

# STUDY OF THE MIGRATION OF NANOIRON PARTICLES IN A 3-D HOMOGENEOUS ARTIFICIAL AQUIFER

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## Abstract

Migration of zero valent iron in the subsurface is a task solved in the long term from different points of view at many workplaces. Experimental equipment in these workplaces mostly enables only one-dimensional assignments (laboratory columns) to be studied in different orders with various levels of detection of migrant substances. Three-dimensional experimental equipment from the VEGAS research facility, University of Stuttgart with large scale dimensions of approximately 8m x 1m x 3m (L x W x H) enables the migration and interaction of nanoiron particles to be studied in a homogeneous artificially created aquifer under conditions approaching the real conditions of a contaminated site. The whole experiment is linked to the international research project NANOREM, which aims to show that the application of nanoparticles is a useful and in particular reliable method for remediation of contaminated soil and groundwater.

## Key words:

Nanoiron particles, injection of nanoparticles, remediation of contamination source zones, transport and targeted deposition of nanoparticles in the subsurface

## Introduction

Artificially created DNAPL (Dense Nonaqueous Phase Liquid) contamination in 3-D experimental equipment is treated by zero valent iron nanoparticles using the method of direct-push directly into the contamination source. The use of the direct-push method is economical even in hard to reach areas. The application of reactive zero valent iron nanoparticles (nZVI), which are pushed as water slurry into the underground, has many advantages. The nanoscale particles have easier access to the pore space and because of their large specific area react very well with the contaminant. Furthermore, nZVI are applicable to a wide range of pollutants (organic substances, heavy metals, pesticides etc.). [1] The whole system enables the extensive monitoring and visualization of nZVI migration in the subsurface or monitoring of the interaction between the particles and the contaminant.

## Methodology

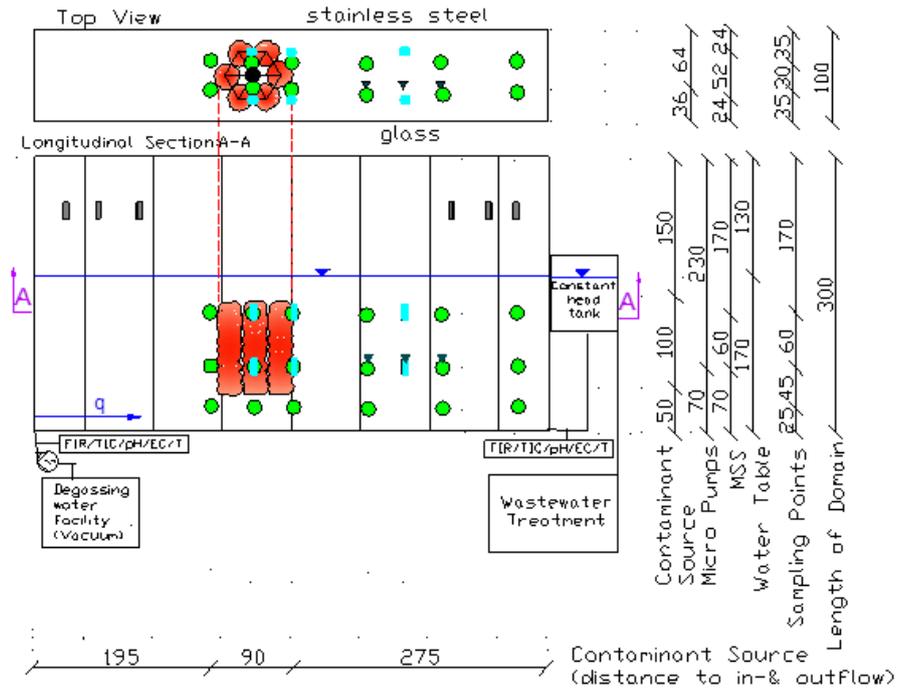
An experimental 3-D large scale box was designed and built in the VEGAS research facility at the University of Stuttgart (Fig. 1). The box is made of stainless steel and the front wall is made of glass. The experimental equipment is 16 meters long, 1 meter wide and 3 meters high. It is subdivided into two separate compartments, each 8 meters long. Remediation of a source zone of contamination by nZVI particles takes place in the first compartment of the experimental box (LSF 1). The nZVI particles produced by NANO IRON s.r.o. have an average particles size of 50 nm, an average surface area of 20-25 m<sup>2</sup>/g, a narrow particle size distribution of 20-100 nm and a high content of iron in the range of 80-90 wt. % [3]. Thirty-six sampling and measurements points are installed in the system. The whole system should introduce a homogeneous soil structure to the unconfined aquifer. Sand with a medium grain size ( $K = 4 \cdot 10^{-4}$ ) was used. The boundary conditions on the inflow site are defined by a constant flux and on the outflow site by a constant head. Degassed water flows into the system at a flowrate of 100 m<sup>3</sup>/d. The experimental box was filled layer by layer. Each layer was manually compacted using tampers. To prevent (or minimize) anisotropies, the tamper surfaces were spiked with nails and a rake was used to roughen the surface of each layer after compacting. The water table was continuously raised following the filling level of the flume. A tracer test was performed prior to the start of the experiment to validate the permeability of the whole flume and to establish the initial conditions in the experiment. Values of pH, ORP, hydraulic conductivity, dissolved oxygen and

flowrate on the inflow and outflow were measured online. Twelve sensors were installed in the flow domain for measurement of magnetic susceptibility for detection of the migration of nZVI particles, 3 micro pumps for water sampling during the injection of particles and 12 piezometers/pressure transducers for monitoring water level/pressure increase in the system during injection (Fig. 2). Further parameters were measured including the concentration of chlorinated hydrocarbons (CHCs), hydrogen, dissolved iron and physical and chemical parameters in the whole system.

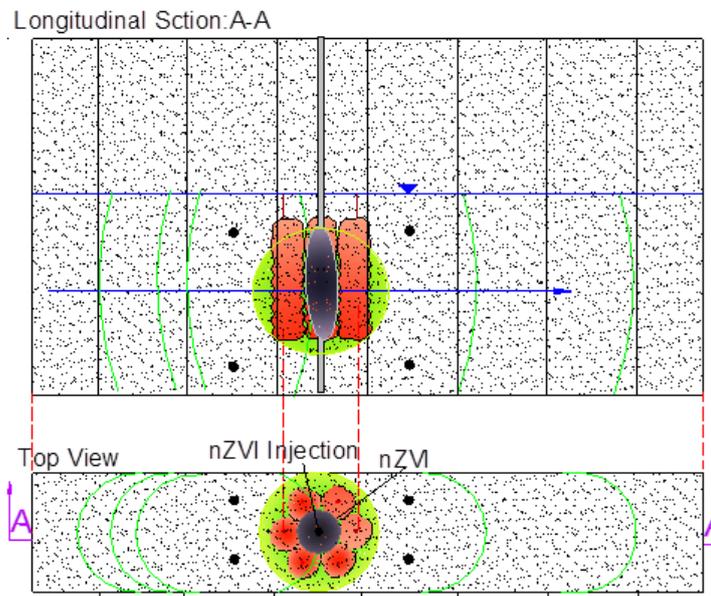


**Fig. 1:** 3-D large scale experiment in the VEGAS research facility, Stuttgart

The application of contamination and injection of nanoparticles (NPs) was performed in the central part of the experimental box. Tetrachlorethen (PCE) was chosen as the model contaminant, which was coloured by the organic red colouring Rhodamin for its better detection in the system. The PCE source was injected at six locations. At each location, 333 g of PCE was injected at 10 different depths with 10 cm intervals (Fig. 2). The centre of the hexagon was kept clean for the drilling wells (Fig. 3). After the PCE application it was necessary to wait approximately 1-2 months for the PCE concentration to stabilize in the porous media. The distribution of the source was regularly monitored during this time period. After the stabilization of PCE the preparatory phases for the nZVI injection were started. The NPs were injected by direct-push with a 1" ID injection well with 4 small openings at the bottom which produce a high injection velocity around the openings (Fig. 4). Based on the preliminary lab batch and column tests 1 m<sup>3</sup> of iron suspension was injected with a concentration of 10 g/L at ten depths. The aim was to have a sufficient concentration of nZVI outside the contamination source zone. The concentrated stock suspension of NANOFER 25S nZVI was diluted online at the required concentration using a dosing unit. The stock suspension was bubbled through inert gas to avoid oxidation of the particles and was mixed to prevent particle sedimentation. Due to safety reasons the monitoring well was installed with a float sensor close to the injection well to control the pressure inside the system during injection of the NPs. Pressure sensors were also installed between the dosing unit and the injection well. After the nZVI injection the whole system was monitored again. The migration of the NPs was detected and the remediation of PCE source was quantified.



**Fig. 2:** Schematic diagram of the 3-D experiment (location of installed monitoring equipment and PCE source placement)



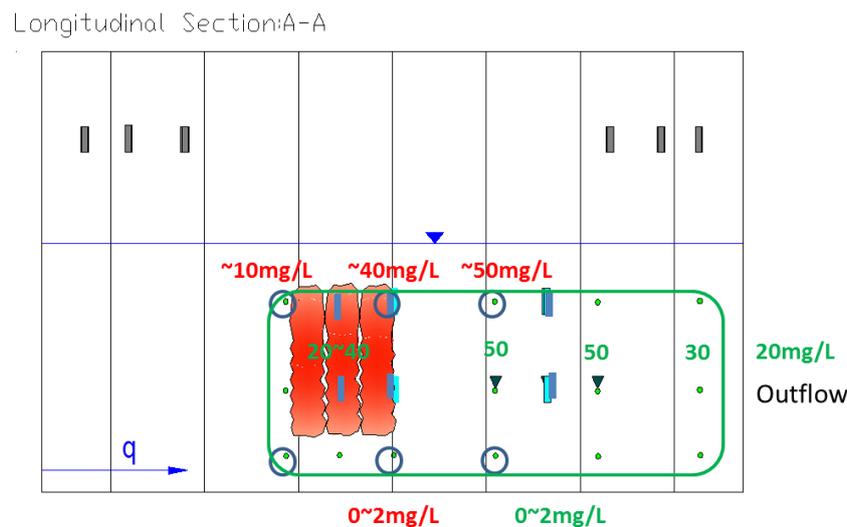
**Fig. 3:** Location of NP injections



**Fig. 4:** Injection well for direct-push (Aquatest a.s., Liberec, Czech republic)

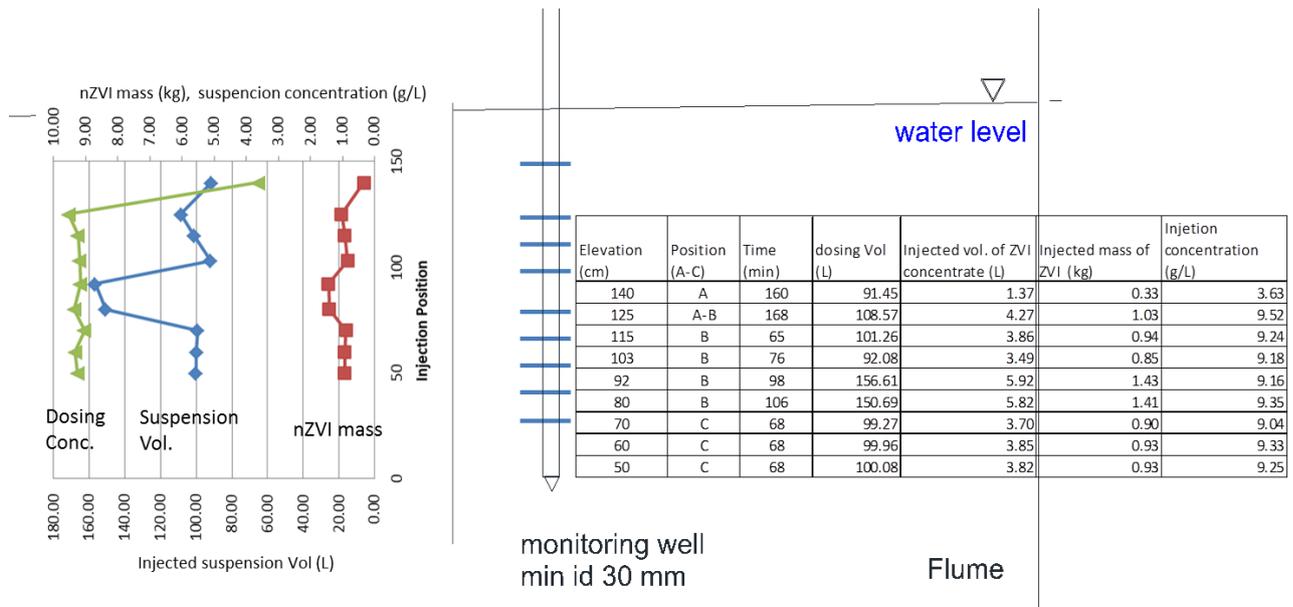
### Results

During the monitoring of PCE distribution in the porous media the first concentrations of PCE in the sampling points close to the location of the application were observed two days after the placement of the source. Two weeks after application the PCE concentration in these sampling points was constant. After 8 weeks, just before nZVI injection, stable PCE concentrations were measured the in all of the sampling points in the system. Rough PCE concentrations before the NPs injection are illustrated in Figure 5.



**Fig. 5:** Monitoring of PCE distribution in the system

The NP injection was planned at ten depths with a total volume of water-iron slurry of 1 m<sup>3</sup>. In each position, we planned to inject 100 L of suspension with a concentration of 10 g/L. Each position should contain 1 kg of nZVI particles. Against the original plan the suspension was only injected into three closely located positions due to clogging of pores, which caused a decrease in pressure in the system. If the pressure was too high the NP injection was stopped and the position of the direct-push well was changed. Nanoiron in form of iron-water slurry was successfully applied at nine depths. With the exception of two positions, approximately 100 L of suspension were applied in each depth according to the original plan. The total injected volume was approximately 1 m<sup>3</sup> of nZVI suspension with a real mass of ZVI 8.75 kg. Except for three positions, each depth contained 1 kg of nZVI. In eight of the nine positions, nZVI was injected at a concentration higher than 9 g/L. (Figure 6)

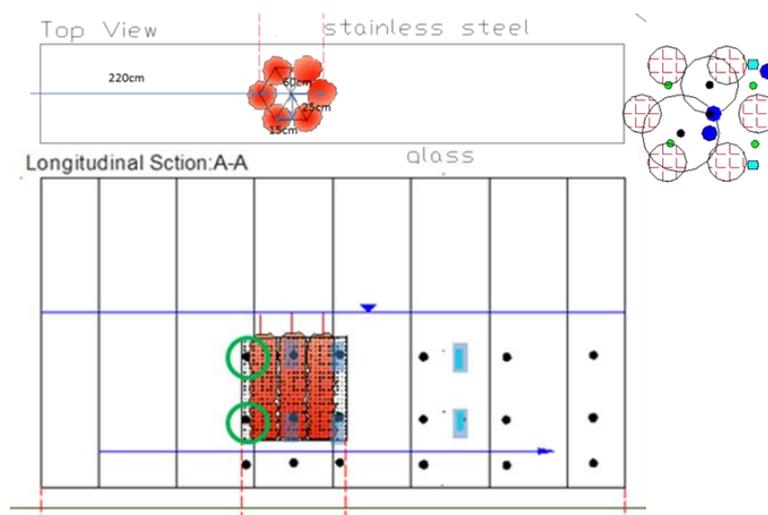


**Fig. 6:** Preliminary results of the first pilot NP injection

Five days after particle injection, free phase PCE was observed during the sampling flowing from each sampling port (Figure 7). One week after injection this effect was still observed in the sampling points close to the PCE application point. From the results of the nanoparticle mobility monitoring it was determined that the NPs did not migrate in the subsurface as far as expected according to previously performed experiments. The installed sensors for the magnetic susceptibility measurements did not detect any NP transport in the system. The nearest magnetic susceptibility sensors were located approximately 25 cm from the nZVI injection point. Soil profiles were sampled for the exact determination of nZVI concentrations in the subsurface. nZVI concentrations were determined in the soil profile in the closest sampling points, approximately 15 cm from the NP injection point. The highest nZVI concentrations were determined in the levels between 70 and 90 cm, between the third and fifth injection positions (Figure 8). The monitoring of the ability of the nZVI particles to migrate in the subsurface showed that the NPs were able to migrate less than 15 cm from the injection point in the system.



**Fig. 7:** Results of nanoparticle injection – sampling of water after nanoiron injection



**Fig. 8:** Monitoring of nZVI transport (soil profile sample points and the position of the magnetic susceptibility sensors)

### Discussion

From the preliminary results of the first pilot injection of the NANOFER 25S nZVI water slurry in the 3-D experimental box it follows that for remediation of PCE contamination a second round of nZVI particle injection is necessary. Due to insufficient migration of the NPs and remobilisation of free phase, the necessary contact between nZVI particles and contaminant was not achieved or only partially and only a negligible amount of PCE underwent reductive dechlorination. The reason for the remobilisation of the PCE free phase could be the flushing with water contained in the injected iron water slurry or with surfactant contained in this slurry during the remediation. On the other hand, the first pilot test verified and completed other objectives of the experiment. The whole experimental set-up was tested and the permeability of porous media was checked by tracer tests. The system was also tested for nZVI particle injection, the dosing unit, the monitoring and sampling equipment and also the system for the application of contaminant to the subsurface. On the basis of the results of the first pilot test additional research is under way in the form of laboratory batch and cascading columns tests. The second pilot test is planned to commence after the evaluation. It is necessary to re-verify whether the iron slurry concentration of 10 g/l is sufficient from the point of view of migration. Then surface modification of the particles should be considered to support their migration in the porous media or the use of other nZVI particles for the whole remediation. It is also necessary to consider the location of the second nZVI particle injection. If it will be in the same place as the first injection it could lead to clogging of pores due to the presence of the NPs in the subsurface from the previous injection. If a new injection location will be selected then it is necessary to consider the placement of the installed monitoring and sampling system in the box.

### Conclusion

This paper presents the preliminary results of a 3-D experiment after the first pilot test, which enables the study of migration of nZVI particles, its interaction with the contaminant and quantification of the whole remediation in a homogeneous artificially created aquifer under conditions close to those encountered at field sites. The 3-D experiment is performed in the framework of the NanoRem project. The first pilot test verified the functionality of the whole system, tested the injection system and the installed monitoring and sampling equipment. According to the existing results the transport of the NPs was insufficient. The NPs did not migrate as far as expected according to the results of the preliminary 2-D migration experiment [2]. Almost half of the whole applied contamination mass was flushed due to the injection of nZVI particles and the reductive dechlorination process only started in a negligible amount (about 1%) of the applied PCE. The reductive dechlorination process leads to the conversion of PCE to less toxic or non-toxic products. On the basis of these facts and the findings

additional research is under way in the form of laboratory batch and cascading column tests. The second pilot test will take place after the evaluation.

### **Acknowledgement**

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