NanoRem NEWSLETTER

N° 3 Autumn 2015

Nanotechnology for Contaminated Land Remediation

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

NanoRem So Far – First 30 Months

The aim of the NanoRem project is to showcase the application of nanoparticles (NPs) as a practical and reliable method for the treatment of contaminated soil and groundwater. As described in previous newsletters (see www.nanorem.eu) the project is looking at many different aspects to help build up this knowledge. Detailed below is an update of the different activities over the last year building on previous newsletters.

Investigating nanoparticles

One of the key parts of the NanoRem project is to provide a direct link between the production and application of NPs. NanoRem NP production falls into two domains: nano zero valent iron (nZVI) and others including non-zero valent iron (non ZVI) and composite NPs.

- The nZVI NPs have been produced by solid-state thermal reduction or milling. These products are now being tested in unmodified or surface modified forms, as slurries or dry powder in large-scale field test injections on sites.
- For the non ZVI and composite NPs, the project has progressed the particle design, optimised the self-manufacture of particles and also purchased some particles. These particles are all now available for injection at field test sites.

Mobility and fate of nanoparticles

Characterisation, mobility and reactivity tests of all the available NPs have now been completed. Based on these results further NP optimisation testing for stability and mobility properties has been carried out with only a few optimised NP tests still pending. As described previously the preliminary results indicate that a significant improvement of

Photo 1: Partners preparing a Carbo-Iron® suspension at VEGAS. Source: VEGAS/USTUTT, University of Stuttgart.

particle properties (particularly mobility and reactivity) has been achieved. These properties are now being evaluated during the field scale work.

Environmental impact of reactive nanoparticles

The ecotoxicity of NPs has been tested on both terrestrial and aquatic organisms with the highest toxicity being seen for one batch of milled Fe particles. The effect of soil

Highlights

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

constituents and ageing on ecotoxicity has also been studied using groundwater from the large-scale laboratory-based experiments and field sites. So far, no toxicity has been observed at three injections, including one large-scale laboratory flume and two onsite injections, therefore not allowing the recording of possible toxicity alleviation. Groundwater samples from one site in the Czech Republic were observed to be highly toxic prior to nFeOx injection with toxicity alleviation happening within a few hours to weeks after nFeOx injection, but this was shown to be transient. Microbial community analyses on soil and groundwater samples from the field sites is ongoing, to determine microbial interactions during and after remediation with NPs. Further information on the ecotoxicity testing can be found on page 3.

Field based analytical methods

The various analytical methods available for nZVI and other Fe-based NP characterisation that have been developed and tested in the large-scale tank experiments and in the pilot field site applications have continued and refined. These included *in situ* magnetic susceptibility arrays, as well as on site sampling and analysis. The methods have been successful in tracking the movement of NPs during injection, in assessing transformation processes and tracking renegade particles through rare earth element signatures. New methods for tracing Carbo-Iron® and Fe-Zeolites are also being tested during field applications.

Modelling tools

Modelling tools have continued to be used to simulate the movement of NPs in the subsurface to assist with the design and interpretation of laboratory and field tests. The numerical tool for macro-scale simulation of NP transport in porous media called MNMs and RT3D has been adapted and extended for the use by the consortium to aid modelling at some of the field sites.

Up-scaling large tank trials, risk and sustainability

The set-up of three large-scale experiments for up-scaling to the field scale, including emplacement of contaminant sources / plumes, and injection of different NPs has been completed. Performance parameters are being measured continuously with sustainability and preliminary life cycle assessment approaches continuing to be advanced.

Field tests at case study sites

All the field sites have now been confirmed and investigated with most installations completed. Conceptual site models have been compiled, remediation goals defined and evaluated, and injection permits obtained. Three of the sites have had NPs injected, and a smaller scale test injection has been performed on one of the Czech Republic sites.

Photo 2: Spreading of Carbo-Iron® suspension in the large scale flume experiment. Source: VEGAS/USTUTT, University of Stuttgart.

Dissemination, dialogue and exploitation

Initial recommendations for risk assessment of NP deployment and considerations of the sustainability and market prognoses for nanoremediation have now been produced based on workshops, literature review and wider stakeholder engagement. This information is primarily based on nZVI however other NPs are now being incorporated over the second half of the project. The initial nZVI findings are now being reviewed as the project progresses across the NanoRem project. Summaries and downloads are regularly updated to the website (www.nanorem.eu), in particular as “information for decision makers”.

The NanoRem website (www.nanorem.eu) is also continuing to be updated with project reports and news items as they become available.

The project consortium also had a really large presence at AquaConSoil 2015 through platform presentations, poster sessions and special sessions which allowed for wide engagement with many different stakeholders (see page 12).

Future

The next 12 months will be extremely important for NanoRem, with results from the site works nearing completion and the writing up of the results beginning, being more widely shared and showing that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater.

Exciting Initial Ecotoxicity Results from the NanoRem Project

NanoRem has recently announced that no significant toxicological effects have been found on soil or water organisms when ecotoxicological tests have been undertaken for a range of nanoparticles (NPs) that could be used for remediation projects that are being tested as part of the project. The NPs tested are:

- NanoFer 25S, made from nanoscale zero-valent iron, used for the remediation of chlorinated hydrocarbons in the large-scale flume pilot experiment, and at Spolchemie I, Czech Republic.
- Carbo-Iron®, a composite made from activated carbon and zero-valent iron, to be used for the remediation of chlorinated hydrocarbons in the large-scale flume pilot experiment, and at Balassagyarmat, Hungary.
- Fe-Oxide, nanoscale goethite, used for the remediation of toluene in the large-scale container pilot experiment, and at Spolchemie II, Czech Republic.
- Fe-Zeolites, aluminosilicate containing an iron catalyst, used in lab-scale remediation studies.
- Bionanomagnetite, (with and without 5% Pd), nanomagnetite produced by bacteria, used in lab-scale remediation studies.

NanoRem tested for their effects on a range of organisms, mostly using standard methods published e.g. by the Organisation for Economic Co-operation and Development (OECD). These organisms were:

- *Eisenia fetida*, earthworm, used for its relevance upon ingesting soil and skin contact with contaminants in soil.
- *Lolium multiflorum* (ryegrass) and *Raphanus sativus* (radish), representing monocotyledon and dicotyledon plants, used for their relevance in contact exposure of germinating seeds and roots.
- *Daphnia magna*, aquatic crustacean, used for its relevance for ingesting suspended particles and contaminants in water.
- *Lumbriculus variegatus*, freshwater oligochaete, used for its relevance for ingesting sedimented and suspended particles and filtering freshwater.
- *Pseudokirchneriella subcapitata*, microscopic green algae, used for its relevance in contact exposure in aquatic environments.
- *Vibrio fischeri*, bioluminescent marine bacterium, used for its high sensitivity to contaminants, and relevance to marine environments.

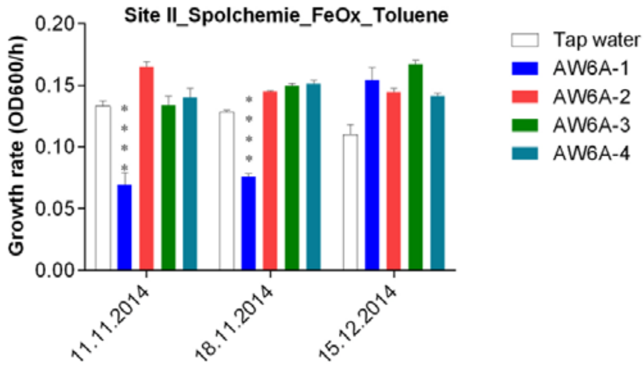

Figure 1. Graphs showing reduced toxicity of groundwater close to an injection well (monitoring well AW6A-1) at the polluted site Spolchemie II (assessed as growth rate of the bacterium *Clostridium perfringens* by the Technical University of Liberec), within three weeks after iron oxide (FeOx) NPs.

A part of the NanoRem project ecotoxicity testing is a key aspect as it provides additional evidence to the stability of these NPs in the environment. The project team will continue ecotoxicity testing if any new NPs or formulations are developed as the project progresses.

The project has also been looking at how NPs reactivity and toxicity change with time. It is believed that as NPs interact within the soil matrices they become less reactive, and therefore less toxic with time. NanoRem's findings confirm this anticipated trend which is very similar to how chemicals in general react in soil. As chemical contaminants age in the soil, their reactivity is reduced along with their bioavailability and toxicity.

There are currently widespread concerns that NPs are being used to treat pollutants that may not fully degrade them, but transform the pollutants into more toxic compounds. NanoRem has investigated whether this phenomenon may be occurring, both in large-scale pilot experiments and in the field using bioassays to investigate toxicity. These bioassays have used sensitive test organisms and have also investigated whether there are changes to the indigenous populations of microorganisms. This work is still ongoing, but the initial results indicate no enhancement of pollutant toxicity (or NP toxicity) even within a few metres of the injection wells and shortly after injection. On the contrary, groundwater samples from one of the field sites (Spolchemie II) were found to be highly toxic prior to injection of Fe-Oxide NPs, but toxicity was significantly reduced within three weeks after the injection (see Figure 1).

Monitoring of the wells around this and other field sites injected with NPs will continue for several months with additional chemical analyses being carried out by other partners within the NanoRem project, to provide detailed evidence of the different processes occurring during the treatment of the different contaminants. The results will be reported to depict the mechanisms of degradation and ecotoxicity that are occurring, but so far they are very promising.

Microbial community analyses from the polluted field sites are in progress, and assays on microbial functioning are scheduled for the second half of the project.

The 2nd Annual Meeting Barcelona / Manresa

NanoRem's 2nd Annual Meeting took place in Barcelona and Manresa from 14th to 17th April 2015 with about 75 participants, including the responsible Project Officer (PO), the Project Technical Advisor (PTA), and external experts of the Project Advisory Group (PAG).

The second year of NanoRem was very productive, good progress was made, many new insights were gained during the research but also the need for exchange of experience, coordination and adjustment of the abundant tasks became obvious. So ahead of the official meeting, on Tuesday and Wednesday morning, problem-oriented sessions were held to discuss overarching issues between different work packages (WPs), strengthening the cooperation and interaction. Moreover, on Wednesday morning the first Project Management Group (PMG) Meeting took place.

A working lunch with the PO, the PTA and the PAG members on Wednesday marked the 2nd Annual Meeting's official start.

After a brief welcome by the PO, Jyrki Suominen, the project coordinator, Hans-Peter Koschitzky officially opened the meeting, giving a brief overview of the "news" since the last annual meeting and the process and goals for the next three days. The opening was followed by the WP leaders giving their presentations about the progress of the 2nd project year. At the end of these presentations, the PO shared his thoughts on the project progress and status and congratulated and thanked the NanoRem team for the progress achieved and the good teamwork and coordination. The day was closed by a financial overview by the project's administrative and financial project manager. In parallel, the first PAG meeting took place.

After two productive days in Barcelona, the meetings on Thursday and Friday took place in Manresa, where one of the NanoRem partners, CTM, hosted the meeting.

Thursday's sessions were dedicated to WP meetings to discuss the upcoming tasks and challenges and agree on a course of action. In the afternoon the PAG and PMG each had a separate meeting, followed by a joint meeting in the late afternoon, where the external experts shared their impressions of the work progress and provided advice and recommendations for the upcoming work to WP leaders.

In the evening, the participants of the meeting enjoyed a visit to the medieval monastery St. Benet near Manresa including a dinner in one of its halls.

On Friday, the PAG summarised their recommendations for the consortium and discussed open questions with the WP leaders. All recommendations and questions will be addressed by the WP leaders and answers provided. Finally, the WP leaders summarised the previous day's WP meetings, including the timelines and data that they needed for the next year. Last but not least the PTA gave his short concluding summary and the coordinator closed the Annual Meeting, thanking all participants, in particular the project partner CTM for organising and hosting the meeting.

The consortium especially would like to thank the project officer for his presence during the WP presentations on Wednesday and his very positive remarks, as well as the PTA for his valuable feedback during the whole meeting. Additionally, the consortium would like to thank the PAG for their constructive remarks during the last year and the very helpful ongoing support.

Photo 1: NanoRem participants at Manresa.

Catherine Leaf

Member of the Project Advisory Group representing NICOLE

Q. Can you tell us a little bit about NICOLE?

A. NICOLE (the Network for Industrially Contaminated Land in Europe) is a European forum focused on progressing the effective management of contaminated land in a cost efficient and sustainable manner. NICOLE is funded by its members which comprise three main groups: Industry (e.g. industrial land owners), Service Providers (e.g. consultants, remediation contractors, analytical laboratories) and Academics and Other Individuals.

The Network is led by its Steering Group which comprises representatives from each of the three Member Groups and specific Working Groups are formed to focus on particular areas of interest – the outputs of the Working Groups are communicated to all members. A new Working Group is in the process of being established (Operating Windows Group) via which there is potential for NICOLE to further its own assessment of the potential for nanoremediation.

Ramboll Environ (formerly ENVIRON) is a member of NICOLE, thus my involvement with the NanoRem Project enables dual representation of both Ramboll Environ and NICOLE meaning NICOLE has a direct route into NanoRem.

Q. What motivated you to join the NanoRem Project Advisory Group?

A. In 2011, I wrote an article for the European publication AWE on the potential that nanotechnology has as a remediation technique. However there remain a number of unknowns relating to the release of nanoparticles (NPs) in the environment, particularly with respect to their mobility, fate, transport and ecotoxicology. My article repeated previous calls by many others for more collaborative research to further understanding in these areas. Therefore when the opportunity arose to get involved with the NanoRem Project, I leapt at the chance! NanoRem is exactly what my article recommended and I'm delighted to be a part of that.

My role on the Project Advisory Group (PAG) means that I can apply my experience as a contaminated land consultant inputting to the PAG's guidance of the project from the perspective of both consultancy (i.e. those that would design and implement nanoremediation) and the land owners (i.e. the Clients) that want surety over the effectiveness and cost of the remediation. This dual perspective serves NICOLE's membership well and I feed back to the Network and offer myself as a channel of any queries the membership may have.

Q. What do you see as the strengths of the project and what might be the points we need to watch out for?

A. The NanoRem project is a large research project comprising 28 partner organisations supported by the PAG and Management Group. One of the strengths of the project is the vast amount of knowledge and expertise held by the partner organisations and supporting groups. Via this, the NanoRem project is well capable of significantly furthering the understanding of the viability of nanoremediation.

However the size of the project requires highly effective communication in order to ensure that the relevant and required knowledge is shared between the different Work Packages (WPs) in a timely and efficient way. That's not always an easy thing to accomplish within any organisation, especially one whose partners are spread across 13 countries (!) which is why I see it as something to watch out for.

Q. How do you think NanoRem will advance knowledge in nanoremediation?

A. For me, the defining aspect of the NanoRem project which has the potential to really advance knowledge in nanoremediation is the way the project has been structured to have a specific WP focused on outward communication. That WP ensures that the project not only effectively disseminates the outputs of the research and development undertaken by the other WPs but also actively engages with organisations such as NICOLE and Common Forum to provide opportunities for their members to input to the project with their queries on nanoremediation. Without this vital function, the results of the hard work undertaken by the other WPs would be at risk of remaining in the academic arena and not reaching those of us that operate in the commercial arena which is after all where the future of nanoremediation will really be determined.

Miroslav Cernik

Leader of Work Package 2

Q. What interested you in nanotechnology/nanoremediation in the first place?

A. I worked as a consultant in the environmental engineering and consultancy company AQUATEST a.s. for a number of years and tested many methods of groundwater/soil remediation. However, some of the methods were very boring, longwinded and ineffective (e.g. pump-and-treat). The Czech National Property Fund, which was responsible for remediation of properties sold by the State to the private sector, preferred these methods due to their simplicity and because they easily showed the amounts of extracted contaminants. At many sites these methods were not sufficient and the estimated duration of site remediation was in the range of several decades. At the beginning of this century new methods began to be tested, including *in situ* treatments. The application of zero-valent iron began at this time in the USA and since the beginning we have collaborated in this field with Golder Associates. At first the method looked very simple and straightforward. Of course nothing is as simple as it looks at the beginning. What interests me about this method is how we can improve, optimise and get it to work. It is nanotechnology (in general) which has been successfully applied in the Czech Republic. In addition to remedial applications we are also interested in the issues of nano safety and toxicity, etc.

Q. Can you tell us a little bit about the work you are leading in NanoRem?

A. The aim of Work Package 2 is to improve the properties of Fe-based nanoparticles (NPs) and scale-up the production to an industrial level. Both industrial partners (NANOIRON and UVR-FIA) had the capacity to produce NPs in hundreds of kg per month before the project started. During NanoRem, the production procedure was improved and then up-scaled from the laboratory to industrial level. An example is the production of dry particles, which were developed at UPOL, then tested at TUL and the optimal thickness of the oxidic protective layer was achieved. UPOL transferred the production to NANOIRON who up-scaled it from grams to hundreds of kilograms. But this is not the end of the story. NPs have to be stabilised, not for storage and transport like before but for improvement of their migration in the subsurface environment. This is a different process and due to the oxide layer on the surface, different stabilisers are also needed. In addition, we found that dry NPs have to be initialised prior to their application. So, optimal NP production at a laboratory scale, as well as their testing, characterisation and then up-scaling are the major tasks that I am leading.

Q. What do you think are the benefits and opportunities of nanoremediation compared with other *in situ* remediation technologies?

A. I can tell you in a few words: it is a relatively simple, fast and efficient method which is more environmental-friendly compared to most other technologies. The groundwater is naturally in a chemically reductive condition, so the popular oxidation methods need to dramatically change it, which is linked to the oxidation of all organic matter and the surface of minerals. This depletes the source of carbon for possible consequent bioreduction and releases heavy metals. The other reductive methods can be used together with nanoremediation in a combined approach. The opportunity is to bring a successful and environmentally friendly remedial technology to the market and demonstrate its advantages.

Q. What are your views of the current challenges?

A. Currently, we are concentrating on the activation process and surface modification of NANOFER STAR. The particles have to be activated prior to their use in order for them to be sufficiently reactive and this process is currently being studied in detail. Additional surface modification for improvement of NP migration is an additional challenge. Carboxymethyl cellulose is tested together with axilates, natural gums, starch and other candidates. The dispersion process is an important step in NP activation ensuring that there is a good distribution of particles in groundwater. The NPs are tested for their reactivity with Cr(VI) and chlorinated hydrocarbons and for their mobility in a laboratory column. Tests with real contaminated groundwater samples from contaminated sites are also performed in order to select the right NP for each site.

Q. How does your work help expand the opportunities for nanoremediation and address the challenges it faces?

A. Improvement in the properties of NPs is a key factor affecting their applicability. Other factors include psychological barriers e.g. it is a new method without any broad experience, the magic world "nano" and also groundless fears of their possible toxicity. So, let's do our job and show how nanoremediation is a good card in the pack of remedial methods.

Katrin Mackenzie
Leader of Work Package 3

Q. What interested you in nanotechnology/nanoremediation in the first place?

A. My research group has been involved in the whole process of method development for water treatment over the last two decades. Twenty years ago the use of iron filings was the subject of intensive investigation owing to their reactive properties leading to a new remedial methodology. An interest in nanoscale particles is a logical consequence of this work, given their higher reactivity. Nanoparticles (NPs) play a role for me in several directions. In all cases halogenated water pollutants are the targets to be destroyed. We use reagents such as iron, with or without catalysts such as palladium (Pd), to achieve this.

The NanoRem project has given me the opportunity to extend my research interests by focusing on other NPs. Within the project we are developing new particles such as Carbo-Iron® which will extend the range of treatment approaches that can be used using NPs.

I see nanotechnology/nanoremediation as a very attractive scientific field to work in, however it is very challenging. Working with NPs is complex and time consuming and there are perception challenges that need to be addressed, but it is worth it when we succeed.

Q. Can you tell us a little bit about the work you are leading in NanoRem?

A. In NanoRem I am leading Work Package 3 which focuses on composites and also non-ZVI NPs. This is complementary to the activities in Work Package 2, which is exclusively focussing on studying nano-iron particles. Our part of the project aims at design, optimisation and supply of all the “other” particles.

Most of these “other” particles are newly developed or are employed in new uses. With these particles we want to extend the range of treatment approaches from reduction to include also oxidation and sorption strategies, thus increasing the range of treatable contaminants in NanoRem. The range of particles includes nano-iron oxides for enhanced natural attenuation, bio-generated nanomagnetite, a C-Fe composite known as Carbo-Iron®, non-iron metals as reducing agents, and oxidation catalysts Fe-zeolites. Two of these particles have been selected for field application: (1) Nano-iron oxides which strongly support iron-reducing microbial degradation processes leading to pollutant oxidation and (2) Carbo-Iron®. With Carbo-Iron® we have developed an alternative to nanoiron particles for reductive dehalogenation which are designed to have a higher and more adjustable mobility than nanoiron and can combine strong sorptive enrichment of the contaminants to more efficiently utilise the iron for the dechlorination reaction.

Q. What do you think are the benefits and opportunities of nanoremediation compared with other *in situ* remediation technologies?

A. When we compare nanoremediation with established *in situ* technologies, such as *in situ* bioremediation, injection of reactive liquids and soil flushing etc, each of these technologies has their advantages and disadvantages. The main differences are:

- When a reactive solution is injected it travels with the groundwater flow, therefore mixing with the groundwater occurs but causes the injected reagent to often react only with the outer regions of the injection bulb. Therefore the real radius of influence is lower.
- However an injected nano particle zone is stationary. This allows the polluted groundwater to flow through the injected zone, thereby creating a more reactive zone of influence.
- Most dissolved reagents have a shorter life-time than NPs which can live much longer.
- *In situ* bioremediation works as a stationary zone, is long-lasting but can often produce unwanted persistent intermediate products (e.g. in the case of perchloroethene reduction where dichloroethenes and vinyl chloride are generated and are not further reduced).

Q. What are your views of the current challenges?

A. We need to ensure that the aspects which do not work perfectly for the existing solutions are addressed using NPs. The scientific community, public and authorities also need convincing that there is no risk posed to the environment by the application of our NPs.

Concerning the risk, I deeply believe that with the NPs we are currently studying, the risks to the environment are marginal or non existent and this has to be seen also in the light of what they can offer us (i.e. effective remediation of contaminated sites). NanoRem intentionally designed the particles in such a way that for the best of our knowledge and extensive experience, all means have been taken to avoid risks. In addition, all NPs are thoroughly tested before any application is conducted.

However, we do know that there are other NPs which are not studied in NanoRem, where we would not have the same belief in their environmental compatibility. These include metals that are known to be ecotoxic or biocides (e.g. Ag) or where highly reactive species are generated when in contact with light (photocatalysts, e.g. TiO_2). Unfortunately, these types of particles are used extensively and discredit the term “nano” and therefore also “nanoremediation”. Therefore it makes it more difficult to gain acceptance.

Q. How does your work help expand the opportunities for nanoremediation and address the challenges it faces?

A. Firstly, we are specifically designing particles. In this process we include our knowledge gained from the performance of other particles and are therefore not being the pioneers in particle design but are using our own experience and that of other groups to learn from.

As an example, using the process for Carbo-Iron®: We learnt from nanoiron that on the one hand its reactivity is high and should be maintained. However, its subsurface transport is insufficient to efficiently generate reactive zones in contaminated aquifers. Also its affinity to organic solvents (NAPL phases) is low. As we had previously also worked on sorption barriers, we brought both ideas together: sorption and reaction. We combined activated carbon particles with nanoiron by embedding the iron structures within the activated carbon grain. In doing so, we mix the properties of both materials. The iron does not agglomerate as bare nanoiron particles do and the carbon gives porosity, a lower density, lower surface charge and most importantly strong sorption properties (with enrichment of organic pollutants of several orders of magnitude in concentration). In addition, activated carbon has a high affinity to undissolved organic pollutant phases which would be one precondition for source remediation. We also learnt that “nano” is not always the best size range for transportation purposes. Particle sizes around 1 µm and embedded into iron nanostructures are better. This does not only help to improve transport but brings the particles away from the critical size of ecotoxicological concern. Thorough study of the material expands our knowledge on its properties but also its efficient use. We are now able to either place the particles near the injection port when we target a certain (source) zone or let them travel within a distance of 8 to 10 m for plume control. This and the fact that the particles are stable in air is an enormous improvement for particle handling in the field.

Case Study Site: Field Injection Trial at Solvay Zurzach

Judith Nathanail Land Quality Management, Norbert Klaas & Juergen Braun University of Stuttgart and Randi Bitsch Solvay

The project demonstration site in Zurzach, Switzerland, is a former Solvay chemical works which produced perchloroethene (PCE). The nanoparticles (NPs) injected were milled zero-valent iron NPs (nZVI) to treat the PCE and related chlorinated solvent contamination within groundwater. The injection was carried out by Aquatest in March 2015.

Nanoparticle injection

The milled ZVI was supplied as a dark grey slurry in ethylene glycol by UVR-FIA GmbH in small 15 litre drums. The small volumes allowed any unforeseen stability and viscosity problems to be handled. The slurry was then mixed on site to discourage aggregation. A lithium tracer was added to the slurry to assist with tracking the subsurface migration of the injected liquid.

This slurry was gravity fed to the Vulcanus dosing unit (Photo 1) then mixed with tap water at doses of 10 g nZVI/l, and pumped into the injection wells at 5-7 bar injection pressure. In total 100 kg of nanoiron was injected in each of the five wells.

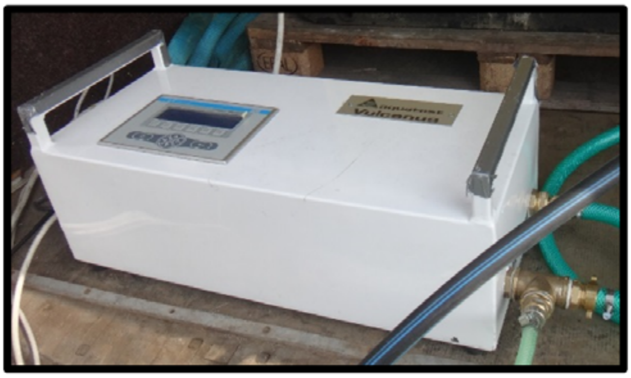

Photo 1. Vulcanus dosing unit. Source: Judith Nathanail.

The five injection wells had been drilled earlier in the project (Figure 1) and comprised 2” PVC pipe with horizontally slotted screen in the bottom 0.75 m of the well. The geology is interbedded sands and gravels, with average permeabilities between 2E-3 to 2E-2 m/s although in the gravel it may be higher.

The injection rod had an integral packer (the black section in Photos 2a and 2b). Once at the correct depth, the packer was

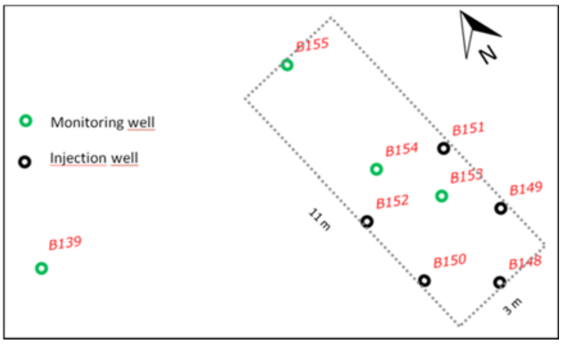

Figure 1. Borehole locations. Source: Solvay.

Photos 2a and 2b. The injection rod being inserted. Source: Judith Nathanail.

inflated allowing the nZVI to be injected at selected depths within the well. After inflation, injection began; at the surface, all that was visible was a gentle rise and fall of the rod in line with the strokes of the pump.

Monitoring subsurface nanoparticle migration

The design of the monitoring equipment was a key part of the injection as there is a need to understand both NP migration and effectiveness of remediation in the subsurface.

Three new monitoring wells (B153, B154 and B155, Figure 1) were drilled for the NanoRem project in which sensor arrays measuring temperature (at 3 depths) and magnetic susceptibility had been placed.

The temperature sensors showed the progress of the injected liquid; the magnetic susceptibility sensors were used to detect the presence of the iron NPs.

The sampling equipment was a Solinst pump powered by nitrogen gas. The system is a low flow sampling technique which minimises sample disturbance. It works by changing the pressure in the inner and outer tubes which forces the water upwards.

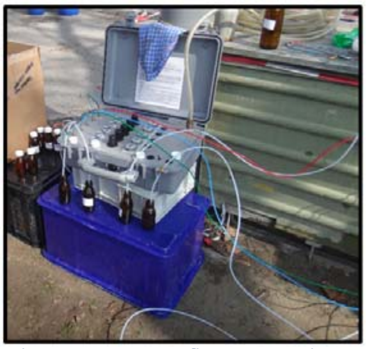

Photo 3. Low flow sampling. Source: Judith Nathanail.

Sampling was carried out every two hours during the injection. Photo 3 shows the collection of the low flow samples.

Samples were tested for lithium at the Solvay chemistry laboratory and for hydrogen and ethene by VEGAS. The location of the boreholes is shown in Figure 1.

Early Results

Whilst on site, it was evident that the NPs were moving distances of at least 2m; the sampled water turned black which indicated the presence of iron particles (Photo 4). NPs were detected in monitoring wells B153 and B154 from all three sampling levels during injection but were not observed in B155, which is further from the injection wells.

Photo 4. Nanoparticles present in water samples. Source: VEGAS/USTUTT, University of Stuttgart.

The lithium tracer indicates the distribution of the injected liquid which moves ahead of the NPs and provides an indication of flow direction. Lithium was found in B155, (where nanoiron has not been detected) suggesting B155 is on the flowpath (Figure 2)

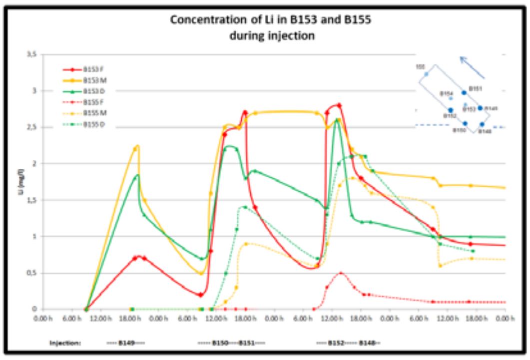

Figure 2. Tracer concentration over time. Source: Solvay.

Figure 2 shows the concentration of the lithium tracer at each monitoring depth with time and the period of injection for each of the wells B148 to B152. As expected, there was a bigger time delay for the tracer to reach B155 (dashed lines) compared to B153 (solid lines).

The field trial shows that the milled iron NPs can successfully be injected into the subsurface. Monitoring of contaminant and reaction product concentrations is ongoing to evaluate the impact of the milled iron NPs on the chlorinated solvents in the groundwater.

Case Study Site: Application of Carbo-Iron® in Balassagyarmat, Hungary

Matthias Kraatz Golder Associates

One of the six pilot sites to carry out field demonstrations of injecting nanoparticles (NP) is a site in Balassagyarmat Hungary. Here the application of an emerging NP called Carbo-Iron® is being trialled as part of the NanoRem project between February 2013 and January 2017.

The field testing work is being conducted by Golder Associates GmbH, Germany and Golder Associates (Magyarország) Zrt. in Hungary. NP specification involves the production and injection of Carbo-Iron® NPs, which are being produced by SciDre in Dresden, Germany. Planning and field application of NPs at each pilot site is supported by lab-scale testing, conceptual and hydraulic modelling and sustainability assessment, all in close coordination with the associated work package groups such as the German research facilities UFZ Leipzig and VEGAS Stuttgart.

This pilot test is based on field experience gathered when the project team applied iron NPs for subsurface remediation on a research project in Germany between 2010 and 2014 ("FE-Nanosit") into a contaminated aquifer situated at an industrial brownfield site. Here the subsurface was contaminated primarily from an off-site source of chlorinated hydrocarbons (CHC) (PCE, TCE, DCE), creating an on-site plume of approximately 15 kg PCE into a sandy and silt aquifer layer with the groundwater table being situated at about 3 m below ground level. To date, no remediation has been legally required or initiated by pertinent authorities on site.

Upon the NanoRem project kick-off and the Balassagyarmat Hungary site being selected as one of the pilot sites, a detailed site investigation and evaluation of the legal permitting framework was performed by Golder. Based on the analytical results, a conceptual site and contamination transport model was developed, and the pilot site with an area of approximately 150 m² was selected.

Sampling points (Continuous Multi channel Tubing (CMT) wells and standard monitoring wells) were installed in the contaminated zone up and downstream of the proposed three injection points in early 2015. The wells were located next to a sports field on the plume zone side of the groundwater contamination. In the fall of 2015, Carbo-Iron® NPs were installed using the direct push injection technique to a depth of about 12-14 m where the major contaminant concentration and highest conductivity was encountered, ensuring that the clay aquiclude remained intact below.

Figure 1: Chlorinated hydrocarbon concentrations in groundwater at the study site. Source: Golder Hungary.

Following the injection, the chlorinated hydrocarbons concentrations in the groundwater will be monitored following the agreed monitoring plan and during the remaining course of the NanoRem project. In addition to the groundwater monitoring, soil and groundwater samples from the pilot site will be taken and analysed to meet the project objectives for each of the different NanoRem work packages.

After injection of Carbo-Iron® NPs in autumn 2015, groundwater sampling at 7 monitoring events (-7 to 360 days) shall be conducted at all suitable wells (6 x CMT at 3 different channels), upstream and downstream of the injection area to verify that the treatment of the contaminants is occurring due to the injection of Carbo-Iron® NPs into the aquifer.

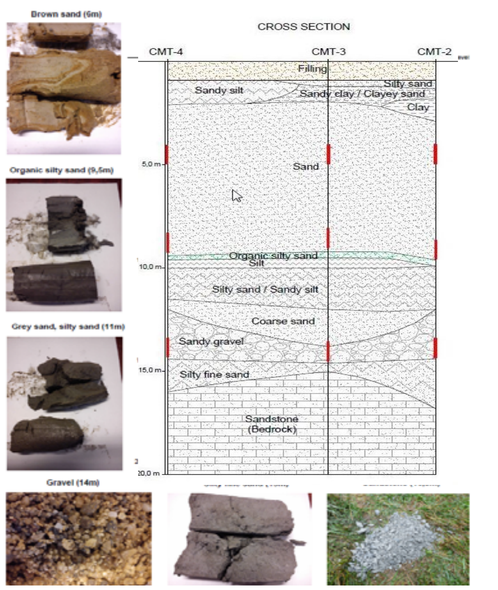

Figure 2. Cross section of soil profile with wells and sampling points. Source: Golder Hungary.

The NanoRem Sustainability and Markets Workshop - Oslo, Norway

Yevgeniya Tomkiv Norwegian University of Life Sciences

The measurement of sustainability is an important criterion to include into a decision-making process when considering to undertake soil and groundwater remediation. The process should consider which remediation techniques provide best net environmental, economic and social impact in dealing with the remediation problem. Nanoremediation is a technique that now extends the range of available *in situ* remediation methods, but how sustainable is it?

The NanoRem project is focusing on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. Therefore, it needs to understand the environmental risk-benefit of nanoremediation, market demand, overall sustainability and stakeholder perceptions. To do so, the project is supporting dialogue and engagement with various stakeholders across Europe in order to explore consensus about appropriate uses of nanoremediation.

One of the stakeholder engagement activities of NanoRem in 2014 was a workshop on Sustainability and Markets, which took place on the Holmenkollen hills overlooking Oslo on 3rd-4th December 2014. The workshop gathered a variety of expert and professional stakeholders from research, regulation and industry. In total, 36 participants from nine different countries (Austria, Belgium, Czech Republic, France, Germany, The Netherlands, Norway, Poland and United Kingdom) attended this event (Photo 1).

The aim of the workshop was to collect opinions from a range of stakeholders on key sustainability issues, ethical concerns as well as market development opportunities in the medium to longer term related to nanoremediation. The workshop focus was on developing a realistic understanding of the stakeholders' opinions on: (1) the sustainability of nanoremediation and issues influencing perceptions of its sustainability; (2) sustainability of nanoremediation compared to other remediation technologies; and (3) factors that might influence the market development of nanoremediation.

Photo 1. Participants of the Oslo workshop. Source: Hans-Peter Koschitzky.

Photo 2. One of the groups during the discussion. Source: Hans-Peter Koschitzky.

The workshop used interactive discussions in smaller groups, following The World Café™ style (Photo 2), allowing every participant to contribute their views.

Discussion on how nanoremediation scores across three pillars of sustainability (environmental, economic and social) revealed both the beneficial and potentially disadvantageous characteristics of nanoremediation. Important environmental benefits include that nanoremediation may be less invasive and can have a lower impact compared to some alternatives. Environmental concerns were largely related to the perceived potential intrinsic hazards of nanoparticles (NPs) themselves. From the economic point of view, it was felt that nanoremediation could be faster and cheaper compared to some alternatives. However, some concerns were raised about the currently high production costs for NPs. The stakeholders thought that nanoremediation technology has potential to create new job opportunities and therefore a greater number of contaminated sites could be remediated. Concerns relating to social aspects included the public perception of NPs, existing knowledge gaps and uncertainties relating to nanoremediation.

When nanoremediation was compared to alternative remediation technologies, it was felt that there was little to differentiate between nanoremediation and *in situ* bioremediation apart from uncertainty and evidence. However, many aspects differentiated nanoremediation from pump and treat technology, the most important being that pump and treat used natural resources and generated waste.

The participants agreed that addressing sustainability as part of the evaluation of remediation technologies demands a broad perspective, including intergenerational aspects and a better understanding of the relationships between environmental, social and economic factors. Discussions about the sustainability of nanoremediation needed to be site specific and has to include comparisons with other *in situ* technologies. For this to occur a clear technical understanding of what the advantages and limitations are should be available and evaluated. While many of the generic issues regarding the sustainability of nanoremediation are similar to those for other remediation technologies, uncertainties in risks and benefits related to use of nanoremediation technology were deemed to be one of the most important factors impacting on its future development.

In addition to the issue of uncertainties, the workshop identified the following challenges for improving the sustainability of nanoremediation:

- reduction of production costs for the different NPs,
- enhancing the transport mobility of the particles in the subsurface (or strictly speaking in the aquifer),
- increasing the lifetime of the product in order to justify the production cost,
- identification of possible synergies with other *in situ* remediation techniques, and
- establishment of a controlled analysis to determine environmental fate of particles.

It is also worth mentioning that these challenges are already being addressed by the NanoRem project.

Finally, workshop participants scored a series of factors determining the evolution of the market for nanoremediation in Europe according to their importance. These results were used to elaborate scenarios of potential market development and derive recommendations for use in an exploitation strategy for nanoremediation.

For more information about the workshop, please have a look at the report. It can be found on the NanoRem website www.nanorem.eu

TOMKIV, Y., BARDOS, P, BARTKE, S., BONE, B. AND OUGHTON, D. (2015). The NanoRem Sustainability and Markets Workshop, Oslo, Norway, December 2014. NanoRem Report.

NanoRem at AquaConsoil 2015

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, and focuses on sustainable use and management of soil, sediment, water resources and remediation. 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 introductory presentation on nanoremediation, an introduction to the NanoRem project was provided and showed how the project is aiming to address

Photo 1. Delegates paying close attention during the nanoremediation scene-setting session at AquaConSoil 2015.

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 co-ordinator. 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 is using.

Photo 2. Juergen Braun describing the NanoRem test sites at AquaConSoil 2015.

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.

Photo 3. A selection of the NanoRem posters displayed at AquaConSoil 2015.

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 uncertainly 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

Cellulose Nanomaterials in Environmental Cleanup Technologies

Mark Wiesner Duke University , Durham, USA

Cellulose, is the most abundant organic polymer on earth, and is an important structural component of plants. With the improvement of analytical techniques scientists have been able to investigate the nanoscale cellulose structures within plants and also discover its strength properties.

Cellulose nanomaterials represent a new class of sustainable materials with already recognised potential in improving paper and packaging, automotive, construction, personal care, and textile industries but it is the use of cellulose nanomaterials in environmental engineering applications and the potential for water treatment and remediation technologies that Duke University Superfund Research Program (Duke SRP) has been concentrating its work.

The research has compiled the different physical and chemical properties, production costs, and current use of cellulose nanomaterials for the use in environmental remediation and water treatment.

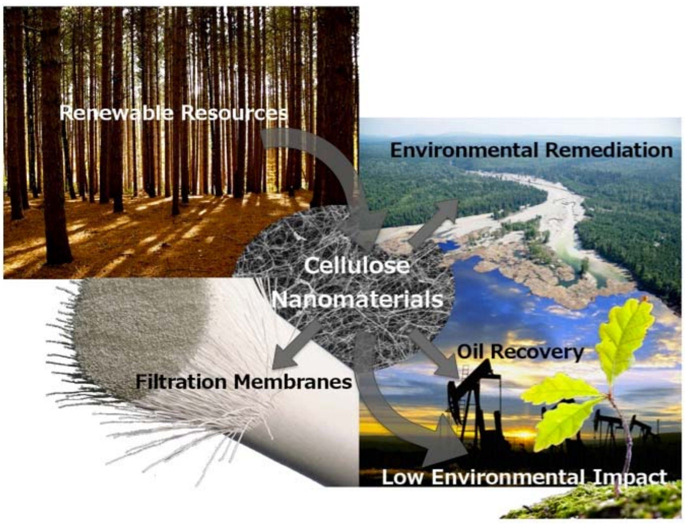

Figure 1. Duke SRP researchers describe the potential benefits of advancing the use of cellulose nanomaterials in water filtration and environmental remediation technologies. Source: Charles de Lannoy.

Environmental remediation

Cellulose nanomaterials are environmentally inert, naturally abundant, low cost and have a high surface area-to-volume ratio, offering a promising alternative to activated carbon for sequestering contaminants.

Scientists have demonstrated that they can increase the sorptive nature of cellulose nanomaterials by using carboxylation (which adds acid structures to the cellulose nanomaterials). Some forms of cellulose nanomaterials derived from bacteria have shown positively to absorb heavy metals whereas other modified cellulose nanomaterials have demonstrated absorption of a wide range of organic contaminants.

Although the results are extremely positive, further research is needed to ensure that any chemical modifications do not alter the nontoxic nature and biodegradability of cellulose nanomaterials. In addition more work is needed to be carried out to determine if the higher cost of cellulose nanomaterials, as compared to the popular activated carbon, will be offset by potentially lower deployment costs.

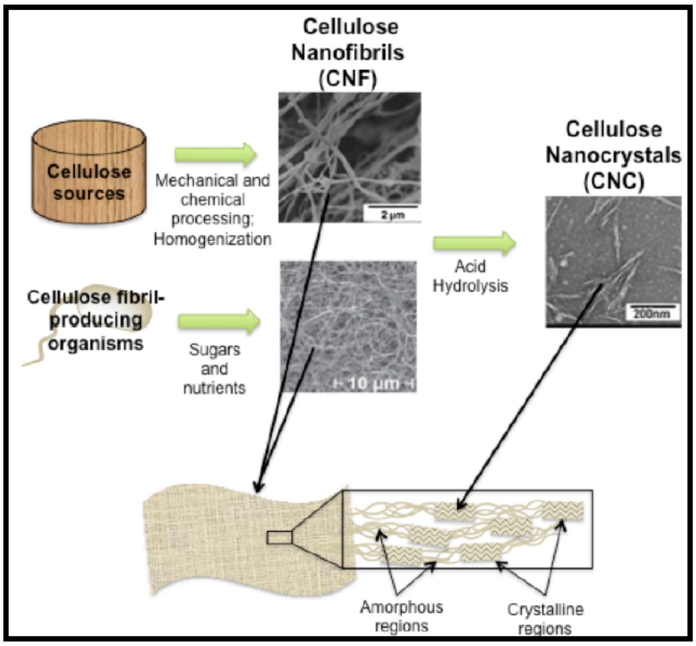

Figure 2. Cellulose nanomaterials are categorised into two groups – cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). CNFs are isolated by breaking down cellulose feedstocks or they can be directly produced by certain types of bacteria. CNCs are produced using acid to extract only the crystalline region of the nanomaterials. Reprinted with permission from (Carpenter *et al.* 2015 Copyright (2015) American Chemical Society.

Water filtration

Membranes to be used in water filtration can also be created from cellulose nanomaterials because of their dimensional capacity and strength. There are however concerns with the biodegradability of cellulose nanomaterials when incorporated into membranes that interact with bacteria. This concern has been addressed by using the cellulose nanomaterials as an additive to polymer membranes, which would protect the cellulose from degradation.

Advantages of cellulose nanomaterials

The researchers at Duke SRP have also compared the properties and application of carbon nanotubes with cellulose nanomaterials, and conclude that the latter may be a suitable replacement for carbon nanotubes used in water treatment technologies. They suggest this because cellulose nanomaterials are biodegradable, a naturally occurring renewable resource, much cheaper and less energy-intensive to produce than carbon nanotubes.

Due to cellulose nanomaterials fibrous nature, remarkable mechanical properties, low cost, biocompatibility, and sustainable source, there is huge potential for many markets including water filtration membranes and environmental remediation applications. This is evident in the growth of cellulose nanomaterial-related patents in the last 10 years. Hopefully interested parties will work together to develop these materials to their full potential.

For further information about this research, refer to:

Carpenter AW, de Lannoy C-F, Wiesner MR. 2015. Cellulose Nanomaterials in Water Treatment Technologies. Environ Sci Technol 49:5277-5287. doi: 10.1021/es506351r

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You can find our full list of partners on our project website (www.nanorem.eu). If you would like any further information please contact Hans-Peter Koschitzky at koschitzky@iws.uni-stuttgart.de. Contact information for each Work Package is shown below:

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