

# Aging of Iron Nanoparticles in Water: Effects on Structure and Reactivity

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## Abstract

We studied the aging of Fe<sup>0</sup>-core/oxide-shell nanoparticles in water with a focus on changes in (i) the composition and structure of the particles (by XRD, TEM, XPS, and bulk Fe<sup>0</sup> content), and (ii) the reactivity of the particles (by carbon tetrachloride reaction kinetics, electrochemical corrosion potentials, and H<sub>2</sub> production rates). The results show that nano-Fe<sup>0</sup> becomes more reactive between 0 and ~2 days exposure to water, and then gradually loses reactivity over the next few hundred days. The behavior of unaged nano-Fe<sup>0</sup> in our laboratory experiments may be similar to that in field-scale applications for source-zone treatment due to the short reaction times involved. However, nano-Fe<sup>0</sup> that has been aged in water for >3 days acquires properties that are relatively stable over weeks or even months.

## Introduction

Most nanoparticles that are used in environmental applications are reactive in ways that alter the particle's properties over time. This process is responsible for the apparent aging of these materials and is a primary determinant of their longevity. Aging (or longevity) and transport in aqueous media are among the most important and potentially limiting factors in the use of nano-Fe<sup>0</sup> to reduce contaminants in groundwater remediation. However, while transport of nano-Fe<sup>0</sup> in the subsurface is now receiving a great deal of investigation, few studies have explicitly addressed the issue of aging.

From a priori considerations—and results from the few prior studies that have significant bearing on the aging issue (Liu and Lowry 2006; Sohn et al. 2006)—we anticipate the following fundamental processes will be responsible for nano-Fe<sup>0</sup> aging under environmental conditions: (i) breakdown of the oxide shell by hydration, autoreduction, etc.; (ii) oxidation of the exposed surface coupled with reduction of solutes; and (iii) aggregation of particles and subsequent cementation. Two additional considerations are (iv) potential feedbacks between the above primary effects (e.g., between *i* and *ii*, which alter solution chemistry of the medium, or between *ii-iii*, which are affected by solution chemistry) and (v) the relative timing (i.e., kinetics) of the above primary effects, which vary so widely that some processes are essentially independent of others.

The multiplicity of processes that contribute to aging—combined with uncertainties regarding their relative significance, relative timing, and interactions—makes the pursuit of a complete and balanced understanding of the problem quite challenging. To achieve this goal, we have employed expanded and novel set of complementary characterization methods for both particle structure and reactivity. The scope covers the whole range of aging regimes (concentrated slurry and dilute suspensions, with and without contaminants present), and therefore the results have implications for laboratory and field-scale applications of nano-Fe<sup>0</sup> in any aquatic media.

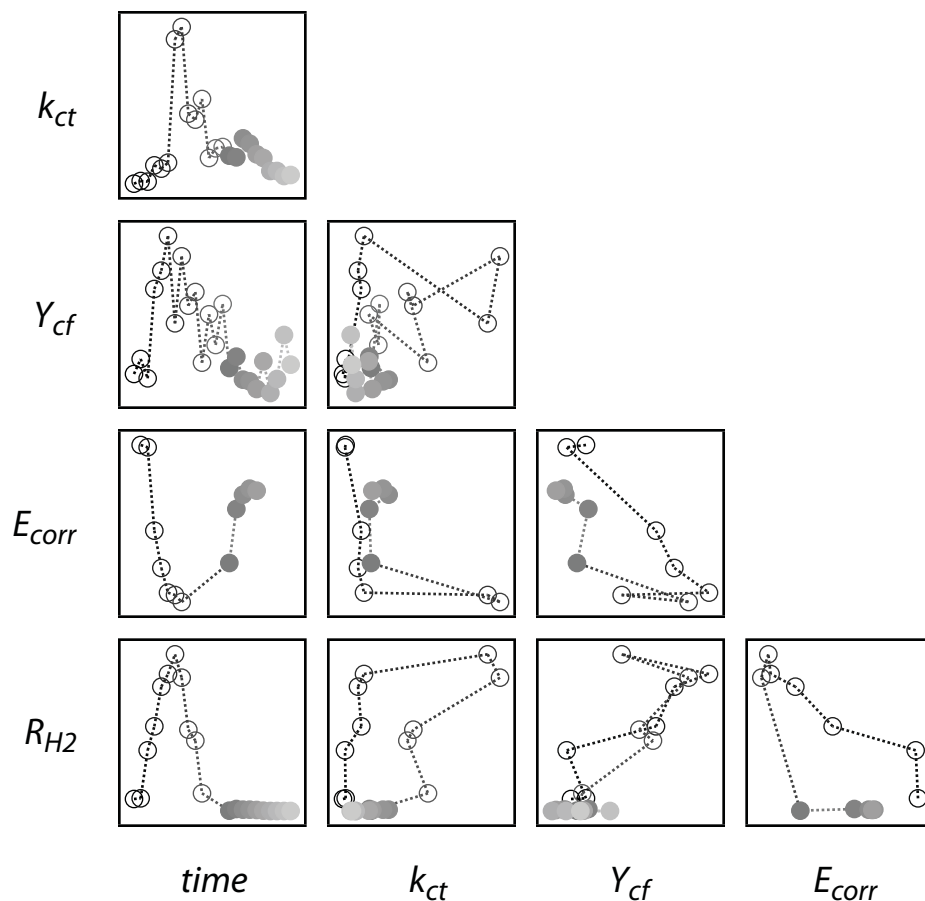
## Methods

We used two preparations of Toda RNIP-10DS (Fe<sup>H2</sup>): one that had never been exposed to water (Fe<sup>H2(D)</sup>) to represent short-term aging effects, and one that had been in an aqueous slurry for approximately a year (Fe<sup>H2(W)</sup>) and therefore reflected long-term aging. For both of these types of materials, we characterized the time dependent changes in (i) the structure of the iron particles, using spectroscopy and microscopy (XPS, XRD and TEM); (ii) the Fe<sup>0</sup>-content and rate of H<sub>2</sub> production by reaction of Fe<sup>0</sup> with H<sub>2</sub>O (using manometry of H<sub>2</sub> pressure); (iii) the kinetics and pathway of reaction (focusing on carbon tetrachloride, CT); and (iv) corrosion potential of the iron-oxide particles using electrochemical experiments. Details of the treatment regimes and analytical methods are given in (Sarathy et al. 2008).

## Results and Discussion

While the Fe<sup>0</sup>-content of the nanoparticles decreased with aging time, as has been reported previously by others (Liu and Lowry 2006; Sohn et al. 2006), most of the other properties show more complex behavior, with a period between 0 and a few days exposure to water where the Fe<sup>H2(D)</sup> becomes more reactive followed by a gradual decline in reactivity of the next few hundred days. In Figure 1, this can be seen in the kinetics of CT reduction, yield of chloroform from CT, corrosion potential, and hydrogen production rate (i.e.,  $k_{CT}$ ,  $Y_{CF}$ ,  $E_{corr}$ , and  $R_{H_2}$ , respectively).

Between  $Y_{CF}$  and  $R_{H_2}$ , nearly all the data fall on a line because both properties peak at the same time (1 day) and the rates of change on the sides of the peaks are similar. In contrast,  $k_{CT}$  and  $R_{H_2}$  gives a correlation with marked hysteresis, even though both of these parameters also peak at 1 day, because the rate of change in  $k_{CT}$  is less than that for  $R_{H_2}$ . The time series are less complete for correlations involving  $E_{corr}$  because aging data were only collected up to 2 days. Nevertheless, the correlations between  $E_{corr}$  and  $k_{CT}$  or  $Y_{CF}$  have similar features to those involving H<sub>2</sub> production rate because the data for Fe<sup>H2(W)</sup> apparently are sufficient to represent the effect of long term aging. In this case, the correlation between  $k_{CT}$  and  $E_{corr}$  shows no hysteresis (and also is nonlinear); whereas the correlation between  $Y_{CF}$  and  $E_{corr}$  shows modest hysteresis. In general, correlations without hysteresis imply a more direct relationship between two variables. Therefore, it appears that  $R_{H_2}$  is better at describing the effect of aging on  $Y_{CF}$ , whereas  $E_{corr}$  comes closer to explaining changes in  $k_{CT}$ . These relationships are mechanistically plausible given that (i)  $E_{corr}$  reflects the particle's potential to donate electrons (Nurmi and Tratnyek 2008), and accepting electrons is generally regarded as determining  $k_{CT}$ , and (ii) H<sub>2</sub> production involves formation of reduced forms of hydrogen (Reardon et al. 2008), and the availability of reduced forms of hydrogen probably control  $Y_{CF}$ .



**Figure 1.** Matrix of scatter plots showing all combinations of four measured properties of  $\text{Fe}^0$  (pseudo first order rate constants for carbon tetrachloride disappearance,  $k_{CT}$ ; yield of chloroform from carbon tetrachloride,  $Y_{CF}$ ; corrosion potential,  $E_{corr}$ ; and the rate of hydrogen production due to reduction of water,  $R_{H_2}$ ) and aging time. Open symbols are for  $\text{Fe}^{\text{H}_2(\text{D})}$  and solid symbols are for  $\text{Fe}^{\text{H}_2(\text{W})}$ . Symbol color scales from black to gray with increasing age. Data adapted from (Sarathy et al. 2008).

## Conclusions

In general, decreasing  $\text{Fe}^0$  content, and concomitant shrinking of the  $\text{Fe}^0$  core, are the primary characteristics of aging nano- $\text{Fe}^0$ . However, while these changes in structure eventually must result in the loss of reactivity, the short- and medium-term effects of aging on two types of reactivity—hydrogen production or contaminant degradation—seem to vary with the type of aging regime and other reaction conditions. These changes in reactivity correlate with evidence for rapid destruction of the original  $\text{Fe}(\text{III})$  oxide film on  $\text{Fe}^{\text{H}_2}$  during immersion and the subsequent formation of a new passivating mixed-valence  $\text{Fe}(\text{II})$ - $\text{Fe}(\text{III})$  oxide shell. These dynamics have implications for in situ remediation applications of nano- $\text{Fe}^0$ , because the oxide shell must mediate reaction of the core with all solution species, including contaminants (Scherer et al. 1998).

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## Conference Questions and Answers

No questions.

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