

The Reaction Specificity of Nano Particles in Solution

Effects of Aging on Structure, Composition, and Reactivity of Nano-Sized Zero-Valent Iron

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Background

Iron oxides form a film on iron metal under aquatic conditions, and the role of this film in mediating the reactivity of iron in the environment has been studied extensively [e.g., 1]. Despite this, much remains to be learned about the overall dynamics of these oxide films because the processes involved are many and coupled.

Two other major areas of research interest are the environmental fate and effects of nanoparticles, and the factors that control branching among contaminant degradation pathways that yield wanted and unwanted products. The foremost example of the former, is the remediation of groundwater contaminants with nano Fe⁰, and a prototypical example of the latter is the formation of harmless products (e.g., CO, CH₄) rather than chloroform from reduction of carbon tetrachloride (CCl₄).

We are participating in a multi-investigator project that encompasses these three areas of research and ranges in approach from batch experimentation to theoretical computation. Previously [2], we have reported a detailed comparison of the structure and reactivity of the two leading types of nano Fe⁰. Throughout our work, we have repeatedly found evidence that aging (controlled and uncontrolled) has profound effects on the structure and reactivity of Fe⁰ nanoparticles [2,3]. Recently, we have begun to focus on the aging process, and some of our recent results are summarized here.

Structure vs. Reactivity

In general, the reduction of solutes by Fe⁰ occurs via either defects in—or charge transfer through—the oxide film [1].

The latter is more favorable for nanoparticles of Fe⁰ because charge transfer (e.g., by tunneling) across a film that is only a few nanometers thick will be much more facile than charge transfer through the thicker oxide films that form on larger grains of Fe⁰.

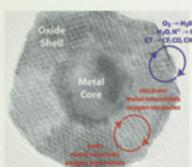
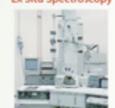


Figure 1. Nanoparticle with Fe⁰ core and iron oxide shell, showing the coupling between processes involved in aging of the shell (autooxidation, etc.) and processes leading to reduction of solutes (oxygen, water, and contaminants). Background image is a transmission electron micrograph (TEM) of an iron nanoparticle produced by sputtering gas aggregation [4].

Approaches to Characterization

Ex Situ Spectroscopy



TEM, XPS, XRD
Core-shell structure
Composition of oxide shell
Passivation, Aging, Reactivity

Batch Reactions



Gas/Liquid Chromatography
Kinetics and products
Process variables
Mass transport

Electrochemistry



Voltammetry, Amperometry
Interfacial kinetics
Electrode potentials
Electrode kinetics

In Situ Spectroscopy



EPR, FTIR
Radical species
Adsorbed species
Reactivity changes

Surface Characterization

Fresh nano Fe⁰ from Toda Kogyo Corp. (Fe⁰) has been thoroughly characterized by us [2,3] and others. The primary particles have a well-defined core-shell structure, with the core being Fe⁰ and the shell being oxide.

XRD (not shown) also indicates the particles are ca.70% Fe⁰ and 30% magnetite.

Both Fe⁰ and iron oxides are observed in the fresh Fe⁰ (red). Upon flash drying, exposure to air, or aging, much of the near-surface Fe⁰ is oxidized (black, green and blue curves).

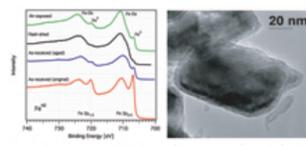


Figure 3. XPS photoemission spectra of the Fe 2p_{1/2} and 2p_{3/2} regions of Fe⁰.

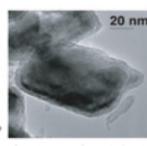


Figure 2. TEM showing the core (Fe⁰) and shell (magnetite) structure of Fe⁰.

Surface Characterization - Aging

Aging, among other factors like pH, ionic strength and redox conditions can affect the composition of the oxide shell. Since even de-oxygenated water is an oxidant with respect to Fe⁰, the oxide thickness increases with exposure to solution.

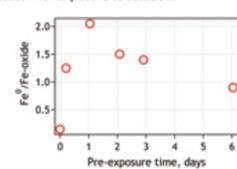


Figure 4. Metal/oxide ratio at the particle surfaces (obtained from XPS) versus aqueous exposure time at pH 6.5. The data suggest initial dissolution of the oxide layer over 1 day followed by passivation.

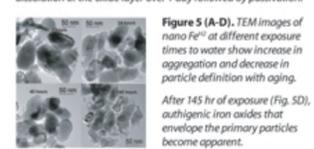
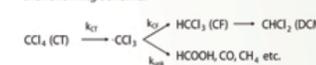


Figure 5 (A-D). TEM images of nano Fe⁰ at different exposure times to water show increase in aggregation and decrease in particle definition with aging. After 145 hr of exposure (Fig. 5D), authigenic iron oxides that envelope the primary particles become apparent.

Batch Reactions

Carbon tetrachloride (CT) is a convenient and relevant molecular probe for aging effects on reactivity. CT reduction is believed to branch at a radical intermediate into two pathways as shown in the following scheme.



The top pathway forms the undesirable products CF and DCM, while the bottom pathway produces completely dechlorinated products that are harmless (formate, etc.).

As we did in [2], the rate of CT reduction is described by pseudo first-order disappearance rate constants (k_{ct}) and the branching between the two product formation pathways is described by the yield of chloroform (Y_{CF}).

Branching between these two pathways (as represented by Y_{CF}) may be influenced by a number of factors. Of particular interest is the availability of H donors, which presumably will favor CF production by H-addition to the $\cdot\text{CCl}_3$ intermediate. Another factor that might effect Y_{CF} is the reduction potential of the electron-donor. Both of these may be influenced by aging of the oxide film.

Electrochemistry - Aging Results

We have measured the open-circuit or corrosion potential (E_{corr}) vs. time using powder disk electrodes of Fe⁰ and, for comparison, (micron-sized) Fisher electrolytic Fe⁰ (Fe⁰). Representative chronopotentiometric data are shown in Fig. 6A, with the corresponding anodic polarization curves in Fig. 6B. The y-axes are aligned for comparison.

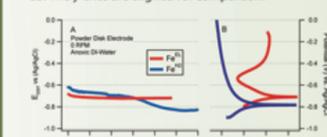


Figure 6A. Chronopotentiograms obtained with micron sized iron (red, Fe⁰) and nano sized iron (blue, Fe⁰). B. Anodic polarization curves for Fe⁰ and Fe⁰ under the same conditions.

Fig. 6A shows that E_{corr} of the Fe⁰ drops rapidly to potentials consistent with the active region in Fig. 6B. E_{corr} of the Fe⁰ drops to similar potentials, then after 17 hours, drops again to a more cathodic potential consistent with the active region for Fe⁰ (Fig. 6B). The second drop in E_{corr} for Fe⁰ is consistent with the aging kinetics suggested by the XPS (Panel 5) and EPR data (Panel 9).

Short Term Aging Effects

To determine how reactivity with solutes is affected by changes in the composition and reactivity of the oxide shell due to aging, batch reactions were carried out with Fe⁰ that was exposed to DI water for various times prior to addition of the probe reactant/solute (e.g., CT).

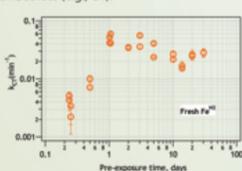


Figure 7. Pseudo-first order disappearance rate constants for CT (k_{ct}) plotted against pre-exposure time (or aging) in days. Data are for "fresh" Fe⁰. Note the log time scale to show the short term effects.

For 1 day or less of pre-exposure time, k_{ct} increases dramatically. This is consistent with the initial dissolution/depassivation of oxide with solution seen with XPS and chronopotentiometry.

EPR Analysis of Aging Effects

Recently, we have begun to explore *in situ* spectroscopic methods for studying the effects of aging on passive film structure and branching among reduction pathways for CT.

EPR was used by reacting Fe⁰ with a spin trap agent (DMPO), which is EPR visible only after it is reduced. When DMPO is reduced by electron transfer, 3 peaks are seen by EPR, whereas additional peaks are observed when DMPO is reduced by hydrogen transfer.

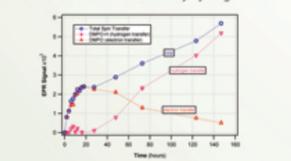


Figure 8. EPR signal intensity for electron transfer, hydrogen transfer and the sum of both plotted versus pre-exposure time in hours.

Electron transfer is the dominant mechanism of DMPO reduction observed during the first 20 hours. From 24 to 60 hours, the contribution of hydrogen transfer increases to equal and then surpasses electron transfer.

Long Term Aging Effects on k_{CT}

Batch experiments with CT were carried out using Fe⁰ that was shipped dry ("fresh") and Fe⁰ that was shipped in an aqueous slurry and then flash-dried. The latter sample was ca. 1 year old, so it was used to represent long term aging of the dry iron.

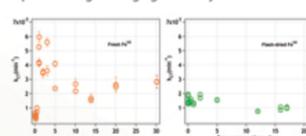


Figure 9. Pseudo first order disappearance constant for CT (k_{ct}) plotted against pre-exposure time of Fe⁰ to deoxygenated water for (A) fresh Fe⁰ and (B) flash-dried Fe⁰.

Fig. 9A shows that k_{ct} for dry Fe⁰ increases sharply for ca. 24 hr, then declines gradually over 30 days of pre-exposure to water. Fig. 9B shows that k_{ct} for flash-dried Fe⁰ starts off just below where dry Fe⁰ left off and then decreases gradually with further pre-exposure to water.

The results in Fig. 9 are reminiscent of those obtained by XPS (Fig. 4), CP (Fig. 6), and EPR (Fig. 8) and are generally consistent with growth of the particles' oxide shell.

Long Term Aging Effects on Y_{CF}

The same series of experiments shown above (Fig. 9) also provided data on how Y_{CF} is affected by long-term aging.

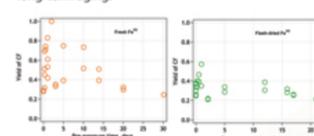


Figure 10. Yield of chloroform from CT (Y_{CF}) plotted against pre-exposure time of Fe⁰ to deoxygenated water for (A) fresh Fe⁰ and (B) flash-dried Fe⁰.

Fig. 10A shows too much scatter between 0 and 10 days preexposure to conclude that there is any effect on Y_{CF} , but the average value of Y_{CF} is well over 0.5. After 10 days, the data for Y_{CF} converges and decreases to ca. 0.2. Fig. 10B shows similar behavior for flash-dried Fe⁰ except the data for short preexposures show less scatter and lower average Fe⁰ (ca. 0.4).

Again the fresh and flash-dried Fe⁰ appear to give a logical progression suggestive of long-term aging, and the aging effect is consistent with growth of the (magnetite) oxide shell, which seems to correlate with low Y_{CF} .

Why Aging is a Concern

The aging of iron nanoparticles under conditions of groundwater remediation (i.e., their "diagenesis") is one of the most fundamental issues in understanding (and predicting) remediation results in the field.

Aging occurs throughout the lifetime of nanoparticles, from their original production to ultimate dissipation. Throughout this timeline, the conditions will vary and this will greatly affect the rates and processes of particle aging.

Some practical implications of this are illustrated in Fig. 11. In the two modes of application shown, particle aging will occur under very different circumstances. In A, the conditions will be like that of a conventional PRB, but in B, the conditions will be like that of chemical flooding.

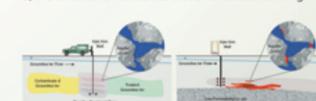


Figure 11. Two approaches to application of nano iron particles for groundwater remediation: (A) a "reactive treatment zone" formed by sequential injection of nano-sized iron to form overlapping zones of particles adsorbed to the grains of native aquifer material; and (B) treatment of non-aqueous phase liquid (DNAPL) contamination by injection of mobile nanoparticles. [5]

Conclusions

- Under environmental conditions, nanoparticles of Fe⁰ are protected by a shell of oxide.
- The structure and composition of the iron oxide shell strongly influences the particles' reactivity, including rates and pathways of reaction with solutes.
- Aging effects on the properties of these particles tend to show relatively rapid changes in the first 24 hours after exposure to water, followed by gradual reversal (over 10's of days) of the changes in some properties.
- XPS shows that the proportion of Fe⁰ near the particle surfaces increases for 24 hr after exposure, suggesting breakdown of the oxide shell, followed by repassivation.

- Chronopotentiometry shows that corrosion potentials converge to values consistent with highly activated Fe⁰.
- EPR experiments suggest that reaction of the spin trap is predominantly due to electron transfer in the first 20 hours, after which hydrogen transfer gains importance.
- Rates of CT reduction increased from 0 to 24 hours of pre-exposure to water, and then decreased gradually, suggesting the same effects seen by XPS and EPR.
- Yield of CF decreases with increasing pre-exposure time possibly due to increasing thickness of the magnetite shell.