in commercially available fine grained quartz sand (DORSILIT® Nr.8, Gebrüder Dorfner GmbH Co, Hirschau, Germany) under field relevant injection conditions of 100 m d<sup>-1</sup>. The maximal travel distance (LT) of 12 m calculated for agar agar (1 g L<sup>-1</sup>) stabilized milled ZVI suspension compared to the non-stabilized suspension (LT < 10 cm) revealed that agar agar as stabilizer significantly improve particle mobility. Finally, lab-scale batch degradation experiments were performed to determine the impact of agar agar on the reactivity of milled ZVI and investigate the apparent corrosion rate of particles by quantifying the hydrogen gas generated by anaerobic corrosion of milled ZVI. The results indicated that despite agar agar had positive impact on the milled ZVI stability and mobility, adverse impact on the reactivity towards trichloroethene was observed compared to the non-stabilized material. On the other hand, this study shows that the apparent corrosion rate of milled ZVI particles was not impacted by the presence of agar agar and longevity of particles action was significantly prolonged compared to the nZVI particles.

### 2.3.4 Demonstrating Nanoremediation in the Field - The NanoRem Test Sites

*Juergen Braun (University of Stuttgart, DE), Randi Bitsch (Solvay AG, SE), Matthias Kraatz (Golder Associates GmbH, DE), Jorge Gonçalves (Geoplano-Consultores, S.A, PT), Nerea Otaegi (Tecnalia Research & Innovation, Geldo, ES), Noam Weisbrod (Zuckerberg Institute for Water Research, Blaustein Institutes for Desert Research, Ben Gurion University of the Negev, IL), Petr Kvapil (AQUATEST a.s., CZ)*

NanoRem (Nanotechnology for contaminated land Remediation) is a research consortium (EU, FP7) dedicated to develop in-situ groundwater remediation technologies based on the injection of nanoparticles in the subsurface. For a successful transfer to the end user, nanoremediation technology performance and applicability has to be shown at realistic scales (pilot sites, field applications), including considerations of cost and wider impacts. Successful field demonstrations allow for the test

of different injection methods for difficult geological conditions. Selected NPs developed in NanoRem are being tested on several sites in different hydrogeological, hydrochemical and climatic environments and also against different contaminant distributions and target contaminants. Efficient performance requires a suitable injection technology, confirmation that NPs can be transported to the required treatment zone and that their longevity guarantees an economical application (but not a hazardous long term persistence in the environment).

A total of seven field injections are being conducted in six countries in the NanoRem project: In the Bad Zurzach (CH) site CHC were detected in residual concentration in an alluvial aquifer with a fairly high groundwater flow velocity. Milled nZVI particles (UVR-FIA) will be injected to reduce the contaminants.

The Spolchemie Site (CZ) shows a CHC plume and some residual saturation. Groundwater velocities in the alluvial aquifer are moderate. Nanofer 25s (NANOIRON) will be injected to chemically reduce the contamination. In the southeastern part of the Spolchemie site a toluene contamination has been located and delineated. The toluene plume migrating towards the Elbe river is to be intercepted by ironoxide NP (Goethite, HMGU) to enhance microbial degradation and thus to stop the plume.

Barreiro (PO) is an abandoned industrial complex close to the sea with a high content of various heavy metals in both the saturated and unsaturated zone. An additional challenge of this site is the low pH of the groundwater. Different particles are tested to immobilize the heavy metals on small plots on that site.

In Balassagyarmat (HU) next to a company formerly manufacturing electronic equipment (now closed) CHC in plume and some residual saturation has been detected. These contaminations are to be treated using an injection of Carbo-Iron (UFZ, SciDre).

A second heavy metal site is located in Bizkaia (ES). The site is located on an alluvial aquifer next to a river and, in contrast to the Portuguese site, does not show a pH reduction. Goethite NP (HMGU) will be utilized to address this contamination.

The Besor-Secher site in Israel is distinguished by a much more arid climate and a fractured aquifer. While the site offers a range of contaminants from an industrial complex nearby, at this time the main focus on the site is on transport and targeted deposition of various NP in this complicated hydrogeological system.

In summary: Particles tested include different kinds of nZVI, Carbo-Iron® and iron-oxide (Goethite) NP. Each of these particles targets specific contaminants (organic, inorganic, chlorinated hydrocarbons etc.), in other words they enhance specific remediation processes (chemical reduction or oxidation, microbial dechlorination or oxidation etc.). Moreover, each NP suspension has specific requirements with respect to hydrogeological (coarse or fine grained porous material, fractures) and hydrogeo-chemical (pH, salinity, redox conditions etc.) site conditions.

The talk gave an overview of the NanoRem sites including their specific goals and challenges and also gave preliminary results from some test sites.

### 2.3.5 Performance of Carbo-Iron particles in in-situ groundwater plume and source treatment approaches

*Katrin Mackenzie, Steffen Bleyl, Frank-Dieter Kopinke (Helmholtz Centre for Environmental Research, DE)*

PCBs are highly recalcitrant compounds that have traditionally been relegated to “dig and dump” and “dig and incinerate” remedial solutions. Recent projects have shown, however, that in-situ thermal remediation presents a repeatable solution that foregoes excavation.

Soils at the subject site were primarily contaminated with Polychlorinated Biphenyl Aroclors 1254 and 1260. These contaminants were introduced into the subsurface from 53 transformers that were part of the former manufacturing plant. The volume of impacted soil was estimated at 7,800 cubic meters, and is generally comprised of clay and silty clays. Average combined PCB concentrations of 5,900 mg/kg were present in the soil, both in saturated and unsaturated zones. Remedial goals of < 4.0 mg/kg toxic PCB congeners was required to achieve total regulatory compliance.

The initial laboratory study determined that when the actual site soils were subjected to a treatment temperature of 250°C for 72 hours, over 99% of PCBs could be removed from the test matrix. Based on these results, a pilot study test of 200 m<sup>3</sup> was conducted. Thermal treatment extended from grade to 5 m bgs. The unsaturated soils (0 – 4m bgs) were heated to an average temperature of 250°C, and the saturated soils (4 – 5m bgs) were heated to an average temperature of 100°C over 69 days of active thermal treatment. The information obtained from the pilot study was used to optimize the design and energy delivery in the full scale project.

The field application pilot study confirmed that average soil reductions of PCBs from 5,900 mg/kg to < 1 mg/kg were realized in the unsaturated zones of the project, confirmed via hot soil validation sampling. The full-scale project reached all temperatures, specifications, and remedial goals.

### 2.3.6 Nanoiron and Carbo-Iron® particle transport in aquifer sediments - Targeted deposition

*Steffen Bleyl, Katrin Mackenzie, Anett Georgi, Frank-Dieter Kopinke (Helmholtz Centre for Environmental Research, DE)*

The applicability of nanoiron-based materials for in situ groundwater remediation has been shown in several lab and field studies within the last decade(s). Compared to larger iron particles, nano-sized zero valent iron (nZVI) shows increased reactivity towards a variety of aliphatic chlorinated hydrocarbons. For this reason and their injectability as colloidal suspensions into contaminated aquifers, the application of nZVI for groundwater treatment seems to be a promising innovative technology. However, the success of a tailored in situ remediation technology is strongly affected by intrinsic particle properties and the environmental conditions (hydrogeological and chemical). As known for bare nZVI colloids, the particles show a pronounced agglomeration tendency which limits targeted reagent transport in water-saturated sediments. Therefore, the research on injectable reactive particles has been focused on optimization of suspension stability and mechanistic understanding of colloid deposition on sediments in different natural environments.

Nanoiron-based materials like Nanofer 25S® (provided by NANOIRON, Czech Republic) and Carbo-Iron® (developed by UFZ, Germany), which are designed as agents for in situ groundwater remediation, are studied within the framework of NanoRem (EU funded research project

within FP7). Nanofer 25S is supplied as a stabilized nZVI suspension containing 20 wt-% metallic iron. Carbo-Iron is a composite material consisting of nanoiron clusters on colloidal activated carbon ( $d_{\text{particle}} \approx 1 \mu\text{m}$ ). Both iron-based materials were tested regarding their colloid stability and their mobility in sediment-packed columns using glass columns ( $L = 0.25 \dots 1 \text{ m}$ ) filled with tightly packed water saturated sediments. The influence of suspension composition, water constitution (e.g. water hardness) and injection mode (e.g. injection flow velocity) on particle breakthrough are key questions to be addressed. Depending on the remediation approach – plume treatment with low contaminant concentrations or source attack where particles are encountered with highly contaminated groundwater and DNAPL – different requirements have to be met by the material development and suspension composition. For Carbo-Iron suspensions (20 g/L) a tailored approach using carboxymethylcellulose as stabilizing additive in defined concentration ranges leads to either high mobility (LT<sub>99.9</sub> = 12 m) or targeted deposition within a certain transport range (e.g. 93% deposition within 1 m). For targeted deposition, injection in a superposed manner (i.e. with intervals of injection at high flow velocity and intermittent low-flow periods) was successful; no clogging occurred. This is a crucial prerequisite for source treatment, where delivery of a sufficient amount of reactive metallic iron is necessary for efficient contaminant degradation.

The presentation focused on particle transport in 1D-column experiments and gave an insight into the tailored design of colloidal nanoiron-based reagents. Furthermore, the influence of particle concentration, water constitution and injection procedures on particle mobility and targeted delivery was be discussed.

### 3 NanoRem Talks outside the special sessions

#### 3.1 Thematic Session 1C.17 In Situ Chemical Oxidation (ISCO) 2

##### 3.1.1 Barium ferrates for in-situ chemical oxidation of BTEX contaminants

*Norbert Klaas, Christine Herrmann, Karin Hauff*

Ferrate(VI) has a high oxidizing capacity - under acidic conditions, its redox potential is even higher than the one of ozone - making ferrate(VI) a very promising agent for water and wastewater treatment processes. It has been shown that various types of organic compounds like for example phenol or thiourea can be oxidised by ferrate(VI) [1].

The work presented here is especially focusing on the potential applicability of barium ferrate for in-situ groundwater remediation. To the best of our knowledge currently no material, except for oxygen-releasing compounds being applied for in-situ bioremediation, is tested for passive oxidative remediation. Since barium ferrate offers slow-release properties it could be utilized to form zones of strong oxidation potential with the possibility of producing a depot-effect in the aquifer. BTEX contaminants (benzene, toluene, ethyl benzene, and xylenes) represent one major category of contaminants affecting groundwater [2] and hence have been chosen as target pollutants to study the use of barium ferrates for in-situ chemical oxidation.

Ferrates(VI) can either be prepared by dry oxidation, wet oxidation or electrochemically. Here, the electrochemical preparation is used because it offers several advantages like for example a shorter synthesis time and reduced costs [3]. The electrochemical synthesis of ferrate(VI) is based on the oxidation of an iron metal anode in alkaline media [4]. Barium ferrate is obtained by subsequent precipitation and characterised by titrimetric chromite analysis [5] and X-ray diffraction. In order to investigate the reactivity of barium ferrate towards BTEX contaminants batch tests have been conducted using toluene as a model contaminant. The results were presented along with considerations towards the potential applicability of the material for field application, including aspects of a later remediation technology.

[1] M. Alsheyab, J.-Q. Jiang, C. Stanford, *Journal of Environmental Management* 2009, 90, 1350.

[2] P. Panagos, M. V. Liedekerke, Y. Yigini, L. Montanarella, *Journal of Environmental and Public Health* 2013, 2013, Article ID 158764.

[3] X. Yu, S. Licht, *Journal of Applied Electrochemistry* 2008, 38, 731.

[4] S. Licht, R. Tel-Vered, L. Halperin, *Journal of the Electrochemical Society* 2004, 151, A31.

[5] S. Licht, V. Naschitz, L. Halperin, N. Halperin, L. Lin, J. Chen, S. Ghosh, B. Liu, *Journal of Power Sources* 2001, 167.

#### 3.2 Thematic Session 1C.18 Miscellaneous remediation topics 1

##### 3.2.1 A Novel Approach for Particle Detection in Porous Media – Fluorescent Labelled Fe-Zeolites

*Glenn Gillies, Anett Georgi, Katrin Mackenzie, Frank-Dieter Kopinke (Helmholtz Center for Environmental Research - UFZ, Leipzig, DE)*

In-situ chemical oxidation (ISCO) by means of Fenton reagents is an established method for treating groundwater pollution. The utilization of the Fenton cycle for the production of highly reactive OH-radicals from hydrogen peroxide needs auxiliary materials. Complexing agents and/or acids are required in order to keep the catalytically active Fe-cations in the dissolved state. In

the EU-project NanoRem a variation of the conventional Fenton-based ISCO process is developed. The disadvantages of dissolved Fe are avoided by the use of Fe-loaded zeolites as catalysts. Contrary to Fe-ions as catalyst, the formation of OH-radicals at the Fe-zeolite takes place at neutral pH without the necessity for other agents. Furthermore, the zeolite framework adds sorption properties to the system, so the reactive species are formed at the centres of the highest local concentration of the target contaminant. This system offers some target selectivity due to its sorption properties towards non-polar molecules and the size-selectivity provided by the zeolite framework.

For the intended application, colloidal suspensions of Fe-zeolites with a particle size in the lower  $\mu\text{m}$ -range shall be injected into the subsurface where they will be immobilised on the sediment after a certain travel distance. The zeolite particles form a permeable sorption barrier which will cut off contaminant plumes by means of adsorption. After particle loading by sorption, the barrier will be regenerated by the injection of  $\text{H}_2\text{O}_2$ . Therefore, the injection of catalyst and oxidant is separated in time and space, offering safety and economic benefits compared to common Fenton-based ISCO. In case of plume treatment, the combination of sorption and subsequent oxidation should provide a more efficient use of  $\text{H}_2\text{O}_2$  per mass of target contaminant.

Tracking Fe-zeolite particles in sediment is a very challenging task. Methods based on element composition cannot be used, since Fe-zeolites are composed of ubiquitous elements (Fe, Si and Al). Other sum parameters like turbidity only work under well-defined conditions, and inherent zeolite properties like their high specific surface area can be used but are not applicable in a routine analysis setup.

In this talk, results on the issue of Fe-zeolites monitoring in water and sediment matrices were presented. Since fluorescence as detection principle has the potential to solve many issues in tracking particle fate in the environment, a method to irreversibly label zeolites with a fluorescent dye was developed. A fluorescent dye molecule is synthesized inside the framework of the zeolites from educts which are small enough to enter the channel system. The resulting product, on the other hand, is too big to exit the channel system. This type of process is called ship-in-a-bottle synthesis. Verification of the applicability for zeolite tracing includes experiments on detection limits in various water and sediment matrices, stability against leaching and oxidants and representativeness (i.e. exclusion of impacts of labelling on particle key properties such as mobility).

## 4 NanoRem Posters

During the conference, the NanoRem project did have a strong presence in the poster area. Members of the NanoRem project exhibited about 20 posters, both in the nanoremediation area as well as in other thematic areas. A comprehensive list of the NanoRem posters is shown in Table 3, the posters can be found in the following paragraphs.

**Table 3:** NanoRem posters exhibited at the AquaConSoil Conference in Copenhagen, 2015.

| ACS No. | Authors   | Title   |
|---------|---|---|
| 1A-21   | N. Klaas, H. Li, A. Buchau, H. Hermes   | The Use of Sensor-Data for Investigating the Transport and the Reactivity of Fe(0) Nano-Particles   |
| 1B-18   | R. Hjorth, C. Coutris, N. Nguyen, A. Ševců, A. Baun, E. Joner                           | Ecotoxicity Testing of Nanoparticles for Remediation of Contaminated Soil and Groundwater   |
| 1C.2-2  | A. Georgi, G. Gillies, K. Mackenzie, F.-D. Kopinke                                      | Colloidal Fe-zeolites - A novel material for sorption-supported in-situ chemical oxidation (ISCO)   |
| 1C.5-18 | G. Giannelli, S. Bleyl, R. Sethi, J. Braun  | Small Flume Experiment for the Transport Evaluation of Carbo-Iron® Particles in a Confined Aquifer  |
| 1C.5-28 | N. Joshi, M. Watts, V.S. Coker and J.R. Lloyd   | Surface functionalization of microbially-synthesized magnetite for improved mobility and reactivity   |
| 1C.5-42 | N. Otaegi, E. Cagigal, M. Cernik, J. Slunský, J. Bosch                                  | Testing on emerging nanoparticles for arsenic removal under real conditions on a pilot field site, in Asturias, Spain                                     |
| 1C.5-46 | A.-K. Schlotter, A. Engelbrecht, J. Braun   | Transport of Carbo-Iron® in porous media: Optimization based on cascading column experiments  |
| 1C.6-1  | M. Cernik, R. Zboril, M. Auffan, S. Thümmeler   | Remediation laboratory tests of different nanoparticles based on zero valent iron   |
| 1C.6-2  | J. Filip, Z. Marková, E. Petala, J. Kašlík, P. Slovák, I. Medřík, J. Slunský, R. Zbořil | Current Trends in the Field of Nanomaterials Designed for Advanced Water-Treatment Technologies   |
| 1C.6-3  | D. Ribas, J.A. Benito, V. Marti, I. Jubany, M. Cernik                                   | Lab Scale Fabrication of Nano Zero-Valent Iron (nZVI) Particles for Groundwater Remediation by Milling  |
| 1C.6-4  | K. Mackenzie, M. Kraatz, T. Laszlo, R. Schöndube, J. Braun                              | Injection of Carbo-Iron® Nanoparticles into a Groundwater Aquifer contaminated with Chlorinated Solvents - approach and first results from one pilot site |
| 1C.6-5  | P. Kvapil, V. Stejskal, J. Slunsky, K. Miyajima   | The application and behaviour of nZVI during the treatment of chlorinated hydrocarbons at the field test at the Spol-                                     |

|         |   |   |
|---------|---|---|
|         |   | chemie site and a large scale container test  |
| 1C.6-6  | R. Bitsch, P. Kvapil, S. Thümmeler, N. Klaas  | Dechlorination of solvents by nanoscale zero-valent iron particles: applying flake shaped nanoparticles in an aerobic aquifer with restricted solvent dissolution |
| 1C.6-7  | J. Bosch, T. Lederer, P. Kvapil   | The application of iron oxides nanoparticles as an alternative electron acceptor for biodegradation of BTEX   |
| 1C.6-8  | D. Ribas, Z. Masopustova, J.A. Benito, V. Marti, I. Jubany, M. Cernik                                     | Study of the Cryomilling Technique for the Production of Nano Zero-Valent Iron (nZVI) Particles   |
| 1C.6-9  | K. Miyajima, A. Engelbrecht, J. Bosch, J. Braun   | In-situ Groundwater Remediation Using Iron-oxides Nanoparticles (Goethite): Large Scale Container Experiment to Investigate Transport and Reactivity              |
| 1C.6-11 | O. Mouvet   | Impact of bacterial biofilm on reactive nanoparticles (NanoFer 25S) mobility in laboratory columns filled with sandy material                                     |
| 1C.6-12 | K. Pešková, J. Nosek, D.R. Fargas, M. Cernik  | Methodology of laboratory test for the description and comparison of the reactive and migration properties of new types of iron nanoparticles                     |
| 1C.6-13 | P. van Gaans, T. Tosco, C. Bianco, A. Raof, A. Fujisaku, D. Rodriguez Aguilera, R. Sethi, M. Hassanizadeh | Modelling nanoparticle transport in porous media across the scales: from the pore scale to the field-scale injection  |
| 1C.6-14 | D. Schmid, V. Micic, M. Velimirovic, S. Wagner, F. von der Kammer, T. Hofmann                             | Aquifer modification: an approach to improve the mobility of nZVI used for in situ groundwater remediation  |

# 1A-21: The Use of Sensor-Data for Investigating the Transport and the Reactivity of Fe(0) Nano-Particles – N. Klaas, H. Li, A. Buchau, H. Hermes



## The Use of Sensor-Data for Investigating the Transport and the Reactivity of Fe(0) Nano-Particles

Norbert Klaas<sup>1</sup>, Hua Li<sup>2</sup>, André Buchau<sup>2</sup>, Hubert Hermes<sup>3</sup>



NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Susceptibility Sensor for Measuring nZVI in Columns

#### Problem

For a detailed description of the transport and reactivity of nZVI (nano zero-valent iron) column experiments are a suitable tool. To be able to measure the concentration of the particles standard analytical methods are inappropriate, since they can only be applied after the experiment, are destructive and limited to an analytical background of iron in the soil material used. In addition, they cannot provide transient information during the experiment.

#### Approach

In order to quantify the concentration of nZVI in such column experiments a special setup was developed (see fig 1). A mobile sensor is moved along the column and measures the magnetic susceptibility with repeated scans. The data obtained is stored in a data base and is being processed after the experiment. In order to get real concentrations along the column various steps of data processing are required. The same setup can be used for transport experiments and for reactivity experiments. The differences in operation are described below.

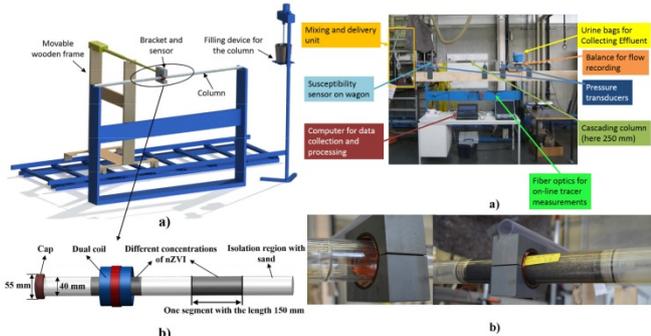
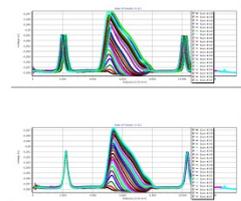


Fig. 1: Measurement setup a) overview with rack, column and wagon, b) detailed view of column and sensor [1]

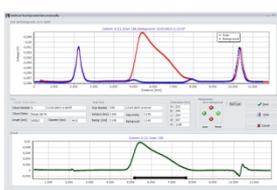
Fig. 2: Photo of transport setup with all installations and measurement devices (a) overview, (b) details

### Data processing

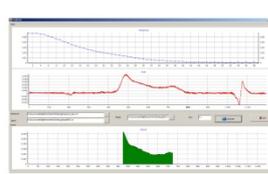
#### Step 1: Horizontal alignment of positions



#### Step 2: Subtraction of background



#### Step 3: Deconvolution

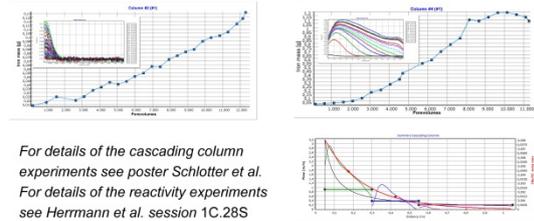


#### Step 4: Calibration



### Investigating Transport

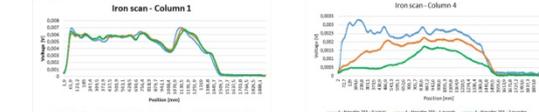
With the setup described above transport experiments can be performed which allow for the detailed description of the transport behavior of nano- or micro-sized iron particles under different conditions and in different formulations (additives). Below the influence of carbomethylcellulose (CMC) is shown for improving the mobility of a specific particle. The left figure shows an accumulation of the iron, whereas the right figure shows a breakthrough after 8 pore volumes.



For details of the cascading column experiments see poster Schlotter et al. For details of the reactivity experiments see Hermann et al. session 1C.28S

### Investigating Reactivity

For the assessment of the reactivity of the particles glass columns are filled with a mixture of sand and the particles. A flow of a contaminant solution is passed through the columns. By taking scans at the beginning of the experiment and after certain times the consumption of the iron can be tracked. Below monthly scans are shown of a column with a low reactive particle (right figure) and a column with a highly reactive particle are shown.



In combination with analytical measurements of the reaction products balances can be made. In this way, the characterisation of the reactivity of the particles can be described and the reactivities of different particles can be compared.

|             | Initial   | After 1 Month |           |       | After 2 Months |           |       | Final        |
|-------------|-----------|---------------|-----------|-------|----------------|-----------|-------|--------------|
|             | Scan area | ZVI           | Scan area | ZVI   | Remaining ZVI  | Scan area | ZVI   | Measured ZVM |
| Column      | [V.mm]    | [g]           | [V.mm]    | [g]   | [%]            | [V.mm]    | [g]   | [g]          |
| 1-Precolumn | 7,55      | 11,22         | 7,76      | 11,53 | 102%           | 7,74      | 11,89 | 11,89        |
| 4-Nanofe255 | 3,70      | 5,5           | 2,48      | 3,68  | 67%            | 1,38      | 2,05  | 37%          |

### Conclusions

A new susceptibility measurement system has been developed for the non-destructive quantification of iron particles in columns. The setup can be used to investigate the transport behavior of particles in columns as well as the reactivity of the particles in long-term experiments. With the data additional analyses are possible in order to describe the behavior of the particles and to compare different types of iron particles.

#### Literature:

- [1] Hua Li, Remus Banacu, André Buchau, Norbert Klaas, Wolfgang M. Rucker (2015, paper accepted): Optimization of a Concentration Measurement Sensor for Nano Sized Zero Valent Iron Using Numerical Simulation. IET Science, Measurement & Technology.
- [2] A. Buchau, W. M. Rucker, C. V. de Boer and N. Klaas, "Inductive detection and concentration measurement of nano sized zero valent iron in the subsurface," IET Sol. Meas. Technol., 2010, Vol. 4, Iss. 6, pp. 289-297.
- [3] Hua Li, C. V. de Boer, A. Buchau, N. Klaas, W. M. Rucker and H. Hermes, "Development of an inductive concentration measurement sensor of nano sized zero valent iron," System, Signals and Devices (SSD), 2012 9th International Multi-Conference, pp. 1-7.



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<sup>3</sup>Hubert Hermes, Hermes Messtechnik, Karlsbader Str. 25, 70372 Stuttgart (mail@hermes.de)

NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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# 1B-18: Ecotoxicity Testing of Nanoparticles for Remediation of Contaminated Soil and Groundwater – R. Hjorth, C. Coutris, N. Nguyen, A. Ševců, A. Baun, and E. Joner



## Ecotoxicity Testing of Nanoparticles for Remediation of Contaminated Soil and Groundwater



Rune Hjorth<sup>1</sup>, Claire Coutris<sup>2</sup>, Nhung Nguyen<sup>3</sup>, Alena Ševců<sup>3</sup>, Anders Baun<sup>1</sup>, and Erik Joner<sup>2</sup>

<sup>1</sup>Department of Environmental Engineering, Technical University of Denmark; <sup>2</sup>Department for Soil Quality and Climate, Bioforsk; <sup>3</sup>Institute for Nanomaterials, Advanced Technologies and Innovations, Technical University of Liberec.

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Background and Objectives

As innovation in remediation technology brings new solutions to old problems, regulatory bodies will require hazard and safety data as new technologies are brought from lab-scale to real-world application.

**Going beyond zero-valent iron**  
A range of nanomaterials are developed in NanoRem in order to extend the spectrum of treatable soil and groundwater contaminants from halogenated organics to non-halogenated substances and non-reducible metals.

**Contributing to hazard assessment of nanomaterials**  
These nanomaterials are meant to help solve the environmental problem of contaminated soil and groundwater, not to create additional ones. Therefore, it is important that their intrinsic toxicity is assessed, as required under REACH.

### Ecotoxicity tests

We have tested a range of particles developed for remediation purposes, using standard ecotoxicity tests to assess their potential hazard towards groups of organisms used for hazard identification for classification and labeling purposes.

- Bacteria: *Vibrio fischeri*, 15 min luminescence, ISO 11348-3
- Algae: *Pseudokirchneriella subcapitata*, 48h growth, OECD 201
- Crustaceans: *Daphnia magna*, 48h immobilization, OECD 202
- Earthworms: *Eisenia fetida*, 48h mortality, OECD 207
- Plants: *Raphanus sativus*, *Lolium multiflorum*, 6d root length, OECD 208

Besides these standardized protocols, we also tested the particles effect on:

- Bacteria: *Escherichia coli*, 6h growth and 24h cell viability
- Algae: *Chlamydomonas sp.*, 48h photosynthesis efficiency
- Oligochaete: *Lumbricus variegatus*, 96h mortality

The tested particles were dispersed as recommended by the producers and the suspensions were characterized by DLS, NTA, ORP, and pH.



### Nanoparticles

|  |  |
|--|--|
| <p><b>Carbo-Iron</b></p> <ul style="list-style-type: none"> <li>Composite of activated carbon and zero-valent iron</li> <li>Adsorption and reduction of halogenated contaminants</li> </ul>  | <p><b>Fe Zeolites</b></p> <ul style="list-style-type: none"> <li>Nanoporous aluminosilicate loaded with iron Fe<sup>3+</sup> catalyst</li> <li>Oxidation of small molecules, e.g. BTEX, MTBE, dichloroethane, chloroform...</li> </ul> |
| <p><b>Fe Oxides</b></p> <ul style="list-style-type: none"> <li>Pristine iron oxides, mostly goethite Fe<sup>3+</sup>O(OH) stabilized with humic acids</li> <li>Oxidation (catalytic effect on bioremediation) of biodegradable contaminants, such as BTEX</li> </ul> | <p><b>Milled zero-valent iron</b></p> <ul style="list-style-type: none"> <li>Mechanically ground zero-valent iron</li> <li>Reduction of halogenated contaminants (same spectrum as for nZVI produced by thermal reduction)</li> </ul>  |

### Results and Discussion

|             |    |    |    |  |  |  |  |    |  |
|-------------|----|----|----|--|--|--|--|----|--|
| Carbo-Iron  |    |    |    |  |  |  |  |    |  |
| Fe Oxides   |    |    |    |  |  |  |  |    |  |
| Fe Zeolites |    |    |    |  |  |  |  |    |  |
| Milled ZVI  | ND | ND | ND |  |  |  |  | ND |  |

EC<sub>50</sub> >100 mg/L    EC<sub>50</sub> <100 mg/L

Standard ecotoxicity testing of nanoparticles has in general proven technically difficult and it may be questioned whether proper hazard identification of engineered nanoparticles needed for environmental risk assessment is currently feasible. Aggregation, agglomeration, sedimentation, shading, and other physical effects are known to interfere with the measuring principles behind the tests and these inferences were also observed for the particles in the present study.

This was pronounced for tests on algae, bacteria, and crustaceans for all particles tested and require inclusion of additional controls to ensure a correct data interpretation. E.g. a reduction in luminescence is seen as a sign of toxicity in the *V. fischeri* assay, but the turbidity of the tested particles absorb the light emitted by the bacteria before detection and is thus not a toxic effect.

### Conclusions

The low toxicities found in the standard organisms do not lead to any hazard classification according to EU regulation for any of the tested particles and the results indicate that the particles, except the milled ZVI particles, can be considered non-toxic.

Nanomaterials with the lowest toxicity profile should be preferred over other materials with similar field scale efficacy and reactivity towards the target contaminants.

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# 1C.5-18: Small Flume Experiment for the Transport Evaluation of Carbo-Iron® Particles in a Confined Aquifer – G. Giannelli, S. Bleyl, R. Sethi, J. Braun



## Small Flume Experiment for the Transport Evaluation of Carbo-Iron® Particles in a Confined Aquifer

Giulia Giannelli <sup>(1)</sup>, Steffen Bleyl <sup>(3)</sup>, Rajandrea Sethi <sup>(2)</sup>, Jürgen Braun <sup>(1)</sup>

<sup>(1)</sup> VEGAS, University of Stuttgart; <sup>(2)</sup> POLITO, Torino; <sup>(3)</sup> UFZ, Leipzig

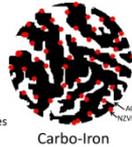


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NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Motivation

- Carbo-Iron® is a new injectable composite material which targets both chlorinated solvents plume and source remediation:
  - Carbo-Iron particles consist of clusters of nZVI embedded in colloidal activated carbon (AC) particles
  - The AC framework functions as a spacer between the nZVI structures lowering their agglomeration tendency which leads to better transport
  - The addition of the environmentally benign stabilizer CMC further enhances suspension stability and mobility by electrosteric stabilization
- A suspension containing 20g/L Carbo-Iron and 4g/L CMC was identified as the best recipe for fully optimized transport
- Carbo-Iron contains 10-25w/w% of nZVI:
  - one single injection (ZVI = 1.48 g/L<sub>soil</sub>) of the optimized suspension into the source zone (PCE = 0.5g/L<sub>soil</sub>) does not suffice for a successful remediation (ZVI=2.6 g/L<sub>soil</sub>)



Carbo-Iron

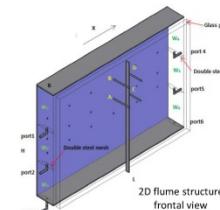
### Goals



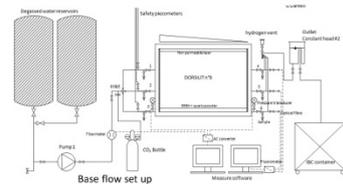
Small Flume Experiment

- Test of a multi-step injection strategy to emplace and accumulate a sufficient mass of Carbo-Iron in a predefined target zone
- Optimization of the injection interval needed to let the previous particles settle
- Confirmation of the Carbo-Iron enhanced mobility features in a quasi 2D system
- Procedure for comparison of particle migration using suspensions of different particles

### 2D Flume



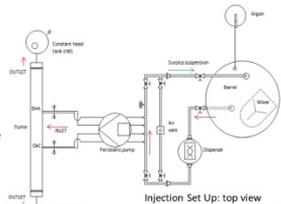
- Stainless steel flume:**
  - L / W / H = 1.00 / 0.12 / 0.70 m (quasi 2D)
  - Frontal glass pane for visual observation
- Confined aquifer simulation:**
  - Dorsilit n°8 sand (0.3-0.8mm), degassed water
  - Horizontal base flow
  - Inflow BC: constant flux, outflow BC: constant head
  - Porosity: 0.37, PV<sub>flume</sub> = 26 L
  - average hydraulic conductivity: 5.87 10<sup>-05</sup> m/s



- Measurements:**
  - MID (total base flow)
  - pressure transducers (Δh in-out)
  - optical fibers (fluorescence)
- Uranine Tracer Test:**
  - visual
  - Using optical fibers

### Experimental Procedure

- Suspension preparation:**
  - 20 g/L Carbo-Iron, 4 g/L CMC
  - Hydraulic mixer, dispenser, argon supply
- Three Carbo-Iron Multi-Step injections:**
  - no base flow, outflow BC: constant head
  - 4 injection ports at the back side of the flume
  - liquid samples from outflow
  - continuous monitoring of injection pressure
- Recovery intervals:**
  - No base flow
  - 1<sup>st</sup> recovery: d = 24 h, 2<sup>nd</sup> recovery: d = 48 h
- Restoration of the base flow:**
  - horizontal base flow
  - q = 1.1 \* 10<sup>-05</sup> m/s, d = 33 h



| n° inj | V [L] | d [min] |
|--------|-------|---------|
| 1      | 15    | 48      |
| 2      | 10    | 34      |
| 3      | 10    | 35      |

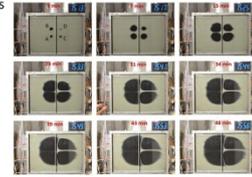
Back side of the flume

### Mobility of Carbo-Iron

- Homogeneous and fast spreading of particles
- No pore clogging
- Mobility Factor** for transport assessment:

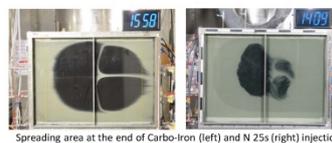
$$M [-] = \frac{V_{NIP}}{V_{inj}} = \frac{A_{spread} \cdot W \cdot n}{V_{inj}}$$

- Ratio between volume from the visual spreading and volume injected
- M = 0: infinite retention
- M = 1: conservative tracer



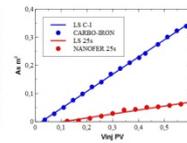
Time lapse analysis from the first injection. (Relative time in upper centre)

- Migration comparison between Carbo-Iron and NANO FER 25s®
  - Carbo-Iron may be considered perfectly mobile particles



Spreading area at the end of Carbo-Iron (left) and N 25s (right) injection

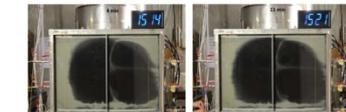
| Parameter                              | Carbo-Iron | NANO FER 25s |
|--|------------|--------------|
| PV <sub>inj</sub> [-]                  | 0.58       | 1.64         |
| final A <sub>s</sub> [m <sup>2</sup> ] | 0.34       | 0.16         |
| M [-]                                  | 0.95       | 0.11         |
| α [-]                                  | 0.61       | 0.14         |
| Fe(0) [w/w-%]                          | 10-25      | 80-90        |



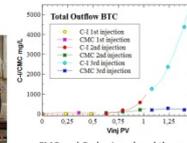
| α [-] angular coefficient |      |
|---------------------------|------|
| C-I                       | 0.61 |
| N25s                      | 0.14 |

### Emplacement of Carbo-Iron

- Particles which are still suspended in the pore water are pushed away by the new injected suspension

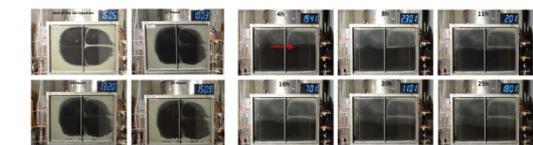


Expansion of the particle zone during the 2nd injection; (left) 4 min and (right) 11 min after start of the 2nd injection



CMC and Carbo-Iron breakthrough curves in the outflow Carbo-Iron BTC shows a rising trend

- Particles migrate downwards during the recovery intervals in the absence of external gradients as well as during the restoration of the base flow (presumable due to higher density of the suspension)
- After restart (restoration) of base flow particles not yet immobilized are further transported in the direction of flow



Time lapse analysis during the 24h recovery interval (left) and the restoration of the base flow (right)

- Analysis of solid samples and concentration mapping**
  - Max ZVI available with a single injection of 1PV (15 L): 1.48 g/L<sub>soil</sub>
  - Max ZVI remaining in the target zone after injection of 2.3PV (35 L): 1.36 g/L<sub>soil</sub> < 1.48 g/L<sub>soil</sub>

### Conclusions and Outlook

- For perfectly mobile particles the Multi-Step Injection method does not increase the amount of ZVI emplaced
- The suspension needs to be tuned for better control. "Deoptimization" of the suspension is achieved adjusting CMC concentration from 4g/L to 1g/L (presentation S. Bleyl).



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## 1C.5-28: Surface functionalization of microbially-synthesized magnetite for improved mobility and reactivity – N. Joshi, M. Watts, V.S. Coker and J.R. Lloyd



### Surface functionalization of microbially-synthesized magnetite for improved mobility and reactivity

N Joshi, M Watts, V.S Coker and J.R Lloyd

School of Earth, Atmospheric and Environmental Sciences, University of Manchester



NanoRem is a four year, €14 million research project funded through the European Commission FP7.

#### Introduction

- Iron nanocomposites have potential for remediation of heavy metals and organic compounds
- Conventional manufacturing methods are synthetic and involve harsh chemical regimes
- Nano-scale biogenic magnetite synthesized by the reduction of ferrihydrite by the anaerobic subsurface bacterium *Geobacter sulfurreducens* offers a benign alternative<sup>1, 2</sup>
- Bionanomagnetite (bnm) is amenable to surface engineering to enhance its reactivity<sup>3</sup>
- Bnm offers a sustainable option for *in situ* remediation of heavy metals and organic compounds

#### Objectives

- Column studies to assess transport properties of biogenic magnetite
- Identify the stabilizers that could enhance its mobility in porous medium
- Assess the impact of stabilizers on the reactivity of biogenic magnetite
- Functionalization of bnm with palladium to enhance reactivity against metals and organics

#### Research methodology

- Microbiological methods to synthesize biogenic magnetite
- Analytical techniques including XRD and ICP-AES to characterize the magnetite for purity and total iron content
- Column studies involving fine quartz sand (0.3-0.8 mm diam.), as porous medium with an injection velocity of 100 m/d
- Stabilization studies using a variety of coatings to enhance mobility and transport in columns
- Reactivity studies using model organic (PCE) and metal (Cr(VI)) target compounds for remediation

#### Results

Reductive precipitation of palladium (II) onto the surface of bnm makes it an effective catalyst for the reduction of heavy metals and organic compounds in presence of external electron donor<sup>4</sup>

#### 1. Functionalization of bionanomagnetite for remediation of chromium and organic solvents

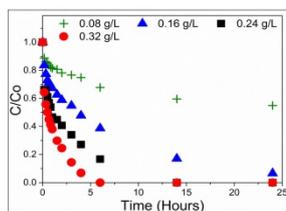


Fig. 1 Cr(VI)/Cr(III) of aqueous Cr(VI) concentration over time with Pd-Bnm / H<sub>2</sub> gas in a model Cr(VI) solution. Cr<sub>0</sub> denotes the starting Cr (VI) concentration, Cr (VI) level determined by diphenyl carbazide assay

The palladized bionanomagnetite promotes rapid decomposition of organic compounds nitrobenzene, perchloroethylene and trichloroethylene

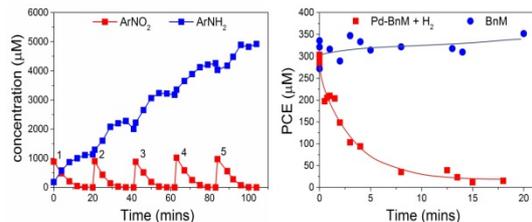


Fig.2 The concentration of the starting contaminant (ArNO<sub>2</sub>) and accumulation of the reduced product ArNH<sub>2</sub> as a function of time, in the presence of Pd-Bnm/H<sub>2</sub>. The number annotations refer to the repeated spiking of the batch experiment with 1000 µM ArNO<sub>2</sub>

Fig.3 PCE concentration for synthetic groundwater treated with 1 g/L Fe Bnm (blue circles) and the 0.025 g/L Fe Pd-Bnm supplied with an excess of H<sub>2</sub> (red squares)

#### 2. Mobility of biomagnetite through columns

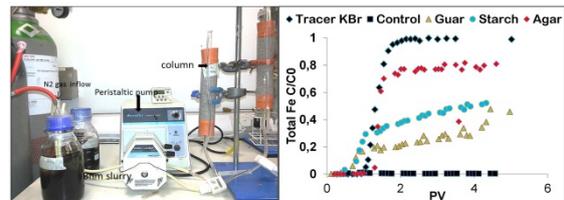


Fig. 4 (a): Columns set up for transport study Fig. 4 (b): Breakthrough curve for tracer (KBr), Control (uncoated) bnm and stabilized slurries with guar, agar and starch. Mobility was enhanced in the order agar>starch>guar>no coating.

#### 3. Impact of the coatings on the reactivity of biomagnetite

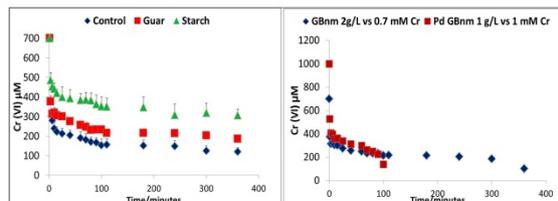


Fig. 5 Reactivity of bnm (control) and stabilized forms (guar and starch), reactivity was reduced, but remained significant, and could be enhanced with Pd additions. Fig.6 Bnm with guar (GBnm) and Pd bnm with guar (Pd GBnm).

#### Conclusion

- Pd bnm has significant potential for the remediation of pollutants
- Stabilization of bnm with guar (3g/L), agar (2g/L) and starch (2g/L) significantly improves its mobility in porous medium, while retaining activity
- The reactivity of coated bnm can be further improved by doping its surface with Pd (0)

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NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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# 1C.5-46: Transport of Carbo-Iron® in porous media: Optimization based on cascading column experiments – A.-K. Schlotter, A. Engelbrecht, J. Braun



## Transport of Carbo-Iron® in porous media: Optimization based on cascading column experiments

Ann-Kristin Schlotter, Alexander Engelbrecht, Jürgen Braun  
VEGAS, University of Stuttgart, Germany

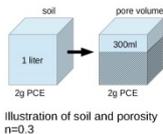


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NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Motivation

- The NanoRem research project aims at **directly injecting reactive compounds into a contamination source** for faster treatment of the pollution.
- Carbo-Iron® are particles composed of 80 wt% activated carbon and 20 wt% nZVI. Carboxymethyl cellulose (CMC) is added to the suspension to facilitate transport.
- The **stoichiometrically required mass** for remediation of 1g PCE is 1.3g nZVI. With a safety addition 5g nZVI are required.

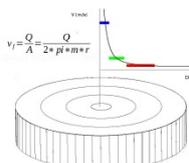


Assuming there is a 20kg PCE contamination in 10m<sup>3</sup> of soil, with 2g PCE per liter of soil, or rather 2g PCE per 300ml of pore volume (PV), then 10g ZVI per 300ml PV are required for the remediation.

### Goal

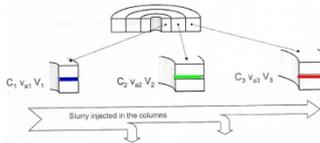
- A slurry of 20g/L Carbo-Iron® contains 4g/L ZVI (20wt%), i.e. there are 1.3g nZVI in 300ml of slurry. With regard to the assumption above, 10g nZVI are needed.
- There are two options to deposit the required mass:
  - Multiple injections, if the mass is not provided with one injection
  - higher Carbo-Iron® concentrations in the slurry to achieve a better deposition with only one injection**
- This study aims at **optimizing the transport behaviour** of Carbo-Iron® to achieve **maximal deposition** of the particles in the subsurface using cascading columns (CC).

### Cascading Columns



- Around an injection well the **Darcy flux decreases hyperbolically** with  $r$ .
- The cascading column scheme **reduces the 3D radial flow to quasi-1D experiments**.
- Column length represents thickness of section area.

- In radial system:  $v$  decreases,  $A$  increases  $\rightarrow Q = \text{const.}$
- In column:  $v$  decreases,  $A = \text{const.} \rightarrow Q$  decreases



### Migration Properties

- The original Carbo-Iron® slurry was designed for ideal transport, not for controlled deposition.
- The migration properties are influenced by:

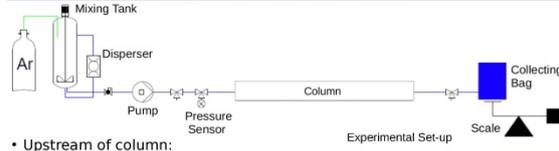
|                             |  |  |
|-----------------------------|--|--|
| Injected flowrate $Q_{inj}$ | $\rightarrow$ defined by boundary conditions | Define input parameters for CC: duration, injected volume... |
| Carbo-Iron® conc.           | base case and variations                     |  |
| CMC concentration           |  |  |

### Injection Scheme and Sampling



- The prepared slurry is injected into the first column whose outflow is injected into the subsequent column (at the appropriate velocity) etc.
- Deposition may then be **compared via mass balance**.

### Experimental Procedure



- Upstream of column: Argon as inert gas, dispenser and stirrer to **avoid sedimentation and agglomeration**, peristaltic pumps, pressure sensor for monitoring the pressure, sampling valve for inflow sample.

Preparation of slurry: gradually dissolving CMC, slowly mixing in Carbo-Iron®, filling suspension in mixing tank.

- Column: Plexiglass column, diameter 44mm, variable filter head with mesh screen to adjust length and detain sand.



Preparation of columns: filled with sand, flushed with argon, saturated with degassed water  $\rightarrow$  **bottom-up method**, check porosity and hydraulic conductivity (goal:  $n=0.3$  and  $K=4 \cdot 10^{-4} \text{m/s}$ ).

- Downstream of column: Bag for collection of outflow, sampling valve, scale to monitor the flow.

### Results

| Column | Initial slurry          | Iron_in [g/L] | Iron_out [g/L] | Deposition within a radius of 1m [%] |
|--------|-------------------------|---------------|----------------|--------------------------------------|
| S1.1   | 20g/L Carbo-Iron        | 2.4           | 0.86           | > 90.8 (iron analysis)               |
| S1.2   | 2g/L CMC                | 0.86          | 0.22           |                                      |
| S1.3   |                         | 0.22          | -              |                                      |
| S2.1   | 20g/L Carbo-Iron        | 1.29          | 0.47           | 96.9 (iron analysis)                 |
| S2.2   | 1g/L CMC                | 0.47          | 0.26           |                                      |
| S2.3   |                         | 0.26          | 0.04           |                                      |
| S3.1   | 40g/L Carbo-Iron        | 4.5           | 4.7            | 88.9 (TOC analysis)                  |
| S3.2   | 2g/L CMC                | 4.6           | 3.5            |                                      |
| S3.3   |                         | 2.6           | 0.5            |                                      |
| S4.1   | 40g/L Carbo-Iron no CMC | 4.6           | -              | clogged at 17.5cm                    |
| S5.1   | 20g/L Carbo-Iron no CMC | 2.3           | -              | clogged at 8cm                       |
| S6.1   | 40g/L Carbo-Iron        | 5             | 1.8            | 100 (TOC analysis)                   |
| S6.2   | 0.5g/L CMC              | 2.3           | 0.6            |                                      |
| S6.3   |                         | 0.8           | -              |                                      |

Nomenclature: Sx.y is column y of set x.

### Conclusion and Outlook

- The initial composition of 20g/L Carbo-Iron® and 2g/L CMC was adjusted to 40g/L Carbo-Iron® and 0.5g/L CMC. Given this concentration, a **total deposition within 0.75m** was achieved.
- Additional experiments investigating slightly higher CMC concentrations between 0.5g/L and 1.0g/L to reach an economically more feasible radius are recommended.

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**NanoRem** - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

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# 1C.6-2: Current Trends in the Field of Nanomaterials Designed for Advanced Water-Treatment Technologies – J. Filip, Z. Marková, E. Petala, J. Kašlík, P. Slovák, I. Medřík, J. Slunský, R. Zbořil



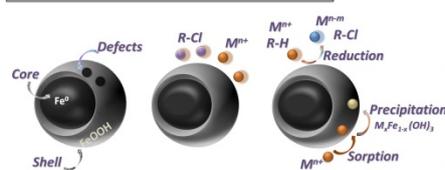
## Current Trends in the Field of Nanomaterials Designed for Advanced Water-Treatment Technologies

Jan Filip<sup>1</sup>, Zdenka Marková<sup>1</sup>, Eleni Petala<sup>1</sup>, Josef Kašlík<sup>1</sup>, Petr Slovák<sup>1</sup>, Ivo Medřík<sup>1</sup>, Jan Slunský<sup>2</sup>, Radek Zbořil<sup>1</sup>

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### Nanoscale Zero Valent Iron (nZVI)



Nano Zero Valent Iron (nZVI) can reduce and remove effectively various contaminants through different mechanisms (absorption, reduction, co-precipitation)

Modified nZVI have highly enhanced remediation ability (less observed agglomeration, air-oxidation protection, higher surface area, homogeneous dispersion and narrower size distribution).

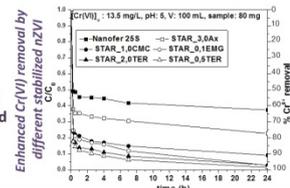


### Surface Modified nZVI

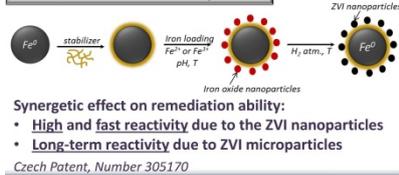
Surface modification by stabilizers provides physically more stable and chemically more reactive nZVI. Prevents particles from agglomerating, increase sorption properties and mobility.



- Stabilizers:**
- poly(acrylic) acid
  - poly(ethylenglycol)
  - carboxymethylcellulose
  - potato starch
  - alginate
  - chitosan
  - polyoxyethylenesorbitane monooleate
  - Axilate 32S dispersion of sodium salt of polyacrylic acid
  - poly(methyl) methacrylate
  - polyaspartate
  - poly(styrene) sulfonate
  - triblock copolymer (PMAA48-PMMA17-PSS660)
  - polyvinyl alcohol-co-vinylacetate-co-itaconic acid
  - xanthan and guar gums



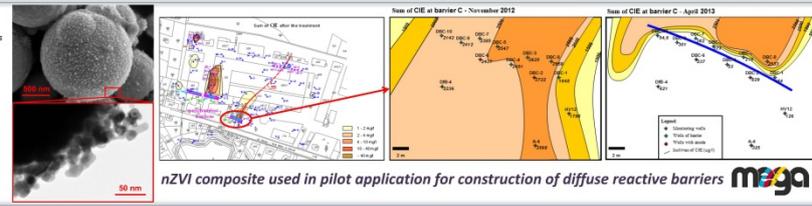
### Nano/Micro ZVI Composite



Synergetic effect on remediation ability:

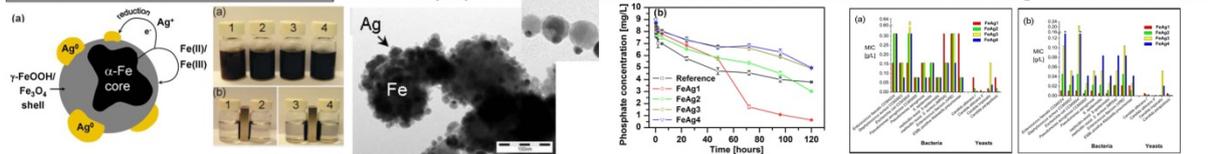
- High and fast reactivity due to the ZVI nanoparticles
- Long-term reactivity due to ZVI microparticles

Czech Patent, Number 305170



### Bimetallic Fe-Ag nanocomposites

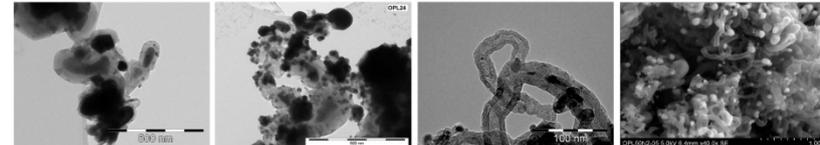
Enhanced properties due to the combination of antibacterial, reductive and magnetic characteristics!



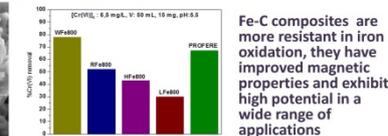
Marková Z. et al, Environ. Sci. Technol., 2013, 47 (10), pp 5285–5293

### Fe-C Composites

Preparation of composites based on nZVI and carbon (i.e., carbothermal reduction)

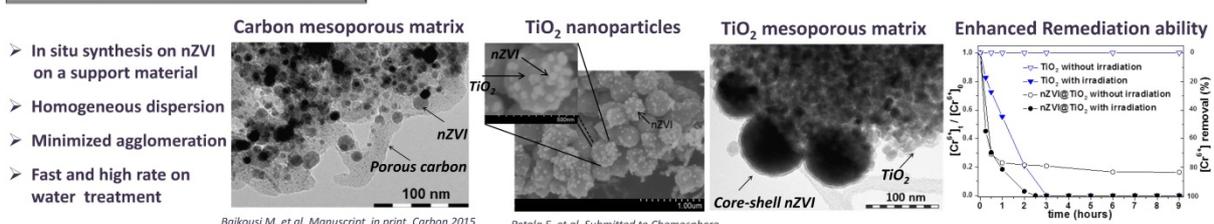


Cr(VI) removal by different Fe-C composites



Fe-C composites are more resistant in iron oxidation, they have improved magnetic properties and exhibit high potential in a wide range of applications

### nZVI supported on different matrices



- In situ synthesis on nZVI on a support material
- Homogeneous dispersion
- Minimized agglomeration
- Fast and high rate on water treatment

Baikousi M. et al, Manuscript in print, Carbon 2015

Petala E. et al, Submitted to Chemosphere



Project No. TE01020218



## 1C.6-3: Lab Scale Fabrication of Nano Zero-Valent Iron (nZVI) Particles for Groundwater Remediation by Milling – D. Ribas, J.A. Benito, V. Marti, I. Jubany, M. Cernik



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### LAB SCALE FABRICATION OF NANO ZERO-VALENT IRON (nZVI) PARTICLES FOR GROUNDWATER REMEDIATION BY MILLING



Ribas D.<sup>1,3</sup>, Benito J. A.<sup>2,3</sup>, Marti V.<sup>1,3</sup>, Jubany I.<sup>3</sup>, Cernik M.<sup>4</sup>

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 Institute for Nanomaterials, Advanced Technologies and Innovation - Technical University of Liberec

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

#### Introduction

Nano Zero-Valent Iron (nZVI) particles are being used for contaminated groundwater remediation because exhibit an extreme reactivity [1].

These nZVI particles can be produced by a borohydride chemical reduction of ferrous/ferric solution (bottom-up approach), the reduction of ferric iron oxides by hydrogen at a high temperature [2-3] and by milling from microscopic particles (top-down approach) [4].

The present work includes the milling in ethanol and Mono Ethylene Glycol (MEG), a pre-treatment as hydrogen embrittlement and a mid-treatment using an abrasive.

#### Materials and methods

##### Milling in ethanol tests

In a first approach milling in ethanol was selected. The preparation of nanoparticles by wet milling in ethanol started from 1.5 g of microscale iron (< 18 µm) using steel and stainless steel (SS) shots in 250 ml stainless steel vials. The milling was performed under argon atmosphere in a Planetary ball mill (Fritsch Pulverisete-5) at 400 rpm.

##### Milling in MEG tests

Ethanol was changed to MEG due to the lower risk of flammability of MEG in contact with nZVI. An initial powder BASF GmbH CIP-SM iron was selected for MEG milling. The initial size characteristics, by volume has a mean of 2.8 µm and a 4.7% of the volume < 1 µm. The milling was carried out in low-carbon steel grinding media and in a specially designed vials to avoid contamination, Figure 1.



Figure 1. H<sub>2</sub> Reactor.

##### Hydrogen embrittlement tests

The exposure of iron to hydrogen increases embrittlement of iron which could improve performance of milling. This is a known phenomenon and has the advantage to avoid contamination of iron. This operation was performed in a reactor (Figure 2) operating at 150 °C and 40 atm for 1 week, that are the theoretical conditions that allow and absorption of 7 g H<sub>2</sub>·Ncm<sup>-3</sup> per each 100 g of iron.

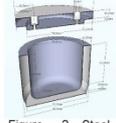


Figure 2. Steel Vial.

##### Abrasion with alumina tests

As post-treatment method, a first step of wet milling with MEG was combined with a second step in which alumina was added as abrasive (Al<sub>2</sub>O<sub>3</sub>).

##### Particle characterization

All milled samples were manipulated in a glove box under nitrogen atmosphere (Jacomex 2P), then samples were stored in absolute ethanol.

For the Scanning Electron Microscope (SEM) studies, the samples were deposited and led to evaporate into the glove box over standard pins.

For size characterization, Laser Diffraction Particle Sizing (LDPS) was chosen. Samples were previously mixed in an ultrasonic bath and then immediately analyzed directly in ethanol. Finally, data was post processed with the Fraunhofer optical model by volume.

#### References

- [1] X. Q. Li, D. W. Elliot, W. X. Zhang, Critical Reviews in Solid State and Materials Science, 31 (2006) 111-122
- [2] C. B. Wang, W.X. Zhang, Environmental Science Technology, 31 (1997) 2154-2156.
- [3] R. A. Crane, T. B. Scott, Journal of Hazardous Materials, 211-212 (2012) 112-125
- [4] D. Ribas, Z. Masopustova, J.A. Benito, V. Marti, I. Jubany, M. Cernik, Study of the cryomilling technique for the production of nano zerovalent-iron (nZVI) particles. Aquaconsoil, 9-12th June 2015, Copenhagen

#### Results and discussion

##### Milling in ethanol

SEM results showed that iron behaved as a ductile metal since very large deformation was produced. Substantial changes from spherical to large flakes shape were observed in the iron particles (Figure 3), in which lengths of several µm together with thickness of only 50 nm were measured.

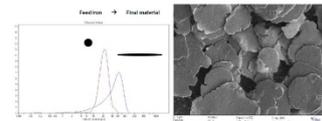


Figure 3. LDPS Evolution of particle size in milling of solutions of iron powder with ethanol. Final SEM picture

Table 1. Relevant tests with ethanol

| Ref.  | Grinding media   | Material | SFR | Milling time | Mean (µ) | < 1 µm | Laser Diffraction (Dv, vol%) |
|-------|------------------|----------|-----|--------------|----------|--------|------------------------------|
|       |                  |          |     | h            | µm       | %      |                              |
| NA 8  | Cr/Ni 60         | SS       | 166 | 16           | 45.3     | 2.7    |                              |
| NA 11 | Cr/Ni 20         | SS       | 166 | 16           | 7.99     | 3.3    |                              |
| NA 12 | Cr/Ni 60         | SS       | 166 | 16           | 46.7     | 0.1    |                              |
| NA 13 | [Ni]<br>Cr/Ni 60 | SS       | 166 | 24           | 41.9     | 0.1    |                              |
| NA 16 | Cr/Ni 60         | SS       | 166 | 24           | 5.93     | 3.4    |                              |
| NA 17 | Cr/Ni 60         | SS       | 166 | 20           | 6.24     | 1.8    |                              |
| NA 18 | Cr/Ni 60         | SS       | 166 | 24           | 4.69     | 7.1    |                              |

Once the flakes were formed, no significant evolution to smaller particles was found with time and different milling media. LDPS analyses showed that milled material had, in general, a scarce fraction of powder < 1 µm (results not shown).

From the conditions of Table 1, it was noticed by SEM-EDX an increase of the powder fraction < 1 µm in stainless steel Cr/Ni vials and balls. This means the breaking of the flakes was observed due to an embrittlement of the iron by Cr alloying.

##### Milling in MEG

In the case of MEG milling (Figure 4), with increasing milling times (24 to 96 hours) there was a reduction in the size of iron particles and a slight increase of the number of iron particles below 1 µm.

However, the flake form was the dominant morphology as in the case of ethanol.

In order to increase the yield of nZVI particles, pre-treatment and post-treatments were tested to facilitate the breaking of the large flakes formed due to the ductile behaviour of iron. measured.

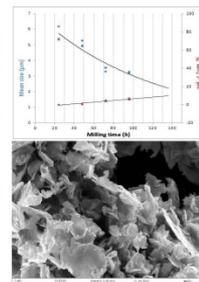


Figure 4. Evolution of particle size in milling of solutions of iron powder with MEG

##### Pre-treatment

After hydrogen embrittlement pre-treatment no significant differences were observed comparing milling between the untreated and the treated iron, thus, this option was discarded.

##### Mid-treatment

Abrasion tests have shown good preliminary results with more than 40% of NPs below 1 µm (see Figure 5) and open further study of this alternative. Confirmation of homogeneous milling and repeatability and reproducibility of the process must be checked, together with the study of the effect of residual alumina on the elimination of contaminants.

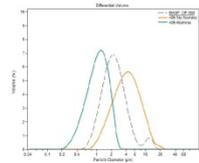


Figure 5. Same conditions with/without alumina.

#### Conclusions

As a conclusion, the use of ethanol and MEG allowed to obtain non oxidized iron in flake form, with a thickness that matches to the definition of nanoparticle but a flat dimension higher than the starting material. New mid-treatment approaches with abrasives allow to obtain smaller nZVI particles to improve its mobility and reactivity in groundwater.

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# 1C.6-4: Injection of Carbo-Iron® Nanoparticles into a Groundwater Aquifer contaminated with Chlorinated Solvents - approach and first results from one pilot site – K. Mackenzie, M. Kraatz, T. Laszlo, R. Schöndube, J. Braun



**NanoRem - Injection of Carbo-Iron® particles into a groundwater aquifer contaminated with chlorinated solvents - approach and first results from one pilot site**



Kraatz, M.; Mackenzie, K.; Laszlo, T.; Schöndube, R.; Braun, J.

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

## Pilot site application of Carbo-Iron® particles

### Project Background:

Pilot site application of Carbo-Iron® particles will be conducted within the NanoRem project (*“Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment”*) granted by the European Union Seventh Framework Programme (Project Nr.: 309517). Pilot Site Applications and Field Demonstrations are to be implemented between February 2013 and January 2017.

### Project Site:

The NanoRem pilot site for applying Carbo-Iron® particles into contaminated groundwater is located in the outskirts of the city of Balassagyarmat, Hungary. Balassagyarmat has 16.000 inhabitants and is located approx. 80 km north of Budapest. The production of electrical components for industry on site started in the 1970s. In 1994 production ceased and the buildings were removed. Nowadays, the area of groundwater contaminated with chlorinated solvents (CHC) is about 250 m wide (E-W) and 700 m long (N-S). At the moment, the site is an industrial brownfield (source zone), parts of the area (plume zone) are used as a soccer pitch.



Figure 1: Encircled pilot site area with former electronic component facility (CHC source, southern square) and selected pilot site injection area (northern square)

### Project Partner:

Pilot site applications are performed by *Golder Associates GmbH*, Germany and *Golder Zrt.* in Hungary. Particle specification involves the production and injection of Carbo-Iron® particles, which will be produced by *SciDre* in Dresden, Germany. Planning and field application of Carbo-Iron® at the pilot site is supported by lab-scale testing, conceptual and hydraulic modeling, sustainability assessment and others, all in close coordination with the associated work package groups like the German research institutions *UFZ Leipzig* and *VEGAS Stuttgart*.

### Contaminant situation:

The groundwater table at the pilot site is found at about 3 m below ground level. The major contamination of about 21,000 µg/L CHC at the pilot sites is mainly situated in a depth of about 12-14 meters within the gravel aquifer with a porosity of 0.4 and conductivity of 5 x 10<sup>-3</sup> m/s, followed by a clay aquiclude. Plume contamination is estimated to about 15 kg CHC (95 % PCE). The redox potential in groundwater is in the range of: +86 - +138 mV with dissolved oxygen between 1,59 mg/l and 2,87 mg/l; Figure 2).

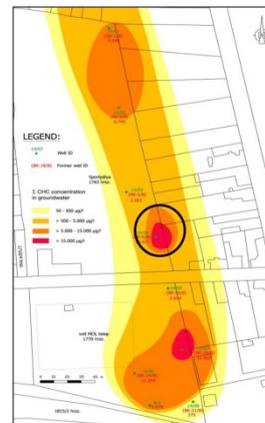


Figure 2: Encircled pilot site area with CHC contaminant distribution

Based on the geological information and the previous groundwater monitoring results, four CMT wells (screened in 3 different intervals) were installed at the site in November 2014. The CMT wells are located at 3 m, 4 m, 10 m and 14 m of distance from the proposed injection points (I1-3) in down-gradient direction. There are 2 monitoring wells, where data loggers will be installed to gain geochemical data during the injection (M; Figure 3).

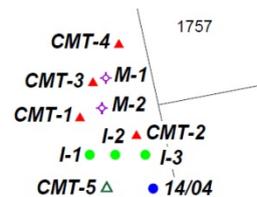


Figure 3: Pilot site area with the sampling points (CMT 1-5, M, 14/4) and proposed injection points

Golder Associates GmbH, Vorbruch 3, 29227 Celle, Germany;  
Golder Associates (Magyarországi) Zrt., 1021 Budapest Hővízvilágyi út 54, Hungary.



NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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**NanoRem - Injection of Carbo-Iron® particles into a groundwater aquifer contaminated with chlorinated solvents - approach and first results from one pilot site**



Kraatz, M.; Mackenzie, K.; Laszlo, T.; Schöndube, R.; Braun, J.

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

**Pilot site application of Carbo-Iron® particles**

**Conceptual Site Model (CSM)**

Based on the analytical results, a conceptual site and contamination transport model were generated and the pilot site with an area ca. 150 m<sup>2</sup> was selected. The CSM has outlined the risk associated with the subsurface contamination transport of chlorinated hydrocarbon towards different receptors in the pilot site test area. As well, a scheme was presented to address the proposed remedial effect of Carbo-Iron® injection at the pilot site (Figure 4).

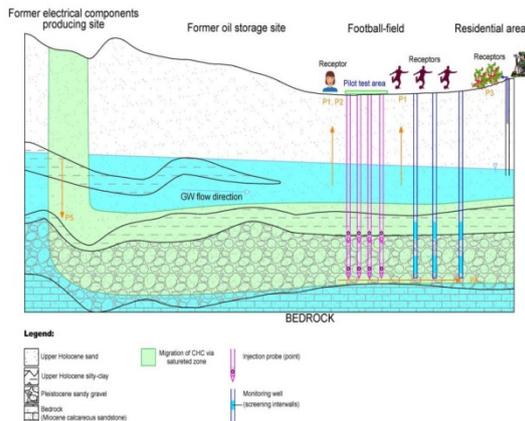


Figure 4: Cross section of pilot site with injection and monitoring scheme

**Injection and Monitoring Planning**

- In summer 2015, Carbo-Iron® injection will be conducted at a gravel aquifer contaminated with chlorinated solvents (CHC)
- Injection shall happen in 3 injection points at the depths of major contamination perpendicular to GW flow direction ;
- 4 monitoring CMT wells are installed to verify the injection results in designated three depths (screened section marked with red lines in Figure 5);
- Chemical groundwater analysis shall indicate CHC reduction as well as associated parameters like vinyl-chloride, hydrogen, dissolved iron, ethane, ethene;
- The technical equipment includes direct push penetrometer, nitrogen supply, water, mixing and injection tanks, high pressure membrane pump, with associated monitoring wells (Figure 6)
- Beyond the groundwater monitoring soil and groundwater samples from the pilot site will be analyzed within the project objectives of selected NanoRem work packages.

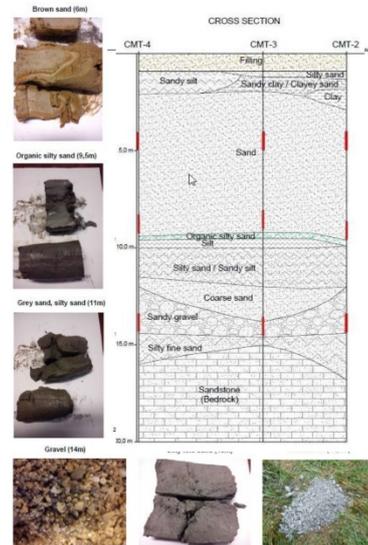


Figure 5: Cross Section of soil profile with wells and sampling points



Figure 6: Technical injection equipment

**Outlook**

After injection in Summer 2015, groundwater sampling at 7 monitoring events (-7 to 360 days) will be conducted at all suitable wells (4 x CMT a 3 Channel), and monitoring wells upstream and downstream of the injection area with the intention to verify contaminant mitigation due to Carbo-Iron® injection into the aquifer.

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# 1C.6-6: Dechlorination of solvents by nanoscale zero-valent iron particles: applying flake shaped nanoparticles in an aerobic aquifer with restricted solvent dissolution – R. Bitsch, P. Kvapil, S. Thümmeler, N. Klaas



**Dechlorination of solvents by nanoscale zero-valent iron particles: applying flake shaped nanoparticles in an aerobic aquifer with restricted solvent dissolution**



Randi Bitsch<sup>1)</sup>, Petr Kvapil<sup>2)</sup>, Silke Thümmeler<sup>3)</sup>, Norbert Klaas<sup>4)</sup>

<sup>1)</sup>SOLVAY (Schweiz) AG, <sup>2)</sup>AQUATEST a.s., <sup>3)</sup>UVR-FIA GmbH, <sup>4)</sup> Research Facility for Subsurface Remediation (VEGAS)

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

## Motivation

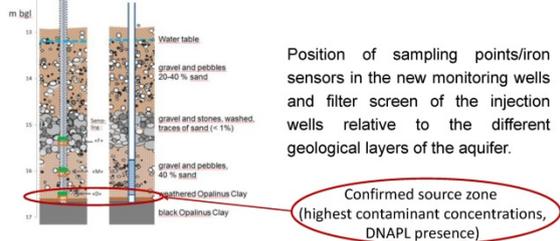


The Zurzach site is located in the Rhine valley in northern Switzerland. The main groundwater contaminants are PCE, TCE and Hexachloroethane (HCA) which were manufactured at this site until 1976.

A pump-and-treat system has been in operation for 12 years, but the efficiency of this installation is decreasing, thus there is an interest in alternative technologies for groundwater remediation. Injection of nanoscale zero-valent iron (nZVI) is an innovative technology, which could have the potential to expedite the remediation. The flake shaped, milled nanoiron FerMEG12 was selected for this field-scale pilot test because of its special physical-chemical properties.

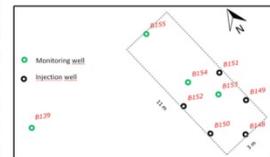
## Geology and Hydrogeology

The test field ground consists of unconfined alluvial sediments of sand and gravel. However, stones and boulders prevalent in distinct layers in the vadose zone prevent the use of direct push techniques. The bedrock (Opalinus Clay) is found at 16.5 m bgl and the average water table at 13 m bgl.



## Set-up of pilot test

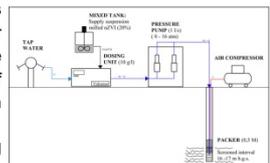
The map is showing the location of the new injection wells and monitoring points relative to the old monitoring well B139. The orientation of the pilot area is determined by the expected flow direction of the deeper ground water. Upper ground water might flow in the direction of B139.



## Injection - Monitoring

A total of 500 kg of milled nanoiron was injected into 5 injection wells at the site. The nanoiron suspension was prepared with the use of a continual injection dosing system. The nanoiron concentrate was stored in a mixing tank, the dosing was provided with the use of an automatic system; the final concentration of 10 g/l was fixed as constant and was dosed automatically according to the water flow into the wells. Five injection wells were screened at the required depth (bottom 1 m screen interval) according to the proved vertical contaminant distribution.

The final nanoiron suspension was injected with the use of a packer system to limit the residence time and to increase the flow velocity of the suspension in the wells and in the pipeline system.

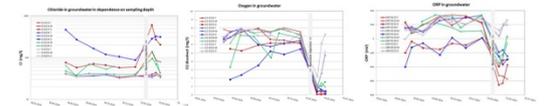


The injection pressure was adjusted between 5 and 7 atm.

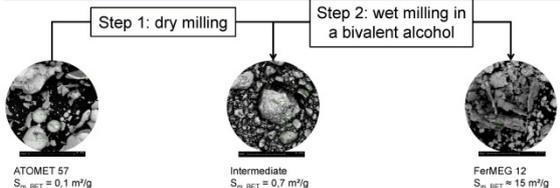
During the pressure injection Lithium tracer applied to follow the horizontal and vertical spreading of the liquid. Breakthrough curves confirmed the communication between all monitoring and injection wells.

## Preliminary Results - Conclusions

- The travel distance of nanoiron particles is confirmed by water sample analysis from monitoring points (black color, iron concentrations).
- Nanoiron travelling distance > 2,0 m (iron particles found in all sampling levels of B153 and B154)
- Oxygen depletion and changes in ORP proves the activity of Nanoiron. Nanoiron is still active 6 weeks after injection.
- Final degradation products – H<sub>2</sub>, ethane, ethene and chloride – are found in significant concentrations.
- Promising initial data show extensive degradation of chlorinated contaminants at some sampling points. Further monitoring is needed before final evaluation of test results.



## FerMEG 12 - Particles



The particles are produced in a two-stage top-down process. Dry grinding to get particles < 40 µm, followed by grinding in a bivalent alcohol to avoid H<sub>2</sub>. With this technology, nanostructured, flake-shaped particles with thicknesses less than 100 nm are obtained. Complete dry grinding without alcohol is in the planning stage.

|               |                       |                  |                |                                   |
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NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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# 1C.6-7: The application of iron oxides nanoparticles as an alternative electron acceptor for biodegradation of BTEX – J. Bosch, T. Lederer, P. Kvapil



## The application of iron oxides nanoparticles as an alternative electron acceptor for biodegradation of BTEX



Julian Bosch<sup>a</sup>, Tomas Lederer<sup>b</sup> and Petr Kvapil<sup>b</sup>

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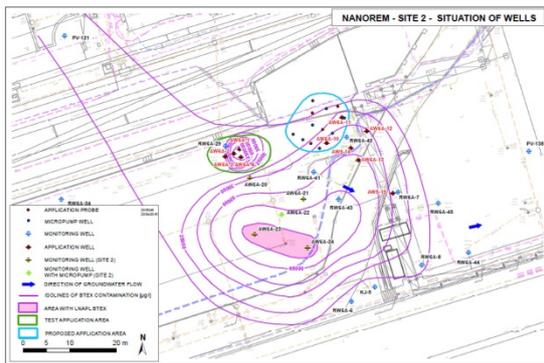
www.nanorem.eu

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Motivation and Goals

Colloidal iron oxide nanoparticles can be used, after injection into contaminated groundwater aquifers, as electron acceptor for the microbial degradation of BTEX. We want to demonstrate the feasibility of this approach at a large scale, BTEX-contaminated field site at Usti nad Labem, CZ.

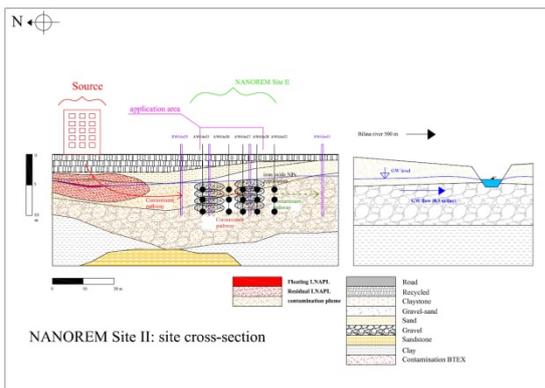
### Field Site



Spolchemie is one of the leading synthetic resin manufacturers in Europe. Besides synthetic resins it also produces other chemicals (e.g. potassium and sodium hydroxide, epichlorohydrin, allylchloride, sodium hypochlorite, perchloroethylene, hydrochloric acid, liquid chlorine).

This production site is located in an area of approx. 52 hectares at Usti nad Labem (Czech Republic) in the heart of Europe. The main Spolchemie complex comprises industrial buildings, roads and railway sidings, with a few vegetated areas. The plant was established in 1856, and began the production of inorganic chemicals followed by the manufacture of organic dyes at the turn of the 20th century, and from the middle of the last century Spolchemie started to produce resins and freons based on tetrachloromethane and tetrachlorethene.

The production, treatment, storage and distribution of these various raw materials and products has led to extensive contamination of the subsurface by chlorinated ethenes and methanes and organic solvents including BTEX compounds, which in many cases have dispersed widely from the original source areas. Some parts of the subsurface are also contaminated by high concentrations of iron and other organics (mainly chlorides and sulphates) which have increased the salinity of the groundwater.



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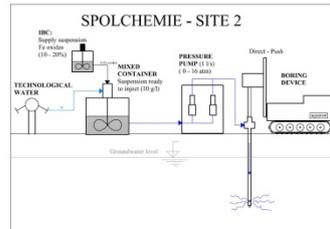
\* For more background information, please see poster 4643 – "In-situ Groundwater Remediation Using Iron-oxides Nanoparticles (Goethite): Large Scale Container Experiment to Investigate Transport and Reactivity" by Myiama et al.

### Remediation Plan

The injection will be done by direct push, as the site soil matrix is dominated by fine sands and clay.

The FeOx-NPs will be delivered as a stock solution and diluted on-site using the local tap-water supply.

The location of the injection and monitoring wells will depend on current monitoring results.



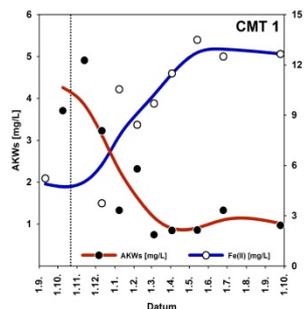
### Test Injection



Test Injection of 3000 L of FeOx-NP in November 2014. Results are currently used for the preparation of the final remediation layout.



### Outlook



Data from a previous, small-scale field site: After the injection of iron oxide nanoparticles (dashed line), BTEX concentrations decline, while ferrous iron is generated.

Currently, the baseline monitoring and installation of injection and high-resolution monitoring wells is taking place at the field site

In parallel, an injection and remediation concept is under development.

Meanwhile, up to 30 m<sup>3</sup> of FeOx-nanoparticle suspension is produced for injection.

The injection event (supported by NanoRem WP6 – Monitoring) is scheduled for Mid-August 2015.

After injection, we expect a local, but sustained remediation (about 1/5 of the source zone), which would open the perspective for a full removal of the total source by our technology.



## 1C.6-8: Study of the Cryomilling Technique for the Production of Nano Zero-Valent Iron (nZVI) Particles – D. Ribas, Z. Masopustova, J.A. Benito, V. Marti, I. Jubany, M. Cernik



### STUDY OF THE CRYOMILLING TECHNIQUE FOR THE PRODUCTION OF NANO ZERO-VALENT IRON (nZVI) PARTICLES



Ribas D.<sup>1,3</sup>, Masopustova Z.<sup>4</sup>, Benito J. A.<sup>2,3</sup>, Marti V.<sup>1,3</sup>, Jubany I.<sup>3</sup>, Cernik M.<sup>4</sup>

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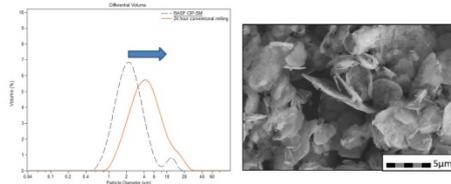
Foundation CTM Technological Centre

Institute for Nanomaterials, Advanced Technologies and Innovation - Technical University of Liberec

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

#### Introduction

Particle size reduction is still an important challenge to obtain zero valent iron nanoparticles suitable for the application in subsurface water remediation. To date, conventional milling has been limited by the high iron ductility. Typically iron milling at room temperature produces large flakes of several microns in width and a thickness of tens of nanometers [1] without any significant evolution with time or energy, e.g.: *Figure 1*. However, at cryogenic temperatures the iron ductility is dramatically reduced.



*Figure 1*. Size distribution (left) and SEM image of conventionally milled particles (right).

#### Materials and methods

##### Experimental Design

In order to figure out the evolution of the material through the process, four milling times were chosen: 20, 40, 60 and 90 minutes, respectively, 3 g of iron powder CIP-SM from BASF GmbH were used in each assay. The temperature was maintained cryogenic (77 K) all the milling.

##### Feeding Iron

BASF GmbH CIP-SM iron was selected, these were the initial size characteristics, by volume: a mean of 2.8  $\mu\text{m}$  and a 4.7% <1  $\mu\text{m}$ .

##### Cryogenic Mill

The 6870 Freezer/Mill - SPEX SamplePrep mill was used. Magnetic coil moves a cylinder from face to face of the vial smashing the sample. The main advantage of this specific model is the complete immersion of the vial into liquid nitrogen ensuring always a cryogenic temperature and an inert atmosphere, *Figure 2*.



*Figure 2*. Magnetic coil surrounding the Vial (Top), Vial container (Bottom).

##### Particle characterization

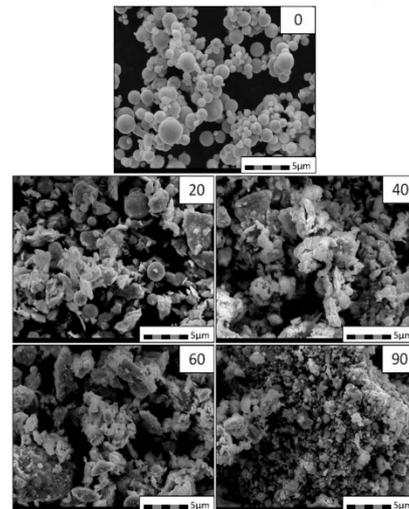
All milled samples were manipulated in a glove box under nitrogen atmosphere (Jacomex 2P), then samples were stored in absolute ethanol.

For the Scanning Electron Microscope (SEM) studies, the samples were deposited and led to evaporate into the glove box over standard pins.

For size characterization, Laser Diffraction Particle Sizing (LDPS) was chosen. Samples were previously mixed in an ultrasonic bath and then immediately analyzed directly in ethanol. Finally, data was post processed with the Fraunhofer optical model.

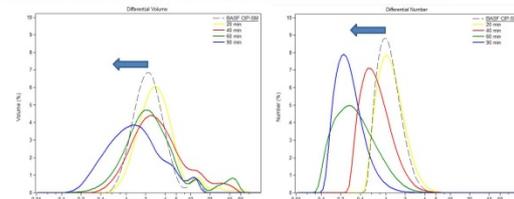
#### Results and discussion

As SEM images shows, a diminution of particle size through time can be observed, but signs of aggregation were detected especially for longer millings. Interestingly no flakes were formed entailing a fragile behavior, *Figure 3*.



*Figure 3*. SEM images: 0 (initial powder), 20, 40, 60 and 90 min milling.

Analysis by LDPS, *Figure 4*, stated that the bonding in the aggregated particles was soft and an important percentage of small particles come off from the surface after ultrasonic pretreatment. By volume, there was an initial period in which a raise in mean particle size was observed but increase in particle fraction of <1  $\mu\text{m}$  started to grow at 40 min. With increasing milling time, the overall particle size decreased and a growth in sub-micron fraction was incremented, with a value of 36.2% and a mean of 2.3  $\mu\text{m}$  at 90 min.



*Figure 4*. Particle size distribution by volume (left) and by number (right).

#### Conclusions

The use of cryomilling allows to obtain dry milled powder with a clear reduction of the particle size due to the brittle behavior of iron at cryogenic temperatures. In comparison with room temperature milling, the final particle size is high improved taking into account the small running times.

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- Köber R., Hollert H., Hornbruch, G., Jekel, M., Kamplner, A., Klaas, N., ... & Braun, J. (2014). Nanoscale zero-valent iron flakes for groundwater treatment. *Environmental Earth Sciences*, 72(9), 3339-3352.

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NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.

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# 1C.6-9: In-situ Groundwater Remediation Using Iron-oxides Nanoparticles (Goethite): Large Scale Container Experiment to Investigate Transport and Reactivity – K. Miyajima, A. Engelbrecht, J. Bosch, J. Braun



In-situ Groundwater Remediation Using Iron-oxides Nanoparticles (Goethite): Large Scale Container Experiment to Investigate Transport and Reactivity



Kumiko Miyajima<sup>a</sup>, Alexander Engelbrecht<sup>a</sup>, Julian Bosch<sup>b</sup> and Jürgen Braun<sup>a</sup>

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www.nanozem.eu

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Motivation

Nanoscale iron-oxide particles (Goethite) can effectively enhance microbial degradation of a wide range of contaminants.

Due to their small size, Goethite nanoparticles can be dispersed in water and directly injected into the subsurface to create reactive zones to promote contaminant degradation.

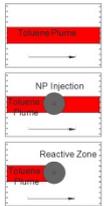


Large Scale Container at VEGAS research facility

→ Experimental proof of Goethite injection as promising technology for in situ remediation of contaminated aquifers is required.

### Goals

- Remediation of a BTEX (toluene) plume utilizing iron-oxide (Goethite) nanoparticles
- Transport and targeted deposition of Goethite nanoparticles (NP) in the subsurface ( $r = 1.5$  m with sufficient concentration)
- Quantification of remediation (degradation) rates and longevity of NP (reinjection intervals)

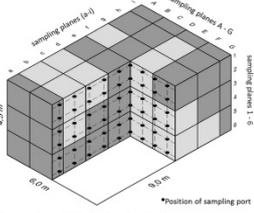


BTEX plume intercepted by injected Goethite NPs

### Set-Up of Large Scale Container Experiment and Monitoring

The Large Scale Container at VEGAS is built of high grade stainless steel and has the dimensions 9.0 x 6.0 x 4.5 m (L x W x H), with a volume of 243m<sup>3</sup>. The container is filled with two types of sand as blockstructure.

- 60 sand blocks in 3 layers (1.75m, 1.45m, and 1.3m high)
- Random distribution of coarse (0-4mm) and medium (0-8mm) sand blocks



Geometry of block structure in large scale experiment: (Light grey = coarse sand, dark grey = medium sand, black dots = location of liquid sampling points)

#### Boundary Conditions

- Unconfined aquifer
- Inflow BC: const. head,  $h_{in} = 3.782$  m
- Outflow BC: const. head,  $h_{out} = 3.775$  m
- Flow rate:  $Q = 3.1$  m<sup>3</sup>/d ( $q = 0.14$  m/d)
- Inflow DO concentration: < 1 mg/L

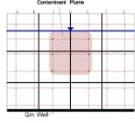
#### Monitoring strategy of each location (inflow, outflow, flow domain)

|                | Monitoring set-up                          | Parameter  |
|----------------|--|--|
| Inflow/Outflow | Installed sensor for continuous monitoring | Q, pH, DO, EC, ORP, T  |
| Flow domain    | 378 liquid sampling points, piezometers    | $h$ , $C_{NP}$ , $C_{toluene}$ , $CO_2$ , buffer capacity, TIC, pH, anion, $Fe^{2+}$ , $Fe^{3+}$ |

### Plume Emplacement

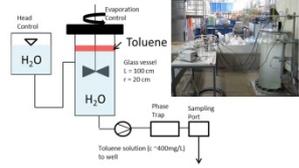
#### Requirements

- Toluene plume to be located in upper and middle block layer
- Cross-sectional area: 2m x 2m = 4m<sup>2</sup>
- To be intercepted by 9 sampling ports on a vertical sampling plane



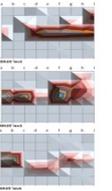
Cross section depicting sampling positions (where red lines cross), block geometry and plume

#### Set-up of continuous toluene solution supply system



Mixing unit and injection pump for concentrated toluene solution (left: Flow chart, right: set-up)

#### Distribution of $C_{tol}$ in the container



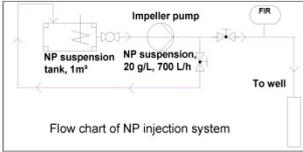
Upper layer at  $z = 3.3$  m  
 Middle layer at  $z = 2.6$  m  
 Bottom layer at  $z = 1.8$  m

$C_{tol}$  in the container before NP injection: Orange > 200mg/L, dark red > 100 mg/L, light pink < 20mg/L

### Nanoparticle Injection

#### Design parameters (based on MODFLOW)

- Reactive zone**  
 $r = 1.50$  m,  $z = 2.20$  m,  $PV \sim 6$  m<sup>3</sup>  
 → residence time of toluene:  $t \geq 7$  days  
 @  $v \sim 0.4$  m/d base flow
- NP Injection system**  
 Gravity driven injection  
 → Injection well: ID = 3",  
 Lscreen = 2.0 m,  
 $z = 1.7 - 3.7$  m  
 → Injection suspension Q = 700 L/h,  
 $t = 8.5$  h,  $c_{NP} = 20$  g/L,  $m_{NP} = 120$  kg

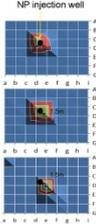


Flow chart of NP injection system

### Preliminary Result

#### NP transport (based on gravimetry method of liquid samples)

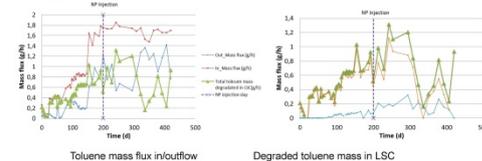
- NPs were transported around 1.5 m from the injection well with sufficient concentration of NP (~13g/L)
- Slight migration of unsedimented NPs by baseflow was observed until 5 weeks after the injection



Distribution of NP concentration during NP injection: (at 4h of injection): yellow: ~13g/L, red: ~5g/L, blue: < 1g/L

#### Remediation (Enhancement of biodegradation)

- Toluene degradation in the container was ~20% increased for 100 days after NP injection (left graph, green curve)
- However the sand in the container contains geogenic  $Fe^{3+}$ , and the inflow GW contains sulfate, so high toluene degradation was observed even before NP injection. Therefore no clear enhancement of biodegradation by NP was observed (right graph, orange curve)



Toluene mass flux in/outflow and Degraded toluene mass in LSC



NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment  
 This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.  
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# 1C.6-12: Methodology of laboratory test for the description and comparison of the reactive and migration properties of new types of iron nanoparticles – K. Pešková, J. Nosek, D.R. Fargas, M. Cernik



## Methodology of laboratory test for the description and comparison of the reactive and migration properties of new types of iron nanoparticles



www.nanorem.eu

Pešková Kristýna, Nosek Jaroslav, David R. Fargas, Černik Miroslav

NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Introduction

Research is underway in the framework of the project NANOREM, aiming to develop new types of iron nanoparticles for the remediation of the rock environment that are stable in air and do not have to be stored in an inert atmosphere. This greatly simplifies handling of the material during remediation (transport and preparation onsite). The pyrophoric properties of these nanoparticles are suppressed by stabilizing their surface using an inorganic shell, which prevents rapid oxidation (degradation) on contact with air. The aim of presenting methodologies for laboratory tests is to confirm the influence of activation of new type of iron nanoparticles (NANOFER STAR) on their reactive and migration properties. The activation process involves leaving a prepared stock slurry in a concentrated state (usually 20% wt.) for 48 hours and causes disintegration of the inorganic surface shell.

### Methodology

**Migration tests:** details of methodology see Fig. 1. Vertical orientation and washing against the direction of gravity. Concentration of nZVI at the input to the column ca. 1,2 g/L. Concentration of total Fe in time measured in output water. pH and ORP measured continuously. At the end of test measured the concentration of total Fe in whole column. Breakthrough curves of each type of nZVI and distribution curves of the nZVI in the columns evaluated and compared with each other.

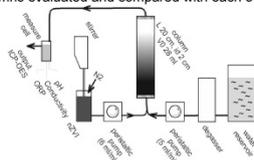


Fig. 1: Block diagram of the column test

**Reactivity tests:** using reagent 100, 250, 500 ml bottles with a Teflon septum. Each sample container used for a single sample and therefore constitutes one time step of the kinetics. The reactor tests - an extension of the batch tests. Using a working stirred reactor with 2.5 litres of contaminated water into which the nZVI dosed. The decrease in the concentration of contamination after the application of the acid and changes in the pH, ORP monitored (CHC: GC/MS – Varian 3800/Saturn 2200; pH, ORP: WTW 3430). Concentration and kinetic tests with water from sites.



Fig. 2: Left – Reagent bottles for kinetic batch tests; Right – reactors

### Results

#### Column tests:

| Type of nZVI                    | NF STAR 197 non-activated | NF STAR 197 activated |
|---------------------------------|---------------------------|-----------------------|
| Fe (mg/l)                       | 1850 mg/l                 | 1275 mg/l             |
| Total Fe on the output (mg) (%) | 47 mg (2.5%)              | 72 mg (5%)            |
| Total Fe in the column (mg) (%) | 2421 mg (98%)             | 2592 mg (97%)         |
| Length of acid bed (cm)         | 21.3                      | 21                    |
| Pore volume of the column (ml)  | 25.2                      | 27.0                  |

Fig. 3: Overall balance of nZVI before and after activation process

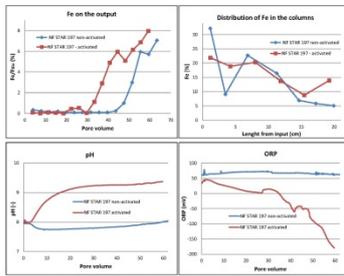


Fig. 4: Comparison of migration properties of non-activated and activated NF STAR and changes in physical-chemical parameters

#### Batch tests:

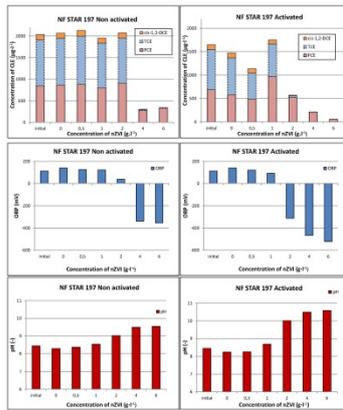


Fig. 5: Reactivity tests with CHC using different concentrations of non-activated and activated NF STAR and changes in phys.-chem. parameters

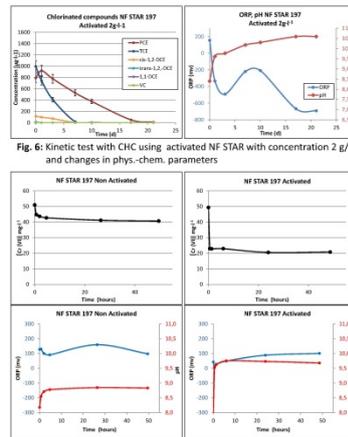


Fig. 6: Kinetic test with CHC using activated NF STAR with concentration 2 g/L and changes in phys.-chem. parameters

- The results of the performed tests show that the activated NF STAR iron nanoparticles are significantly more reactive and achieve better migration parameters. The disintegration of the inorganic surface shell causes that the particles have more negative Zeta-potential. This fact improve their migration and contribute to better distribution in the rock environment.
- The pilot and field tests confirmed that dilution to low application concentrations and dilution with the groundwater during transport in the rock environment does not lead to the disintegration of the inorganic surface shell (to the activation of the nanoparticles). This causes lower reactivity and increase of the remediation costs.

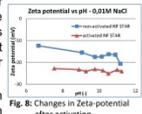


Fig. 8: Changes in Zeta-potential after activation

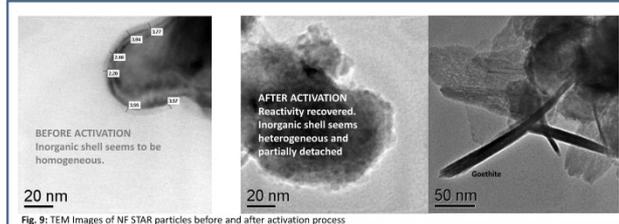


Fig. 9: TEM Images of NF STAR particles before and after activation process

Kristýna Pešková<sup>1</sup>, Jaroslav Nosek<sup>1</sup>, David R. Fargas<sup>2</sup>, Miroslav Černík<sup>1</sup>

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NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517. This poster reflects only the author's views. The European Union is not liable for any use that may be made of the information contained therein.

www.nanorem.eu



# 1C.6-13: Modelling nanoparticle transport in porous media across the scales: from the pore scale to the field-scale injection – P. van Gaans, T. Tosco, C. Bianco, A. Raouf, A. Fujisaku, D. Rodriguez Aguilera, R. Sethi, M. Hassanizadeh



## Modelling nanoparticle transport in porous media across the scales: from the pore scale to the field-scale injection

Pauline van Gaans, Tiziana Tosco, Carlo Bianco, Amir Raouf, Asako Fujisaki, David Rodriguez Aguilera, Rajandrea Sethi, Majid Hassanizadeh



NanoRem is a four year, €14 million research project funded through the European Commission FP7.

### Rationale

The design of a field-scale injection of engineered nanoparticle (NP) suspensions (e.g. zero-valent iron nanoparticles) for remediation of polluted sites requires a reliable estimation of the particle distribution after injection. In addition, regulators will require information on the longer term mobility of the injected particles in case they do not encounter and react with the contaminant.

While numerical models for the simulation of dissolved contaminant transport are widely available, field-scale models for the transport of NPs, with proven predictive ability, are yet developed. This is, in part, due to the lack of understanding of fundamental controlling mechanisms for the transport of NPs in the subsurface at the field scale.

Therefore, as part of the EU research project NanoRem, WP7 set out to develop a NP transport simulation module, based on fundamental physics, to be incorporated into the existing reactive transport models like RT3D. The research aim is approached from both ends: understanding NP behaviour at the pore scale and finding up-scaled relationships that are validated using experimental or field data at the macro-scale.

### General Approach

**NanoPNM: physically based pore-scale modelling**

**MNMs: Modelling transport in 1D and radial geometry**  
<http://areweb.polito.it/ricerca/groundwater/software/mnms.php>

**RT3D/MNM3D: Modelling transport at field scale in 3D geometries**  
 To 4 days

**WP8: large scale laboratory experiments**

**WP10: field pilots**

### Basic Equations

**Transport equations for liquid and solid phase:**

$$\frac{\partial(cC)}{\partial t} + \nabla \cdot \frac{\partial(pD_s)}{\partial t} + \frac{\partial(qC)}{\partial t} - \frac{\partial^2(\alpha D_s C)}{\partial t^2} - qC = 0$$

$$\frac{\partial(pD_s)}{\partial t} = nk_{a1}(1 + AS)^{-1} - p_1 k_{d1} S_1$$

$$\frac{\partial(pD_s)}{\partial t} = nk_{a2} C - p_1 k_{d2} S_2$$

**Influence of ionic strength:**  
 Salt concentration is coupled with colloid equations via semi-empirical relationships:

$$\frac{\partial(cw_s)}{\partial t} + \nabla \cdot \frac{\partial(\alpha D_s)}{\partial t} - q_s w_s = 0$$

**Attachment Kinetics**      **Detachment kinetics**      **Max. solid phase concentration**

**Equations/parameters to be refined based on NanoPNM model experiments**

**Influence of velocity and flow-rates:**  
 Flow velocity decreases with distance from the injection well. At high flow rates, drag forces increase, reducing retention of particles. Conversely, low flow rates at distances from the well facilitate NP deposition.

### Pore-scale Modelling (NanoPNM)

Using pore-network modelling, PoreFlow, we simulate fluid flow and transport of NPs within a network of interconnected pores. Colloidal processes such as deposition and aggregation are implemented at the scale of individual pores. Averaging over the network domain composed of thousands of pores, we derive macro-scale parameters to be used within macro-scale model.

represented by:

regular network of pores

Pore connectivities, with maximum of 26 connections

Parameters:

- Lattice distance
- Pore size distribution (mean and variance)
- throat radius: pore radius
- elimination rate (connection number)
- pore scale NP attachment/detachment

Results from a column test using iron oxide NPs, from WP4, were simulated with NanoPNM. There is a good match, however, due to the high flow velocity used in the column experiment, no significant attachment was observed.

### Macroscale models for 1D (MNMs) and 3D (MNM3D) geometries

Validation of MNM3D in 1D geometry was performed against both experimental data of a Ferrhydrite microparticle column test and MNMs simulation results (figure on the left; a: 5 mM, b: 10mM).

An application in 3D geometry (figure below) simulated the water flow and the hypothetical NP transport in a large-scale container (LSC) located at the VEGAS facility in Stuttgart University (Germany), where particles will be injected as part of NanoRem WP8. The simulation involved the NP injection through 4 wells and, then, flushing with a lower ionic strength solution (i.e., 50, 30, 10 and 1mM).

| Size (L x W x H)           | 9m x 6m x 4.5m   |
|----------------------------|--|
| Aquifer type               | Unconfined   |
| Soil structure             | Blocks with 2 different types of sand (medium sand and coarse sand) "randomly" distributed |
| Inflow boundary condition  | Constant flux: 12 injection wells  |
| Outflow boundary condition | Constant head  |

**LSC set-up**

Colloid concentration in liquid phase compared with an ideal conservative tracer (µg/L)

A = End of the injection of the colloidal particles (24h);  
 B = 8 hours after the beginning of the ionic strength lowering (102 h);  
 C = Ionic strength decrease completed and particles release at an advanced stage (129 h).

<http://areweb.polito.it/ricerca/groundwater/software/MNMs.php>

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NanoRem - Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment  
 This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.  
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# 1C.6-14: Aquifer modification: an approach to improve the mobility of nZVI used for in situ groundwater remediation – D. Schmid, V. Micic, M. Velimirovic, S. Wagner, F. von der Kammer, T. Hofmann

## Aquifer modification: an approach to improve the mobility of nZVI used for *in situ* groundwater remediation

Department of Environmental Geosciences  
Doris SCHMID, Vesna MICIĆ, Milica VELIMIROVIĆ, Stephan WAGNER, Frank von der KAMMER & Thilo HOFMANN

BACKGROUND

**Limited mobility** of nanoscale zero-valent iron (nZVI) remains an obstacle for the nZVI-based groundwater remediation.

Beside straining and sedimentation, also attachment to positively charged "patches" on the **mineral grain surfaces hinders the mobility of nZVI**.

**Hypothesis:** An increase in mobility of nZVI may be achieved by increasing the negative surface charge of the mineral grain surfaces (modifying aquifers) via pre-injection of inexpensive polyelectrolytes into sand.

EXPERIMENTAL SETUP

MATERIALS

**SAND**  
Chemical composition [%]: SiO<sub>2</sub>: 98.5; Al<sub>2</sub>O<sub>3</sub>: 0.47; Fe<sub>2</sub>O<sub>3</sub>: 0.18; CaO: 0.02; MgO: 0.01; Na<sub>2</sub>O: 0.02; K<sub>2</sub>O: 0.07; TiO<sub>2</sub>: 0.11; P<sub>2</sub>O<sub>5</sub>: 0.01.  
Grain size [mm]: d<sub>10</sub>: 0.36; d<sub>50</sub>: 0.65; d<sub>90</sub>: 0.88.  
Mineralogy [%]: quartz: 96; feldspar: 2; kaolinite: 1.

**WATER**

- MQ (electrolyte-free) water (Millipore, Elix@5-Milli-Q® Gradient A10). Electrical conductivity: 0.054 µS/cm at 25°C.
- EPA (electrolyte-rich) water (U.S. EPA moderately hard standard water)[mg/L]: [Na<sup>+</sup>]:26.8; [K<sup>+</sup>]:2.3; [Ca<sup>2+</sup>]:13.8; [Mg<sup>2+</sup>]:11.2; [Cl<sup>-</sup>]:2.2; [SO<sub>4</sub><sup>2-</sup>]:79.3; [NO<sub>3</sub><sup>-</sup>]:0.6; [HCO<sub>3</sub><sup>-</sup>]:67.3; Electrical conductivity: 297 µS/cm at 22.6°C.

**nZVI**  
Nanofer 25S suspension (polyacrylic acid coated-nZVI, Nanoiron, s.r.o., CZ). Particle concentration: 1 g/L.

**AQUIFER MODIFIERS**

- Water-soluble sodium lignin sulfonate (Otto Dille® Baeck GmbH & Co. KG, DE).
- Water-soluble sodium humate (Humintech® GmbH, DE).

Tentative structure of lignin sulfonate monomer  
Source: <http://www.chemicalregister.com>

Tentative structure of humic acid monomer  
Source: [doi:10.1039/b001869a](https://doi.org/10.1039/b001869a)

CHARACTERIZATION OF MATERIALS

Lignin sulfonate [mg/L]

Humic acid [mg/L]

**Zeta (ζ) potential of nZVI** (calculated from the electrophoretic mobility) and of **sand** (calculated from the streaming potential) measured in a sand column modified with **lignin sulfonate (A) and humic acid (B) solutions in MQ and in EPA water**. Note that the ζ potential of both sand and nZVI is significantly lower in MQ than in EPA water and that the nZVI aggregates are larger in EPA than in MQ water.

THE CONCEPT OF AQUIFER MODIFICATION

nZVI injection  
into the sand with natural surface charge heterogeneities

**limited nZVI mobility**

nZVI injection  
into the sand having altered surface charge with aquifer modifiers

**enhanced nZVI mobility**

RESULTS

in MQ water: d<sub>50</sub> (nZVI): 2.8 µm

in EPA water: d<sub>50</sub> (nZVI): 6.2 µm

**Mean breakthrough curves of nZVI (measured as Fe<sub>tot</sub>) before and after injection of different solutions of aquifer modifiers.** n is number of replicates. Error bars show standard deviation for n > 3.

(A) Modification of sand surfaces with lignin sulfonate (LS) solutions in electrolyte-free (MQ) water increases the mobility of nZVI independent on LS concentrations. (B) Only after aquifer modification with 10 mg/L of humic acid (HA) solution in MQ water the mobility of nZVI was improved.

In electrolyte-rich (EPA) water is nZVI practically immobile. (C) Aquifer modification with LS solutions in EPA water does not improve mobility of nZVI. (D) Only after aquifer modification with 10 mg/L of HA solution in EPA water mobility of nZVI was improved.

CONCLUSIONS

- ▶ The **ζ potential of sand decreased** when its surface was modified with the solution of **modifiers prepared in MQ water**, but not in EPA water.
- ▶ The two types of modifiers have different effects on the nZVI transport depending on the type of water.
- ▶ Aquifer modification with different concentrations of lignin sulfonate (LS) in MQ water shows a potential to increase mobility of nZVI with the Fe<sub>tot</sub> breakthrough varying between 0.5 and 0.7. Conversely, modifying the aquifer with LS solution in EPA water shows no effect on nZVI mobility with the Fe<sub>tot</sub> breakthrough remaining < 0.2.
- ▶ Aquifer modification with a 10 mg/L humic acid solution in both MQ and EPA waters enhances mobility of nZVI, while the higher concentrations show no effect on mobility of nZVI.
- ▶ Further work will be dedicated to better understanding the mechanisms behind these observations.

This research receives funding from the European Union's Seventh Framework Programme FP7/2007-2013 under grant agreement n°309517.

## 5 NanoRem promotional material

### 5.1 NanoRem – A unique opportunity!

An A5 sized leaflet with information on all the special sessions held by the NanoRem consortium.



**AquaConsoil 2015** offers a number of keynote papers and three specific sessions on **nanoremediation**, brought to you by the FP7 NanoRem project, which could be all you need to know to decide how this technology might be of interest to your organisation:

- Solving problems for site owners
- Offering opportunities for service providers
- Providing evidence based technical information for regulators.

This concentration of information is unique, and will not be found at other events. It is also unlikely to be repeated in the near future.

#### ***Nanoremediation all you wanted to know - a practical guide to nanoremediation***

SpS 1C.23S, Thursday June 11, 9:00 – 10:30, Auditorium 11

*Providing a practical grounding in nanoremediation theory and practice with particular reference to applied examples in the field*

- What nanoremediation is and what it can and cannot do
- Practical experience in nanoremediation
- Regulatory perspective on nanoremediation use
- The NanoRem experience: large scale and case study testing
- Question and answer session,

#### ***Nanoremediation - your future business opportunities***

SpS 1C.24S, Thursday June 11, 11:00 – 12:30, Meeting Room 17

*Providing business and strategic intelligence on market scenarios*

- What will drive the EU nanoremediation market till 2025
- Discussion of possible market trends and opportunities.



Learning about nanoremediation at



## European advances in nanoremediation technology

SpS 1C.28S, Thursday June 11, 14:00 – 15:00, Auditorium 10

Six presentations showing investigations and results of the EU FP7 NanoRem project:

- In-situ Groundwater Remediation Using Carbo-Iron®: Large Scale Flume Experiment to Investigate Transport and Reactivity in a source-treatment approach
- Reactivity tests in columns for simulating source zone and plume remediation of chlorinated hydrocarbons by zero-valent metal particles under subsurface-like conditions
- Agar agar stabilized milled zerovalent iron particles for in situ groundwater remediation
- Demonstrating Nanoremediation in the Field - The NanoRem Test Sites
- Performance of Carbo-Iron particles in in-situ groundwater flume and source treatment approaches
- Nanoiron and Carbo-Iron particle transport in aquifer sediments - Targeted deposition
- Other presentations from the NanoRem will be made in 1C.15,1C.17, 1C.18,

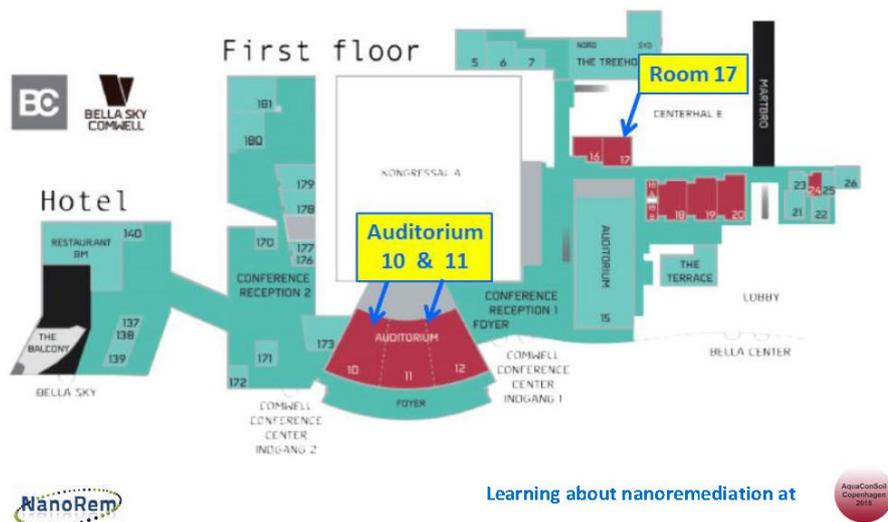
## Nanoremediation - poster session

Tuesday June 9, 17:30 – 18:30

NanoRem will show detailed results on about 20 posters, the authors will be happy to answer questions and to discuss results.

See the map below for where to find these sessions

Floor plan Bella Center



## 5.2 NanoRem – What’s it about?

A leaflet with information on the NanoRem project, with project information on the front and contact information for all work package leaders on the back.



### Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

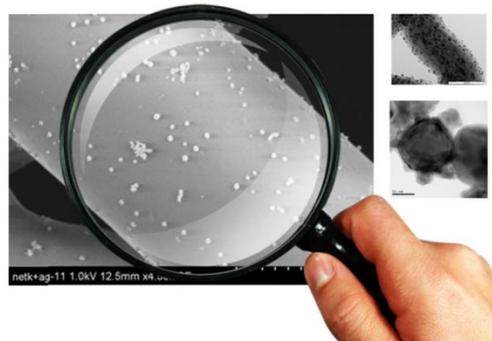
A four year, €14 million research project funded through the European Commission FP7



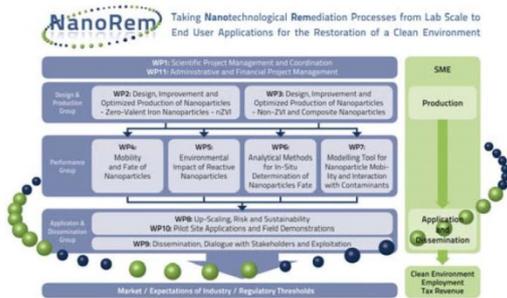
#### What’s it about?

NanoRem will focus on facilitating practical, safe, economic and exploitable nanotechnology for in situ remediation. This will be 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 project is designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and so support both the 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 EU environmental sector.



#### Scientific Structure



#### The Project Partners

The NanoRem consortium is multidisciplinary, cross-sectoral and transnational. It includes 29 partners from 12 countries organized in 11 work packages. The consortium includes 18 of the leading nanoremediation research groups in the EU, 10 industry and service providers (8 SMEs) and one organisation with policy and regulatory interest. The consortium is co-ordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany.

Determine the mobility and migration potential of nanoparticles in the subsurface, and relating these both to their potential usefulness and also their potential to cause harm.

Develop a comprehensive set of tools to monitor practical nanoremediation performance and determine the fate of nanoparticles.

Develop lower cost production techniques and production at commercial scales of nanoparticles.

Engage in dialogue with key stakeholder and interest groups to ensure that the work meets their needs, is most sustainable and appropriate whilst balancing benefits against risks.

Identify the most appropriate nanoremediation technological approaches to achieve a step change in remediation practice.

Carry out a series of full scale applications in several European countries to provide realistic cost, performance, fate, and transport findings.



www.nanorem.eu



| WORK PACKAGE | ORGANISATION  | NAME                  | CONTACT DETAILS                            |
|--------------|---|-----------------------|--|
| WP 1 & WP 11 | Universitaet Stuttgart / VEGAS<br> University of Stuttgart<br>Germany            | Hans-Peter Koschitzky | Hans-Peter.Koschitzky@iws.uni-stuttgart.de |
|              | Karlsruher Institut fuer Technologie<br> Karlsruhe Institute of Technology       | Markus Stacheder      | Markus.Stacheder@kit.edu                   |
| WP 2         | Technicka Univerzita v Liberci<br>   | Miroslav Cernik       | Miroslav.Cernik@tul.cz                     |
| WP 3         | Helmholtz-Zentrum fuer Umweltforschung GMBH – UFZ<br>                            | Katrin Mackenzie      | Katrin.Mackenzie@ufz.de                    |
| WP 4         | Universitaet Wien<br> universität wien  | Thilo Hofmann         | Thilo.Hofmann@univie.ac.at                 |
| WP 5         | Norwegian Institute for Agricultural and Environmental Research – BIOFORSK<br> | Erik Joner            | Erik.Joner@bioforsk.no                     |
| WP 6         | Universitaet for Miljo Og Biovitenskap<br>                                     | Deborah Oughton       | Deborah.Oughton@nmbu.no                    |
| WP 7         | Stichting Deltares<br>   | Pauline van Gaans     | Pauline.vanGaans@deltares.nl               |
| WP 8 & WP 10 | VEGAS / Universitaet Stuttgart<br>   | Jürgen Braun          | juergen.braun@iws.uni-stuttgart.de         |
| WP 9         | r3 Environmental Technology Limited<br>  | Paul Bardos           | Paul@r3environmental.co.uk                 |

## 5.3 Nanoremediation: What's in it for me?

A 4 page brochure including a nanoremediation Q&A, Expert interviews, Information on the project, field trials and particles that are being investigated in the project.



# NANOREMEDIATION: WHAT'S IN IT FOR ME?

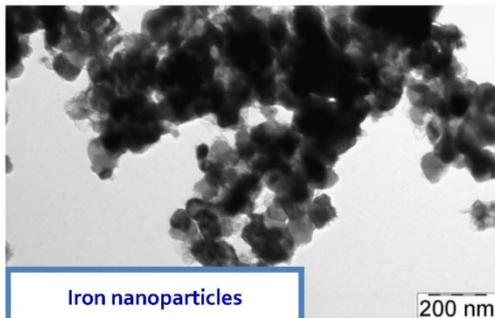
June 2014

## Nanoremediation Q & A

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

### What are nanoparticles?

Nanoparticles (NPs) are usually defined as particles with one or more dimension of less than 100nm.



### What is nanoremediation?

Nanoremediation describes the *in situ* use of NPs in the treatment of contaminated groundwater and soil. Nanoremediation processes generally involve reduction or oxidation, which in some cases may be facilitated by an embedded catalyst.

### Why use nanoremediation; what are the benefits?

As a result of their size, NPs have unique properties, which may give nanoremediation benefits over competing technologies. Anticipated benefits of NP use in remediation include increasing the speed and degree of contaminant destruction, extending the range of treatable problems and avoidance of generating intermediate breakdown products.

### How are nanoparticles deployed?

The most common form of NP deployment is direct injection. The most frequently used NP in remediation to date is nanoscale zero valent iron (nZVI). However a variety of NP types have been trialled or are under development, for example in the NanoRem project.

### What contaminants have nanoparticles been used to treat?

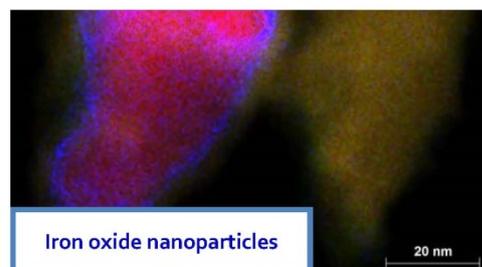
Most deployments of nZVI have focussed on the degradation of chlorinated solvents, although pilot studies have also demonstrated successful treatment of BTEX, perchlorates, hexavalent chromium, diesel fuel, PCBs and pesticides.

### Are there environmental risks?

Fear of risks of environmental impacts from nanoparticles have led to concerns about their application in remediation. However, these risks are thought to be low owing to limited persistence and transport in the subsurface. However, as with any agent applied *in situ* there are potential risks, and some information needs remain, which NanoRem is addressing. A detailed risk-benefit appraisal for nZVI use is available from [www.nanorem.eu](http://www.nanorem.eu).

### How can the particles, or their impacts, be monitored in the environment?

Few direct methods are available to monitor the impact of NPs. Indirect methods rely on measuring the changes of the hydro-chemical milieu (e.g. redox conditions), increasing concentrations of dissolved reaction products such as chlorides or other indicators, and decreasing concentrations of the contaminants down-gradient of the injection zone. Direct methods are more difficult, but the NanoRem project is looking to develop, and test at selected sites, a comprehensive tool box for field-scale observation of NP performance.



This project receives funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No. 309517.

## What is NanoRem?

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) is a research project, funded through the European Commission's Framework 7 research programme.

NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for in situ remediation. This is being undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of NPs, market demand, overall sustainability, and stakeholder perceptions.

The project is designed to unlock the potential of nanoremediation processes from laboratory scale to end user



The NanoRem Consortium includes  
28 partners from 12 countries

applications and so support both the 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 EU environmental sector.

## Expert Interview: Miroslav Cernik

### *How did you become interested in nanoremediation and why?*

I worked as a consultant in an environmental consultancy for a number of years. We applied or tested many methods for groundwater/soil remediation, some of these had only limited effectiveness and long treatment times (e.g. pump-and-treat). While these methods were preferred by some owing to their simplicity, on many sites these methods were simply ineffective, with some sites being estimated to require many decades of treatment.

My interest in nanoremediation was sparked by a connection I had with Golder Associates and learning about their original trial application of nZVI. The method looked very simple and straightforward. Of course, nothing is as simple as it looks! The challenge of improvement and optimization of nZVI (to get it to a stage suitable for practical testing and use in the Czech Republic) piqued my interest in this method. Why do I believe in nanoremediation? Because it is a simple, targeted, fast and economically affordable method for site remediation.

### *What can nanoremediation already do better than other in situ remediation technologies?*

There are quite a few things!

- 1) A much smaller amount of material is needed compared to the other chemical and/or biological remediation methods.
- 2) As nanoremediation with nZVI is a chemically reductive method, the environment is significantly less affected compared, for example, with methods involving oxidation. Additionally, the environment returns very fast to "normal" state. Products of nZVI oxidation are iron oxides, analogous to natural compounds.

3) Compared with other reductive methods or bioremediation, nanoremediation works for all chlorinated ethenes and no toxic intermediates are accumulated.

4) Nanoremediation is relatively quick.

5) There is no migration of chemicals out of the contaminated sites.



Prof Miroslav Cernik  
Technical University of  
Liberec

### *How do you think these advantages will develop in the future?*

As development continues, NPs will be aimed at specific contaminants. Their migration and reactivity could be tuned to specific site properties and contaminants. NPs will be injected directly to where they are needed only. The cost of treatment is also likely to decrease.

### *How can these benefits help consultants and industry deliver better site and groundwater remediation?*

Nanoremediation provides a tailored technology for particular types of contamination at specific sites. It can be a cheaper remediation with a lower negative impacts on the environment compared with other methods; a lower amount of chemicals is needed and it is a potentially faster method. It can also be possible to combine nanoremediation with other methods such as bioremediation.

## Is NanoRem carrying out field trials?

Yes, an essential part of the NanoRem project is the proof of concept of NP based remediation at a range of field sites. Particles tested include different kinds of nZVI, Carbo-Iron® and iron-oxide (Goethite) NPs, see below. Each of these particles targets specific contaminants (e.g. organic, inorganic, chlorinated hydrocarbons). They enhance specific remediation processes (chemical reduction or oxidation, microbial dechlorination or oxidation etc.). Moreover, each NP suspension has specific requirements with respect to hydro-geological (coarse or fine grained porous material, fractures) and hydro-geo-chemical (pH, salinity, redox conditions etc.) site conditions.

As of May 2015, different particles have been injected in pilot sites in Zurzach (CH), Usti nad Labem 1 (CZ) and Besor-Secher (IL). Within 2015 four additional applications will take place in Usti nad Labem 2 (CZ), Balassagyarmat (HU), Barreiro (PT), and Nitrastur (ES).



Preparing nanoparticles for injection, Zurzach site, Switzerland

## What particles are NanoRem investigating?

NanoRem is investigating a range of nanoparticles, including available commercial products, customisations and adaptations to these nanoparticles, nanoparticles emerging into production, and also novel particles being generated through research. Table 1, below, summarises the principal nanoparticle types currently under investigation in the NanoRem project.

Table 1—Summary of NanoRem NPs

| Name  | NanoFer 25S                               | NanoFer Star  | Milled Iron                        | Carbo-Iron  | Fe-oxides   | Bio-Fe-oxides, Biomagnetite         | Bio-magnetite / Pd   | Fe-Zeolites   |
|---|---|---|------------------------------------|---|---|-------------------------------------|--|---|
| Type of particle  | Nano scale zero valent iron (nZVI)        | Air-stable powder nZVI  | Mechanically ground nZVI particles | Composite of Fe(0) and activated carbon               | Pristine iron oxides stabilized with HA                     | Produced from nano-Fe(III) minerals | Biomagnetite doped with palladium                                  | Nanoporous aluminosilicate loaded with iron-oxides                              |
| Process of contaminant removal                          | Reduction                                 | Reduction   | Reduction                          | Adsorption and Reduction                              | Oxidation (catalytic effect on bioremediation)              | Adsorption and Reduction            | Reduction (catalyst)   | Oxidation (catalyst)  |
| Target contaminant                                      | halogenated hydrocarbons and heavy metals | halogenated hydrocarbons and heavy metals   | halogenated hydrocarbons           | halogenated hydrocarbons (cont. spectrum as for nZVI) | biodegradable organics, (pref. non-halogenated) e.g. BTEX   | heavy metals, e.g. Cr(VI)           | e.g. halogenated substances (cont. spectrum broader than for nZVI) | Wide spectrum e.g. BTEX, MTBE, dichloroethane, chloroform, dichloromethane, ... |
| Lab-scale   | X   | X   | X                                  | X   | X   | X                                   | X  | X   |
| Large scale Lab. experiments                            | X   | (X)   |                                    | X   | X   |                                     |  |   |
| Field scale tests (planned)                             | X   | (X)   | X                                  | X   | X   |                                     |  |   |
| Field sites:<br>Site name (country */ main contaminant) | Spolchemie 1 (CZ / PCE)                   | Spolchemie 1 (CZ/PCE)<br>Barreiro (PT / heavy metals)<br>Nitrastur (ES / arsenic) | Zurzach (CH / PCE)                 | Balassagyarmat (HU / PCE)<br>Neot Hovav (IL / n/a)    | Spolchemie 2 (CZ / Toluene)<br>Barreiro (PT / heavy metals) |                                     |  |   |

\*Country Key

CZ – Czech Republic; CH – Switzerland; HU – Hungary; IL – Israel; PL – Poland; ES – Spain; PT – Portugal

## Expert Interview: Katrin Mackenzie

### *How did you become interested in nanoremediation and why?*

Originally I worked in the field of catalysis - somewhere between homogeneous and heterogeneous catalysis. Strictly speaking, we find nanostructures at the surface of most heterogeneous catalysts...and they were working in clean-up processes long before we talked about nanoremediation. My interest in NP use in nanoremediation comes from water treatment. As I have worked in the field of water treatment for a long time, it was inevitable I would come to "nano" eventually!

### *What can nanoremediation already do better than other in situ remediation technologies?*

NPs have a much higher reactivity than their micro-scale counterparts. They offer a larger outer surface area for reactions and often special properties compared to the bulk material.

All established remediation technologies (e.g. as pump & treat, *in situ* bioremediation, soil flushing etc.) have advantages and disadvantages. The main strength of NP injection is the flexibility it offers. We can reach very deep zones and built over/sealed aquifers. We only need a well/bore hole. Other injection techniques can do the same, but it is difficult to "mix" reagent and groundwater. If we simply inject a reactive solution, the solution is transported with the groundwater flow. With NPs, we create an immobilized reactive zone through which the contaminated water flows. This is the principle we know from permeable reactive barriers, but without the need for the excavation works required for PRBs.

### *What are the particular benefits of Carbo-Iron®?*

One of the materials I have been working with is Carbo-Iron®. This is a composite material of colloidal activated carbon and zero-valent iron. With Carbo-Iron® we offer a new air-stable material, which forms stable suspensions and can be easily injected into the subsurface, creating broad reactive treatment zones. The sorption properties of the composite material enhance the effectiveness of the metallic iron reagent. Carbo-Iron® can undergo all iron-specific chemical reduction reactions but the combination of both materials – iron and carbon – allows the strong enrichment of pollutants in the vicinity of the iron. Carbo-Iron has also been shown to support biological degradation processes.

## Feedback and further information

If you have any feedback or queries related to the special session; have a specific question regarding nanoremediation or NPs; or would like to find out more about nanoremediation or the NanoRem project, please contact the Information Manager, Prof Paul Bardos at [paul@r3environmental.co.uk](mailto:paul@r3environmental.co.uk). Alternatively, further information on nanoremediation and the NanoRem project, including news and downloads, can be found at: [www.nanorem.eu](http://www.nanorem.eu).

### *How can these benefits help consultants and industry deliver better site and groundwater remediation?*

Nothing is a secret weapon against all contamination issues in all site circumstances. This question must always be coupled with site knowledge and a comparison of available methods. I see the benefits of Carbo-Iron®'s properties in a whole toolbox of treatment possibilities. We need to provide the information to help consultants and industry to choose the right one.

### *What are the plans for commercially developing and using Carbo-Iron®?*

Carbo-Iron® is currently produced by our industry partner, Scientific Instruments Dresden GmbH. They, together with NanoRem and a partner who will bring the material into the remediation market, will push the commercialization of the product. As the material is new, it needs scientific support and its success needs to be demonstrated in field trials. We also hope to collectively ensure that the product is used at sites where it will be of maximum benefit and that misuse of the product (e.g. improper handling, use at inappropriate sites), which could lead to discredit, is restricted.

In addition, we are eager to gain as much knowledge as possible via accompanying laboratory studies, as we are talking about a new material which has to compete with the established track-record of existing methods and materials. The NanoRem project includes many studies aimed at better understanding of particle fate, transport, reactivity, behaviour towards organisms, and long-term performance.

### *How can people find out more?*

Performance of Carbo-Iron® will be presented in several oral presentations at the AquaConSoil in the NanoRem Thursday sessions. Scientific papers and user-friendly material descriptions will be offered.



**Dr Katrin Mackenzie**  
UFZ, Germany

## 5.4 Nanoremediation: Enquiry Form



# NANOREMEDIATION: ENQUIRY FORM

|              |  |
|--------------|--|
| <b>Name:</b> |  |
|--------------|--|

|                      |  |
|----------------------|--|
| <b>Organisation:</b> |  |
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| <b>Email Address:</b> |  |
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|   |
|---|
| <b>Would you like to receive further general information about (please tick):</b> |
| <input type="checkbox"/> Nanoremediation  |
| <input type="checkbox"/> The NanoRem Project                                      |
| <input type="checkbox"/> Other  |

|   |
|---|
| <b>Please state any specific queries or questions you may have:</b> |
|   |

|  |
|--|
| <b>Any further comments or feedback:</b> |
|  |

You can return this form, or contact us with other queries at [nanorem@r3environmental.co.uk](mailto:nanorem@r3environmental.co.uk). Comments will be received by NanoRem partner r3 Environmental Technology and responses will be provided by the NanoRem consortium. Further general information on nanoremediation can be obtained at [www.nanorem.eu](http://www.nanorem.eu).



FP7 Project Nr.: 309517

## 6 List of References

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