Surface Chemistry in Water Treatment: Reactions at the Solid-Liquid Interface

Roger C. Bales

Recent work in surface chemistry gives fresh insight into the rate of many processes in water treatment that are subject to chemical control and offers a clearer framework for predicting behavioral differences resulting from changes in master variables such as pH. Processes of interest in water treatment involving surface-chemical reactions that can be treated in this manner include dissolution, precipitation, coagulation, deposition, and surface catalysis. A common chemical step in these processes is complexation at the solid-liquid interface—attachment of a specific chemical species onto a surface of defined composition.

The notion that a quantitative description of specific chemical interactions can be used to help describe the overall behavior of a process in water treatment has been well developed by researchers in the field but not widely applied. In most cases, the rate-controlling step in a process can be either a chemical reaction at the solid-solution interface or a physical (transport) step such as diffusion of reactants to or from a particle surface. For cases in which a chemical step is rate limiting, and the rate of that chemical step depends on the formation of some surface complex, a thermodynamic (equilibrium) description of the system can be used to examine the effect of changes in composition on the rate of the process.

Background

The importance of specific chemical reactions at the solid-solution interface is apparent in nearly every aspect of drinking water treatment, including precipitation, coagulation, water filtration, adsorption, ion exchange, and chemical oxidation-reduction reactions. With the exception of adsorption onto activated carbon and certain ion exchange reactions, a chemical step will often limit the rate of each of these treatment processes.

In the literature that is related to water treatment processes, only limited recognition is given to the role of differing solution and surface conditions in determining the rate or extent of chemical reactions (adsorption, dissolution, precipitation) at the particle surface and in determining the resulting surface properties (charge, mineral identity, and ability to form chemical bonds). In practice neither the identity nor the stoichiometry of the particle surface is generally taken into consideration. Rather, the particle-water system is treated as a physical system, and strictly empirical relations derived from bench-scale experiments (e.g., jar tests) are used to determine the optimal conditions for water treatment. Partial consideration of the effect of chemical conditions, by way of accounting for stoichiometry, enters in cases such as use of particle counting, particle size distributions, and electrophoretic mobility to arrive at design and operating strategies.

Solid surfaces of primary interest are those on suspended particles—metal oxides, silicates, carbonates, organics, or some combination of these—sand filter grains, or particles formed from addition of chemicals (Table 1). Very little is known about the mineral identity of particles in water or about the chemical behavior of these unknown surfaces. The dominant role of dissolved natural organic matter (NOM) in determining particle surface properties has been shown for suspended and colloidal material in seawater and for selected particles in freshwater having a NOM concentration above a few milligrams per liter. It is thus plausible that chemical properties of many particles in raw water are determined less by the underlying nature of the mineral than by their organic coating. One exception is silica, which adsorbs smaller amounts of NOM. Because of the influence of organic anions, and because silica surfaces carry a negative charge, positively-charged particles are generally not found in natural waters. Particles formed in water treatment, however, may have an inorganic surface or a mixed organic-inorganic surface.

Models of surfaces

Physical picture of surface. At a molecular level, the surface of a hydr(oxide) mineral consists of oxide (or hydroxide) ions present at a density determined by the crystal structure of the mineral, generally from 3 to 12 ions/nm² (0.48 to 2 × 10⁻⁴ mol/cm²). Two possible arrangements are shown in Figure 1. The first is a magnesium hydroxide surface, as might occur on an unweathered chrysotile asbestos fiber. The surface is composed of close-packed hydroxide ions, with a density of 12 ions/nm² (2 × 10⁻⁴ mol/cm²). Each surface hydroxide is coordinated to three underlying magnesium ions and each magnesium is coordinated to six hydroxides—three on the particle surface and three in the oxide layer immediately beneath the surface. Each surface hydroxide is a possible adsorption site for protons, hydroxide ions, or other ions. The second example shows an oxide mineral with less dense packing than magnesium hydroxide. Surface oxides are spaced such that a water...
### TABLE 1
Composition of suspended and colloidal particles

<table>
<thead>
<tr>
<th>Identity</th>
<th>Size $\mu m$</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clays</td>
<td>&lt;2</td>
<td>Aluminum hydroxide, silica, natural organic matter</td>
</tr>
<tr>
<td>Mineral fragments</td>
<td>0.001-10</td>
<td>Hydrous oxides of aluminum, iron, manganese, magnesium; silica; natural organic matter</td>
</tr>
<tr>
<td>Calcite precipitates</td>
<td>&lt;50</td>
<td>Carbonate</td>
</tr>
<tr>
<td>Bacteria, algae</td>
<td>1-10</td>
<td>Organic</td>
</tr>
<tr>
<td>Decaying organic matter</td>
<td>&lt;1</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>Floc</td>
<td>1-20</td>
<td>Hydrous oxide, natural organic matter</td>
</tr>
</tbody>
</table>

### TABLE 2
Surface complexation model

**Equilibrium constants**

\[
K_{\text{int}} = \frac{\{\text{M-OH}\} [\text{H}^+]}{\{\text{M-OH}^+\}} e^{-\varepsilon\Phi/kT} \quad (1)
\]

\[
K_{\text{int}} = \frac{\{\text{M-OH}\} [\text{OH}^-]}{\{\text{M-OH}^+\} [\text{OH}^-]} e^{-\varepsilon\Phi/kT} \quad (2)
\]

\[
K_{\text{L1}} = \frac{\{\text{M-OH}\} [\text{OH}^-]}{\{\text{M-OH}\}^2} e^{-\varepsilon\Phi/kT} \quad (3)
\]

**Surface charge**

\[
\sigma = \sigma_c - [\{\text{M-OH}^+\} - \{\text{M-O}\} + \{\text{M-OC}^+\} - \{\text{M-L}^-\}] \quad (6)
\]

**Material balance**

\[
S_T = \{\text{M-OH}^+\} + \{\text{M-OH}\} + \{\text{M-O}\} + \{\text{M-OC}^+\} + \{\text{M-L}^-\} \quad (7)
\]

**Charge-potential relation**

\[
C = \sigma/\Phi \quad (8)
\]

**Notation**

- $B_i$ = concentration of surface species $i$ (mol/cm$^3$)
- $[B_i]$ = concentration of solution species $i$ (mol/L)
- $e$ = charge on electron (1.6 x 10$^{-19}$ Coul)
- $k$ = Boltzmann constant (1.38 x 10$^{-23}$ J/K)
- $T$ = Temperature (K)
- $\psi$ = surface potential (V)
- $\sigma$ = surface charge (Coul/cm)
- $F$ = Faraday (96,490 Coul/mol)
- $C$ = capacitance, a constant (Coul/V$^{-1}$/cm$^2$)

### TABLE 3
Reported acid-base character of surfaces—constant capacitance model

<table>
<thead>
<tr>
<th>Material</th>
<th>$pK_{a1}^*$</th>
<th>$pK_{a2}^*$</th>
<th>$\Delta pK$</th>
<th>$pH_{pc}$</th>
<th>$S_T$ mm$^{-2}$</th>
<th>Electrolyte</th>
<th>Capacitance /m$^2$/ Farad</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>7.4</td>
<td>10.0</td>
<td>2.6</td>
<td>8.7</td>
<td>1.3</td>
<td>0.1M NaClO$_2$</td>
<td>0.89/2.6</td>
<td>17</td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>6.4</td>
<td>9.25</td>
<td>2.85</td>
<td>7.8</td>
<td>4</td>
<td>0.1M NaClO$_2$</td>
<td>1.8/2.9</td>
<td>18</td>
</tr>
<tr>
<td>am-SiO$_2$</td>
<td>7.5</td>
<td>6.4</td>
<td>1.0</td>
<td>5.9</td>
<td>5</td>
<td>0.1M NaCl</td>
<td>1.25</td>
<td>19</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>5.4</td>
<td>6.4</td>
<td>1.0</td>
<td>5.9</td>
<td>5</td>
<td>0.1M KCl</td>
<td>3.6</td>
<td>20</td>
</tr>
<tr>
<td>Mg$_2$Si$_2$O$_5$ (OH)$_4$</td>
<td>8.0</td>
<td>10.0</td>
<td>2.0</td>
<td>8.9</td>
<td>5</td>
<td>0.1M NaCl</td>
<td>3.6</td>
<td>14</td>
</tr>
</tbody>
</table>

*First number is observed below pH$_{pc}$, second is above pH$_{pc}$: Farad = Coul/V.
*Data of Bêtre and deBruyn.
*Data for >Mg-OH surface sites only.

![Figure 2](image1.png)

**Figure 2.** Possible complexation reactions at an amphoteric, hydrous, metal-oxide surface, involving coordination of protons, ligands, or cations.

![Figure 3](image2.png)

**Figure 3.** Speciation and surface charge for three oxide surfaces at concentrations relevant to natural waters (calculated using model of Table 2 and constants adopted from Table 3; solids concentration = 2 mg/L. $S_T = 1.6$ nm, and specific surface area = 3.85 m$^2$/g).
molecule can be placed between each oxide, over each metal ion. Sharing of protons between bound water molecules and structural oxides gives rise to a hydrogen-bonded network of greater density than that in the magnesium hydroxide example. The number of sites available to bind protons or other ions, however, has generally been found to be from one half to one fourth that suggested by Figure 1. A physical picture of an organic or organic-coated surface may be quite different. For example, adsorbed NOM may not be uniformly distributed but may be patchy, or cover only portions of a mineral surface. At higher NOM concentrations the coverage may be more complete. The binding strength of exchangeable protons (i.e., carboxyl or hydroxyl groups) would also be less uniform than on a hydroxide surface. An organic or organic-coated surface may also have a greater three-dimensional character, resulting in fundamentally different surface associations than occur on a two-dimensional surface (i.e., hydrophobic partitioning). Adsorbed polymeric molecules may adopt either a flat configuration or extend into solution depending on the density of coverage, charge of the surface, and polarity of the molecule.

Surface complexation model. Possible reactions at an amphoteric surface are illustrated in Figure 2. A surface-complexation model for describing the equilibrium adsorption and charge properties of this surface is listed in Table 2. Specifying total concentrations of components in this model, along with equilibrium constants, permits calculation of surface charge and adsorption as a function of pH and solution composition.

Figure 3 gives an example of calculated results for a simple situation, showing surface complexation and charge. Two extremes of behavior are illustrated. Silica has an acidic surface; >Si-OH groups (surface hydroxides) tend to dissociate at natural-water pH values, giving them a negative surface charge. Magnesium hydroxide has a basic surface: the net charge is positive at natural-water pH values due to protonation of >Mg-OH groups. Computer programs for chemical equilibrium calculations, modified to allow surface speciation, are particularly useful for computing surface-chemical equilibria and estimating parameters.

Other models of the particle surface that are more involved than the constant-capacitance model of Table 2 have been developed. Complexation models that specifically account for nonuniformity of binding sites are also in use. For most of the ill-defined or partially-defined systems encountered in water treatment, additional sophistication will not provide a better fit to experimental data.

As a further example, Figure 4 shows the calculated aluminum oxide fractional coverage (organic adsorption) and surface charge resulting from various organic models. Calculations are presented for salicylate, a low-molecular-weight organic acid that has some properties in common with NOM (i.e., -COOH and -OH groups). At the higher coverages, surface charge approaches large negative values, near those for a silica surface.

Kinetics of heterogeneous reactions. Overall reactions at the solid-liquid interface involve the sequential processes of adsorption of reactants, chemical reaction, and desorption of products. Both diffusion and complex formation are involved in adsorption and desorption. Either diffusion or chemical reaction may limit the rate of the overall reaction. Figure 5 illustrates a succession of possible events leading to adsorption of a molecule or ion. Desorption would involve the reverse process. This conceptual model is analogous to that for reactions at single crystal surfaces, the theory behind which evolved from the early terrace-ledge-kink (TLK) model of growing or subliming surfaces.

The overall rate for a reaction involving surface species can be expressed by Eq 9 of Table 4. Rates for heterogeneous reactions are properly referred to per unit of reactive surface area, or preferably, per unit active site. The number of surface sites is not known with as much certainty as is the unit surface area, and most recent investigations report rates per unit surface area of solid.

For processes involving a sequence of reversible reactions, the rates of which can be formulated from transition-state theory, the overall rate can be expressed as a function of the free-energy change of the system (Eq 10). The affinity A is equal to the negative of the free-energy change for the reaction (-ΔG) and is equal to the sum of the affinities of the sequential reactions (ΣΔA).

Often, a single slow step within the sequence will determine the rate of overall reaction. In that case,  = / for k ≠ j. Formulating j from transition-state theory as the rate of decay of an activated complex gives Eq 11. Writing Eq 11 in terms of the activated-complex precursors, the species that react to form the activated complex in step j, gives Eq 12.

Far from equilibrium A is large and the exponential term is small; the rate is then independent of the affinity or overall free-energy change (Eq 13). Near equilibrium A is small, and a series expansion of the exponential term (truncated after first term) gives Eq 14, in which the rate is directly proportional to the affinity.

Possible activated-complex precursors for reaction of interest include adsorbed protons, cations, or ligands (i.e., species of Figure 2). The concentrations of the species postulated provide the q terms in Eq 12. Writing the rate expression in terms of an observed constant, and assuming that a single species is the precursor, gives Eq 15.

Applications of surface-chemical models

Colloid stability and coagulation. Current models of coagulation and filtration separate these processes into two steps; one is a purely physical step (particle transport) and the other is a combination of physical and chemical steps (adsorption). In a surface-chemical framework, this second combination physical-chemical step is analogous to other processes—dissolution, nucleation, and surface catalysis—noted previously.

The stability of colloidal dispersions—the degree to which colloids will stick together or adhere to other surfaces—depends on the ability of the surfaces to approach each other and form physical and chemical bonds. Where interactions are dominated by the adsorption of potential-determining ions, stability can be calculated using a surface-complexation model and appropriate assumptions about particle geometry.

Table 5 lists equations used to calculate colloidal stability for the case of spheres approaching because of Brownian diffusion. Only van der Waals and electrostatic forces are considered; hydrodynamic corrections are not included in Eq 16. V (Eq 17) is an energetic...
term, whereas \( W \) (Eq 16) is a kinetic coefficient; both have been applied to relate changes in aggregation rate resulting from particle interaction energies. Equations 19 and 21, together with the equations of Table 2, have been solved numerically to provide a solution for the potential between two flat plates.\(^{30}\) The force of interaction between two flat plates is given by Eq 22, and Eq 23 gives the interaction energy for two flat plates. Equation 24 is the integrated form, for spherical particles at small separation, using Derjaguin's method of approximating two interacting spherical surfaces as a series of flat plates.\(^{32}\)

Figure 6 shows the results of sample calculations for stability ratio using the model of Table 5. It is assumed that \( \text{H}^+ \) is the potential-determining ion and that the background electrolyte is monovalent and noninteracting.

The importance of quantitatively considering purely chemical factors in addition to the theory of the electrical double layer, which embodies essentially physical concepts, when determining colloidal stability was emphasized by researchers in the early 1960s.\(^{31}\) That is, specific chemical interactions between ionizable functional groups at the surface of colloids (e.g., carboxyl and hydroxyl groups of natural organic matter) and solution species (typically polyvalent metal ions and polynuclear complexes) may determine colloidal stability to a greater extent than does purely electrostatic counter-ion adsorption. In the model of Table 5, the effect of simple double-layer compression, or counter-ion adsorption, is reflected in \( s \), whereas specific chemical interactions are treated in the surface-complexation models.

In principle then, the colloid stability can be estimated from a knowledge of the acid-base and adsorption properties of the solids, together with a specification of the composition of solution. In practice, colloid stability can be estimated from a knowledge of the acid-base and adsorption properties of the solids, together with a specification of the composition of solution. In practice, colloid stability can be estimated from a knowledge of the acid-base and adsorption properties of the solids, together with a specification of the composition of solution. In practice, colloid stability can be estimated from a knowledge of the acid-base and adsorption properties of the solids, together with a specification of the composition of solution.

**Table 4**

<table>
<thead>
<tr>
<th>Kinetics of heterogeneous reactions(^{27,28})</th>
</tr>
</thead>
<tbody>
<tr>
<td>General model</td>
</tr>
<tr>
<td>[ r = \frac{1}{s} \frac{du}{dt} = \frac{v}{s} \frac{dq}{dt} ]</td>
</tr>
<tr>
<td>[ r = \frac{1}{q_j} k_T \frac{A_j}{a_j^{2g}} ]</td>
</tr>
<tr>
<td>Far from equilibrium</td>
</tr>
<tr>
<td>[ r = \frac{1}{q_j} k_T \frac{A_j}{a_j^{2g}} ]</td>
</tr>
<tr>
<td>Near equilibrium</td>
</tr>
<tr>
<td>[ r = \frac{1}{q_j} k_T \frac{A_j}{a_j^{2g}} ]</td>
</tr>
</tbody>
</table>

**Table 6**

<table>
<thead>
<tr>
<th>Dissolution model</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ r = k_j \left( -M-\text{OH}_2 \right)^{\delta} ]</td>
</tr>
<tr>
<td>[ r = k_s \left( -M-\text{OH}_2 \right)^{\delta} ]</td>
</tr>
<tr>
<td>[ r = k_g \left( -M-\text{OH}_2 \right)^{\delta} + k_s \left( -M-\text{OH}_2 \right)^{\delta} ]</td>
</tr>
</tbody>
</table>

**Table 7**

<table>
<thead>
<tr>
<th>Energetics and kinetics of precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equations</td>
</tr>
<tr>
<td>[ \Delta G_R = \Delta G_{\text{bulk}} + \Delta G_{\text{interface}} = -n k_B T \ln \Omega + nA ]</td>
</tr>
<tr>
<td>[ r = k_1 \left( 1 + \frac{1}{\Omega} \right) ]</td>
</tr>
</tbody>
</table>

**Notations**

- \( n \): number of ions precipitated
- \( k_B \): Boltzmann constant
- \( T \): temperature
- \( \Omega \): ratio of ion activity product to equilibrium constant (\( QR^{-1} \))
- \( A \): surface area of the crystal
- \( r \): reaction rate (mol/cm\(^2\)/s)
- \( k_1 \): overall (empirical) rate constant
TABLE 5
Calculations of colloid stability

<table>
<thead>
<tr>
<th>Equations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W = (r_1 + r_2)^2/r_1 + r_2 \exp{(V_T/RT - \frac{\Delta H}{kT})}$</td>
<td>(16)</td>
</tr>
<tr>
<td>$V_T = V_A + V_g$</td>
<td>(17)</td>
</tr>
<tr>
<td>$V_A = \frac{A}{6} \left( \frac{1}{2} \right) \left( r_1 + r_2 \right)^2 \left( 1 + 1.77 \rho \right)$</td>
<td>(18a)</td>
</tr>
<tr>
<td>$V_g = 2A \left( \frac{1}{2} \right) \left( r_1 + r_2 \right)^2 \left( 1 + 1.77 \rho \right) \left( \frac{2.45}{60} + \frac{2.17}{180 \rho^2} + \frac{0.53}{420 \rho^2} \right) \left( \rho &gt; 0.57 \right)$</td>
<td>(18b)</td>
</tr>
<tr>
<td>$\frac{d^2 \phi}{dx^2} = \frac{e_i^2}{kT} \left( \frac{\gamma}{kT} \right)^2 \sinh \left( \frac{\gamma}{kT} \right)$</td>
<td>(19)</td>
</tr>
<tr>
<td>$\alpha = \frac{2 \pi d^2 \phi}{kT} \left( \frac{\gamma}{kT} \right)^2 \sinh \left( \frac{\gamma}{kT} \right)$</td>
<td>(20)</td>
</tr>
<tr>
<td>$\frac{d \phi}{dx} \bigg</td>
<td>_{x=0} = 0$ (boundary condition)</td>
</tr>
<tr>
<td>$F(h) = -\frac{\rho_0}{2} \left( \frac{d \phi}{dx} \right)^2 + 2kT \ln(\cosh \frac{\gamma}{kT}) - 1$</td>
<td>(22)</td>
</tr>
<tr>
<td>$V_T = \int_0^l F(s) , ds$</td>
<td>(23)</td>
</tr>
<tr>
<td>$V_g = \frac{2 \pi r_1 r_2}{r_1 + r_2} \int_0^l V_T(s) , ds$</td>
<td>(24)</td>
</tr>
</tbody>
</table>

**Notation (see also Table 2):**

- $W$: stability ratio, inverse of coagulation efficiency (dimensionless)
- $V_T$: energy of interaction between two charged particles (J)
- $V_A$: energy of attraction, due to van der Waals forces (J)
- $V_g$: energy of repulsion, due to electrostatic forces (J)
- $r_i$: radius of particle $i$ (cm)
- $r$: distance between centers of two approaching particles (cm)
- $h$: $r - r_1 - r_2$ (cm)
- $p$: $2\pi k T$ (dimensionless)
- $\lambda$: London wavelength (cm)
- $\kappa$: double-layer thickness (cm)
- $\varsigma$: charge on electrolyte ion (dimensionless)
- $\varepsilon$: Hamaker constant (J)
- $\varepsilon$: relative dielectric permittivity, equal to 80 for water (dimensionless)
- $\varepsilon_0$: permittivity in a vacuum, (8.854 x 10^{-12} Coul/cm)
- $x$: separation distance for flat double layers (cm)
- $F_T$: energy of interaction between two charged flat plates (J)
- $F(s)$: force exerted by two flat plates separated by distance $s$ (J/cm)

**Particle deposition and filtration.** Equations 16-24 also apply to deposition of a spherical particle onto a flat collector, by letting $r_2$ go to infinity. From these equations, $\phi_i$ and $\phi_g$ (potentials on colloid and collector surfaces) would appear to be of equal importance in determining $V_T$. Deposition rates calculated using the model of Table 2 are sensitive to every parameter affecting the potential energy of interaction, including Hamaker constant, ionic strength, $pK_a$ values, and mechanism of charge development.

**Dissolution.** In many cases of interest in water treatment, dissolution of solids is fast relative to physical processes and relative to the detention time of water in a unit operation. For example, a 0.1-μm calcite particle should dissolve in approximately 1 min at neutral pH in an undersaturated solution. Dissolution is strictly limited by diffusion at the surface. In this case, an equilibrium model can be used to predict the dissolution or precipitation of solids, given thermodynamic data applicable to the system. Approximate relations such as the Langmuir index have been developed for selected cases; more general multicomponent equilibrium models employing computer calculations are also in use.

Dissolution of less soluble minerals may require a significantly long time and be limited by chemical reaction involving coordination of a reacting ion at the solid-liquid interface rather than by diffusion. For example, at neutral pH, dissolution of a 0.1-μm brucite colloid would require about two days, and dissolution of a 0.1-μm chrysotile particle would require approximately 10 years.

Dissolution is a multistep process involving both redistribution of components in space by diffusion and chemical reactions at the solid-liquid interface (Figure 7). Either diffusion (steps A-C, G-I) or chemical reaction (steps D-F, J) may be rate limiting. Steps A-D give an alternate picture of the adsorption process shown in Figure 5. Steps F-I (involving the product) are the reverse of steps A-D (involving reactants). As illustrated, it is assumed that dissolution occurs preferentially (faster) at sites of higher energy.

For a reaction-limited process, it is thought that decay of a suitable activated complex is often the rate-determining step. Prior steps (A-E) and subsequent steps (G-J) are faster than the ratelimiting step (F) and can be described by an equilibrium model. Electron transfer, ion exchange, or complexation reactions can alter the rate of product transfer from kink sites to bulk solution by slowing or speeding a surface-chemical process. A study conducted by Lelterman and Iyer found reasonable agreement between flocculation efficiency observed in laboratory experiments and that calculated using a model incorporating surface complexion.
reaction or by changing the rate of diffusion. For example, protonation of surface \( >\text{M-}\text{OH} \) groups and ligand exchange—formation of suitable intermolecular complexes of the form \( >\text{M-L} \)-weaken adjacent structural metal-oxide bonds and enhance detachment of the \( >\text{M-L} \) or \( >\text{M-OH} \) group. Alternately, specifically-adsorbing solutes may block access to surface sites and prevent proton or ligand attack.

As in the previous set of examples, the model of Table 2 can be used to describe the behavior of surfaces. For a reaction limited by the decay of a suitable activated complex, the dissolution rate can be expressed as a function of the concentration of that complex. If adsorption of a single proton by a sequence like that depicted in Figure 8 is involved, the rate expression (far from equilibrium) would be given by Eq 25 in Table 6. If \( n \) protons are involved, the expression would be Eq 26. If a ligand is also involved in the dissolution, via a parallel reaction, the multiterm expression (Eq 27) follows by analogy.

Figure 9 shows the effect of varying \( \text{pH} \) on the dissolution of one solid. Calculations shown are for a magnesium hydroxide surface on the mineral chrysotile. Data points are from experiments with chrysotile and suggest a value for \( n \) of 0.75. That is, an average of less than one adsorbed proton is needed to bring about release of one \( \text{Mg}^{2+} \) ion from the surface.

Stone has shown that a variety of organic ligands can bind to manganese oxide particles and enhance dissolution.\(^{30}\) In this case, the organic ligand is oxidized, \( \text{Mn} \) is reduced either on or near the surface, and \( \text{Mn}^{(II)} \) is released into solution. It is thus quite plausible that NOM could dissolve colloidal manganese oxide particles, even following water treatment. Photoreduction dissolution of iron has also been shown to be enhanced by organic ligands, with the reaction also being significantly slower in the dark.\(^{31}\)

**Precipitation of solid phases.** The overall process of mineral precipitation is traditionally divided into two stages—nucleation and crystal growth.\(^{32}\) Nucleation involves the growth of submicron nuclei and is accompanied by an increase in free energy, as evidenced by the second term in Eq 28 of Table 7. Homogeneous nucleation occurs by collision, attachment, and dehydration of hydrated metal ions or polymeric hydrolysis products in solution. In heterogeneous nucleation, the nuclei form on the surface of seed crystals. If the solution species readily bind to the seed material, there may be essentially no free-energy increase associated with the process (A will be essentially constant), and crystal growth will dominate. In sediments, because of a very high density of potential seeds, it is likely that nucleation is almost always heterogeneous.\(^{32}\) The same should be true, although to a lesser extent, in water treatment.

Heterogeneous nucleation and subsequent crystal growth can then be viewed as a multistep sequence analogous to that for dissolution illustrated in Figure 7. After being transported to a reactive site on the particle surface (steps A-C), a reactive ion would attach to the reactive site, exchanging water molecules in its coordination sphere for structural hydroxides (in the case of an oxide or hydroxide mineral). A water molecule (or other ligand) would then be released from the surface (steps G-I). The similarity between precipitation and formation of soluble complexes, in terms of changes in metal-ion coordination, is well recognized.

The rate of crystal growth may be limited by transport (steps A, B, or C of Figure 7) or by chemical reaction. For surface-reaction-controlled growth the precipitation rate would be of the form of
Eq 29, in which \( K_i \) is an overall rate constant that depends on activation energy for attachment and the rate at which an activated complex decays to produce (e.g., dehydration). For large supersaturation \( \Delta G_{sp} \) is large, and Eq 29 resembles Eq 25 for dissolution. For small deviation from equilibrium, the rate would be directly proportional to \( \Delta G_{sp} \) as noted in Table 4.

The degree of oversaturation will be important in many cases in water treatment. As \( \Delta G_{sp} \) approaches zero, the exponential term becomes particularly important (for \( 1 \leq \Delta \leq 1.1 \), near saturation). At higher degrees of oversaturation, changes in \( \Delta G_{sp} \), the concentration of active surface sites, will be more important.

An important precipitation process that is encountered in water treatment is adsorption involving oxide surfaces. The adsorption model is described by the following equation:

\[
 \Delta G_{sp} = -RT \ln K_i \]

where \( K_i \) is the equilibrium constant for the adsorption process. The rate of adsorption is given by:

\[
 \frac{d[A]}{dt} = k_i [A] \]

where \( k_i \) is the rate constant for adsorption.

The degree of oversaturation will be important in many cases in water treatment. As \( \Delta G_{sp} \) approaches zero, the exponential term becomes particularly important (for \( 1 \leq \Delta \leq 1.1 \), near saturation). At higher degrees of oversaturation, changes in \( \Delta G_{sp} \), the concentration of active surface sites, will be more important.

An important precipitation process that is encountered in water treatment is adsorption involving oxide surfaces. The adsorption model is described by the following equation:

\[
 \Delta G_{sp} = -RT \ln K_i \]

where \( K_i \) is the equilibrium constant for the adsorption process. The rate of adsorption is given by:

\[
 \frac{d[A]}{dt} = k_i [A] \]

where \( k_i \) is the rate constant for adsorption.

**Conclusions**

A general surface-complexation model, together with an appropriate physical description of the system, enables the role of differing solution and surface conditions in determining the role of extent of a chemical reaction occurring at the particle surface and in determining the resulting surface properties. In a surface-chemical framework, the different reactions noted can be treated in an analogous manner. The rate equations presented are formulated in terms of the surface species involved in the rate-limiting step. This differs from rate equations for surface reactions formulated in terms of solution species in two key ways. First, expressions in terms of surface species give more direct insight into reaction stoichiometry. Second, the rate equations should apply over a wider range of conditions as the effects of surface potential are explicitly accounted for in the equilibrium model.

Primary applications for models of this sort are in interpreting the behavior of well-defined systems and in predicting the sensitivity of the systems to changes in pH, organic-matter concentration, or other control variables. Use of a surface coordination-chemical approach enables directly coupling solute solution composition with surface behavior.

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**References**

Chemical Products and Toxicologic Effects of Disinfection

Benjamin W. Lykins Jr., Wayne E. Kofsky, and Robert G. Miller

Four disinfectants commonly used in US water treatment—chlorine, monochloramine, chlorine dioxide, and ozone—were applied to four parallel streams in a pilot plant in Jefferson Parish, La. Several organics, including surrogate coffins such as total organic carbon and total organic halide, were evaluated to investigate the effects of disinfection and treatment by sand filtration and granular activated carbon (GAC) adsorption. Five toxicologic tests were also conducted to determine the general toxicity and the mutagenic carcinogenic potential of disinfection or GAC adsorption. Results of the study showed that ozonation of clarified sand-filtered water produced fewer organics than the other disinfectants studied. The short-term animal toxicologic studies revealed difficulties in analyzing actual drinking waters for detectable toxic effects.

Many drinking water utilities have recently changed, or are seriously considering changing, from disinfection with chlorine to some alternative disinfectant as a result of regulations to control trihalomethanes. The water utilities that have changed to alternative disinfectants have often done so without evaluating possible chemical impacts or health effects associated with the alternative disinfectant.

One of the river systems that provides the water source for many of these drinking water utilities is the Mississippi. Near its terminus, this river is used as the source of drinking water for Jefferson Parish, La., where an alternative disinfectant pilot plant was constructed to evaluate four parallel streams dosed with four different disinfectants (chlorine, monochloramine, chlorine dioxide, and ozone). These streams, along with a fifth parallel stream without disinfection (control), were evaluated for chemical constituents, microbiological changes, and health effects.

The objectives of this one-year study were to (1) identify chemical and biological contaminants in filtered water prior to disinfection, (2) evaluate chemical by-product formation and biological effects after disinfection, (3) evaluate the effec-

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