

NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin describes a remediation pilot study using nanoscale zero-valent iron to treat groundwater contaminated with chlorinated hydrocarbons.

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NanoRem Pilot Site – Spolchemie I, Czech Republic: Nanoscale zero-valent iron remediation of chlorinated hydrocarbons

1. INTRODUCTION

This bulletin describes a pilot study of *in situ* nanoscale zero-valent iron (nZVI) remediation. It was undertaken as part of the NanoRem Project (Taking Nanotechnological Remediation Processes from Lab-Scale to End-User Applications for the Restoration of a Clean Environment), which was funded through the European Union Seventh Framework Programme.

The Spolchemie site was chosen as one of the NanoRem pilot sites to test two types of nanoparticles (NPs): nZVI, the subject of this bulletin, and the iron oxide, Nano-Goethite, which is described in NanoRem Bulletin #8. nZVI was applied for the remediation of chlorinated hydrocarbons (CHCs), mainly perchloroethylene (PCE), trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-1,2-DCE), and Nano-Goethite for remediating benzene, toluene, ethylbenzene and xylenes (BTEX). Nanoremediation was seen as giving an opportunity to enhance remedial works that have been ongoing since 2005 and the pilot study will be used to validate its suitability as a full-scale remediation option.

The main aim of the study was to verify migration characteristics and remedial efficiency of two types of nZVI, NANOFER 25S and NANOFER STAR, using advanced procedures for monitoring NPs and vertical stratification of contamination. NANOFER 25S is an aqueous dispersion of nZVI particles with a surface modification based on the combination of a biodegradable organic and inorganic stabiliser and NANOFER STAR is a Surface stabilised, Transportable, Air-stable and Reactive (i.e. STAR) powder, meaning it is much easier to store and process compared to pyrophoric NANOFER 25S.

2. SITE DESCRIPTION

Spolchemie is one of the leading synthetic resin manufacturers in Europe, located at Usti nad Labem, Czech Republic in the heart of Europe. The plant started to produce resins and freons based on perchloromethane and tetrachloroethene in the middle of the last century. The production, treatment, storage and distribution of these various raw materials and products has led to extensive

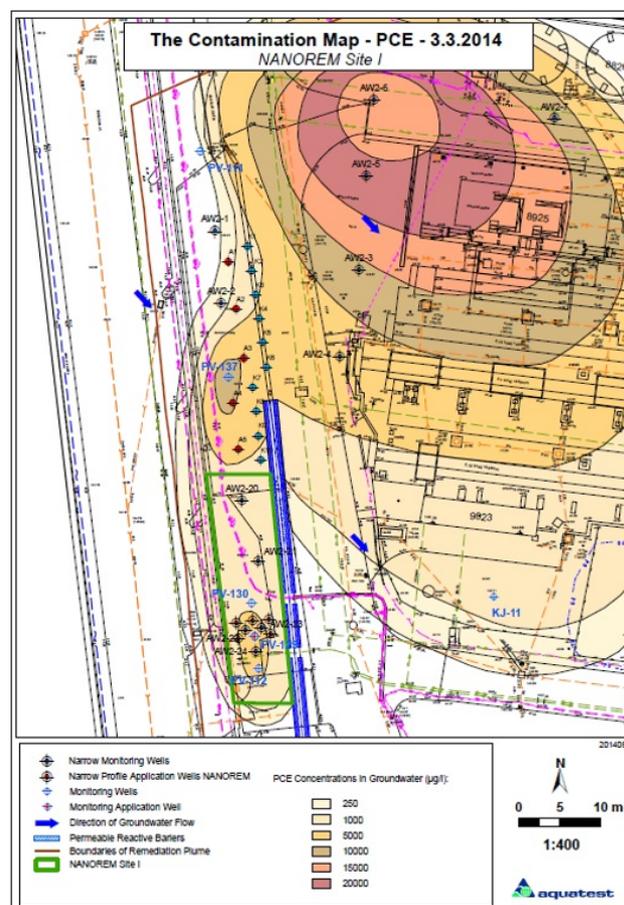


Figure 1. Site plan of the Spolchemie I site.

contamination by chlorinated ethenes and methanes, which in many cases have dispersed widely from the original source areas.

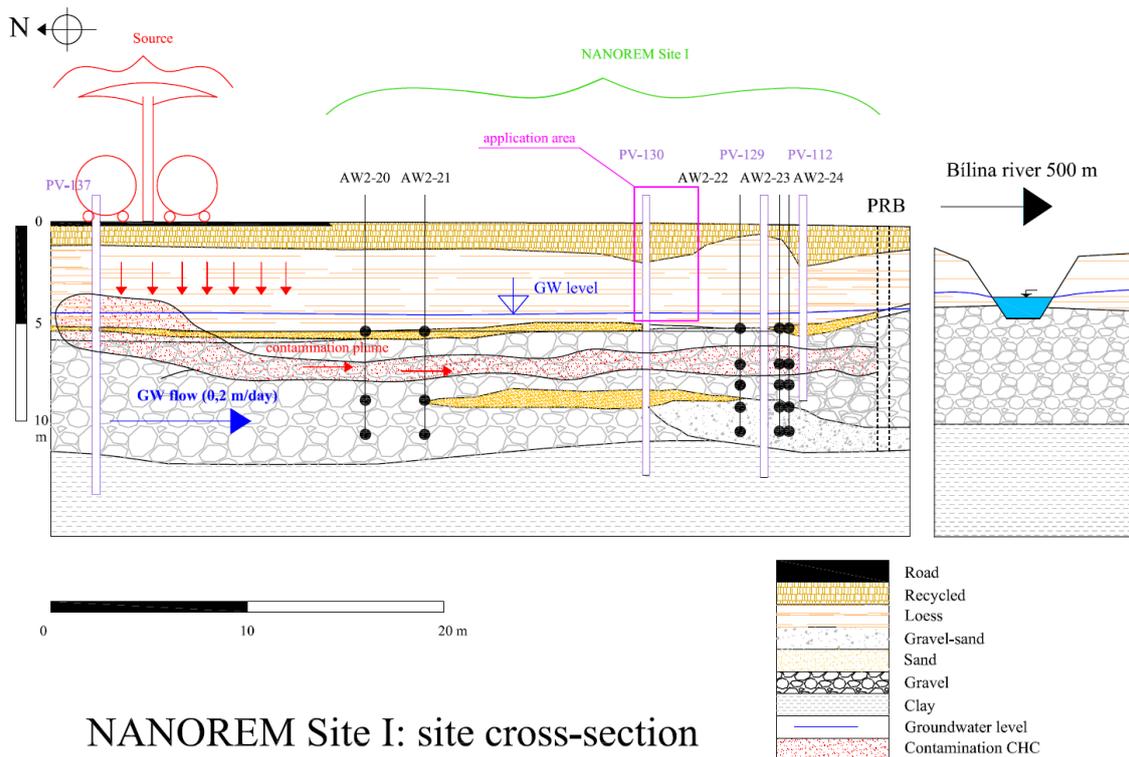
The pilot study area, named "Spolchemie I", is approximately 10 m x 20 m and is located in the southwestern corner of the factory compound. Figure 1 provides a site plan of the site and illustrates the location of monitoring and injection wells and the distribution of the main CHC contaminant, PCE, across the site.



Taking **Nanotechnological Remediation Processes** from Lab Scale to End User Applications for the Restoration of a Clean Environment.
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NANOREM Site I: site cross-section

Figure 2. Cross-section of the Spolchemie I site.

Figure 2 shows a cross-section of the site and the distance to the primary receptor, the river Bilina. The subsurface at this location consists of quaternary sand and gravel with a thickness of approximately 10 m underlain by a clay aquitard. The quaternary sand and gravel terrace is the only hydrogeologic unit where the CHC contamination has been found. The groundwater level is 4 m below ground level (bgl), thus the unconfined aquifer has a thickness of 6-7 m. The groundwater flow velocity has a south-easterly direction and is approximately 0.2 m/d.

Figure 3 shows the proportion of the different CHCs on site (PCE, cis-1,2-DCE, TCE, perchloromethane (PCM), trichloromethane (TCM)) and their vertical distribution. The highest CHC concentration was found 6.5 mbgl (30,000 µg/l in total), in contrast the total CHC concentration at 11 mbgl is only 1500 µg/l.

The study site area is separated from the main Spolchemie compound by a permeable reactive barrier which encloses the DNAPL CHC source zone. Pools have not been detected and back diffusion from the underlying aquitard is also very unlikely.

3. PROJECT MANAGEMENT

3.1 Project Team

The pilot study involved the successful cooperation of several NanoRem project partners: NANO IRON s.r.o. - the producer of the NPs, AQUATEST - a private company performing *in situ* remediation, VEGAS, University of Stuttgart - responsible for large-scale experiments with NPs, Palacký University of Olomouc - responsible for monitoring particle migration and fate, and Technical University of Liberec - responsible for microbiological analyses.

3.2 Regulatory Approval

For the Spolchemie site, permission has been granted by the local authorities (Regional government of Ústí nad Labem region - Krajský úřad Ústeckého kraje) for the injection of three tonnes of iron NPs per year. AQUATEST is permitted to distribute this quantity across the whole Spolchemie site according to its needs.

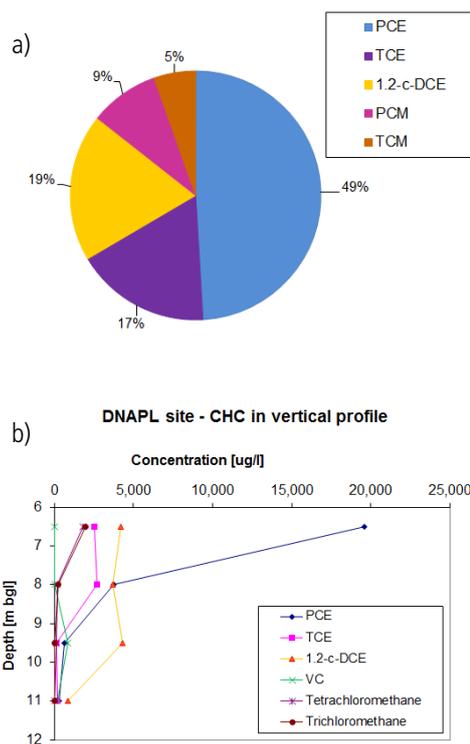


Figure 3. a) Relative proportions of CHCs and b) vertical concentration profile of contaminants on the Spolchemie I site.

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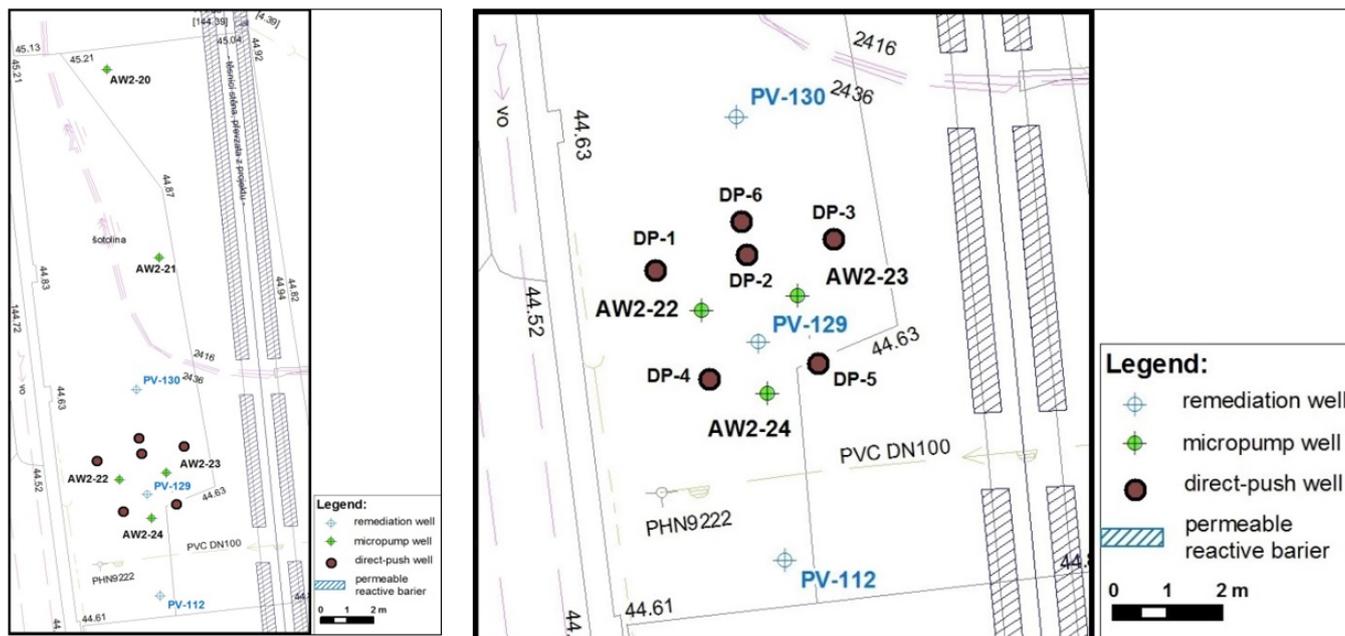


Figure 4. Test field for the injection of NANO FER STAR (left overview, right details).

4. DESIGN, INSTALLATION AND OPERATION

4.1 Monitoring System Design

The first application of the nZVI NANO FER 25S on the Spolchemie I site took place in November 2014 and was monitored until the summer of 2015. By that time only 6 of the 15 sensors used in the system for the *in situ* measurement of magnetic susceptibility had remained operational. Magnetic susceptibility sensors are used for monitoring nZVI migration. Thus, prior to the second injection, this time using NANO FER STAR, the sensors together with the micro-pump system for groundwater monitoring were replaced (in September 2015). Three new boreholes were drilled to replace wells AW2-22, AW2-23 and AW2-24. All of them are located in approximately the same position as the previous ones and equipped with micro-pumps at depths of 5.5, 6.5, 8, 9.5 and 11 mbgl. Unfortunately, due to the very dry summer, all three micro-pumps situated at 5.5 mbgl did not have enough water for groundwater sampling.

In addition to the wells AW2-22, AW2-23 and AW2-24 (12 sampling points) there are three monitoring wells PV-112, PV-129 and PV-130 (diameter 160 mm, open screen) on the site and two micro-pump wells on the inflow to the site (AW2-20 and AW2-21). The placement of all the wells is shown in Figure 4.

4.2 Injection of nZVI and Tracer

In total 1000 kg of a 20% suspension of NANO FER 25S was injected at a concentration of approximately 2.2 g/l. In total, 91 m³ of suspension was injected. Five direct-push probes were situated around well PV-129, with an application fluid pressure of between 1 and 12 bars. The application started at 5 mbgl and continued to 10.5 mbgl in 0.5 m increments (e.g. 5 m, 5.5 m... ..10 m, 10.5 m). The nZVI suspension was continuously stirred during the injection. The set up of the injection system is shown in Figure 5.

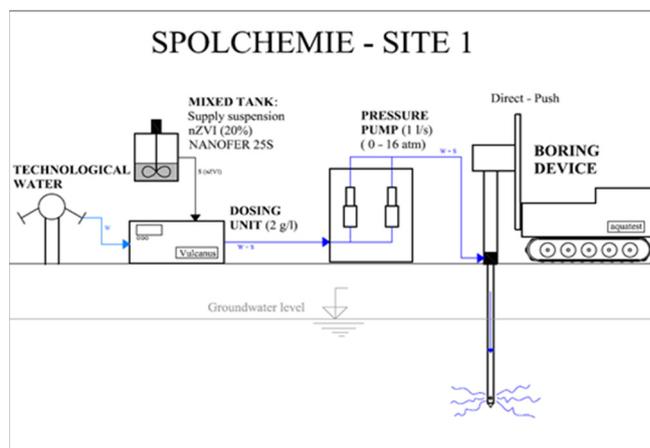


Figure 5. Set up of NANO FER 25S direct-push injection.

Lithium chloride (LiCl) was injected as a tracer together with the nZVI to make it easier to monitor the migration of the nZVI. In total, 165 g of lithium was injected in the first cubic metre of the suspension. The monitoring points were the traditional wells PV-112, PV-129, PV-130 and 12 micro-pump points (AW2-22 – 6.5 m, 8 m, 9.5 m, 11 m; AW2-23 – 6.5 m, 8 m, 9.5 m, 11 m; AW2-24 – 6.5 m, 8 m, 9.5 m, 11 m). Samples were taken from these points in 15 monitoring rounds during a 4 month period (intensively only during the first 4 weeks).

The second nZVI direct-push injection nZVI (NANO FER STAR) was carried out in October 2015 together with a tracer (LiCl), but after experience with the first injection LiCl was diluted in the whole volume of the injected suspension. 300 kg of nZVI were injected (1500 kg of 20% suspension) to six injection points. The depth was from 6.5 mbgl to 10 mbgl. Injection parameters for the direct-push injection of NANO FER STAR are shown in Table 1.

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Table 1. NANO FER STAR injection parameters

Well	Date	ZVI conc (g/l)	Vol. (m ³)	Q (m ³ /h)	nZVI (kg)	LiCl (g)	Inj. Pressure (bar)	Inj. Depth (mbgl)
DP-5	15.10.15	5	12	1.8	60	200	1-12	6.5-10
DP-1	16.10.15	5	12	1.8	60	200	1-12	6.5-10
DP-3	16.10.15	5	12	1.8	60	200	1-12	6.5-10
DP-4	17.10.15	5	12	1.8	60	200	1-12	6.5-10
DP-2	17.10.15	5	9	1.8	45	150	1-12	6.5-10
DP-6	18.10.15	5	3	1.8	15	50	1-12	6.5-7.5
Total	15.10.15-18.10.15	5	60	1.8	300	1000	1-12	6.5-10

5. RESULTS AND DISCUSSION

5.1 NANO FER 25S Injection

Tracer test and total iron content

The injection of LiCl as a tracer resulted in a very small increase in lithium concentration at the micro-pump wells (AW2-22, AW2-23 and AW2-24). In contrast, a significant increase in lithium concentration (i.e. 1-2 orders of magnitude to 2.2 - 3.1 mg/l) was observed in groundwater in wells PV-129 and PV-130 (Figure 6). The lithium concentration increased even in the groundwater from PV-112 at the outflow of the Spolchemie site; therefore, the tracer tests proved the expected groundwater flow direction.

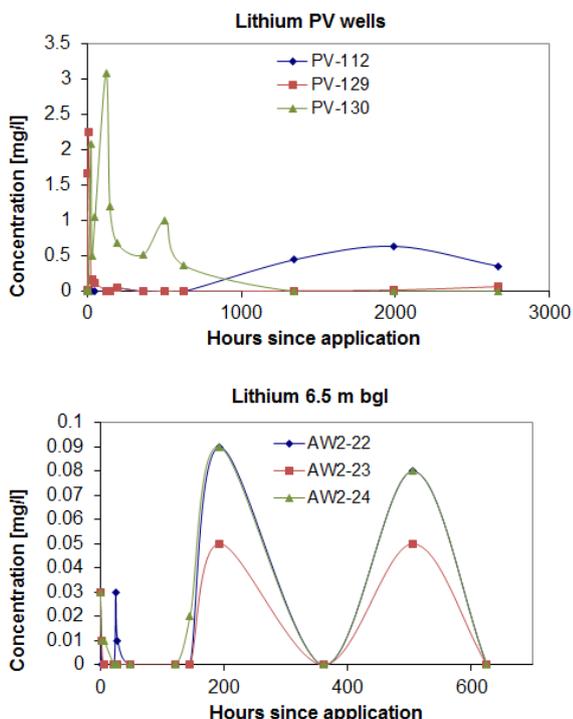


Figure 6. Lithium chloride tracer concentrations after NANO FER 25S injection.

An increase (up to 30 mg/l) in total iron content was observed in groundwater in PV-129 and PV-130 (Figure 7). An even higher increase was observed in the micro-pump monitoring points in monitoring wells AW2-22 and AW2-24 (AW2-22 depth 6.5 mbgl and AW2-24 6.5 m and 8.0 mbgl). These results confirm the contact between the contaminants and the nZVI. The following interpretation focuses on these monitoring points in particular.

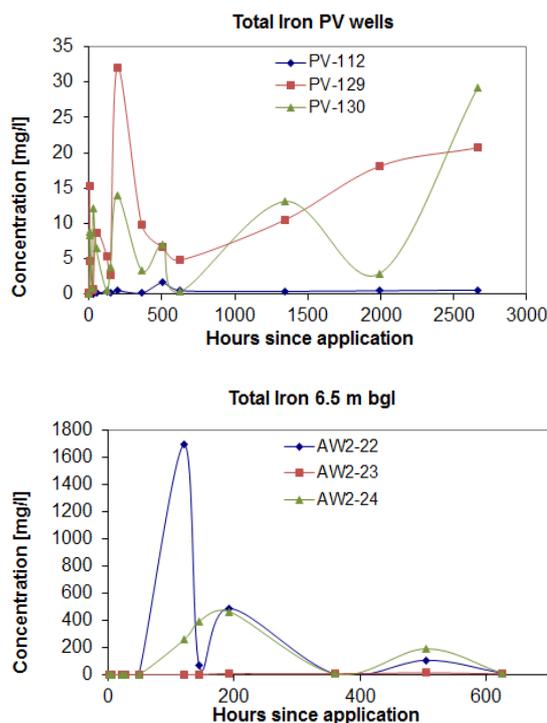


Figure 7. Total iron concentrations after NANO FER 25S injection.

Redox measurements

Figure 8 shows that the injection of NANO FER 25S caused a significant decrease in oxidation-reduction potential (ORP) in the groundwater. The ORP decreased in the most influenced monitoring points, from +400 to -300 mV. This rapid reduction lasted only 20-50 days. Fifty-six days after nZVI injection the ORP increased to between -180 and +5 mV. One-hundred and twelve days after injection the ORP value stabilised around +100 mV. The ORP value remained around 100 ± 50 mV until the end of the monitoring period 277 days after the NANO FER 25S injection.

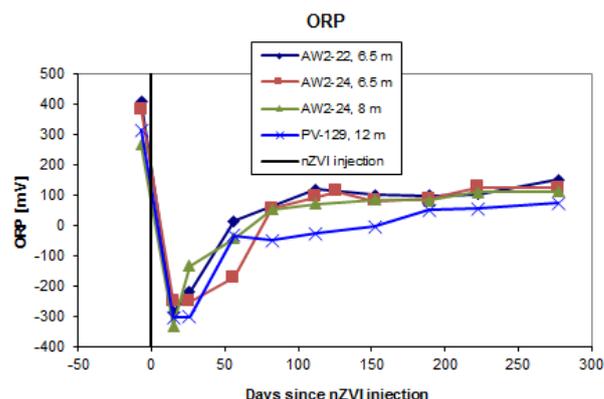


Figure 8. Redox potential after NANO FER 25S injection.

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Contamination

Figure 9 shows a rapid decrease of PCE concentration in groundwater across the Spolchemie I site after injection of NANOFER 25S. This effect was partially caused by injection of NPs mixed in non-contaminated Elbe water and partially (especially in the long term) caused by CHC reduction. The PCE concentration decreased immediately after the nZVI injection. A reduction of PCE in groundwater at monitoring wells PV-112 and PV-130 was observed for 277 days; the concentration decreased from 35,000 – 40,000 µg/l to 10,000 µg/l (72-80% long-term PCE reduction). In contrast, concentration of PCE in the injection area rebounded after a few months. The PCE concentration in groundwater at PV-129 was still at 10% of the pre-injection value 5 months (152 days) after injection. After this, the PCE concentration increased continuously and 277 days after injection was at the same value as before the nZVI injection. A very similar trend was observed at AW2-22, 6.5 mbgl. In contrast, AW2-24, 6.5 mbgl had faster rebound and after 112 days from the nZVI injection the PCE concentration increased to the pre-injection value. The lowest impact of nZVI injection on the PCE concentration was monitored in groundwater at AW2-24, 8 mbgl. Here PCE decreased only for 3 monitoring rounds and after 82 days it was again at the level of pre-injection values.

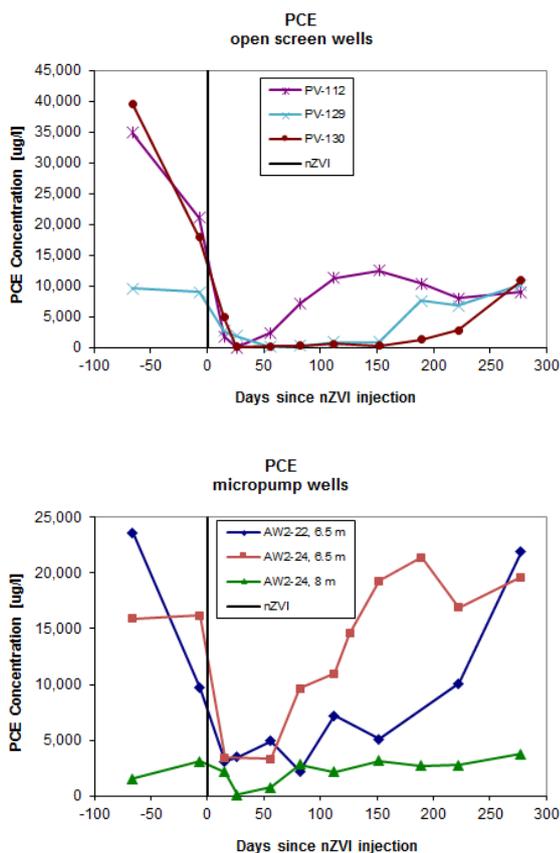


Figure 9. PCE concentrations in groundwater after NANOFER 255 injection.

Figure 10 shows a similarly significant decreasing trend in the PCM concentration (compared with PCE concentration) in groundwater across the Spolchemie I site after injection of NANOFER 25S, albeit at different concentrations to those observed for PCE. This effect was also attributed to the injection of NPs mixed in non-contaminated Elbe water and by CHC reduction. PCM is an important contaminant especially in the upper (6.5 mbgl) horizon of monitoring wells fitted with micro-pumps. The PCM concentration decreased immediately after nZVI injection and its reduction in groundwater lasted at least 277 days. The PCM concentration decreased from 9000 µg/l to a few hundred µg/l. The relative reduction of PCM in the majority of the monitoring wells between 15 and 222 days after nZVI injection exceeds 50% compared with the pre-injection concentration. The PCM concentration rose between 222 and 277 days after injection and reached approximately 60% of the pre-injection concentration. The lowest concentration of PCM was monitored in groundwater in AW2-24 8 mbgl, but even at this monitoring point the relative decrease is significant. The long-term reduction (277 days after injection) of PCM at this point is 60%.

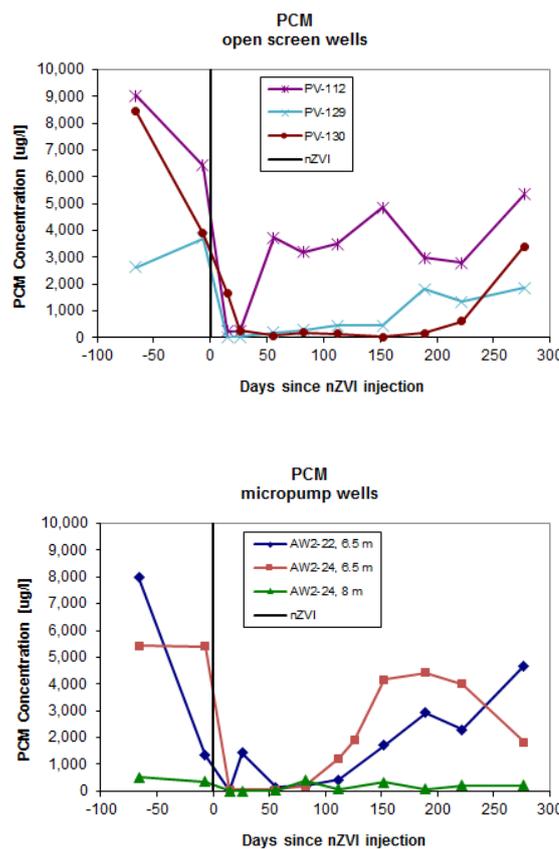


Figure 10. PCM concentrations in groundwater after NANOFER 255 injection.

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Degradation products

The concentration of degradation products (ethane and ethane) of chlorinated ethenes increased rapidly after injection of NANOFER 25S (Figure 11). Monitoring for degradation products was carried out only on wells PV-112, PV-129 and PV-130 due to their higher influx. The primary degradation product, ethane, increased by one order of magnitude 56 days after the injection. At the same time, the concentration of ethane in groundwater from monitoring wells PV-112 and PV-129 also peaked. After that, a continuous decrease of both degradation products was observed until the end of the monitoring campaign (277 days after nZVI injection). The concentrations of ethane or ethene have not returned to their pre-injection concentrations.

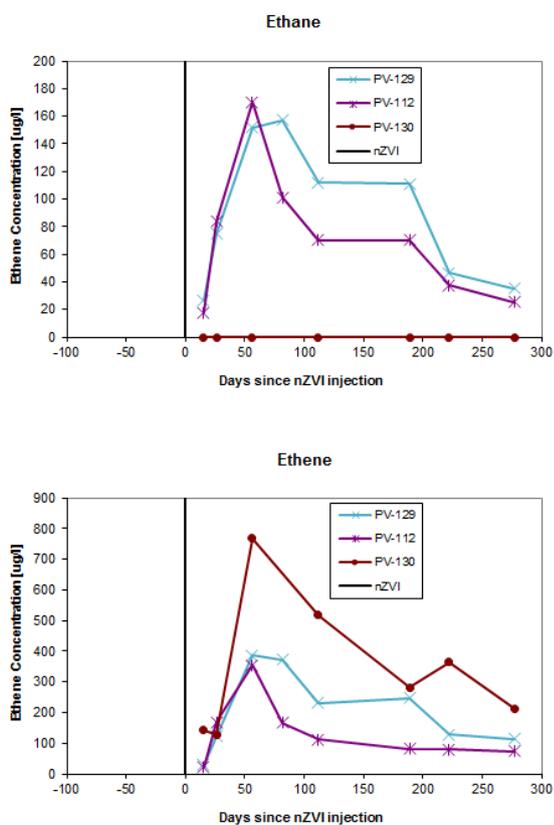


Figure 11. Ethane and ethene concentrations in groundwater after NANOFER 255 injection.

NPs transformation

When introduced into the environment, NANOFER 25S transforms predominantly to magnetite (Fe^{II}/Fe^{III} oxide) and carbonate green rust (Fe^{II}/Fe^{III} hydroxide-carbonate) in the presence of dissolved carbonate anions (Figures 12 and 13). In some cases metastable Fe(OH)₂ was also observed (layered structures surrounding α-Fe cores, shown in Figure 13), but this phase usually undergoes transformation due to the presence of oxygen in the monitoring well or during transport and sample preparation.

5.2 NANOFER STAR Injection

Tracer test and total iron content

Figures 14 and 15 show the total iron concentrations and LiCl tracer measured after injection of NANOFER STAR.

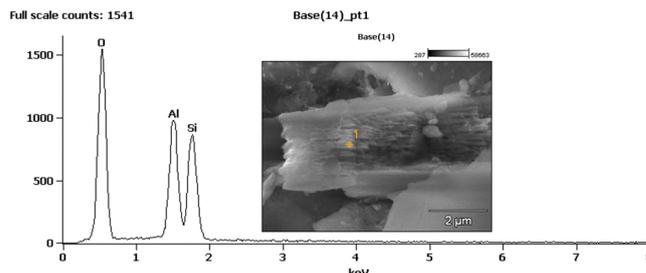


Figure 12: SEM image and ESD of background sediment taken from well PV-129 before application of NANOFER 25S.

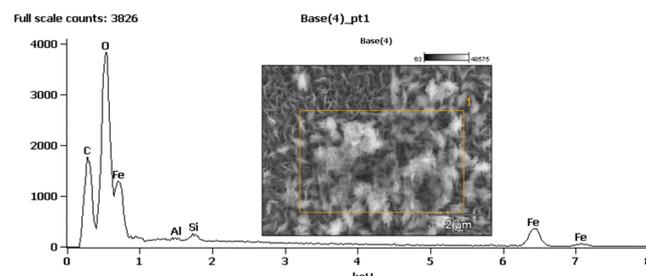


Figure 13: SEM image and ESD of sediment taken from well PV-129 7 months after application of NANOFER 25S; the layered structures are typical for Fe(OH)₂, metastable product of nZVI transformation.

The application of the nZVI suspension caused a significant increase in total iron content in the groundwater of two remediation wells (except PV-112 on the outflow) and in all micro-pumps in the application depths (6.5, 8.0 and 9.5 mbgl). The deepest horizon of micro-pump wells (11.0 mbgl), however, showed almost no reaction to the nZVI injection. The increase in total iron concentration lasted only for 8 - 15 days after the start of the nZVI injection (4 - 11 days after its end), indicating that most NPs had most likely been immobilised in the treatment zone area after this period.

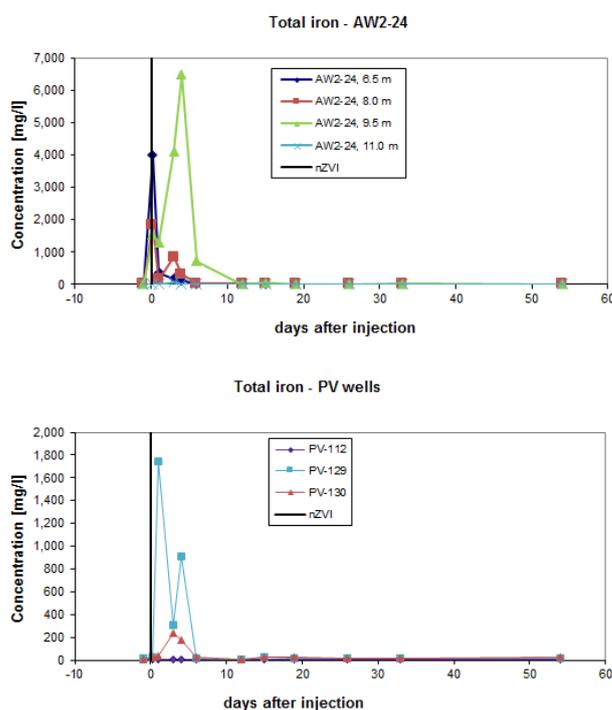


Figure 14. Total iron concentrations after NANOFER STAR injection.

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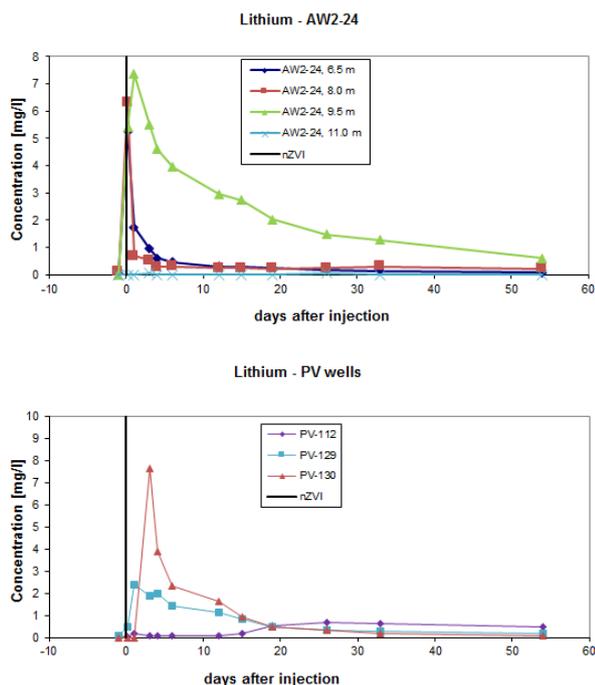


Figure 15. Lithium chloride tracer concentrations after NANOFER STAR injection.

The lithium concentration increased significantly immediately after the injection of NPs in the same monitoring points where an increase of total iron content was observed. Compared with the increase in the iron concentration, the increase in lithium concentration lasted much longer (33 - 54 days or even longer), due to the higher mobility of the lithium ion. Nineteen days after the start of the application, an increase of lithium was observed in the groundwater of monitoring well PV-112, which proves that water influenced by the application of NPs flowed a distance of 4 m from the application area. An important conclusion of the tracer test at the Spolchemie I site was that layers between 6.5 to 9.5 mbgl in the application area were very well saturated with the nZVI suspension. Contact between contaminated groundwater in the monitoring points and NPs was proven.

The time taken to reach the peak concentration of total iron (4000 mg/l) in AW2-24 (6.5 mbgl) was only 4.5 hours. Since the distance between the current application probe and this monitoring point is 1 m the conclusion can be drawn that it was possible to induce groundwater flow with moving NPs at a migration velocity of at least 0.2 m/hr using a pressure of 1-12 bars.

Monitoring of the lithium ion concentration during pilot tests helped to trace the injected suspension and yielded information regarding the effect of dilution. Figure 15 shows that the volume of suspension with high lithium concentration injected into the ground was completely replaced by surrounding groundwater in monitoring wells PV-129 and PV-130 after 33 days; in the two upper horizons of the micro-pump wells it was even faster – groundwater was replaced in 12 days after the start of nZVI injection. Therefore, 33 days and 12 days after injection of nZVI any decrease of contamination can be attributed to a dilution effect. After these periods any reduction in CHCs can be attributed to nZVI.

Redox measurements

The injection of NANOFER STAR caused a significant decrease in groundwater redox potential at all monitoring points in the study area. Micro-pumps, which are more connected to the subsurface than open screen wells, showed a permanent (250 days and continuing) decrease from 200 to -100 mV. Figure 16 shows only the most contaminated micro-pump points AW2-23 (6.5 and 8 mbgl) and AW2-24 (same levels). In contrast in the open screen wells (PV-112, PV-129 and PV-130) the ORP decrease caused by nZVI injection lasted only 150 days; in this time all three monitoring wells had already reached 0 mV.

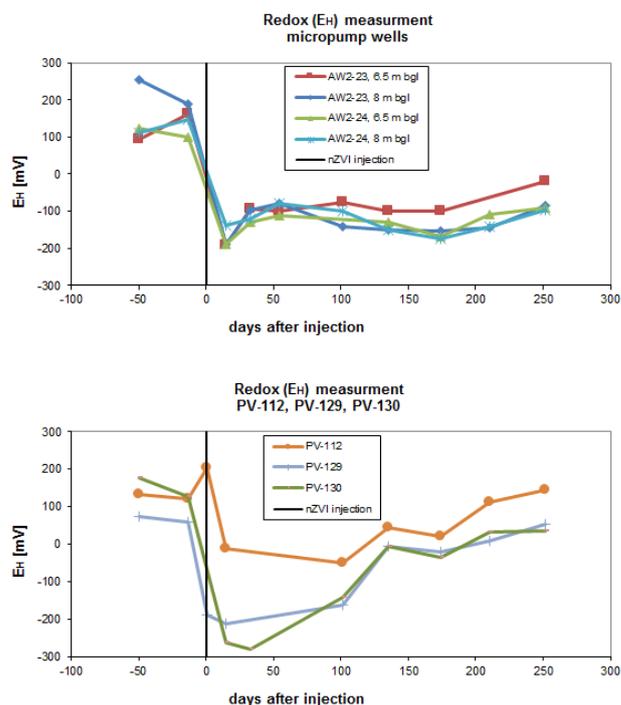


Figure 16. Redox potential after NANOFER STAR injection

Contamination and degradation products

A significant decrease of total chlorinated ethene concentration was observed in the most contaminated micro-pump horizons (at 6.5 and 8 mbgl) immediately after injection of NANOFER STAR (Figure 17). This decrease lasted until the end of groundwater monitoring at the Spolchemie I site. With results from the tracer test it is possible to easily distinguish between dilution and the reduction effect of the injected suspension – 54 days after injection 95% of the injected liquid was already replaced by fresh contaminated water from the surroundings. Between 54 and 250 days since the injection the concentration of chlorinated ethenes in groundwater was still at 20% of the initial value. According to these results and the redox potential ($E_H = -100$ mV) injected NANOFER STAR was still active and reducing contamination to the final degradation products after 250 days (8 months 1 week) (i.e. there was no significant increase of vinyl chloride (VC) or observation of cis-1,2-DCE).

The concentration of chlorinated ethenes in groundwater at the open screen wells was different compared with those with micro-pumps. While PCE and TCE were reduced within 30 days after the injection, primarily to the final degradation products ethane and ethane (and none of them increased in next 250 days to their pre-injection values), total DCE showed a different behaviour (Figure 18).

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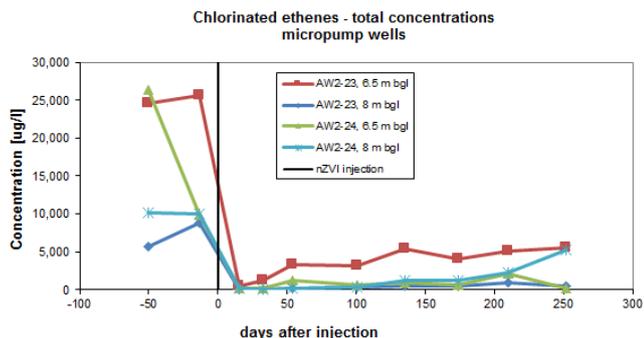


Figure 17. Total chlorinated ethene concentrations in groundwater after NANO FER STAR injection.

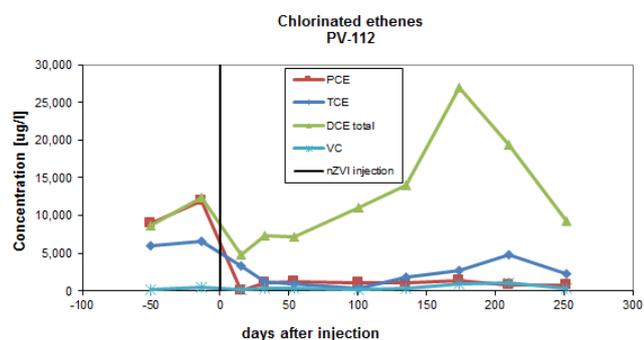


Figure 18. Chlorinated ethene concentrations in groundwater after NANO FER STAR injection.

At monitoring well PV-112 a significant increase of total DCE in groundwater was observed 150 days after the injection. This corresponds to the breakpoint of direct reduction of PCE and TCE to ethane and ethene, because of an increase in ORP above 0 mV (Figure 19). At 174 days after the injection the total DCE concentration peaks and 40 days later it decreased sharply again. This decrease could be induced by reactivation of injected nZVI or DCE degradation under unspecified changes in microbiology. However, it is clear that the concentrations of degradation products confirm the decomposition of CHC in this time.

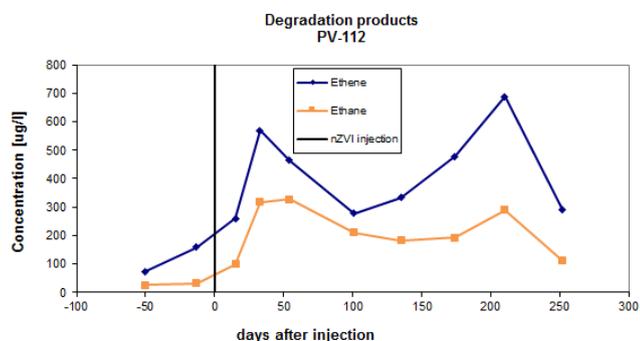


Figure 19. Ethane and ethene concentrations in groundwater after NANO FER STAR injection.

Transformation of NPs

In contrast to NANO FER 25S, carbonate green rust is the dominant product of NANO FER STAR transformation. During one year after the injection a decrease of zero-valent iron (α -Fe) and increase in green rust percentage was observed in monitoring well PV-130 (Figure 20). The last two sampling intervals provided some $\text{Fe}(\text{OH})_2$, most likely originating from deeper anaerobic layers of the sampled sediment.

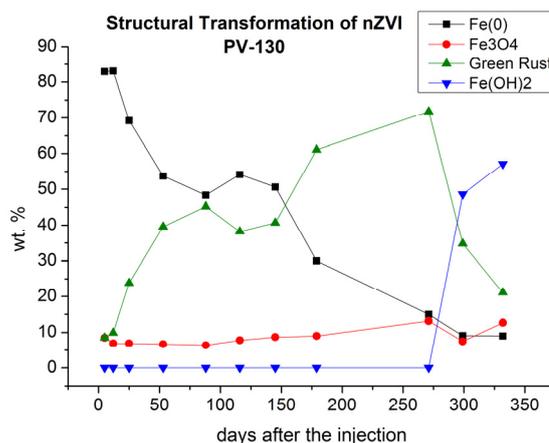


Figure 20. Change in weight percentage of nZVI transformation products one year after injection.

6. CONCLUSIONS AND LESSONS LEARNED

The application of two nZVI NPs, NANO FER 25S and NANO FER STAR to groundwater contaminated with CHCs resulted in a successful pilot study. Contact between the CHCs and each nZVI was confirmed using tracer tests and total iron analyses. Both nZVI products caused a decrease in redox potential, a significant reduction in CHCs (up to 85% for NANO FER 25S, and up to 95% for NANO FER STAR), and an increase in final degradation products, ethane and ethene.

A number of lessons were learned from the pilot study. The use of micro-pumps for groundwater sampling proved very effective and these are considered the best technology to provide representative groundwater samples in vertical profile and time. Vertical profiling of groundwater contamination is required during every in situ injection.

Direct-push injection technology is considered the best solution to inject nZVI into the whole aquifer, regardless of the hydraulic conductivity field. Decisions on exact injection locations (depth, space) can be obtained from results from micro-pumps analyses.

Tracer tests are an inexpensive method that can provide crucial data for further interpretation of all works on site. An intensive sampling regime for total iron and the lithium chloride tracer was used during the first month after injection to provide this data.

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

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