



# Calcium hydroxide coating on highly reactive nanoscale zero-valent iron for in situ remediation application

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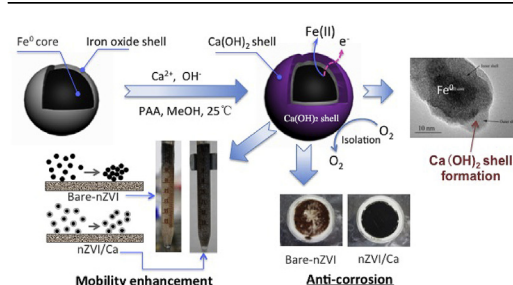
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## HIGHLIGHTS

- The Ca(OH)<sub>2</sub> shell was successfully coated on highly reactive nZVI particle.
- Moderate Ca(OH)<sub>2</sub> coating slowed down the nZVI oxidation in corrosion test.
- Transport of nZVI in sandy column was promoted with Ca(OH)<sub>2</sub> coating.
- nZVI/Ca-0.25 presented a good reduction potential toward to trichloroethylene.
- Ca(OH)<sub>2</sub> coating mediated the phase transformation of nZVI surface.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nano scale zero-valent iron (nZVI), a promising engineering technology for in situ remediation, has been greatly limited by quick self-corrosion and low mobility in porous media. Highly reactive nZVI particles produced from the borohydride reduction method were enclosed in a releasable Ca(OH)<sub>2</sub> layer by the chemical deposition method. The amount of Ca(OH)<sub>2</sub> coated on nZVI surface were well controlled by the precursor dosage. At moderate Ca(OH)<sub>2</sub> dosage ( $R_{Ca/Fe} = 0.25$ ) condition, the increment of Fe<sup>0</sup> content for the obtained nZVI/Ca-0.25 sample was observed. The interfacial reactions between the iron oxide shell and the Ca(OH)<sub>2</sub> saturated environment were delicately elucidated by the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) spectrum. And the coverage of Ca(OH)<sub>2</sub> shell on spherical nZVI surface was found more complete and uniform for the nZVI/Ca sample obtained from the moderate precursor dosage condition ( $R_{Ca/Fe} = 0.25$ ). The Ca(OH)<sub>2</sub> shell before dissolution was demonstrated owning the anti-corrosion capability to slow down the oxidation of Fe<sup>0</sup> core in air, during ethanol storage and in aqueous environment. The mechanism of anti-corrosion capability for nZVI/Ca-0.25 particle was interestingly found to be attributed to the Ca(OH)<sub>2</sub> shell isolation and also be potentially due to the iron oxide shell phase transformation mediated by the outer Ca(OH)<sub>2</sub> shell. An improved trichloroethylene reduction performance was observed for nZVI/Ca-0.25 than bare nZVI. The mobility of nZVI/Ca particles in water-saturated porous media was moderately improved before shell dissolution.

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## 1. Introduction

Nano-scale zero-valent iron (nZVI) technology is a promising

engineering method for in situ remediation of contaminated subsurface environments (soil and groundwater aquifers) that are widely distributed around the world [Zhao et al., 2016; Ahn et al., 2016]. Ideally, nZVI slurry can be simply injected into the polluted subsurface sites, making the application easy to handle, flexible, and probably cost-saving. nZVI particles were demonstrated to have high reactivity towards many contaminants, including chlorinated organic pollutants, heavy-metal ions, nitrates, and others in higher oxidation states [Li et al., 2017; Wang and Zhang, 1997; Sun et al., 2016a, b]. However, in practice, these advantages can be exhibited only if the injected nZVI slurry can be well transported a sufficiently long distance in porous media during the delivery, and if the reducing reactivity is reserved until arrival at the target sites. Unfortunately, the reactivity of nZVI particles could also be quickly lost after their injection or during transport by reacting with non-targeted substances such as oxygen and water [Ahn et al., 2016; Filip et al., 2014; Greenlee et al., 2012]. Poor transport of nZVI particles and blocking of the porous media were observed due to self-aggregation and deposition onto media grains [Phenrat et al., 2007; Guan et al., 2015].

Several methods have been developed to increase the mobility of nZVI and to protect the reactivity of nZVI particles that are required for effective environmental remediation applications [Phenrat et al., 2010; He and Zhao, 2007; Zhan et al., 2008; Guan et al., 2015; Zhan et al., 2011]. Most of these methods feature coating a layer of polymer, surfactant, or oil onto the particles' surface. The polymer adsorption method was proved to be beneficial for aggregation inhibition (and therefore mobility enhancement) due to either increased inter-particle repulsion force (including steric force and electrostatic force) or reduced inter-particle attraction force (van der Waals force and electromagnetic force) [Phenrat et al., 2010; He and Zhao, 2007]. Nevertheless, a moderate reactivity loss after surface modification by polymer adsorption was also reported [Phenrat et al., 2009]. A second group of methods involve encapsulation of the nZVI particles into an inert solid support such as silica [Zhan et al., 2008] and carbon platelets [Guan et al., 2015; Zhan et al., 2011]. However, the issue concerning the effective release of reactive iron from the stable shell coating and the cost of application of these methods should be further considered.

A trade-off between the stabilization of nZVI particles for reactivity reservation during their transport and the release of reactivity towards contaminants when they arrive at the target sites always exists. One kind of releasable inorganic shell on commercial micro- and nano-sized ZVI surfaces was developed in our previous study [Wei and Li, 2013; Wei et al., 2018]. Based on the surface-assisted nucleation process, a calcium hydroxide shell was successfully coated by heterogeneous nucleation on the surface of model micro- and nano-sized ZVI particles as the nucleation seeds. Other than a kind of low-solubility inorganic salt like calcium carbonate, in which it is difficult to control core/shell structure formation due to the likelihood of a single-phase microscale crystal forming by quick homogeneous nucleation [Wei et al., 2018], the moderately soluble calcium hydroxide was proved to be suitable for a thin, amorphous shell coating on the commercial ZVI surface by heterogeneous nucleation. Depending on the solubility of  $\text{Ca(OH)}_2$  (1.62 g/L, 20 °C), the  $\text{Ca(OH)}_2$  coating on ZVI surface was supposed as a releasable shell during application for onsite remediation. For in-situ application, the  $\text{Ca(OH)}_2$  coated ZVI particles are initially delivered by the saturated  $\text{Ca(OH)}_2$  solution to prevent the shell dissolution before injection and the shell commonly begins to dissolve into the background aquatic environment due to the dilution of background  $\text{Ca(OH)}_2$  saturated solution by conceptual water flushing after injection (as indicated by a conceptual model) (Figure S1). Upon this model, remediation performance of  $\text{Ca(OH)}_2$

coated nZVI particle towards to the target contaminant would be greatly dependent on the reactivity of the  $\text{Fe}^0$  core enclosed. Commercial ZVI particles employed in our previous studies were found likely to be stabilized during processing without presenting a high reactivity. So an effective surface oxidation/reduction reaction occurrence after shell dissolution needs to be further achieved by enclosing the highly reactive nZVI in  $\text{Ca(OH)}_2$  shell.

While a uniform and complete  $\text{Ca(OH)}_2$  shell formation on highly reactive nZVI particle is very challenging due to the easy oxidation of  $\text{Fe}^0$  core during the gradual shell growth by heterogeneous nucleation. As we know, the most reactive iron nanoparticles are made by borohydride reduction of aqueous iron (III) salts [Wang and Zhang, 1997]. The smallest nZVI particles obtained from this method with the addition of ethanol have an average diameter as low as 10–20 nm and therefore have the potential merits of intrinsic high reactivity and high surface area provided for surface nucleation. However, the oxidation of nZVI particle during  $\text{Ca(OH)}_2$  coating was easily to be observed due to the inter-reaction between nZVI and surrounding aqueous environment. When the synthesis was conducted in methanol with the assistance of ultrasound to enhance seeds dispersion, oxidation of nZVI particle was observed [Wei and Li, 2013]. Consequently, a practical approach of coating the  $\text{Ca(OH)}_2$  layer on highly reactive nZVI surface need to be developed to ensure a good reduction reactivity retained in the  $\text{Ca(OH)}_2$  shell.

In this study, a simple and effective process to coat a thin  $\text{Ca(OH)}_2$  shell on freshly prepared nZVI particles was established. The shell formation process is analogous to heterogeneous nucleation on an available surface in solution. The  $\text{Ca(OH)}_2$  shell coating was processed in methanol with the assistance of the mechanic mixing at the temperature ranged at about 10 °C. There was no obvious oxidation observed during the  $\text{Ca(OH)}_2$  coating procedure and the quantity of  $\text{Ca(OH)}_2$  coated on nZVI surface was regulated by the calcium precursor dosage. The specific objectives of this study were to optimize the coating methods to form a complete  $\text{Ca(OH)}_2$  shell on the very reactive nZVI particles, to testify the physical and structure characterization of so-formed calcium-hydroxide-coated nZVI particles (denoted as nZVI/Ca), to assess the anti-corrosion capability of nZVI/Ca particles and the mobility of nZVI/Ca particles within fine-grained water saturated porous sandy media, to evaluate the preserved reducing reactivity towards target contaminant.

## 2. Materials and methods

### 2.1. Preparation of bare nZVI particles

Bare nZVI particles, denoted as B-nZVI, were synthesized according to the borohydride reduction method [Wang et al., 2009]. More details can be found in supplementary Information (SI).

### 2.2. $\text{Ca(OH)}_2$ coating onto nZVI particles

A 20 mL well-dispersed B-nZVI (200 mg nZVI particle contained) methanol suspension is prepared by adding a dispersion agent (5 mg poly(acrylic acid), PAA, Sigma) and mechanical stirring (250 rpm) in an anaerobic environment. Mechanical stirring was employed to enhance a homogeneous distribution of B-nZVI particles as nucleation seeds. Consequently, the nZVI particle was suspended in a deoxygenated methanol solution at a relative low temperature of 10 °C without water and oxygen participation. After injecting 10 mL NaOH methanol solution and complete mixing, another 10 mL  $\text{CaCl}_2$  methanol solution was quickly injected into the NaOH-contained nZVI suspension to achieve a instantly oversaturated  $\text{Ca(OH)}_2$  solution. The oversaturation degree was

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