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Aging characteristics and reactivity of two types of nanoscale zero-valent iron particles (Fe^{BH} and Fe^{H2}) in nitrate reduction

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HIGHLIGHTS

- ► Fe^{BH} and Fe^{H2} nanoparticles exhibited substantially different aging characteristics.
- ► Fe(0) core of Fe^{BH} was consumed completely during nitrate reduction.
- ► Formation of goethite as an aging product of Fe^{BH} is reported for the first time.
- ► Aging mechanisms for Fe^{BH} and Fe^{H2} nanoparticles in water were proposed.
- ► Nitrate reduction capacity of Fe^{BH} was 35 times higher than that of Fe^{H2}.

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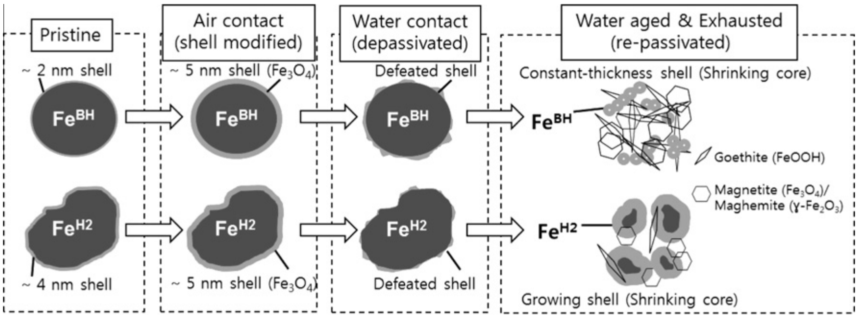
GRAPHICAL ABSTRACT



ABSTRACT

The reactivity towards nitrate and aging characteristics of two types of Fe nanoparticles (Fe^{BH} and Fe^{H2} nanoparticles) were investigated. During shell modification for producing air-stable Fe nanoparticles, the shell layers of Fe^{BH} nanoparticles were passivated more extensively than those of Fe^{H2} nanoparticles were. Column experiments showed that the nitrate-reduction capacity of Fe^{BH} nanoparticles was 35 times higher than that of Fe^{H2} nanoparticles. The Fe(0) core of Fe^{BH} nanoparticles was consumed completely before breakthrough during the nitrate-reduction column experiments, which indicates that the thickness of Fe^{BH} nanoparticles' shell layers remained constant during aging. The Fe^{H2} nanoparticle surfaces were readily passivated, and subsequently depassivated and reactivated by acid flushing, which indicates that the thickness of Fe^{H2} nanoparticles' shell layers increased during aging. Exhausted nanoparticles were examined to obtain information on equilibrium mineral phases. Magnetite was prevalent among the mineral phases in the exhausted Fe^{BH} nanoparticles, unlike in the case of the Fe^{H2} nanoparticles. The formation of goethite as an aging product of Fe^{BH} nanoparticles is reported for the first time herein. Conceptual aging models for Fe^{BH} and Fe^{H2} nanoparticles are proposed on the basis of current and previous experimental results.

Abbreviations: NZVI, nanoscale zero-valent iron; TCE, trichloroethylene; HRT, hydraulic retention time; XANES, X-ray absorption near-edge structure; XRD, X-ray diffraction; TEM, transmission electron microscopy; PAL, Pohang Accelerator Laboratory; PBDE, polybrominated diphenyl ether; JCPDSs, Joint Committee on Powder Diffraction Standards.

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1. Introduction

Nanoscale zero-valent iron (NZVI) has been of interest as an engineered material for remediation of contaminated soil and groundwater. The reactivity of NZVI in removing halogenated organic compounds and heavy metals was greater than that of microsized zero-valent iron due to the higher specific surface area of NZVI [1–4]. The superior reactivity of NZVI for various contaminants, including conventional (trichloroethylene (TCE), nitrate, heavy metals) and emerging pollutants (perchlorate, (polybrominated diphenyl ethers (PBDEs)), dioxins), was reported in numerous studies [5–11]. However, the structural characteristics and aging mechanisms of NZVI particles and their impacts on the chemical reduction of contaminants still not clearly understood. The understanding of NZVI-based subsurface remediation will be improved by performing investigations on the changes in mineralogical and chemical characteristics of NZVI particles when they are aged in air or water, and on the subsequent effects on the reaction between NZVI particles and contaminants [12–14].

Two types of NZVI – Fe^{BH} and Fe^{H2} – that are synthesized by different methods have been widely used in studies on NZVI. Fe^{BH} nanoparticles, which are prepared by borohydride reduction of ferrous/ferric iron solution, are spherical with particle sizes ranging from 30 to 60 nm and have Fe(0) content greater than 95% [12,15]. On the other hand, Fe^{H2} nanoparticles, which are produced by the reduction of ferric iron oxides by H_2 at high temperature, have irregular shapes with particles sizes ranging between 50 and 70 nm, and an Fe(0) content of about 65% [3,16]. The reactivity of Fe^{BH} nanoparticles was two to three times higher than that of Fe^{H2} nanoparticles in TCE reduction [14].

The core/shell structures of the two different Fe nanoparticles also exhibited different aging characteristics in water. The thickness of the shell layer of Fe^{BH} nanoparticles appeared to remain constant and the Fe(0) core shrank during contaminant reduction [17]. However, Liu and Lowry [18] reported that the thickness of the shell layer of Fe^{H2} nanoparticles increased and the Fe(0) core shrank, and that changes in particle sizes were negligible during the aging process. The current study further investigated the aging characteristics of Fe^{BH} and Fe^{H2} nanoparticles during the batch and column nitrate-reduction processes.

In our previous study, atmospherically stable Fe^{H2} nanoparticles were produced by modifying the shell layers of the nanoparticles by the controlled air contact procedure [19]. Fe^{BH} and Fe^{H2} nanoparticles used in this study were initially modified by this procedure. This initial shell modification gives useful information on shell aging in the atmospheric environment and produces Fe nanoparticles that have the advantage of easy handling.

The objectives of this study were to investigate the core–shell chemistries and the reactivities of Fe^{BH} and Fe^{H2} nanoparticles with modified shells, and their aging characteristics under atmospheric and aquatic environments. Nitrate-reduction experiments were conducted using batch and column reactors, respectively. To achieve near-aging equilibrium conditions for the Fe nanoparticles, the nanoparticles were reacted with nitrate solutions and reactivated with acidic solution until their reduction capacities were compromised. Morphological and mineralogical characteristics of Fe^{BH} and Fe^{H2} nanoparticles in various stages of aging were investigated by TEM (transmission electron microscopy), XRD (X-ray diffraction), and XANES (X-ray absorption near-edge structure) analyses.

2. Experimental

2.1. Chemicals and iron minerals

Fe^{BH} nanoparticles were synthesized in the laboratory by $NaBH_4$ reduction of a ferrous iron ($FeSO_4·7H_2O$) solution, as described by Glavee [12]. Fe^{H2} (RNIP-10DS) nanoparticles were purchased from the Toda Kogyo Corp. The other chemicals used were as follows: trichloroethylene (TCE, 99%, Acros Organics), hexane (99% HPLC grade, J.T. Baker), methanol (99% HPLC grade, J.T. Baker), acetone (99% HPLC grade, J.T. Baker), and ethyl alcohol (99% HPLC grade, J.T. Baker). KNO_3 (99.9%, Sigma–Aldrich) was used to prepare the nitrate solution. Among the iron oxide minerals used as reference materials in the XANES analysis, wüstite (FeO, 97%, Kanto Co.) and magnetite (Fe_3O_4, 98%, Kanto Co.) were purchased, and hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and goethite (α-FeOOH) were synthesized, as done in a previous study [20].

2.2. Modification of shell of Fe^{BH} and Fe^{H2} nanoparticles

Before use, the freshly synthesized Fe^{BH} and as-received Fe^{H2} nanoparticles were washed with acetone and dried in an anaerobic chamber (Bactron 1.5, SHEL Lab, USA). The shell layers of the NZVI particles were then modified by the controlled air contact procedure [19] to produce air-stable NZVI particles that were resistant to rapid aerial oxidation. The pristine NZVI particles dried in the anaerobic chamber generally exhibited extreme pyrophoric characteristics and the surface layers of the NZVI particles turned red when exposed to air because of the formation of iron oxides such as hematite (α-Fe_2O_3). However, the shell-modified Fe^{BH} and Fe^{H2} nanoparticles in this study showed no pyrophoric characteristics and were stable in air.

2.3. Batch and column experiments

Batch degradation experiments were carried out in clear borosilicate glass vials (nominal volume of 100 mL) with a Mininert valve (24 mm, VICI, USA) designed to minimize the intrusion of oxygen. Deionized water was used in all experiments without further deoxygenation. Batch reactors contained 100 mL of water solution with a small headspace of ~5 mL.

To initiate the experiments, 0.32 g or less of the relevant NZVI particles were introduced into the reactors that contained a solution with a NO_3–N concentration of 30 mg L^{-1}. The vials were then placed on an orbital shaker (200 rpm) at room temperature (22.5 ± 1.0 °C). At each sampling, 1 or 2 mL of the aqueous samples were withdrawn using a gas-tight syringe for analyzing the nitrate (NO_3–N) and degradation products (NO_2–N, NH_4–N). To obtain NZVI particles that were exhausted in terms of reduction capacities, aliquots of NO_3–N stock solutions with a concentration of 750 mg L^{-1} were added to the reactors at the end of each cycle of NO_3–N degradation in the anaerobic chamber.

For the column experiments, acrylic column reactors with 12-cm length, 3-cm inner diameter, and a volume of 85 mL were fabricated. Shell-modified Fe^{BH} or Fe^{H2} nanoparticles were used in each column experiment. Each column used for nitrate-reduction experiments was packed with a 70-g mixture of the shell-modified Fe^{BH} or Fe^{H2} nanoparticles and industrial sand (Jumunjin sand, Dongho Mining) with a mass ratio of 1–9. The industrial sand had particle diameters ranging from 0.15 to 1.5 mm, surface roughness ranging from 0.6 to 0.8, and a mean diameter (d_{50}) of 0.4 mm. The drainage and exit parts of the column were designed to have 2-cm sand layers. The column for control experiments was packed with only the industrial sand. The packed columns were washed with two pore volumes of 1% HCl solution prior to experiments.

Nitrate solution with a NO_3–N concentration of 30 mg L^{-1} was continuously supplied to the column reactors without any deoxygenation at a flow rate of 0.1 mL min^{-1}. The porosity of the packed column was 0.423 and the hydraulic retention time (HRT) of the nitrate solution was 6 h. Effluent samples were collected after every two pore volumes of elutions and the samples were acidified with hydrochloric acid (1 + 1 v/v) before analyzing the nitrate (NO_3–N)