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Pressure-controlled injection of guar gum stabilized microscale zerovalent iron for groundwater remediation

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ABSTRACT

The paper reports a pilot injection test of microsized zerovalent iron (mZVI) dispersed in a guar gum shear thinning solution. The test was performed in the framework of the EU research project AQUAREHAB in a site in Belgium contaminated by chlorinated aliphatic hydrocarbons (CAHs). The field application was aimed to overcome those critical aspects which hinder mZVI field injection, mainly due to the colloidal instability of ZVI-based suspensions. The iron slurry properties (iron particles size and concentration, polymeric stabilizer type and concentration, slurry viscosity) were designed in the laboratory based on several tests (reactivity tests towards contaminants, sedimentation tests and rheological measurements). The particles were delivered into the aquifer through an injection well specifically designed for controlled-pressure delivery (approximately 10 bars). The well characteristics and the critical pressure of the aquifer (i.e. the injection pressure above which fracturing occurs) were assessed via two innovative injection step rate tests, one performed with water and the other one with guar gum. Based on laboratory and field preliminary tests, a flow regime at the threshold between permeation and preferential flow was selected for mZVI delivery, as a compromise between the desired homogeneous distribution of the mZVI around the injection point (ensured by permeation flow) and the fast and effective injection of the slurry (guaranteed by high discharge rates and injection pressure, resulting in the generation of preferential flow paths). A monitoring setup was designed and installed for the real-time monitoring of relevant parameters during injection, and for a fast determination of the spatial mZVI distribution after injection via non-invasive magnetic susceptibility measurements.

1. Introduction and background

The use of zerovalent iron in the form of microscale or nanoscale particles (mZVI or nZVI) is a promising and cost-effective approach for groundwater remediation. mZVI and nZVI allow to overcome most of the restrictions associated to the use of millimetric iron fillings in permeable reactive barriers (PRBs), mainly related to the difficulties in the excavation of the trench, to the limited depth of application, and to the treatment of the sole dissolved fraction of the contaminants (Di Molfetta and Sethi, 2006; Moraci and Calabrò, 2010; Tosco et al., 2014b; Zhang, 2003; Zolla et al., 2009).

Despite a broad range of laboratory studies have been devoted in recent years to the assessment of reactivity (Freyria et al., 2011; Hosseini et al., 2011) and transport of iron particles in saturated porous media (Dalla Vecchia et al., 2009b; Freyria

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et al., 2011; Hosseini and Tosco, 2013; Tiraferri and Sethi, 2009; Tosco et al., 2014a), successful and well controlled pilot scale studies proving the feasibility of this approach are still limited, and mostly performed using nZVI (Bennett et al., 2010; Elliott and Zhang, 2003; Johnson et al., 2013; Macé et al., 2006; Mueller et al., 2012; O'Carroll et al., 2013; Quinn et al., 2005; Su et al., 2012), while mZVI field injection has been scarcely reported (Flores Orozco et al., 2015; Luna et al., 2013; Truex et al., 2011). The most critical issue in field scale applications of zerovalent iron particles is related to the generation of a wide and homogeneous reactive zone (Cameselle et al., 2013; Cook, 2009; EPA, 2003; Quinn et al., 2005). Several concurrent factors have to be taken into account to achieve optimal results, including (a) stability of the ZVI suspensions, (b) mobility of the ZVI particles, (c) injection approach, and (d) costs.

The emplacement of ZVI particles is hindered by the strong magnetic interactions which lead to aggregation and subsequent gravitational settling of bigger flocs (Dalla Vecchia et al., 2009a; Phenrat et al., 2007; Tiraferri et al., 2008). Such aggregates could also significantly limit transport and clog the porous medium (Kanel et al., 2005; Kocur et al., 2013; Liu et al., 2005; Phenrat et al., 2007; Phenrat et al., 2010; Saleh et al., 2007; Schrick et al., 2004). They also exhibit reduced specific surface area, and therefore reactivity (He and Zhao, 2005; Nurmi et al., 2005). Aggregation and sedimentation of ZVI particles should be prevented for a time sufficient to allow slurry preparation, handling and injection in the subsurface. An improved colloidal stability can be obtained by adding surfactants or food-grade green biopolymers characterized by high molecular weight. Polymers, if dosed in low concentration (fractions of g/l), adsorb on the particle surface, creating a brush layer and thus reducing inter-particle forces (steric stabilization) (Hydutsky et al., 2007; Krol et al., 2013; Phenrat et al., 2008; Schrick et al., 2004; Tiraferri et al., 2008; Tosco and Sethi, 2010). The polymer anchored onto the ZVI particles has a double positive impact on particles mobility: it reduces particle–particle attractive forces, preventing the formation of large aggregates which may be prone to filtration in the porous medium, and at the same time increases the repulsion among particles and porous medium. Since the adsorption of biopolymer chains can hinder the reactivity, it is important to use easily biodegradable biopolymers (e.g. guar gum) which can be removed by enzymatic breakdown (Di Molfetta and Sethi, 2006; Gastone et al., 2014a; Kirschling et al., 2011; Reddy et al., 2011; Velimirovic et al., 2012) or by soil microbial population (Velimirovic et al., 2014b). If the polymer is dosed in significantly higher concentrations (in the order of grams per liter), part of the polymer chains adsorb onto the ZVI surface, until saturation, and part stay in suspension, increasing the viscosity of the dispersing fluid (kinetic stabilization) and consequently significantly reducing aggregation and sedimentation rate (Dalla Vecchia et al., 2009b; Tiraferri et al., 2008; Velimirovic et al., 2012; Xue and Sethi, 2012). Stabilization approaches based on the use of polymeric solutions, characterized by a non-Newtonian shear thinning behavior, showed promising results also in improving particles mobility in porous media (Cantrell et al., 1997; Comba and Sethi, 2009; Dalla Vecchia et al., 2009b; Gastone et al., 2014b; Kocur et al., 2013; Tiraferri and Sethi, 2009; Tiraferri et al., 2008; Tosco et al., 2014a; Xue and Sethi, 2012). In particular, Dalla Vecchia et al. (2009b) and Hydutsky et al. (2007) proved that the transport distances of polymer-coated nZVI and mZVI can be in the order of a meter in laboratory experiments. Furthermore, from a rheological point of view, the shear thinning behavior of guar gum solutions is highly beneficial for field applications, since it helps improving stability without significantly increasing the injection pressure: shear thinning fluids show a viscosity decrease as the shear rate increases, i.e. the viscosity is higher in static conditions (corresponding to the storage before injection) and lower in dynamic conditions (corresponding to the injection in the subsurface, when a limited viscosity is desired in order to limit the overall pressure build-up in the porous medium) (Comba et al., 2011; Sorbie et al., 1989; Xue and Sethi, 2012).

Even if some successful pilot and full scale applications of both nZVI and mZVI have been recently reported using different injection technologies (Elliott and Zhang, 2003; He et al., 2010; Johnson et al., 2013; O'Carroll et al., 2013; Quinn et al., 2005; Su et al., 2012; Velimirovic et al., 2014c), specific studies on the preferable delivery techniques are, to the authors' knowledge, still lacking, and the topic still needs to be further investigated. As a general rule, a field injection can be performed according to two different regimes: (i) permeation injection, which generates a uniform particle distribution in the subsurface and ensures the contact between particles and contaminants, or (ii) fracturing injection, which consists in injecting fluids and particles at a pressure exceeding the porous medium critical pressure, thus generating a non-uniform distribution if the process is not properly designed and controlled. From a theoretical point of view, in order to achieve a homogeneous distribution of the particles around the delivery point, the injection via permeation is preferable to fracturing. Nevertheless, there are several factors that hinder the delivery under permeation regime, namely medium to low hydraulic conductivity of the aquifer system, and mechanical straining of the particles when the ratio of the size of the iron particles to grain size of the aquifer material exceeds a threshold limit, usually reported in the range of 0.8–1% (Bradford et al., 2006; Xu et al., 2006). Moreover, the injection has to be performed in a time shorter than the sedimentation time of the particles, in order to avoid plugging of the injection pipes and of the well. As a consequence, the injection discharge has to be chosen fulfilling two requirements: on the one hand it has to be low enough to avoid pressure build-up exceeding the porous medium critical value, on the other hand it has to be high enough to ensure colloidal stability during the whole injection. Finally, it is worth to point out that adopting very low discharge rates, and consequently increasing the overall delivery time, leads to a significant increase in costs due to longer field injection operations. Similar considerations are also valid for the determination of the stabilizer concentration: on the one hand it should be high enough to maintain the particles suspended for the duration of the injection, on the other hand it should be low enough to prevent excessive pressure build-up in the well.

As highlighted in this paragraph, the design of a field scale injection of ZVI-based slurries is the result of the optimization of several concurrent technical, environmental and economic factors and constraints which have to be simultaneously satisfied. In several field applications a permeation injection is practically unfeasible, due to the constraints mentioned above, and fracturing injection is the only viable approach. As an example, the authors previously reported a field injection in a low permeability contaminated aquifer, where the ratio of