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Core-shell structured mZVI/$Ca(OH)_2$ particle: Morphology, aggregation and corrosion

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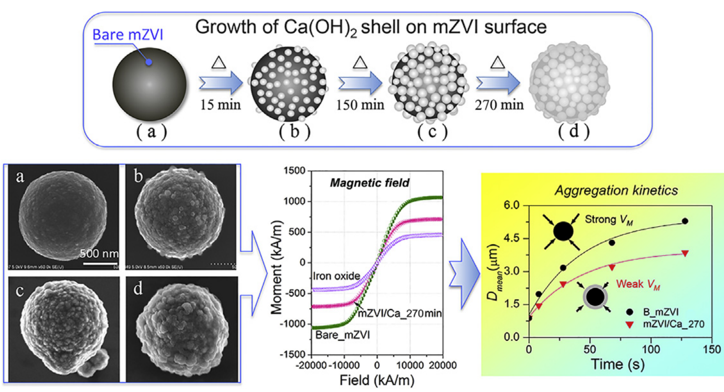
GRAPHICAL ABSTRACT



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ABSTRACT

A calcium hydroxide shell was coated onto the surface of micro-sized zero valent iron (mZVI) particles by hydrothermal approach in oversaturated $Ca(OH)_2$ solution. The heterogeneous nucleation of nano-scale $Ca(OH)_2$ particle on micro-scale spherical ZVI surface was clearly observed by scanning electronic microscope (SEM). The moderate solubility of $Ca(OH)_2$ was demonstrated as the crucial factor in inducing slow nucleation rate and in facilitating the abundant growth of $Ca(OH)_2$ nuclei on mZVI surface. The growth of shell thickness was found to obey the zero order kinetics with the rate constant at about 15 nm/h. The $Ca(OH)_2$ shell was demonstrated to be anticorrosive to protect reactive Fe^0 from oxidation based on standard corrosion test. In addition, the instant aggregation process of mZVI within 120 s was slowed down after $Ca(OH)_2$ shell coating. The saturation magnetization of mZVI, measured by a vibrating sample magnetometer (VSM), was gradually diminished along with the shell formation with a 32% reduction after excluding the Fe^0 content change effect. This indicated that $Ca(OH)_2$ shell coating can partially eliminated particle-particle or cluster-cluster magnetic attraction force to enhance the dispersion stability and resultantly facilitate the transportation. The dissolution of $Ca(OH)_2$ shell was greatly dependent on the pH value of the background water environment. The pH gradient change resulted from the $Ca(OH)_2$ shell dissolution along mZVI particle transport was illustrated by a conceptual model.

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1. Introduction

Micro- and nano- zero valent iron (ZVI) are well known as a promising application for in-situ remediation of recalcitrant organic contaminant and heavy metals owing to their high specific surface area and the resultant high reactivity [1–5]. However, ZVI was frequently found to clog around the injection point and be oxidized quickly by contacting with water and oxygen in early field demonstrations [6–9]. For typical micro- ZVI (mZVI) and nano-ZVI (nZVI) particles, whether be aged or not, a core/shell structure was found to have a Fe^0 core and an iron oxide shell with varied composition depending on the aging time, possibly including Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3 and α-FeOOH phases [10,11]. Fe^0 core was demonstrated to own strong ferromagnetization potential and part of the shell composition such as Fe_3O_4 and γ-Fe_2O_3 are also magnetic [12,13]. The rapid aggregation of ZVI was well substantiated to mainly result from magnetic attraction between particles due to their intrinsic magnetic moments [13]. The formation of aggregates instantly leading to the pore plugging during transport in porous media consequently made a poor performance of ZVI for in-situ remediation.

Developing a coating layer on ZVI surface was well studied to prevent the aggregation and/or to protect the reactivity of ZVI particles. Polymer adsorption was demonstrated to be beneficial for mobility enhancement due to increased inter-particle electrostatic repulsion force [14–15], but without providing the protection of reactivity [16]. A class of solid supports composited with nZVI was developed to stabilize and deliver nZVI into porous media, such as silica-supported nZVI and C-Fe composite [17–20]. These solid supports have the potential to reserve the reactive Fe^0 inside the composite and prevent iron particle from agglomeration by shielding the dipolar interaction. However, the release of encapsulated reactive iron from the stable shell coating and the cost of application of these methods should be further considered.

One kind of releasable inorganic shell on nZVI surface was developed in our previous study [21]. A simple and direct method to form a shell on a core particle can be normally come to heterogeneous nucleation process. The embryos of shell material are directly deposited onto the core surface and continue the formation of nuclei and growth on its own surface, instead of forming new nuclei in the bulk phase [22]. A slow nucleation rate favors the formation of a uniform shell [22–24]. In our previous study, a thin and amorphous calcium hydroxide shell can be observed on the surface of commercial nZVI particle. The shell coating evidently protected the nZVI from the quick corrosion and enhanced the mobility of nZVI particle in water-saturated porous media. However, the heterogeneous nucleation behavior and rate of $Ca(OH)_2$ shell on nZVI surface was very hardly observed in nano-scale dimension. Also, the coating efficiency need to be further improved with more $Ca(OH)_2$ deposited on spherical ZVI surface. The nucleation process could be delicately influenced by the initial nucleus size and the nucleus growth behavior and rate, which would result from the crossing factor including different initial oversaturation degree and oversaturation speed [25].

In this study, we used mZVI as the model particle to observe the inorganic shell formation process by employing the heterogeneous nucleation method. Firstly, the nucleation behaviors of different calcium-containing inorganic salts on mZVI surface were compared to demonstrate the effect of salt solubility on shell formation characteristics. Further, the nucleation of moderately soluble inorganic salt calcium hydroxide on ZVI surface was carefully studied, in that a uniform shell formation was obtained from the thermal nucleation process. The nucleation rate was observed by scanning electron microscopy (SEM) and estimated by the Poisson law [26,27] based on statistical nuclei counting and image analysis. The effects of $Ca(OH)_2$ shell on the magnetic property and corrosion resistance capability of ZVI particles were well substantiated. Based on XDLVO theory, change of the particle-particle interactions after $Ca(OH)_2$ coating was further discussed.

2. Experimental

2.1. Materials and reagents

Carbonyl mZVI, denoted directly as mZVI, was purchased from Nabond (SZ, China) which had a mean diameter of ~1 μm. All mZVI powders for the experiments were wet-ground in ethanol by a ball-milling method in a sealed lead vial. Calcium hydroxide ($Ca(OH)_2$), calcium bicarbonate ($Ca(HCO_3)_2$), calcium chloride ($CaCl_2$) and sodium oxalate ($Na_2C_2O_4$) were purchased from Sigma–Aldich. Stock oversaturated $Ca(OH)_2$ solution was prepared at 4 °C by dispersing 4 g $Ca(OH)_2$ into 1 L fully degassed Milli-Q water (Millipore) in a sealed flask without headspace, followed by overnight dissolution and settling. Organic solvents were also fully degassed before use.

2.2. Nucleation of $CaCO_3$ and CaC_2O_4 on mZVI surface

The solubility of $CaCO_3$ and CaC_2O_4 are about 6.5 mg/L and 6.7 mg/L at 20 °C. Due to the relatively low solubility of the above two calcium-containing salts, the $CaCO_3$ nucleation on mZVI surface was accomplished by the thermal decomposition of $Ca(HCO_3)_2$ under a gradual elevation of temperature to 60 °C. The CaC_2O_4 nucleation was induced in a gradually oversaturated CaC_2O_4 solution by precipitation between $CaCl_2$ and $Na_2C_2O_4$ in a microemulsion system. More details of the above two methods can be found elsewhere [28].

2.3. Nucleation of $Ca(OH)_2$ on mZVI surface

The $Ca(OH)_2$ shell was proposed to coat on the mZVI surface by hydrothermal approach according to the heterogeneous nucleation theory [29]. Clear $Ca(OH)_2$ solution at saturation was obtained from the stock $Ca(OH)_2$ solution (at 4 °C) after filtration through a glass fiber membrane (0.45 μm, Millipore) conducted in vacuum glove box. A well-dispersed mZVI suspension was obtained by dispersing 500 mg mZVI powder into 40 mL clear $Ca(OH)_2$ solution (at 4 °C) followed by ultra-sonication mixing (8891, Cole-Parmer) for 30 min. Temperature of the mZVI–$Ca(OH)_2$ mixture was then gradually elevated from 4 °C to 60 °C, at which shell coating was conducted for up to 270 min. Samples were taken at 15 min, 150 min and 270 min to investigate the nucleation process. The sampled particles, denoted as mZVI/Ca_sampling time, were obtained after several cycles of ethanol washing and quick magnetic separation until a clear supernatant was observed. Peptization by 2-propanol was then conducted to achieve a mono dispersion of the mZVI/Ca suspension [30]. One trial of multi-coating (for four times) of $Ca(OH)_2$ by repeating the above coating procedure, denoted as mZVI/Ca_4 times was engaged for SEM mapping analysis. Control group without mZVI addition under otherwise exactly same experimental condition was set for each trial of experiment.

2.4. Physical properties

The crystalline character was tested by a Bruker AXS D8 X-ray diffraction (XRD) equipment, using Cu K radiation at 40 kV and a step size of 0.04° 2θ at 0.4 s/step. The morphologies of samples were characterized by a scanning electron microscope (Hitachi S-4800 FEG SEM, Japan). The hydrodynamic particle size (D_H) and