STUDY OF THE MIGRATION OF NANOIRON PARTICLES IN THE 2- AND 3-D HOMOGENEOUS ARTIFICAL 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. The 2- and 3-dimension experimental equipment from the VEGAS research facility, University of Stuttgart with large scale dimensions of approximately 1m x 0.12m x 0.7m and 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.

Keywords: Nanoiron particles, injection of nanoparticles, transport and targeted deposition of nanoparticles in the subsurface, interaction of nanoiron particles with contaminants

INTRODUCTION

Nanoscale zero-valent iron (nZVI) is a progressive material for in-situ remediation of contaminated sites. Besides testing the reactivity of iron nanoparticles with a given kind of contaminant (e.g. Cr(VI), chlorinated ethenes, lindane, heavy metals) it is equally important to find out how far the nanoparticles are able to migrate to ensure contact with the contaminant in the subsurface. Artificially created DNAPL (Dense Nonaqueous Phase Liquid) contamination in 2-D and 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 advantageous. 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 large scale system enables the extensive monitoring and visualization of nZVI migration in the subsurface or monitoring of the interaction between the particles and the contaminant. The aim of these experiments is to compare the migration properties of different particles, to calculate the spread efficiency of the particles in the subsurface and in particular to quantify the whole remedial action.

1. MATERIALS TESTED

The nZVI particles NANOFER 25S (NF 25S) and NANOFER STAR (NF STAR) both produced by manufacturer NANO IRON s.r.o were used. The NF STAR particles are air-stable because their surface is stabilized by an inorganic oxide layer. The NF STAR suspension was prepared as 20% water slurry dispersed with a homogenizing and dispersing device. To recover the reactive surface of the iron particles it is necessary to prepare the suspension at least 2 days prior its application. The NF 25S suspension was prepared from pyrophoric NF 25P particles in distilled water with a ratio of 1: 4 (20% water slurry) using an LD 05 laboratory dispersing unit (NANO IRON s.r.o.) in a nitrogen atmosphere immediately prior to application. To stabilise the suspension 3% of organic stabilizer (Axilat - Polyacrylic acid) was used. Both types of particles have an average particle size of 50 nm, an average surface area of 20-25 m^2/g, a narrow particle size distribution of 20-100 nm and a high content of iron in the range of 80-90 wt. % [3]. The used concentration of nZVI in suspensions was 10 g/L.

Volatile chlorinated hydrocarbon tetrachlorethene (PCE) was chosen as the model contaminant. PCE is colourless volatile liquid, very stable and fire-resistant. It is used for dry cleaning of fabrics. PCE was coloured by the organic red colouring rhodamin for its better detection in the experimental system.

2. LABORATORY TEST METHODOLOGIES

2-D experiment (small flume)

The aim of the experiment is to present in the best possible way a homogeneously filled two-dimensional cross-section of a confined aquifer (**Figure 1**). The box is made of stainless steel and safety glass, and the confined state is created by two fixed boundary conditions i.e. Constant Head #1, and Constant Head #2 (see in the circle in **Figure 1**). The box was filled with silica sand (DORSOLIT® Nr.8) and an impermeable layer (Geba weiß - fine-grained silica sand). Two containers located on the inlet side of the box served as deoxygenated water tanks. The contaminant and the iron nanoparticles (NF 25S) were subsequently applied to the porous medium through four injection ports at the rear of the box. Prior to injection of the iron the suspension had to first be prepared in a mixing container. Since iron nanoparticles rapidly clump together and have a tendency to form large impermeable agglomerates the suspension had to be dispersed before and during injection.

The box was first assembled and filled with sand and then the first tracer test was performed to confirm that the system is homogeneously filled and there are no preferential flow paths in the system. Subsequently, the first (reference) migration experiment was performed without the presence of contaminant in order to observe the spread of nanoparticles through the medium without the presence of harmful substances. After the first migration experiment, the second tracer test was carried out in order to observe changes in the water flow after injection of the particles. After the experiment, the box was emptied layer by layer. The individual layers were documented, analyzed and the results were used to calculate the spread efficiency of the particles in the porous medium. The entire migration experiment was then repeated under the same conditions but this time with the presence of PCE. This experiment served to visualize the spread of the iron nanoparticles in the porous medium with the presence of PCE and thus to verify the direct-push method.

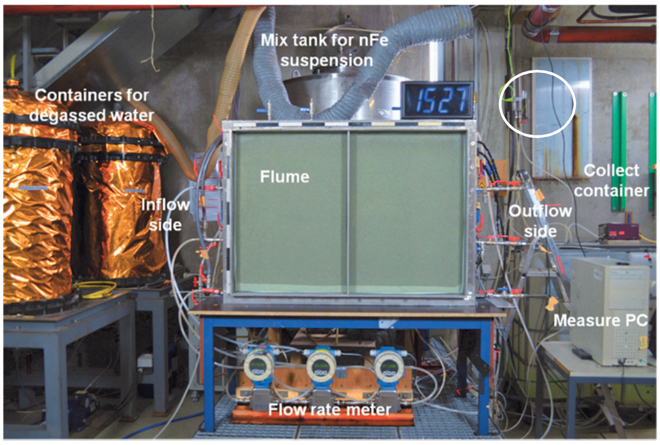

Figure 1 2-D experiment workstation at the VEGAS research centre

3-D experiment (large scale flume-LSF)

The experimental box is made of stainless steel and the safety glass. The equipment is 16 meters long, 1 meter wide and 3 meters high (**Figure 2**). 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 whole system introduces the unconfined aquifer with a homogeneous soil structure. Sand with a medium grain size (hydraulic conductivity - K = $4*10^{-4}$) 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^3/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. 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. Further parameters were measured including the concentration of chlorinated hydrocarbons (CHCs), hydrogen, dissolved iron and physical and chemical parameters through the installed 36 sampling points in the whole system.

The application of contamination and injection of nanoparticles (NPs) was performed in the central part of the experimental box. The PCE source was injected at six locations (**Figure 5**, red colour). At each location, 333 g of PCE was injected at 10 different depths with 10 cm intervals. After the PCE application it was necessary to wait approximately 1-2 months for the PCE concentration to stabilize in the porous media. 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. The stock suspension was bubbled through inert gas to avoid oxidation of the particles and was mixed to prevent particle sedimentation. The injection into the LSF1 was performed in two steps. The first pilot injection was performed in August 2014. Based on the preliminary lab batch and column tests 1 m^3 of iron suspension was injected at ten depths. The concentrated stock suspension of NF 25S was diluted online at the required concentration using a dosing unit. The second injection went in June 2016. On the basis of the results from the 1st injection and additional cascading columns and reactivity tests was injected 1m^3 of NF STAR suspension modified with Carboxymethyl cellulose (CMC) at five depths. After the both nZVI injections the whole system was monitored. The migration of the NPs was detected and the remediation of PCE source was quantified.

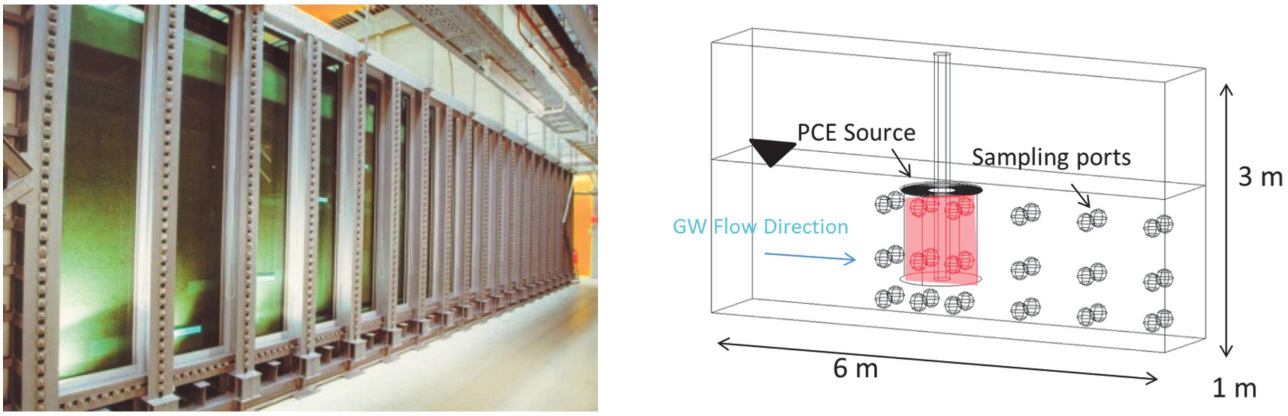

Figure 2 3-D large scale experiment in the VEGAS research facility

3. RESULTS

2-D experiment (small flume)

The experiments demonstrated that iron nanoparticles spread radially from the injection point (**Figure 3**). The transport distance of NF 25S was approximately 0.4 meters within 7 hours. For the NF 25S particles the more mobile disaggregated particle fractions were easily transported. After disassembling the experiment with the NF 25S particles it was apparent that the individual zones of nanoiron were connected in all of the layers and the greatest concentration of particles was very close to the injection points (**Figure 4, right**). The lighter parts of the zones in the flow direction were areas with a lower content of particles. Furthermore, this experiment confirmed that the iron nanoparticles also reached the areas of PCE contamination, whereby providing the necessary contact for the onset of the reaction of PCE with the iron nanoparticles. A limitation of this experiment proved to be the formation and accumulation of gases in the upper part of the box, which was the result of the reaction of the PCE with the nanoiron and anaerobic corrosion. During the tracer test the flow of water completely changed after injection of the nanoiron, with the area affected by the injection of nanoiron being bypassed (**Figure 4, left**).

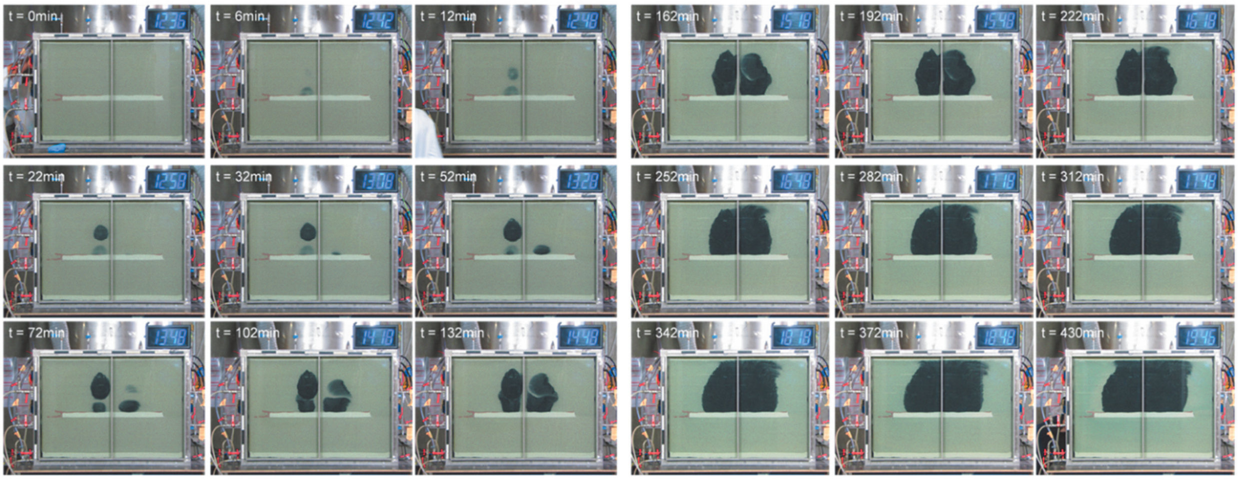

Figure 3 Visualization of the 2D-migration experiment using NF 25S with the presence of a contaminant

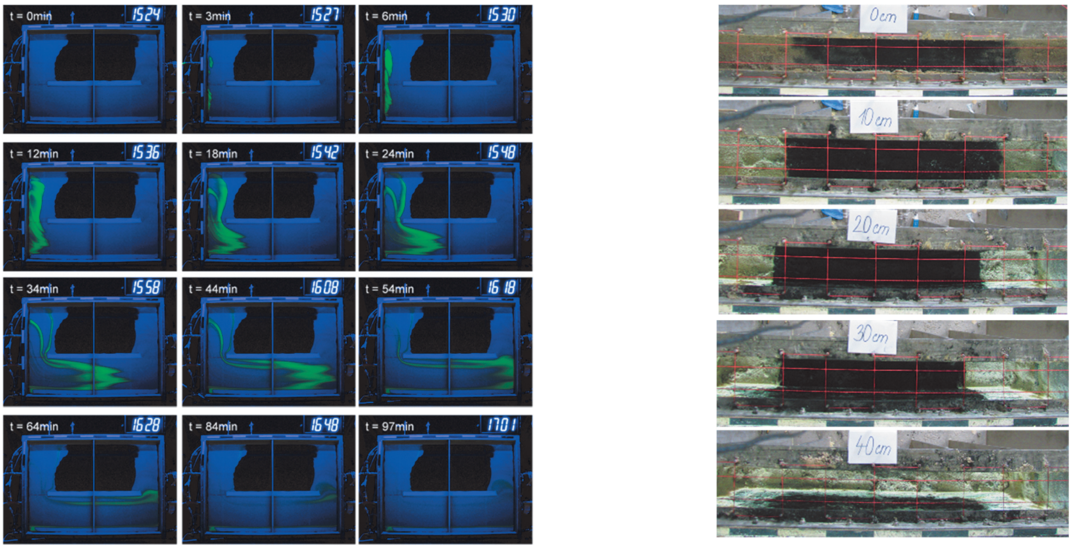

Figure 4 left - Tracer test after nZVI injection; right - Disassembling of the experimental box layer by layer at the end of experiment

3-D experiment (large scale flume-LSF)

The first pilot test verified the functionality of the whole system, tested the injection system and the installed monitoring and sampling equipment. The migration of NF 25S nanoparticles in larger equipment was very limited and significantly lower than expected according to the results of the preliminary 2-D migration experiment [2]. The installed sensors for the magnetic susceptibility measurements did not detect any NP transport in the system. The nearest magnetic susceptibility sensors (MSS) 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. 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. 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 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 the additional research was under way in the form of laboratory batch and cascading column tests.

Before the second injection was necessary to emplace the same amount of PCE into the system because the previous PCE source was flushed out during the first injection. Due to the first injection of NPs the soil pores was clogged. The hydraulic conductivity was too small in areas close to the injection point. The position of PCE source emplacement and second NPs injection was shifted 40 cm downstream (**Figure 5 -left**, violet colour). The new injection position was far enough from the first injection point and the nearest MSS were located 33 cm up/downstream. The position of the nearest sampling ports was 25 cm up/downstream. After the second NPs injection the nZVI particles were detected from six MSS. Five were detected inside of the source zone (33 cm up/downstream) and one was detected at 1.44 m downstream in the middle part. Temperature changes were detected from seven MSS. Four were detected inside of the source zone and three at 1.44 m downstream. After 2 months of the injection the particles were found at LSF glass front (**Figure 6**). The PCE decline at the downstream of the injection has been observed (**Figure 5 - right**). The PCE degradation is still going on.

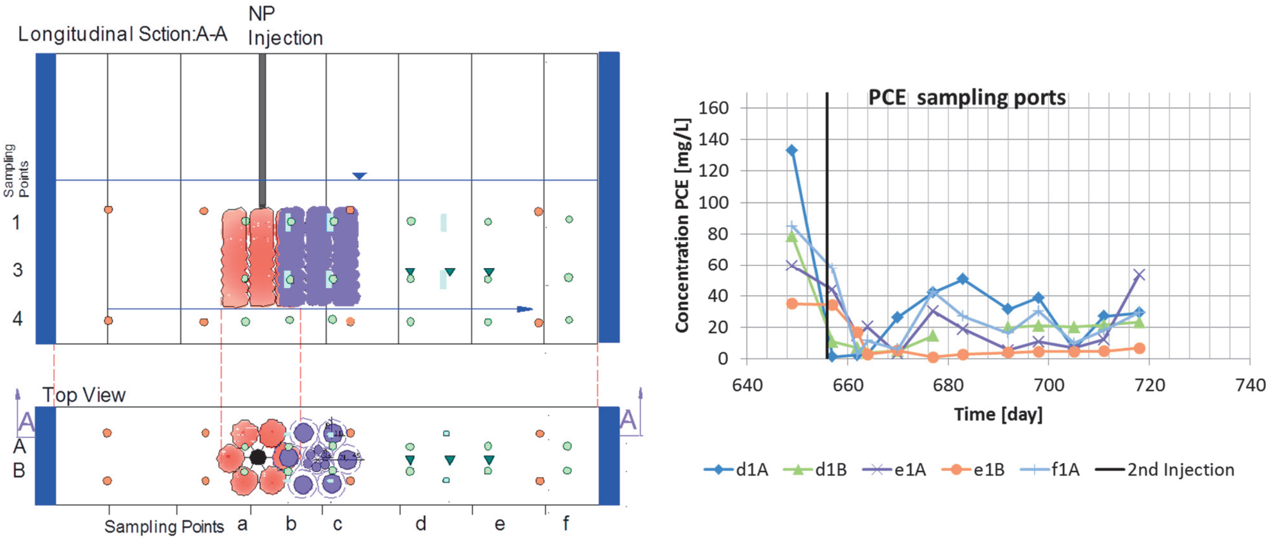

Figure 5 Left - Position of PCE emplacement and NP injection for 1st and 2nd injection; right - Change of the PCE concentration in sampling ports at the downstream after 2nd injection

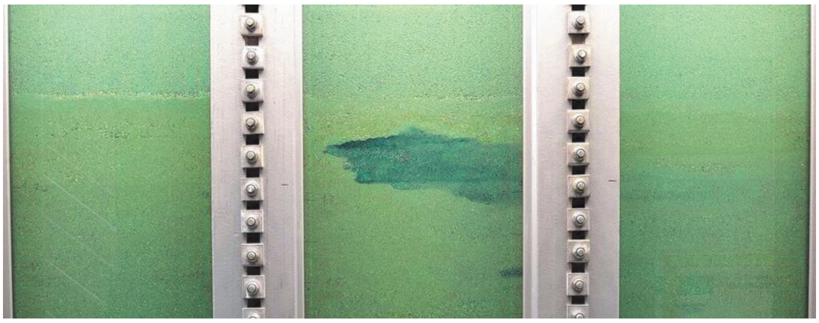

Figure 6 Nanoparticles found at LSF glass front after 2 months of the 2nd injection

4. CONCLUSIONS

The 2D-experiment designed for the purpose of comparing the migration properties of different types of nanoparticles fulfils its task. The experiment can be repeated to determine how the individual particles behave in the given porous medium. By maintaining the same initial conditions of the experiment (the same porous medium, the concentration of particles in the suspension etc.) not only can the migration ability of the particles be compared but also the spread efficiency in the medium.

The 3-D large scale experiment 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 first pilot test verified the whole experimental system and initial conditions. The transport of the NANOFER 25S particles from the injection point was insufficient. During the 2nd injection with use of other type of nZVI particles NANOFER STAR modified with CMC to enhance the migration properties in the porous media was achieved better transport of nZVI in the system. After two months the particles discovered at the LSF glass front. The LSF experiment was designed for a deeper understanding of a real remediation action and to show that the application of nanoparticles is a useful method for remediation of contaminated soil and groundwater.

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REFERENCES

[1] ČERNÍK, M., a kolektiv (2010): Chemicky podporované in situ sanační technologie, VŠCHT Praha, 2010, Czech Republic, ISBN 978-80-7080-767-5.

[2] DE BOER, C. (2012): Transport of Nano Sized Zero Valent Iron Colloids during Injection into the Subsurface, Dissertation, Universität Stuttgart - Institut für Wasser- und Umweltsystemmodellierung, 2012

[3] NANO IRON, s.r.o. (2010): Products, [online]: <http://www.nanoiron.cz/en/nanofer-25s> [24.08.2015, 15:46]