



Electro-osmotic transport of nano zero-valent iron in Boom Clay



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ABSTRACT

One of the many problems that impede the successful remediation of soil and groundwater contaminated with chlorinated hydrocarbons occurs when pollutants diffuse into low permeability zones, and become difficultly accessible. Remediation by reductive dechlorination using nanoscale zero-valent iron (nZVI) is possible, but its delivery into contaminated hot spots is difficult using solely hydraulic gradients.

Recently, electrokinetics has been proposed to transport nZVI, with the assumption that both electrophoresis and electro-osmosis are involved. However, so far no study has focused solely on transport driven by electro-osmotic flow. This driving force could significantly improve field remediation, allowing nZVI to reach low permeability hotspots.

This work describes the experiments carried out to evaluate if nanoscale zero-valent iron can be transported by electro-osmotic advection in a dense clay using a specifically designed laboratory apparatus. It explores how working parameters (such as voltage, injection point and pH) influence transport, and provides an insight into the subsurface behaviour of nanoparticles using micro-XRF.

The results confirm the transport of nZVI by electro-osmotic advection, with an electro-osmotic conductivity in the range $(0.5\text{--}1.0)\cdot 10^{-10} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. The presence of nZVI decreases electro-osmotic conductivities by approximately half and affects geochemical conditions of the system, inducing sharper pH profiles and enhancing cation exchange in the clay.

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1. Introduction

Nano-scale iron materials have been researched to explore their potential for treating contaminated soil and groundwater [1]. Among them, nanoparticles of zero-valent iron (nZVI) have shown their potential for environmental remediation. These particles have been used due to their efficiency to treat and degrade different compounds like organic chlorinated compounds, pesticides, etc.

Recent advances in zero-valent iron (ZVI) technologies have been directed towards delivery techniques that carry the reactive iron towards the contaminant without the extensive trenching methods and disruptions that occur with installation of permeable reactive barriers (PRB's). These techniques require an *in-situ* method based on the injection of ZVI into an aquifer [2] and are alternative methods to the classic PRB's.

One of the challenges when using nZVI is to effectively transport nanoparticles across a significant distance. Usually, it is a function of how far the fluid can be moved before the particles settle by

coagulation. Filtration of particles also limits movement. It has been hypothesized that the nanoscale ZVI particles are so small that they can migrate easily in the aquifer by advection [3] and, therefore, can treat a large volume of the subsurface *in situ* by direct injection [4,5]. Unfortunately, laboratory tests have shown that nanoscale ZVI particles can form much larger aggregates of particles shortly after production [6–8]; these larger aggregates may not migrate through granular aquifers by advection because of their larger size. These problems would be strongly aggravated in transport through fine-grained soils like clays.

To overcome the limitations, a combined technique using nZVI and electrokinetics is being developed [2,9]. Electrokinetics is a technology that has found many applications in environmental contaminants removal. It is particularly effective in removing inorganic and organic compounds from homogeneous and low-permeable soils, such as clay. More recently, the use of electrokinetic phenomena to mediate and enhance chemical oxidation/reduction has been considered. The electrokinetic transport mechanisms can be classified in electromigration i.e. migration of charged ionic species to opposite charged electrodes; electrophoresis i.e. motion of dispersed particles relative to a fluid under the influence of an electric field; and advection by electro-osmosis, motion of liquid induced by the application of an electric field.

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Specifically, electro-osmosis (EO) may be utilised to deliver oxidising or reducing agents by convection in pore water into these low permeability zones, to facilitate the remediation of these contaminants [10].

According to the literature, some studies have been done to evaluate the electrophoretic transport of the nZVI in high permeability soils like sands [11,12]. So far no studies have been found to assess the possibility of using nZVI with EO for transport, allowing nZVI to reach low permeability hotspots.

EO flow is known for more than two centuries, having first been described in 1809, according to [13]. It originates when an electric field is applied to a soil or other porous material in which particles have surface charge. Most clay particles have negative surface charges, and therefore an accumulation of positively charged species from the soil solution occurs around these clay particles, creating an electric double layer. Application of a voltage drop across the soil generates an electric field that causes positively charged ions accumulated near the soil particles' surface to move towards the cathode, dragging along their hydration molecules and thus creating a water flux towards the cathode. This is a simplified vision of the EO phenomenon and a more detailed explanation can be found in [14].

The mobility of nanoparticles in the subsurface environment by EO depends on many factors including the texture of the soil and type of soil particles, solution and soil pH. A deeper knowledge of the subsurface geochemical conditions and interactions between nZVI and the soil is needed, in order to predict nZVI properties during *in situ* treatment and enhance transport into low permeability zones.

This work describes the laboratory experiments carried out to evaluate if nanoscale zero-valent iron could be transported by electro-osmosis in Boom clay, a dense Oligocene clay from Belgium. It describes how working parameters (such as voltage, injection point for nZVI and pH) influence transport and provide an insight into the subsurface behaviour of the nanoparticles and their interactions with soil using micro-XRF techniques. Even though electrophoresis occurs in a compact soil with low permeability, it is not a dominant mechanism [15,16]. Moreover, different authors suggest mass transport by electrophoresis is negligible in low permeability soil systems [16,17]. This work is therefore based on the assumption that electrophoresis is negligible in Boom clay.

2. Experimental

2.1. Reagents

The nanoparticles of zero-valent iron (NANO FER 25) containing less than 1% of Tween as stabilizer were obtained from Nano Iron sro, Czech Republic.

An electrolyte solution was prepared with de-oxygenated water and 10 mM sodium chloride (NaCl, Merck) with an initial pH of 7.08.

All the chemicals used in the experimental procedures were reagent grade.

2.2. Soil sample

The soil used in the experiments was finely ground and compacted Boom clay. Boom clay is a thick deposit of over-consolidated marine clay of Oligocene age [21,22]. The clay consists predominantly of clay minerals and silt and minor sand. It is characterised by a rather constant chemical and mineralogical composition and a low permeability and plasticity. It is of scientific and practical interest because of its high retention capacity for radionuclides. This clay was obtained from Mol (Belgium).

The clay properties are shown in Table 1. The CaCO₃-content of the clay was estimated prior to use in the studies and was lower than 0.5%.

2.3. Experimental setup

To investigate the transport of nZVI, a new cell design based on a previous EO cell design of the University of Utrecht [10] was used, consisting of a one-compartment cylindrical cell with the electrodes located at opposite sides. In the original cell, the electrodes were in contact with the soil sample, so oxygen and hydrogen generation in the anode and cathode could oxidise nZVI and reduce its reactivity. Therefore, active electrodes (platinum) have been separated from soil and placed in open reservoirs at both ends of the main compartment, thus avoiding the release of gas into the soil (Fig. 1) [23]. In order to isolate the soil samples from the reservoirs, porous stones and filter papers were used. The porous stone provides a homogenous distribution of the flow in the cell and the filter papers between porous stones and clay (Whatman n 1) prevents transport of soil particles into the reservoirs. Electrode chambers and extra reservoirs were filled with the processing fluid NaCl.

To measure the real potential difference across the clay sample, a pair of Ag/AgCl reference electrodes was located in the extra reservoirs adjacent to the soil (Fig. 1). The addition of two new reference electrodes in the set-up enables controlling the potential applied across the soil, by excluding the effect due to the polarization.

Experimental design and working conditions are shown in Table 2. In total, 6 experiments were carried out. Experiment 0 aimed at assessing polarization effects and at selecting working voltage. Experiments I and II tested two opposite injection points for nZVI, one near the cathode (exp. I) and the other near the anode (exp. II), measuring transport through a small soil cylinder of 2.5 cm in length and 5.0 cm in diameter. The following experiments (III and IV) were carried out in a longer soil-cell (5.0 cm length; 5.0 cm diameter) and tested EO flow in the presence and absence of nZVI, during 160 hours. Experiment V replicated the conditions in experiment IV, but extended time to 360 hours.

The applied voltage was delivered by a power supply (Agilent 3612A) and potential between the reference electrodes was maintained constant. During the experiments, daily measurements of current and pH at the anode and cathode reservoirs were done using a Fluka multimeter and COMSOL pH meter C830. The electrolyte flow due to the electrokinetic transport was measured in the electro-osmotic flow reservoirs.

2.4. Sample treatment and analysis

After finishing the experiments, the soil sample was removed from the soil compartment, frozen with liquid nitrogen and then longitudinally cut in two half cylinders. One of them was polished and then analysed using Micro-XRF (Edax Orbis®, X-ray optics with capillary focusing to 3 μm spot size). The other one was divided into five sections of similar size 1–5, namely, from anode to cathode (Fig. 1). pH and metal content were analysed in these sections.

Metal content in the soil was determined using AAS & ICP. Previously a chemical extraction procedure was performed in accordance with EPA Method 3050 Acid digestion [24]. pH value of the soil samples was measured by adding 1 M KCl solution to the dry sample in a ratio of 2.5 mL/g according to van Reeuwijk [25].

3. Results and Discussion

From the developed experiments we derived the effect of different working parameters like voltage, current density and pH on the transport of the nanoparticles. Furthermore, the subsurface geochemical conditions, interactions between nZVI-Boom clay and

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