CL:AIRE

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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 pilot study which investigated the transport of iron nanoparticles in fractured chalk.

NanoRem Pilot Site – Neot Hovav, Israel: Transport of Iron Nanoparticles in Fractured Chalk

1. INTRODUCTION

This bulletin describes a pilot study to investigate the transport of iron nanoparticles (NPs) in fractured chalk at a research facility in Neot Hovav, Israel. 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.

Researchers from the Ben-Gurion University of the Negev took advantage of their laboratory fracture system and a unique network of boreholes hydraulically connected by fractures in the field. The field site is located within an industrial municipality where polluting industries were located in the 1970s. Leakages from the industrial area had resulted in major contamination[1] of the underlying aquitard. Since then numerous studies have been conducted investigating the site's hydrogeology, contaminant distribution, characteristics, biodegradation and more (e.g., Kurtzman *et al.*, 2007; Kurtzman *et al.*, 2005; Arnon *et al.*, 2005; Nativ *et al.*, 2003; Nativ and Nissim, 1992; Weisbrod *et al.*, 2002; Wefer-Roehl *et al.*, 2001). To this day the university has good working relations with the municipality and there are several ongoing studies taking place.

Although the injection site itself is outside of the principal areas of contamination, previous work done at the site (Kurtzman *et al.*, 2005) made it attractive and suitable for transport experiments. The tracer tests carried out at the site in Kurtzman's work showed very high tracer recoveries and conceptual and numerical models relevant to the current work have been developed (Kurtzman *et al.*, 2005; Kurtzman *et al.*, 2007).

Since iron NP transport in fractures had not been tested before, the team was interested in taking advantage of the system available to test the feasibility of applying iron NPs in fractured media, focusing mainly on particle transport rather than an *in situ* remediation application itself.

2. SITE DESCRIPTION

The site is located within the industrial area of Neot Hovav in the southern part of Israel, the Negev Desert (Figure 1). It is an arid environment with an average of 180 mm/year of rain. The area of Neot Hovav is 23.7 km^2, of which 8 km^2 are used and the rest is designated for future industrial facilities. Currently there are 24 factories and industrial facilities on site including the Israeli national hazardous waste site and a complex of chemical works including a pesticide factory and a bromide products factory.

In the early 1970s, the industrial area was constructed on the chalk formation with the assumption that the low permeability of the matrix would prevent contaminant transport to the aquifer. The fractures crossing the chalk formation, enabling fast transport of contaminants and water to the underlying groundwater, were overlooked. As a result, contamination occurred and the groundwater level was elevated by leakages from the industries in the area. In order to control, reduce and treat contamination, the fractures were mapped and studied (Nativ *et al.*, 1999). The thickness of the chalk formation ranges from 150 m to 285 m and the fractures go down to about 40-50 m below ground level. Contamination is restricted to the chalk formation and includes various organic (BTEX, chlorinated and brominated hydrocarbons) and inorganic compounds.

To reduce the groundwater level and prevent the seepage of contaminated groundwater at the surface, a network of drainage channels was excavated perpendicular to the major fractures. The drains were then filled with medium-sized gravel at the bottom and coarse gravel on top of it – to allow maximum flow within the channels. These channels were covered with chalk to prevent clogging from flood events. Each of these drains now flows by gravity to a collection shaft from which water is continuously being pumped and treated and groundwater is kept to a level of 2-10 metres below the surface (depending on the location and its altitude) .

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[1] More than 100 different organic compounds, from a complex of 24 different factories, were detected in the local groundwater. Concentrations varied widely among wells and across the year. The nature of a fractured aquitard is that since the volume is small and velocities are high, there is no "typical concentration" as one would expect from a porous aquifer.

Taking **Nano**technological **Rem**ediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment.
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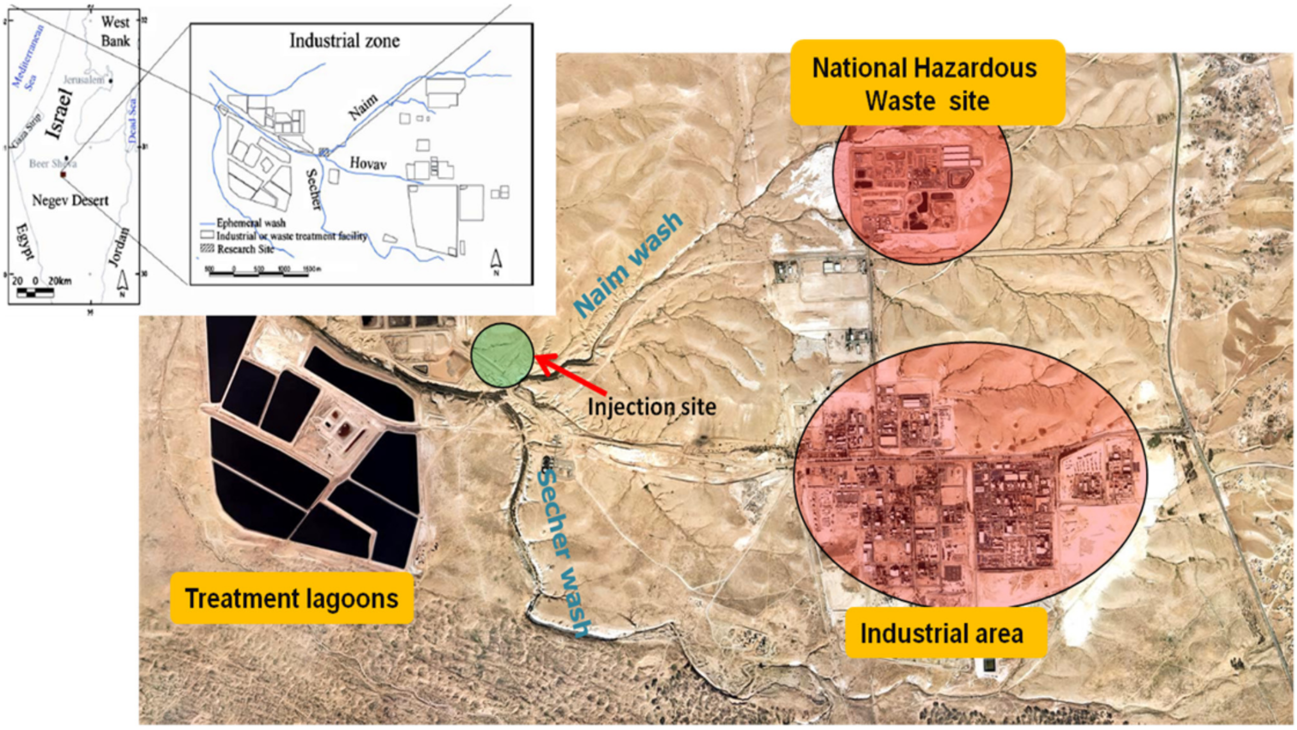

Figure 1. Aerial photo of the industrial municipality of Neot Hovav, on the top left side – the industrial municipality location and research site location (taken from Kurtzman *et al.*, 2005).

Specifically, the field test site is located at the junction of two washes, the Naim and the Hovav washes (Figure 2). In the last two decades several slanted boreholes were drilled in this area, crossing the fracture network below the water table. Previous studies carried out at this site showed through the fractures high hydraulic connectivity between the boreholes in this area.

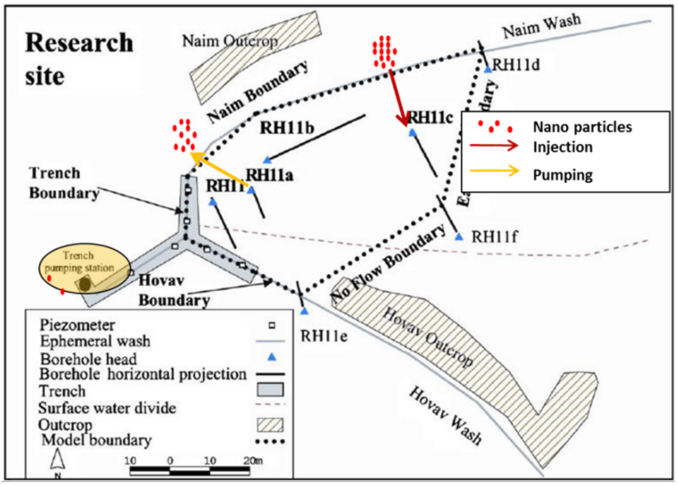

Figure 2.The injection site and proposed injection boreholes. The pumping borehole, as well as the pumping station downgradient, will minimise potential particle loss to the wider groundwater environment (taken from Kurtzman *et al.*, 2005).

3. PROJECT MANAGEMENT

3.1 Project Team

The project team was Prof. Noam Weisbrod, Meirav Cohen – PhD student, Raz Amir – field technician and Roi Cohen – laboratory and field technician; all from the Department of Hydrology and Environmental Microbiology, The Zuckerberg Institute for Water Research at the Ben-Gurion University of the Negev. Carbo-Iron® for the laboratory experiments was provided by The Helmholtz Centre for Environmental Research – UFZ and for the field site by ScIDre GmbH Dresden, Germany.

3.2 Regulatory Approval

The NanoRem project team was authorised to inject NPs at the site by the municipality.

4. DESIGN, INSTALLATION AND OPERATION

4.1 Laboratory Experiments

NP transport experiments were undertaken with several different NPs provided by NanoRem partners – Nano-Goethite, NANOFER 25S, NANOFER STAR and Carbo-Iron® (see NanoRem Bulletin #4 for more information about these NPs). In order to assess the transport potential of these NPs, first they were characterised by measuring their size and stability in two ionic strength solutions and with different stabiliser concentrations. The NPs that showed the highest stability were tested in transport experiments in a laboratory-scale discrete fractured chalk system. The chalk core was excavated from the Avdat Group in the northern Negev Desert. The core was drilled along a vertical single fracture bisecting it in two. Detailed description of the core system set up and saturation can be found in Zvikelsky *et al.* (2006) and Weisbrod *et al.*, (2013). The core and fracture are 43.5 cm long and 18 cm wide.

The laboratory experiments showed that the more stable the particles were, the more recovery there was (Figure 3). On the basis of these results Carbo-Iron® particles were chosen for further work in the laboratory and field.

Carbo-Iron® is an air-stable powder developed at The Helmholtz Centre for Environmental Research - UFZ. Carbo-Iron® consists of activated carbon colloids which are doped inside with nano-iron structures and can be used to target halogenated organic contaminants or heavy metals in groundwater. Carbo-Iron® needs to be stabilised in a suspension using a specific kind of carboxymethyl cellulose (CMC) defined by the producers. The results of previous field applications of Carbo-Iron® are summarised in Mackenzie *et al.* (2016).

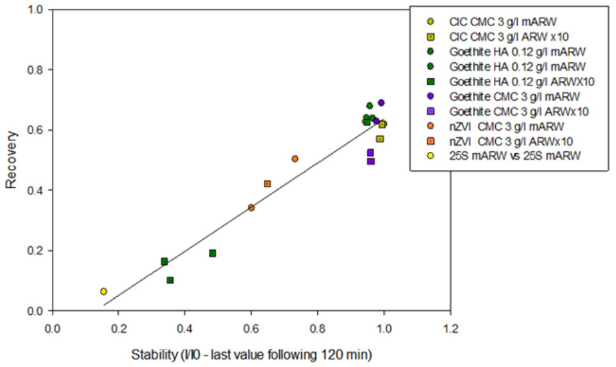

Figure 3. Particles recovery vs. stability laboratory experiment results.

4.2 Preliminary Field Tests

At the field site pumping tests were performed to ensure borehole connectivity and to determine aquifer hydraulic parameters such as storativity, transmissivity and hydraulic conductivity.

A tracer test was carried out using two fluorescent tracers. Well RH11A was pumped continuously throughout the 150 hour experiment while Uranine was injected into RH11C and Na-Naphthionate was injected into RH11F (Figure 2). Note that all three wells are slanted boreholes (20º), drilled at this angle to ensure the penetration of fractures below the water table. The water in the injection wells was mixed using circulation pumps throughout the experiment to ensure homogenous input. Water was pumped from RH11A for 24 hours prior to the tracer injection until steady state conditions were achieved (1.5 m below the natural water table in RH11A). Following the tracer injection, samples were taken at regular intervals for a period of one week.

4.3 Injection of Carbo-Iron® at the Field Site

Two NP transport experiments using Carbo-Iron® were conducted at the field site. In both experiments NPs were injected at RH11C and pumped at RH11A. The distance between the boreholes was 47 m. Most NPs transported should arrive at RH11A and any unrecovered particles should arrive at the pumping station (drainage shaft) downgradient, pumped regularly by the site operators (Figure 2).

The first experiment was conducted in March 2015. 6 kg of Carbo-Iron® particles, 4.8 kg CMC stabiliser (Carbo-Iron®:CMC 1:0.8) and 0.5 kg potassium iodide (tracer) were injected. The Carbo-Iron®-CMC (CIC) suspension was mixed in a 160 L barrel with the local groundwater while nitrogen was being continuously purged into the solution. Sampling took place for approximately 100 hours, until the concentration of NPs in the pumping borehole was below the detection limit.

Carbo-Iron® particles were selected to be injected in this field site due to their high stability even in highly saline groundwater (about 8,000 mg/l) at the site. As the purpose of the first test was to evaluate the maximum potential mobility of the particles, the suspension was stabilised with a very high concentration of CMC. Such high stabiliser concentrations are not usually implemented at the field for remediation. Therefore in May 2016 a second field transport experiment took place, following further laboratory experiments testing the effect of different CMC concentrations on particle transport. Technically, the experiment was identical to the first field experiment but with a lower stabiliser (CMC) concentration, giving a Carbo-Iron® particles to CMC ratio of 1:0.05.

5. RESULTS AND DISCUSSION

Samples taken from the injection and the pumping wells provide the breakthrough curves of the two tracers used (Figure 4). However, Uranine injected at RH11C arrived faster and at higher relative concentrations than Naphthionate injected at RH11F. The direct hydraulic connection and fast migration of the soluble tracers between the boreholes can be observed clearly.

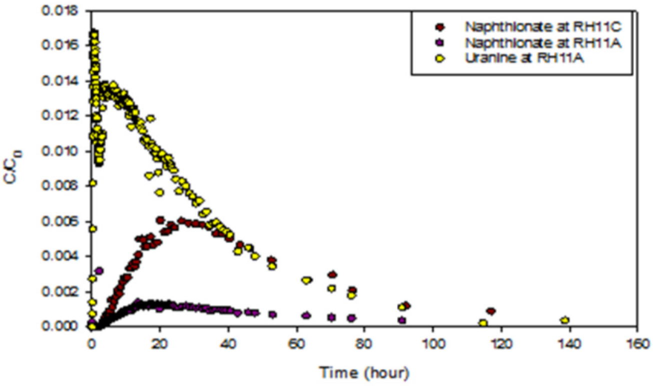

Figure 4. Uranine and Naphthionate recoveries during the preliminary tracer tests.

Similar breakthrough values of Uranine injected at RH11C and pumped at RH11A, were reported by Kurtzman *et al* (2005). The authors indicated that in a forced-gradient tracer test, the water originating from the injection borehole forms only a fraction of the water sampled at the pumping borehole. Therefore, a dilution factor was calculated in order to estimate the volumetric flow rate at the pumping borehole that comes from the injection borehole. Using this dilution factor, Kurtzman *et al.* show that the relative mass recovery of Uranine at the pumping borehole is actually 80%.

Figure 5 shows the breakthrough curves of the Carbo-Iron® and iodide tracer in RH11A for both field experiments. In the first experiment (labelled 2015), the relative concentrations of both the NPs and iodide in the pumping borehole exhibited very similar behaviour with regard to arrival time, peak time and relative concentrations. NPs and tracers arrived very quickly at the pumping borehole and showed high recoveries (i.e. the similar C/C_0 values of iodide and Carbo-Iron® observed in the first experiment indicates high recovery of the tracer and NPs of 60-80%).

It is important to remember that the first experiment was performed under very favourable conditions, in terms of stabiliser concentration, encouraging particle transport and decreasing substantially sedimentation and matrix interactions. Therefore, as expected, Figure 5 also shows much lower recoveries of the NPs in the second experiment. In addition, iodide exhibits a more complex behaviour. Initially, a higher iodide concentration with a very sharp peak at about 3 hours was observed, followed by a sharp decrease in

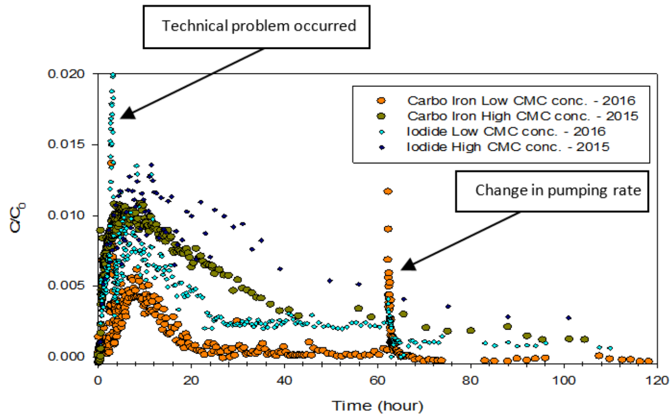

Figure 5. Breakthrough curve of Carbo-Iron® and iodide in both field experiments at RH11A.

concentration, which then increased to approximately the same concentrations as in the first experiment. However, a faster decay in iodide concentrations then followed.

A similar initial sharp peak of Uranine was observed in the tracer experiment (Figure 4) and is attributed to insufficient mixing in the injection borehole, which resulted in higher concentrations at the top of the injection borehole and subsequent transport of concentrated solution through what is assumed to be a high transmissivity fracture at that part of the interval. In the NP injection experiment, a technical problem at the injection borehole at the point in time where the sharp peak is observed (~3 hours) may have resulted in insufficient mixing. Indeed, a peak of both iodide and CIC concentrations was observed at 10 m depth (some 20 m depth samples are missing due to a separate technical problem) in the injection borehole at 2-3 hours (Figure 6). It is considered that the transport of this concentrated solution at that point in time caused both iodide and CIC concentrations to decay faster than the previous experiment in the pumping borehole, and a subsequent faster concentration depletion in the pumping borehole followed. However, while iodide concentrations initially exceeded the previous experiment concentrations, CIC concentrations remained lower due to the particles having lower mobility when stabiliser concentration is reduced.

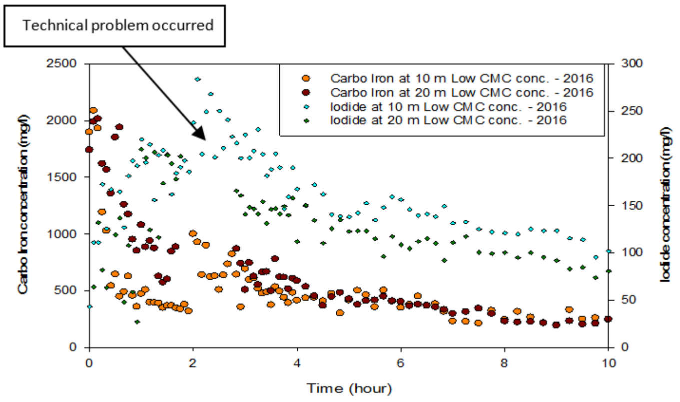

Figure 6. Carbo-Iron® and iodide concentrations at RH11C.

Following significant depletion in NP concentration in the pumping borehole (~60 hours after injection), the influence of increasing the hydraulic gradient on particle transport was tested. After 61 hours, pumping rate was increased, resulting in a 155 cm fall in the water level within the pumping well. This resulted in a significant increase in particles concentrations in the pumped well for a short period of time (Figure 5 – hour 61) – indicating particle remobilisation, presumably due to the increased flow velocity and subsequently higher shear force. These results indicate the potential for NP transport manipulation by changing stabiliser concentration and groundwater flow velocity.

6. CONCLUSIONS AND LESSONS LEARNED

The various tests and experiments (laboratory and field) conducted during this project were aimed at giving an insight into iron NP transport and application in fractured media. Transport was shown to be heavily dependent on the stability of the NP suspension and hence on particles properties, stabiliser concentration and solution properties like viscosity and ionic strength. It was shown that unlike in porous media, transport potential in a fractured rock matrix is high and can be efficiently manipulated by changing stabiliser concentration and particle properties like the single particle size, the aggregate size and the particle stability. Moreover, it was shown that flow velocity impacts particle transport. Nevertheless, generally it can be concluded that (1) iron NPs can be highly mobile in fractured systems; (2) stability analysis of particulate suspensions combined with evaluation of field hydraulic parameters could provide good estimation for NP mobility.

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