NANOSIZE EFFECTS ON THE KINETICS
OF CONTAMINANT REDUCTION BY IRON AND IRON OXIDES

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Introduction
There are many reports suggesting that nano-sized Fe⁰ and FeⅡ oxides exhibit greater reactivity with reducible contaminants than micro-sized particles of the same materials. However, most of these reports are preliminary in that they leave a host of potentially significant (and often challenging) material or process variables either uncontrolled or unresolved. In particular, many studies do not clearly distinguish between mass-normalized and surface-area-normalized rate constants, or do not use robust methods for calculating the latter from the former. Furthermore, secondary factors such as pH can influence comparisons between types of iron because different types of iron can produce different solution pH's and solution pH affects contaminant reduction rates. To take such factors into account when making generalizations about relative reaction rates – without a mechanistic kinetic model more detailed than any that is current available for this system – an alternative approach is needed. Here we explore the use of a graphical tool for assessing relative rates of reactions occurring on particle surfaces.

The format that we have found to be particularly useful is a log-log plot of surface area normalized rate constants ($k_{SA}$, L m⁻² hr⁻¹) vs. mass normalized rate constants ($k_M$, L g⁻¹ hr⁻¹). The data for such plots are calculated from the simple relationship:
\[ k_{\text{obs}} = k_M \rho_M = k_{\text{SA}} a_s \rho_M = k_{\text{SA}} \rho_{\text{SA}} \]  

where \( k_{\text{obs}} \) is the pseudo first order rate constant (hr\(^{-1}\)), \( \rho_M \) is the concentration of particles by mass (g L\(^{-1}\)), \( \rho_{\text{SA}} \) is the concentration of particles by surface area (m\(^2\) L\(^{-1}\)), and \( a_s \) is the specific surface area of the particles (m\(^2\) g\(^{-1}\)). From eq. 1, it is apparent that \[ k_{\text{SA}} = k_M / a_s, \] and therefore:

\[ \log k_{\text{SA}} = \log k_M - \log a_s \]  

Equation 2 defines the disposition of data on \( \log k_{\text{SA}} \) vs. \( \log k_M \) plots and prescribes some of their general features: (i) For a set of experiments on a particular material which is assumed to have a single value of \( a_s \), all the data will fall exactly on a line with slope = 1 and intercept = \( \log a_s \) (ii). Determinate and indeterminate variability in \( k_{\text{obs}} \) will cause the data to be distributed along the diagonal lines defined by eq 2 (iii). Change or uncertainty in \( a_s \) will not alter the distribution of data on the abscissa but will alter its position on the ordinate (i.e. the points will move vertically on the plot).

We first utilized \( \log k_{\text{SA}} \) vs. \( \log k_M \) plots to compare data on the reactivity of three types of Fe\(^0\) with CCl\(_4\) and benzoquinone in Nurmi et al.\(^1\). Since then, we have extended our analysis to include more of our own data for CCl\(_4\), many more types of Fe\(^0\), most of the previously published data for CCl\(_4\) vs. Fe\(^0\) and Fe\(_{\text{II}}\) oxides, and several other contaminants including the major explosives (TNT, RDX, etc.). Inspection of the \( \log k_{\text{SA}} \) vs. \( \log k_M \) plots that we have obtained with these data has provided a number of important insights, some of which are summarized below.

**Results**

A major conclusion that we drew from the \( \log k_{\text{SA}} \) vs. \( \log k_M \) plot for CCl\(_4\) in Nurmi et al.\(^1\) was that nanoparticles have larger \( k_M \)'s than micro-sized iron, but the \( k_{\text{SA}} \)'s are similar. This conclusion was based on only three types of Fe\(^0\): micro-sized electrolytic Fe\(^0\) from Fisher (Fe\(_{\text{EL}}\)), nano-sized Fe\(^0\) made by precipitation from solution with borohydride and obtained from Wei-Xian Zhang (Fe\(_{\text{BH}}\)), and nano-sized Fe\(^0\) made by reduction of Fe\(_{2}\)O\(_3\) with H\(_2\) and obtained from Toda Kogyo Corp. (Fe\(_{\text{H2}}\)). For each type of iron, however, a range of experimental conditions (pH, buffer, etc.) was represented, as was the effect of uncertainty in \( a_s \) for the two types of nano Fe\(^0\). Thus, we anticipated that the conclusions drawn from the figure would be fairly general for CCl\(_4\).

Figure 1 expands our previous analysis to cover almost all available data for CCl\(_4\) by Fe\(^0\), including own our new data for Fe\(_{\text{EL}}\), Fe\(_{\text{BH}}\), Fe\(_{\text{H2}}\), and 5 additional types of nano Fe\(^0\); previously published data for Fe\(_{\text{EL}}\), other types of micro-size high-purity Fe\(^0\) (Fluka, etc.), and various types of low-purity and/or construction-grade Fe\(^0\) (e.g., Peerless and Connelly). The data in Figure 1 show conclusively that \( k_M \) is greater for nano Fe\(^0\) than micro Fe\(^0\) but that there is no nano-size effect on \( k_{\text{SA}} \). In addition, Figure 1 shows that \( k_M \) and \( k_{\text{SA}} \) are both smaller for low-purity iron than high purity iron (nano or micro).

The data in Figure 1 can be further investigated in a number of ways. For example, we are interested in whether there are meaningful differences in reactivity of the various
types of nano Fe$^0$, so we have focused on those data and labeled them in Figure 2. Although most of the data obtained with nano Fe$^0$ from Zhang (Fe$^{BH}$) suggests slightly higher $k_M$ and $k_{SA}$, relative to the data obtained with the sample obtained from Toda (Fe$^{H_2}$), there is a cluster of outliers labeled “Aged BH” that seems to have even higher $k_M$ but lower $k_{SA}$. This material was Fe$^{BH}$ that had been stored (under an anoxic atmosphere) for about 1 year. BET gas adsorption showed that its $a_s$ had increased from ~3 to 35 m$^2$ L$^{-1}$, suggesting that aging restructured the material in a way that gave more surface area that was comparatively less reactive.

**Figure 1.** Log $k_{SA}$ vs. log $k_M$ plot for reduction of CCl$_4$ by Fe$^0$. All available data are included.
Figure 2. Log $k_{SA}$ vs. log $k_M$ plot for reduction of CCl$_4$ by Fe$^0$. Nano Fe$^0$ is shown in red.

This type of plot is also suitable for comparing data from diverse systems – for example, Fe$^0$ vs. Fe$_3$O$_4$ vs. Fe$_2$O$_3$ with adsorbed Fe$^{II}$. The results of such comparisons have implications for some of the larger questions about the reactivity of iron and iron oxides. For example, nanoparticles with an Fe$^0$ core and Fe$_3$O$_4$ shell appear to be more reactive with CCl$_4$ than Fe$_3$O$_4$ or Fe$_2$O$_3$/Fe$^{II}$ under all circumstances (data not shown), suggesting that Fe$^0$ increases the reactivity of the particle even though it may not be in contact with the solution.

Comparisons such as the latter, however, effectively assume that $a_s$ is an adequate (ideally accurate, but minimally unbiased) measure of reactive surface area. This probably is not the case for Fe$^0$ that contains large amounts of oxide or Fe$^{II}$ oxides. Furthermore, it may not be strictly true even for high purity Fe$^0$, as has been noted in a number of studies$^{2,3}$. In principle, most facets of this issue can be represented in log $k_{SA}$ vs. log $k_M$ plots (or variations thereof), but the necessary data are generally not available (e.g. experimentally determined values of the density of reactive sites on the surface). However, log $k_{SA}$ vs. log $k_M$ plot such as those in Figures 1-2 can be used to show that the potential significance of this issue is large for most analyses that involve comparison of rate constants.
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**References**

