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The Coordination Chemistry of the Oxide-Electrolyte Interface; The Dependence of Surface Reactivity (Dissolution, Redox Reactions) on Surface Structure*

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Many heterogeneous processes (formation and dissolution of solid phases, redox and photochemical processes at the solid-water interface are kinetically controlled by a reaction step at the surface (and not by a transport step). Obviously the surface reactivity depends on the surface species and their structural identity, which — in turn — depend on the coordination chemical interactions that occur at the solid water interface. We discuss these processes for oxide-water interfaces in terms of a unifying rate law: $R = kx_a P_j S$, where R is the reaction rate [mol m^{-2} s^{-1}], x_a denotes the mole fraction of the reaction-active surface sites [—], P_j represents the probability to find a specific site in a suitable coordinative arrangement [—], and S is the surface concentration of sites [mol m^{-2}]. Thus, for example, the dependency of the dissolution rate of an oxide mineral on pH can be explained in terms of surface protonation (or surface deprotonation). Similarly the effect of ligands such as oxalate on the dissolution can be accounted for by the concentration of ligand surface complexes. We extend this concept to the reductive dissolution of iron(III) hydroxides, to the oxidation of transition metal ions and other redox- and photorerox-reactions occurring at hydrous oxide surfaces and illustrate the dependence of reaction rates on specifically adsorbed oxidants and reductants.

The cycling of iron as it occurs in natural systems (water, sediments, soils and atmosphere), is used to illustrate the various redox processes, including photocatalyzed reactions, that are mediated by surfaces. Furthermore, we try to illustrate that the concepts of surface reactivity should be applicable to the interpretation of corrosion reactions, specyifically the passivity of iron oxide films.

INTRODUCTION

20 years ago, at the *first Conference (International Summer School) on Solid/Liquid Interfaces*, a preliminary approach to the interfacial coordination chemistry of hydrous oxides was given[1]; the oxide-electrolyte interface was

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considered from a point of view of two paradigmas: 1) the polarized electrode and 2) the aquated oxide surface containing functional OH-groups whose association with H^+, OH^- and metal ions was interpreted in terms of coordination chemistry. And the extent of adsorptive interaction was discussed by mass law expressions in the same way as equilibria in solution. The further development of this concept has been presented in subsequent conferences.[2-5] Originally our interest was motivated by colloid chemistry and the demonstration that specific chemical interactions need to be considered in addition to those of the electric double layer to explain the colloid stability of dispersed systems. Stimulated by Paul Schindler's work[6,7], our attention concentrated on the surface complex formation of metal ions[2,8] and the role of particle interfaces in regulating metal ion concentrations in oceans[6] and lakes.[9-11] The geochemical fate of most trace elements is controlled by the reaction of solute with solid surfaces; simple chemical models for the residence time of reactive elements in oceans[6,16] and in lakes[9,11,17] are based on the partitioning of species between soluble and sedimenting aquatic particles. Significant advances became possible with the quantification of adsorption of anions and weak acids in terms of ligand exchange[3,12,13]; the central ion of a hydrous oxide surface, acting as a Lewis acid, exchanges its structural OH ions against other ligands.

Extensive tabulations on experimentally determined intrinsic surface equilibrium constants reflecting the acid-base characteristic of surface hydroxyl groups and the stability of surface metal complexes, of anion (ligand) complexes and of ternary surface complexes are now available.[14,15] It has been shown[13,14] that such constants can also be estimated from equilibrium constants for corresponding reactions in solution, thus, demonstrating that similar inner-spheric types of complexes are formed on the surface as with their counterparts in solution. It is not sufficient to describe, with the help of the so called site binding models, how reactants (H^+, Me^{n+}, ligands, reductants) are distributed between the surface and the solution. We need to know the structural identity of the surface species. Indeed, spetroscopic evidence[18-22] (electron spin resonance, electron nuclear double resonance spectroscopy, electron spin echo envelope modulation, Fourier trasform infrared, and EXAFS[20,21] (extended X-ray absorption fine structure) have demonstrated the existence of innersphere surface complexes.

More recently[4,5] it was shown that the structural identity of the surface species, *i. e.*, the geometry of the coordination shell of surface sites and of reactants at surfaces, needs to be known for interpreting reaction rates occurring at the oxide-water interface (nucleation, dissolution, redox reactions). Simple rate laws were given illustrating that the rates depend on the concentration (activity) of surface species[4,5]. All kinetic mechanisms of surface controlled processes depend on the coordinative environment of the surface groups.[4,5,23-27] Table I summarizes some factors of the concept of the coordination chemistry of the oxide-water interface and shows some important applications in natural technical systems; some of the kinetic applications discussed here are given in the third column of this table.

TABLE I

Coordination chemistry of the oxide-water interface: concepts and important applications in natural and technical systems

Surface Complex Formation	**Thermodynamic Applications: Distribution of Solutes between Water and Solid Surface**	**Kinetic Applications: Rates depend on Surface Speciation**
Interaction with — H^+, OH^- — Metal ions — Ligands (ligand exchange)	**Binding of Reactive Elements to Aquatic Particles in Natural Systems** — Regulation of metals in soil, sediment, and water systems — Regulation of oxyanions of P, As, Se, Si in water and soil systems — Interaction with phenols carboxylates and humic acids	**Natural Systems** **Dissolution of Oxides and Sicilates** — Weathering of minerals — Proton and ligand promoted dissolution — Reductive dissolution of Fe(III) and Mn(III, IV) oxides
Thermodynamics of Surface Complex Formation — K (mass law constants, corrected for electrostatic effects) — ΔG, ΔH		**Formation of Oxide Phases** — Heterogeneous nucleation — Surface precipitation, crystal growth — Biomineralization
Kinetics of Surface Complex Formation Rates of sorption and desorption	**Binding of Cations, Anions and Weak Acids to Hydrous Oxides in Technical Systems** — Corrosion; passive fims — Processing of ores, flotation — Coagulation, flocculation, filtration — Ceramics, cements — (Photo)electrochemistry (electrodes, oxide electrodes and semiconductors)	**Surface Catalyzed Processes** — (Photo)redox processes — Hydrolysis of esters — Transformations of organic matter by Fe and Mn (photo)redox-cycles — Oxygenation of Fe(II), Mn(II), Cu(I) and V(IV)
Structure of Surface Compounds (Surface Speciation) — Inner-sphere *versus* outer-spere — Monodentate *versus* binuclear — Monodente *versus* bidentate		
Structure of Lattice — Defect sites — Adatoms, kinks, steps, ledges — Lattice statistics		**Technical Systems** — Passive films (corrosion) — Photoredox processes with colloidal semiconductor particles as photocatalyst, e.g. degration of refractory organic substances — Photoelectrochemistry, e.g. photoredox processes at semiconductor electrodes

1.1 Objectives

It is the purpose of this presentation to illustrate the importance of the coordination chemistry of the mineral/water, or specifically the oxide/water interface, in the assessment of surface reactivity, *i.e.* in the prediction of surface controlled reaction rates in the dissolution of minerals or in surface catalyzed redox reactions. The specific objectives of this paper are:

1) To briefly review aspects of coordination chemistry of the mineral water interface and to emphasize that specific chemistry dependent properties (*i.e.* properties dependent on the chemistry and structure of the oxide) need to be considered in addition to the generic properties, common to all oxides (*e.g.* the distribution of counter ions) in characterizing the surface species and their structural identity.

2) To emphasize that by considering surface coordination, lattice statistics and activated complex theory, a unifying kinetic concept can be applied to most surface controlled reactions on dissolution, to surface catalyzed redox reactions, and to many photocatalytic processes.

3) To characterize rates and mechanisms of reductive and of photochemical reductive dissolution of iron(III) hydroxides.

4) To illustrate that in oxygenation reactions of transition metal ions, complex formation with surface hydroxyl groups of minerals produces similar kinetic effects as complex formation with OH^- in solution.

5) To demonstrate that surfaces can mediate the non-biotic geochemical cycling of electrons; specifically to exemplify that the cycling of iron (reduction of Fe(III) oxides to Fe(II) and subsequent reoxidation of Fe(II) to Fe(III) oxides -- of importance in the photic zone of surface waters, in water-sediment and soil systems and in the atmosphere) critically depends on surface controlled processes some of which are influenced by photocatalysis.

6) To propose that certain corrosion reactions, especially some passivity phenomena be explained in terms of specific interactions of H^+, metal ions and ligands with the hydrous oxide passive films.

2. GENERIC AND SPECIFIC ASPECTS OF THE OXIDE-ELECTROLYTE INTERFACE

In the *Gouy-Chapman (Stern) double layer model* the surface is treated as if it were an electrode; the distribution of ions in solution is governed by thermal motion and electrostatic interaction. The (Stern) Gouy-Chapman model has been useful in describing the distribution of charges on the solution side and predicting many phenomena of colloid stability. However, the selectivity of interactions of hydrous oxide surfaces with many solute species can be accounted for only by considering specific chemical interactions at the solid surface. In Figure 1a the *surface complex formation model* is represented schematically. Hydrous surfaces contain functional groups, *e. g.*, hydroxo groups, $>$Me-OH, at the surfaces of oxides of Si, Al and Fe. These surface functional groups represent enormous facilities for the specific adsorption of cations and anions.

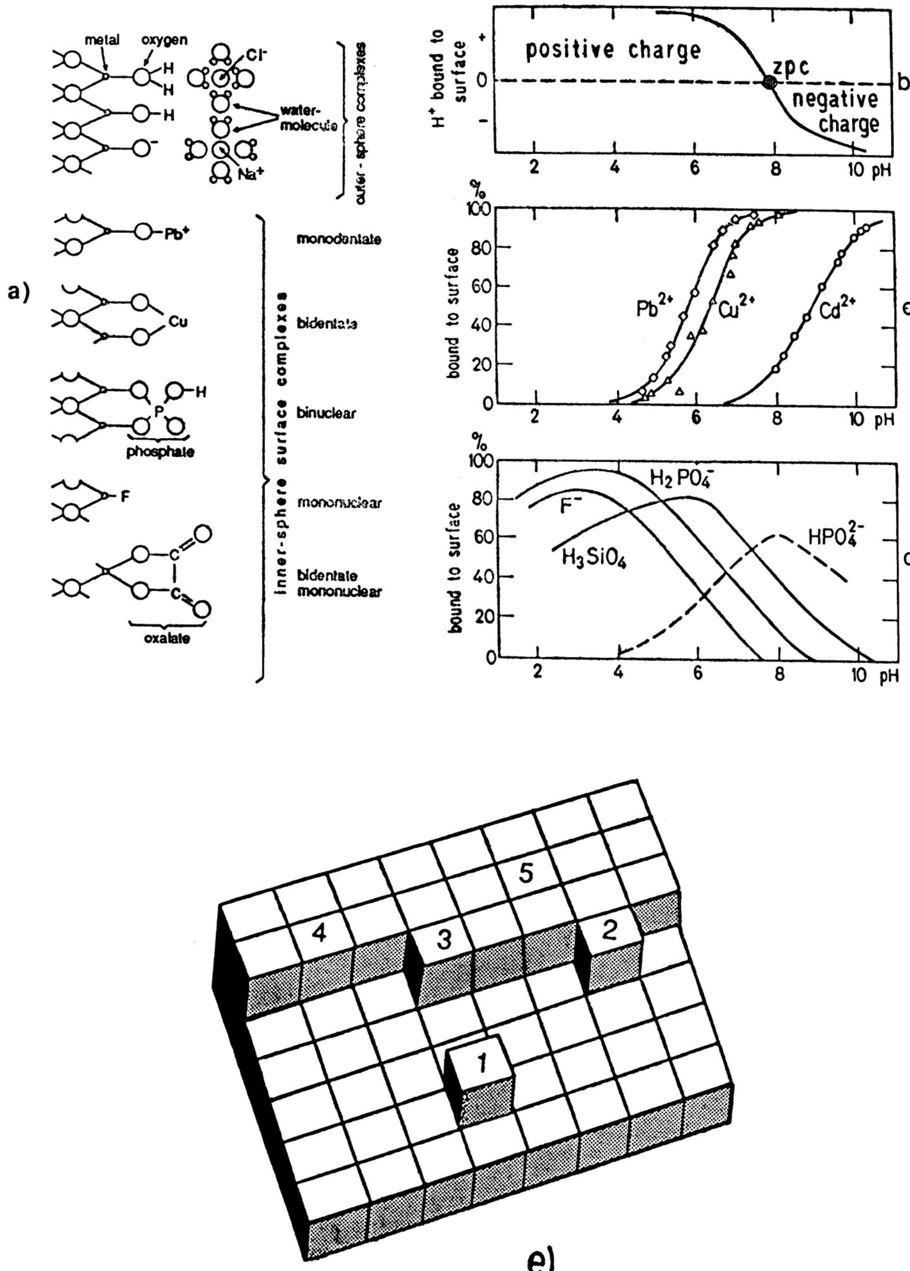


Figure 1. (a) An oxide surface, covered in the presence of water with amphoteric surface hydroxyl groups, $>$M-OH, can be looked at as a polymeric oxyacid or base. The surface OH group has a complex-forming O-donor atom that coordinates with H^+ (b) and metal ions (c). The H^+ bound to the surface can be determined

experimentally by alkalimetric titration of an oxide suspension in a given electrolyte solution; ZPC is the point of zero proton condition (»zero point charge«). The underlying central ion in the surface layer of the oxide acting as a Lewis acid can exchange its structural OH ions against other ligands (anions or weak acids) (d). The extent of surface coordination and its pH dependence can be quantified by mass-action equations and can be explained by considering the affinity of the surface sites for metal ions or ligands and the pH dependence of the activity of surface sites and ligands. The tendency to form surface complexes may be compared with the tendency to form corresponding solute complexes. e) The geometry of a square lattice surface model. The five different surface sites are 1) adatom, 2) ledge, 3) kink, 4) step and 5) face. The five types of octahedral surface complexes are bonded to 1, 2, 3, 4 and 5 neighboring surface links (ligands). From a point of view of surfaca reactivity (*e. g.*, dissolution rate), obviously the various surface sites have different activation energies, the adatomsite (1) is most reactive and the face-site (5) (linked to 5 neighboring sites) is least reactive. The overall dissolution rate is based on the parallel dissolution reactions of all sites, but the overall dissolution kinetics is dictated by the fastest indvidual reaction rate. The latter is essentially given by the product of the first order reaction rate specific for each type of site and the relative concentration of surface sites of each category. Monte Carlo methods, where individual activation energies were assigned to the distinct sites, were able to show that a steady state distribution of the various surface sites can be maintained during the dissolution and that one type of the surface sites essentially accounts for the overall dissolution rate. The model [Wehrli[30]] suggests that the kink-sites (3) — although reacting much slower than ledge and adatom sites, but being present at much higher relative concentrations than these less-linked surface sites — control the overall dissolution rate. (Figure a is modified from Sposito.[29])

The pH dependent charge of a hydrous oxide surface results from proton transfers at the surface. The surface OH groups represent σ-donor groups and are, like their counterparts in solution, able to form complexes with metal ions. The central ion acting as a Lewis acid can exchange its structural OH ion against other ligands such as anions or weak acids (ligand exchange)[3,13]. The concept of surface complex formation has been extensively documented in recent reviews.[14,29] The extent of surface coordination and its pH dependence can be quantified by *mass action equations*. The equilibrium constants are conditional stability constants — at constant temperature, pressure and ionic strength — the values of which can be corrected for electrostatic interaction.[1,14] The nature of surface complexes and the nature of its bonding has far-reaching implications for the mechanism of interfacial processes and their kinetics.

Lyklema[28] has recently proposed to separate adsorption phenomena on hydrous oxides into a *specific* part, determined by the chemical nature of the surface and a generic part, solely determined by the solution side. A simple example is given by Figure 2, illustrating the proton binding at various surfaces[25]. Different oxide surfaces, because of specific chemical interaction, have different affinities for protons. On the other hand if normal behaviour is fulfilled (the surface potential shifts by 59 mV for each pH unit) the pH-axis, corresponding to the potential axis, can be normalized with respect to the point of zero charge (ZPC = point of zero proton condition). If the concentration of the protons bound to the surface of the various oxides is plotted as a function of Δ pH = pH_{ZPC} — pH (Figure 2b), the curves describing the adsorption of protons become congruent; *i. e.* the same protonation curve describes various particle surfaces at constant ionic strength; this illustrates the generic property of the double layer which produces the same surface proton charge on different surfaces. As Lyklema[28] points out, the charge formation is determined from the solution side. On rutile and hematite, and possibly on other oxide surfaces the H^+-dependent surface charge is not only pH-congruent but also temperature-congruent.[28]

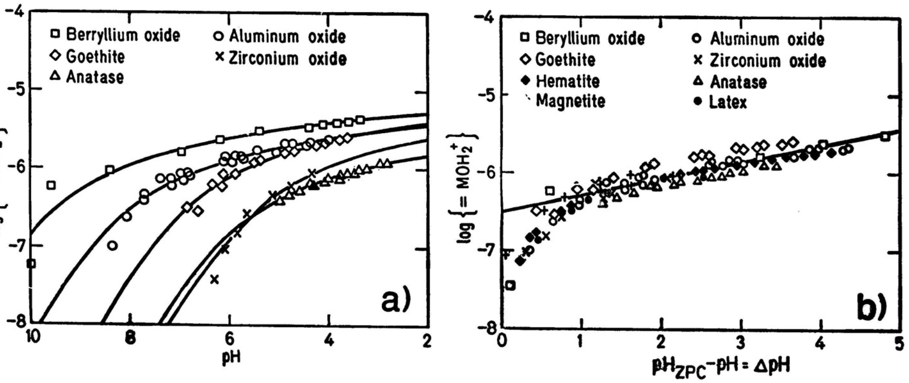


Figure 2. Surface protonation isotherm. Dots represent experimental data from titration curves at ionic strength $I = 0.1$ (Hematite, $I = 0.2$). The concentration of protonated sites $\{\equiv MOH_2{}^+\}$ is given in moles m^{-2}. BET surface data were used to calculate the surface concentrations. (a) Frumkin isotherms. (b) Surface concentration as a function of $pH_{ZPC} - pH = \Delta pH$. The adsorption isotherm at $\Delta pH > 1$ can be interpreted as a Freundlich master isotherm (from Wieland, Wehrli and Stumm[25]).

The specific properties, the chemical interaction with the functional groups of the surface (Figure 1a) reflect the possibilities for the formation of a great diversity of surface complexes. Geometrical considerations and chemical measurements indicate an average surface density of 5 (typical range 2-12) hydroxyls per square nanometer of an oxide mineral. The various surface hydroxyls formed may not be structurally and chemically fully equivalent, but to facilitate the formulation of thermodynamic equilibria one usually considers the chemical reaction of »a« surface hydroxyl group S-OH. These functional groups contain the same donor atoms as found in functional groups of soluble ligands; *e. g.*, the surface hydroxyl group on a hydrous oxide or an organic solid has similar donor properties as the corresponding counterparts in dissolved molecules such as hydroxide ions and carboxylates. We need to consider, however, that the functional groups are bound into a solid framework and their reactivity is in essence, a cooperative property.[29] In a *mean field approach*, a hydrous oxide particle can be treated statistically like a polymeric oxoacid (or base) which tends to undergo protolysis and to coordinate with metal ions and ligands. An inner-sphere complex, as indicated in Figure 1a involves a chemical (often a covalent) bond; no H_2O molecule is interposed between the functional group or the central ion and the bond species.

Outer-sphere surface complexes involve electrostatic binding mechanisms; at least one H_2O molecule is interposed between the complex partners.

The reactivity of the surface (Figure 3), *i. e.* its tendency to dissolve, depends on the type of surface species present; *e. g.* an inner-sphere complex such as that shown for oxalate facilitates the detachment of a central metal ion and enhances the dissolution. This is readily understandable, because the ligands bring negative charge into the coordination sphere of the Lewis acid center and can polarize the critical Me-oxygen lattice bonds, thus enabling the detachment of the central metal ion into solution. Similarly, surface protonation tends to increase the dissolution rate, because it leads to highly polarized interatomic bonds in the immediate proximity of the surface central ions and thus facilitates the detachment of a cationic surface group into the solution. On the other hand, a surface-coordinated metal ion, *e. g.* Cu^{2+} or Al^{3+}, may block a surface group and thus retard dissolution. An outersphere surface complex such as SO_4^{2-} adsorbed to an Al(III) (hydr)oxide has no effect on the dissolution rate. Changes in the oxidation state of surface central ions may have a pronounced effect on the dissolution rate.

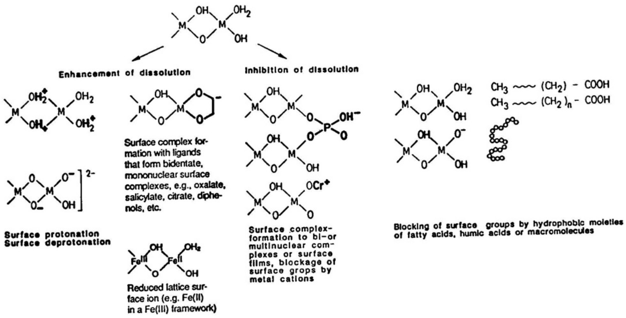


Figure 3. Effect of protonation, complex formation with ligands and metal ions and reduction on dissolution rate. The structures given here are schematic short hand notations to illustrate the principal features (they do not reveal the structural properties nor the coordination numbers of the oxides under consideration; charges given are relative).

The ideas developed here are largely based on the concept of the coordination at the (hydr)oxide interface; the ideas apply equally well to silicates. Somewhat modified concepts for the surface chemistry of carbonate, phosphate, sulfide and disulfide minerals have to be developed.

Energies of interaction of surface functional groups include electrostatic and chemical contributions. The selectivity of interaction of hydrous oxides and silicates with many solute species (metal ions and ligands) can be accounted for only by considering specific interactions.

In a more differentiated picture we have to be aware that several types of OH^- groups may be present at an oxide surface. While the mean field approach permits the formulation of thermodynamic equilibria and the formulation of rate laws, the reactivity of individual functional groups may depend on the specific coordination of the metal site.

A surface metal center, M, of a simple oxide may be characterized as[30]

$$(>\mathrm{MO})_{\sigma 1}\ (>\mathrm{MOH})_{\sigma 2}\ (>\mathrm{MOH_2})_{\sigma 3}\ \mathbf{M}\ (\mathrm{OH})_{\nu 1}\ (\mathrm{H_2O})_{\nu 2}$$

surface ligands terminal ligands

Charges have been omitted. Here (>MOH) denotes a bridging surface OH group which binds the center **M** to the solid, whereas (OH) stands for a terminal hydroxyl group. Terminal groups are coordinated only to one metal center and point towards the liquid. The stoichiometric coefficients σ_Y and ν_Y account for the two different ligand types. The geometry of a square lattice model reflecting in a simplified way an octahedral coordination, is shown in Figure 1e. There are adatoms, ledges, kinks, steps and defect sites. The reaction, *e. g.* the dissolution, is favored at a few localized (active) sites, where the reaction has lower activation energy. The overall surface controlled reaction rate is the sum of the rates of the various types of sites. The reactions occurring at differently active sites are parallel reaction steps occurring at different rates. In parallel reactions, the fast reaction is rate-determining. If the ratio of active sites to total sites remains constant during the reaction, *e. g.* the dissolution, *i. e.*, the reactive sites are continuously regenerated, steady state conditions are maintained and a »mean field« rate law can generalize the dissolution rate.

The fact that for example constant dissolution rates are experimentally obtained over long time periods is in line with this steady state assumption. Further evidence comes from Monte Carlo simulations of the dissolution kinetics. Wehrli[30] has studied the interdependence of surface morphology and the dissolution kinetics of minerals by means of such simulations. This lattice statistical approach was able to model zero order dissolution kinetics and to show the evolution of steady state surface morphologies with constant mol fractions of the different reaction sites. On the molecular scale, the constant roughness of dissolving mineral grains may be regulated by the kinetic process itself.

2.1. Redox Reactions on Oxide Surfaces

Figure 4 illustrates schematically how oxidants and reductants participate in the formation of surface complexes, a prerequisit for surface mediated redox reactions. Furthermore, changes in oxidation state affect the solubility of metal (hydr)oxides. The oxides of transition elements become more soluble upon reduction, other oxides such as Cr_2O_3 or V_2O_3 become more soluble upon oxidation. Reductants or oxidants can enhance the dissolution rate. The reduction of surface metal centers in reducible metal oxides typically leads to easier detachment of the reduced metal ions from the lattice surface. This is readily accounted for by the larger lability of the reduced metal-oxygen bond in comparison to the non-reduced metal oxygen bond; for example, the Madelung energy of the Fe^{II}-O bond in a crystalline lattice is much smaller than that of the Fe^{III}-O bond. Another example is the oxidative dissolution of chromia with MnO_4^-; this reaction involves the adsorption of MnO_4^- at the oxide surface and the subsequent electron transfer and realease of CrO_4^{2-} into solution.[34]

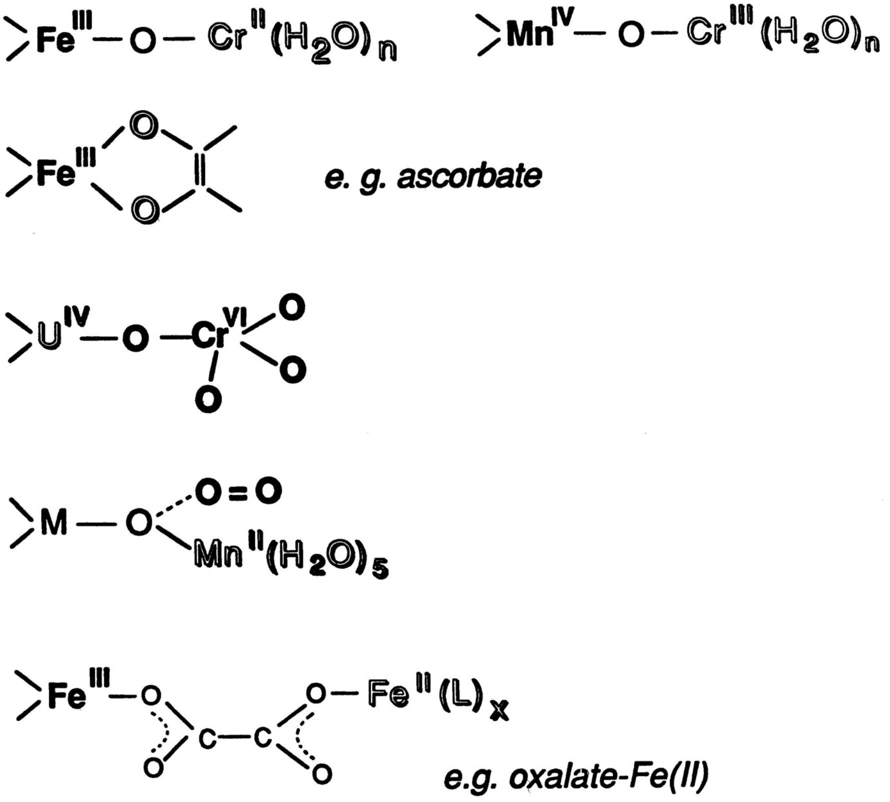


Figure 4. Schematic illustrations on the adsorption of oxidants or reductants directly or through ligand bridges.

Oxidants or reductants can form both, inner-sphere or outer-sphere surface complexes.[31-34] A reductant or oxidant bound inner-spherically to the surface OH-groups behaves entirely differently than one that is in solution or outer-spherically bound. Because the surface site OH-groups act as σ-donor ligands, a Cu(II) ion bound is characterized by a higher electron density at its metal center and its redox potential (with regard to Cu(I) · aq) is lower than if it were in solution. Furthermore, its ligand exchange kinetics (*e. g.* exchange of coordinated water) is faster.[33,34] Fe(II) bound inner-spherically to an oxide mineral, is a much stronger reductant than Fe(II) · aq.

Bridged surface ligands may mediate electron transfer; if the oxidant and the reductant can be coupled by a bridging ligand the electron transfer can be much faster than in the absence of such an electron transferring bridge. Taube[35] has shown such effects in reactions with ternary complexes such as

$$(NH_3)_5CO^{III}\text{-}X\text{-}Cr^{II}$$

where X is a suitable bridging ligand such as Cl^- or oxalate that permits the transfer of electrons and thus, facilitates the reduction of Co(III) by Cr(II).

In the oxidation of U^{IV} by PbO_2, Gordon and Taube[36] have shown with the help of ^{18}O, that the oxygen atoms present in the oxidation product, UO_2^{2+}, originate from the PbO_2, thus indicating that the electron transfer occurred through the surface oxo-bridges $(Pb^{IV}\text{-}O_2)U^{IV} \cdot aq.$) Our discussion on catalytic reductive dissolution of Fe(III) (hydr)oxide will illustrate the kinetic enhancement of a redox reaction by a ligand, that forms a ternary surface complex with the reductant.

Specific binding of transition metal ions such as Cu(II), Fe(III), V(IV), Mn(II) to surface ligands may modify their redox kinetics, *e. g.* the experiments of Tamura *et al.*[32], Wehrli and Stumm[38] and of Davies and Morgan[39] show an increase in the oxidation rate with oxygen if the transition metal ion is adsorbed to an oxide surface. As will be discussed, a specific adsorption to a surface O-group, promotes oxygenation similar as hydrolysis (coordination to a solute hydroxo group), presumably because the hydroxo coordination facilitates the outer-spheric or inner-speric attachment of an O_2 molecule.

2.1.1 Photoredox Reactions

A photoredox reaction is a redox reaction which occurs after electronic excitation of one or several reaction partners. By electronic excitation of a molecule or a solid like a semiconductor a strongly reducing photoelectron and a strongly oxidizing photohole are formed, thus, a compound in an electronically excited state is both, a better oxidant and a better reductant. The ionization potential of an electronically excited species decreases and the electron affinity increases approximately by the excitation energy.

Many natural occurring metal oxides have semiconducting properties. Upon absorption of light with energy equal or higher than the band gap energy of the semiconductor, a band-to-band transition occurs, moving an electron from the filled valence band to the vacant conduction band. In the electrical field caused by the band-bending, photoelectrons move in opposite direction from holes. The charge carriers that reach the surface can undergo redox reactions with adsorbed species at the solid/liquid interface. The thermodynamic requirement for such a redox reaction to occur is that the energy of the highest occupied molecular orbital of the electron donor is less negative than the energy of the valence band edge and that the energy of the lowest unoccupied molecular orbital of the electron acceptor is more negative than the energy of the conduction band edge, Figure 5a. The efficiency of the redox reaction at the solid/liquid interface - which is in competition with the recombination of the photogenerated electron-hole pair - depends on how fast the minority carriers reach the surface of the solid and how fast they are captured through interfacial electron transfer by a thermodynamically appropriate electron donor or acceptor. (For a recent review of photocatalysis on semiconductors, see Pichat and Fox[39]). It is in many cases the surface structure, especially the coordinative interactions taking place at the surface, that determine the efficiency of a photoredox reaction at the solid/liquid interface of a hydrous metal oxide.

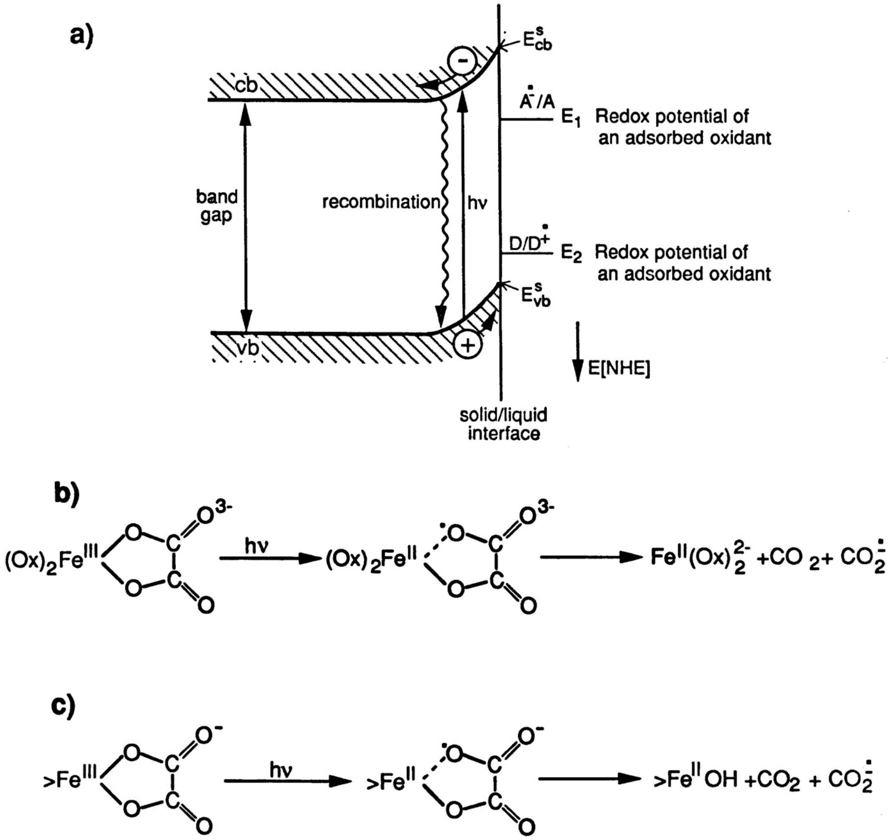


Figure 5. Photochemical redox reactions: a) at the surface of a semiconductor; b) photolysis of a Fe(III) oxalato complex in solution; c) photolysis of a surface Fe(III) oxalato complex.

In photoredox reactions occurring at hydrous metal oxide surfaces also a surface complex formed between a surface metal center and a specifically adsorbed ligand may be the light-absorbing species, responsible for the light-induced electron transfer reaction. Thus, surface complexes may undergo similar photoredox reactions as the corresponding dissolved coordination compounds. Such a mechanism may play a role in the light-induced dissolution of hydrous metal oxide in the presence of a ligand like oxalate Figure 5c. (Waite and Morel[40], Siffert *et al*[41], Sulzberger[27]).

Irrespective of whether the metal oxide itself or a surface complex acts as the primary chromophore, the efficiency of the electron transfer depends on the surface structure. Leland and Bard[42] have reported that the rate constant of photooxidation of oxalate and sulfite varies by about two orders of magnitude with different iron(III) oxides. From their data they concluded that »this appears to be due to differences in crystal and surface structure rather than to differences in surface area, hydrodynamic diameter, or band gap«. Both band gap energy of a metal oxide and surface structure are specific properties.

3. A GENERAL RATE LAW FOR MINERAL DISSOLUTION

Dissolution is a significant link in the global geochemical cycling of elements, in the formation of soils and sediments, and in the regulation of water composition. Biota contributes to the weathering processes globally by providing ligands from exudates and decomposition intermediates (specifically *e. g.* carboxylic acids, hydroxy-carboxylic acids, phenols). Reductive dissolution by reducting ligands is of importance in the redox cycling of Fe and Mn.

We review here briefly the dissolution kinetics discussed in more detail before.[4,5,23-26] The most important reactants participating in the dissolution of a solid mineral are H_2O, H^+, OH^-, ligands, reductants and oxidants (in case of reducible or oxidizable minerals).

$$\text{surface sites} + \text{reactants } (H^+, OH^- \text{ or ligands}) \xrightarrow{\text{fast}} \text{surface species} \qquad (1)$$

$$\text{surface species} \xrightarrow[\text{detachment of Me}]{\text{slow}} \text{Me(aq)} \qquad (2)$$

Although each sequence may consist of a series of smaller reaction steps, the rate law of surface-controlled dissolution is based on the idea (1) that the attachment of reactants to the surface sites is fast and (2) that the subsequent detachment of the metal species from the surface of the crystalline lattice into the solution is slow and thus rate-limiting. In the first sequence, the dissolution reaction is initiated by the surface coordination with H^+, OH^- and ligands which polarize, weaken and break the metal-oxygen bonds in the lattice of the surface. There is much experimental evidence that surface complex formation reactions are usually fast ractions; the order of their reaction rates corresponds to that of the rate constants for the release of a water molecule from the hydrated metal ions in homogeneous metal complex systems. In the case of reductive dissolution, the surface metal center is reduced and hence more weakly bound to the crystal lattice. In a subsequent reaction step to the surface coordination, the metal center (either in is original oxidation state or in reduced form) is detached from the surface. Figure 3 gives a few examples on the surface configurations that enhance or inhibit dissolution. Since reaction (2) is rate-limiting, the rate law of the dissolution reaction will show a dependence on the concentration (activity) of the particular surface species.

$$\text{Dissolution rate} \propto \{\text{surface species}\} \qquad (3a)$$

We reach the same conclusion (Eq. 3a) if we treat the reaction sequence according to the transition state theory. The particular surface species that has formed from the interaction of H^+, OH^- or ligands, reductants or oxidants with surface sites is the precursor of the activated complex.

$$\text{Dissolutin rate} \propto \{\text{precursor of the activated complex}\} \qquad (b)$$

The surface concentration of the particular surface species corresponds to the concentration of the precursor of the activated complex (Eq. 3). This concentration can usually be determined from the knowledge of the number of surface sites and the exent of surface protonation or surface deprotonation or the surface concentration of ligands. Surface protonation or deprotonation can be measured from alkalimetric or acidimetric surface titrations, and ligands bound to the surface sites can be determined analytically from the change in concentration of ligands in solution.

A general rate law on the dissolution of minerals is derived by considering, in addition to the surface coordination chemistry, established models on lattice statistics and activated complex theory:

$$R = kx_a P_j S \tag{4}$$

where R is the dissolution rate [moles $m^{-2}s^{-1}$]; x_a denotes the mole fraction of dissolution active sites [—]; P_j represents the probability to find a specific site in the coordinative arrangement of the precursor complex [—]; S is the concentrationof total surface sites [mol m^{-2}] and k stands for the rate constant [s^{-1}] and is related to the activation energy of conversion of a suitable surface complex (precursor) to an activated surface complex and in turn to the crystal bond energy that has to be broken.

The precursor concentration $C_p{}^s$ corresponds to

$$C_p{}^s = x_a P_j S \tag{5}$$

Thus, the dissolution rate is proportional to the precursor concentration of the activated complex (Eq. 3b).

If one represents the two dimensional surface of a hydrous metal oxide with a chessboard, then each metal ion has maximal four neighbouring oxo- or hydroxo groups that can bound an additional proton. As has been shown by Wieland *et al.*[25] for the case of the acid (proton) promoted dissolution of an oxide, the probability, P_j, of finding a surface metal center that is surrounded by j protonated OH groups is given by the Bernoulli-probability:

$$P_j = \left({n \atop j} \right) x_H{}^j (1-x_H)^{(n-j)} \tag{6}$$

where $\left({n \atop j} \right)$ stands for $\frac{4!}{j!(4-j)!}$ and the exclamation mark stands for the factorial ($4! = 4 \cdot 3 \cdot 2 \cdot 1$); x is the mole fraction of surface sites that are coordinated with j protonated OH groups. In the case of the dissolution, induced by protons, one to four neighbouring groups may be coordinated with an additional proton, thus j = 1-4. The maximum proton density that results from titration experiments is typically 10 times smaller than the crystallographic site density S. As a consequence the mole fraction x_H becomes much smaller than one and equation (6) simplifies to:

$$P_j \propto (x_H)^j \; ; \; P_j \propto (C_H{}^s)^j \tag{7}$$

In other words, the probability to find a metal centar to be surrounded by 1, 2, 3 or 4 excess protons, is proportional to the surface protonation (density of protons) to be first, second, third or fourth power, repectively. Then the rate of proton-promoted dissolution is given by:

$$R = k_H x_a S(x_H)^j \quad (8)$$

For a given hydrous oxide the mole fractions of active surface sites can be considered as constant and included into the rate constant. The rate of the proton-promoted dissolution is then:

$$R_H = k''_H(C_H{}^s)^j \quad (9)$$

where C^s_H is the concentration of surface bound protons in mol m^{-2} (in excess of that at the point of zero charge), $C^s_H = x_H)^1/S$, and k'_H is the rate constant in h^{-1}. It is generally observed that j corresponds to the oxidation number of the central ion of the oxide, *i. e.* j = 4, 3, 2 for SiO_2, δ-Al_2O_3 and BeO.[28,43]

In the ligand promoted dissolution[23] the probability P_j to find a surface site in the form of a surface ligand complex, $>$ML is given by $P^j_\infty \{> ML\} = C_L{}^s$. The same is true for the reductive dissolution[44] (compare Table II).

TABLE II

Rate laws for the dissolution of oxide minerals[1,2]

Reactant	**Rate Law**	**Experimental Rate Law**
1) H^+ (acid)	$R_H = k_H'(x_H)^j S$	$R_H = k''_H(C_H{}^s)^j$
2) OH^-(base)	$R_{OH} = k'_{OH}(x_{OH})^j S$	$R_{OH} = k''_{OH}(C_{OH}{}^s)^j$
3) L (ligands)	$R_L = k'_L x_L S$	$R_L = k''_L C_L{}^s$
4) Re (reductant)	$R_{Re} = k'_{Re} x_{Re} S$	$R_{Re} = k''_{Re} C_{Re}$
5) Ox (oxidant)	$R_{OX} = k'_{OX} x_{OX} S$	$R_{OX} = k''_{OX} C^s{}_{OX}$
6) Re + L	$R_{Re+L} = k'_{Re+L}(x_{Re} x_L)S$	$R_{Re+L} = k''_{Re+L} C^S{}_{Re} C^S{}_L$
7) H_2O	$R_{H_2O} = k_{H_2O}$	

[1] The total rate can usually be expressed as the sum of the individual rate laws, *e.g.*, the pH-dependent rate of dissolution may be expressed as $R_T = R_H + R_{OH} + + R_{H_2O}$; $C_H{}^s, C_{OH}{}^s, C_L{}^s, C_{Re}{}^s, C_{OX}{}^s$, are, respectively, the surface concentrations (mol m^{-2}) of H^+, OH^-, L, reductant and oxidant; the exponent corresponds usually to the valence of the central ion; *e.g.*, j = 2, 3, 4, for BeO, Al_2O_3 and SiO_2, respectively. The mol fractions x_H, x_I *etc.* refer to moles of surface bound protons, ligands *etc.* per moles total surface sites. The surface concentration of a species is related by an adsorption equation (surface complex formation mass law) *cf.* Figure 2b to its solute concentration *e.g.* $c_X{}^S \approx Kc_X{}^a$ (where $a < 1$). Thus, if the rate law is written in terms of solute concentrations (activities) $R = k''C_X{}^a$ the rate shows a dependence on the fractional order of the reactant in solution, C_X.

[2] The rate constants k' have the unit h^{-1}.
The rate constants k'' are experimentaly determined rate constants and include the factors that cannot be determined individually. They have the units $h^{-1} \cdot mol^{-(j-1)} m^{2(j-1)}$.

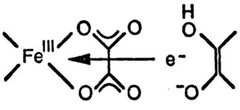
A special case is the reductive dissolution in the presence of a reductant and a surface complex former that does not act as a reductant in the absence of light. It is well known that the combination of a reductant and a complex former is especially efficient for the dissolution of reducible hydrous metal oxides like iron(III) (hydr)oxides. The general rate expression, given in equation (1), can also be applied to this pathway of dissolution. In this case, x_a is the mole fraction of reduced surface sites, and P_j is the probability of finding a reduced surface metal center that is coordinated with a ligand.

3.1. *Case Studies on the Reductive Dissolution, of Iron(III) (Hydr)oxides*

The experiments on the reductive dissolution of iron(III) oxides have been discussed before.[27,33,44-46] We therefore concentrate here on briefly summarizing some of the mechanistic and kinetic features of the various possible pathways illustrating three examples (Figures 6a, 6b and 7). The rate laws are collected in Table II. We interpret the experimental data by implying that all these types of reactions have in common that the dissolution is controlled by the detachment of the reduced iron sites into solution. The concentration of the reduced iron centers at the surface of the solid $\{>Fe(II)\}$ is in turn related to the activity of the dissolution active species on the surface, *i. e.* the concentration of the ascorbate surface complex $\{>Fe^{III}HA\}$, (Figure 6a), the ternary surface complex $\{>Fe^{III}\text{-}C_2O_4\text{-}Fe^{II}\}$, (Figure 6b) and the oxalate-Fe(III) surface complex $\{>Fe^{III}C_2O_4\}$, (Figure 7) respectively.

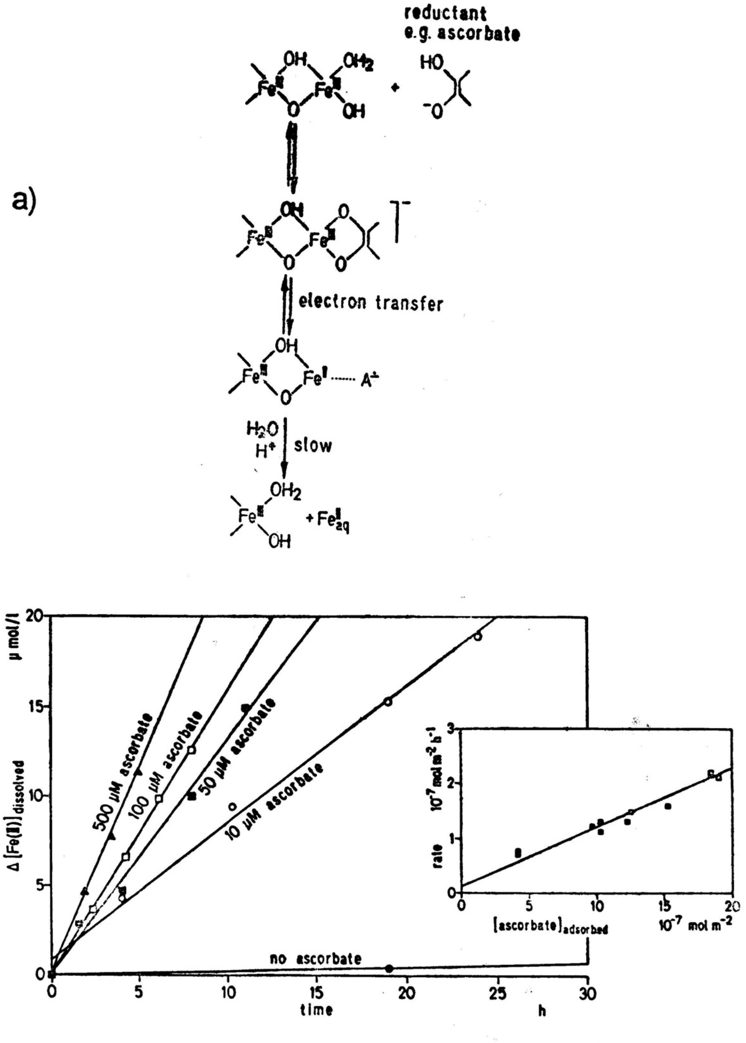
3.1.1. *Reductive Dissolution in the Presence of Ascorbate and Oxalate*

It is well known that a combination of a complex former and a reductant (*e. g.* dihionite-citrate, oxalate-ascorbate) is very efficient in promoting fast dissolution of iron(III) (hydr)oxides. As our data show the oxalate promoted reductive dissolution (with ascorbate) is four times faster than the dissolution due to ascorbate alone despite of the fact that oxalate competitively displaces part of the ascorbate from the surface. We believe that a complex former, such as oxalate, by forming surface complexes, enhances the detachment of the Fe(II) from the solid surface into solution. Oxalate may specifically become bound to the iron oxide surface — at least partially subsequent to the electron transfer with ascorbate. Alternatively a direct electron transfer may occur from ascorbate to a surface iron(III) oxalate complex through the conjugated carbon-bonding system of oxalate acting as an electron bridge:



The rate is linearly dependent on the product of the surface concentration of ascorbate and the surface concentration of oxalate, Figure 8.

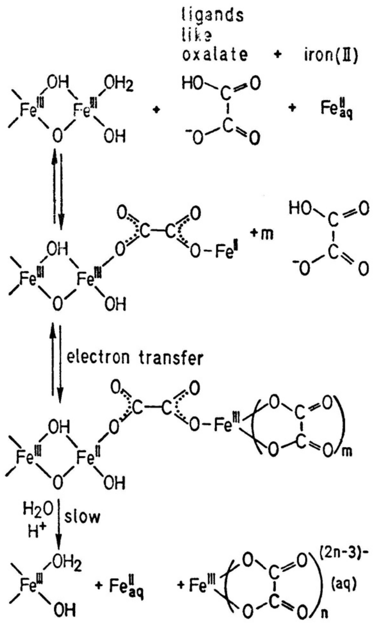
At a given oxalate concentration, the rate of the reductive dissolution, enhanced by oxalate, is linearly dependent on the surface concentration of ascorbate, Figure 6a.[44] The fact that oxalate increases the rate of reductive dissolution, despite of the smaller surface concentration of the reductant, shows that detachment of Fe(II), rather than electron transfer, is most likely the rate determining step in the overall reaction. Other complex formers such as a)

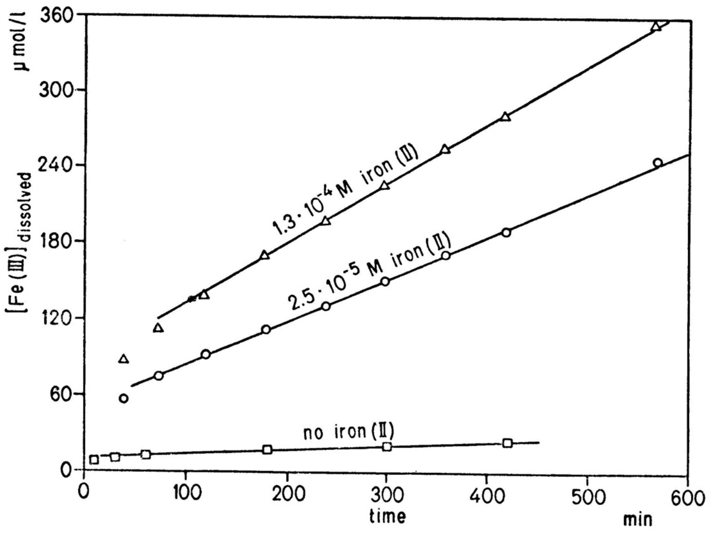


$$R \propto \{>Fe^{III}HA\}$$

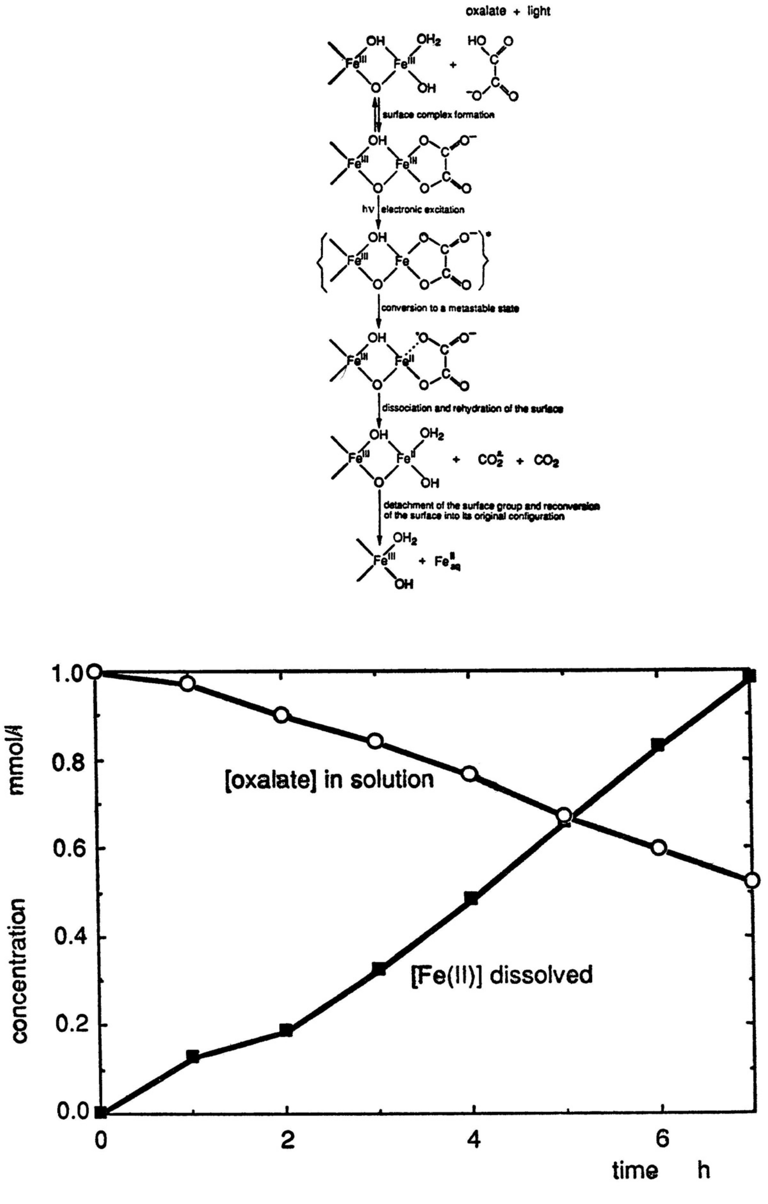
Figure 6. Schematic representation of pathways for the dissolution of α-Fe_2O_3 (hematite) (a) by reductants such as ascorbate that can form surface complexes and transfer electrons inner-spherically; (b) catalytic dissolution of iron(III) (hydr) oxides by Fe^{II} in the presence of a complex former. Below each pathway are some representative experimental results. a) The different ascorbate concentrations corespond to initial concentrations, pH = 3; 0.5 g/l hematite. Fe^{II}-catalyzed dissolution of hematite in the presence of oxalate at pH = 3. Total oxalate concentration: 3.3 mmol/l, 0.5 g/l hematite. The indicated concentrations correspond to the total concentration of added ferrous iron.

b)





$$R\ \alpha\ \{>\mathrm{Fe^{III}}\text{-}\mathrm{C_2O_4}\text{-}\mathrm{Fe^{II}}\}$$



$R \propto \{Fe^{III}C_2O_4\}$

Figure 7. Schematic representation of the photochemical reductive dissolution of α-Fe_2O_3 (hematite) by oxalate in the presence of light, and representative experimental result. Experimental conditions: 0.5 g/l hematite, initial oxalate concentration; 1 mmol l^{-1}; pH = 3; $I_o \cong 4$ kW/m^2; white light from a high pressure xenon lamp after passing a pyrex glass filter, irradiated surface $\cong$ 50 cm^2; reaction volume: 250 ml; nitrogen atmosphere; from Siffert and Sulzberger, in preparation[41].

EDTA show the same effect as oxalate in enhancing the reductive dissolution.[44]

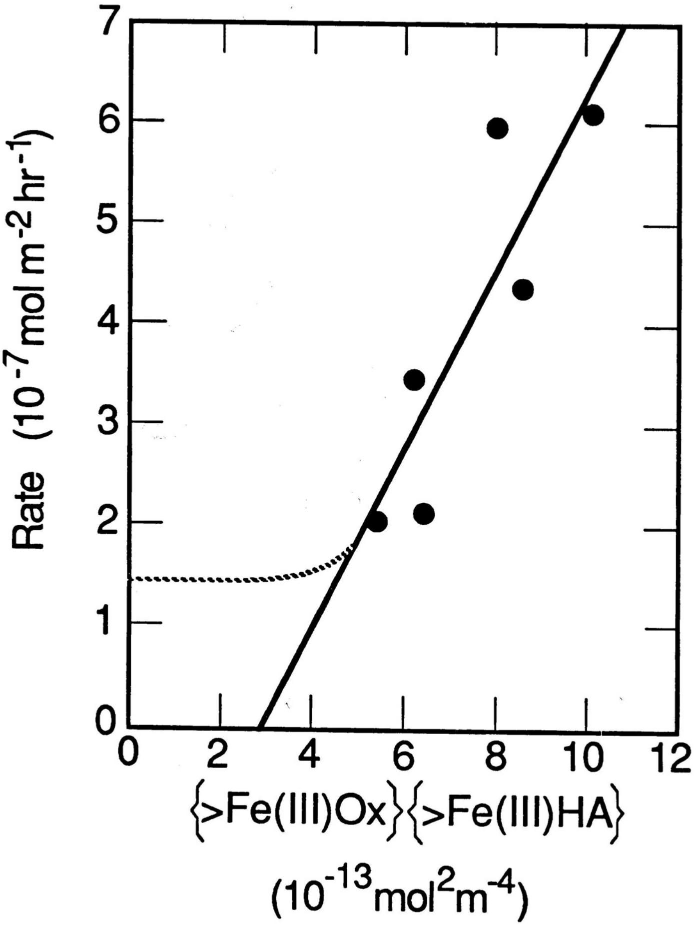
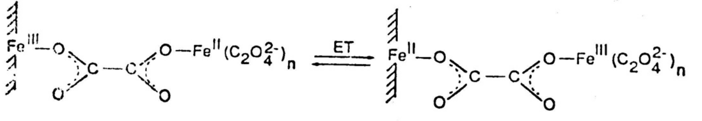


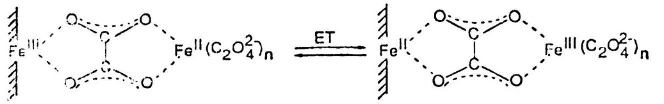
Figure 8. Rate of reductive dissolution of hematite by a reductant and a complex former. The reaction rate can be interpreted as a function of the product of the surface concentrations of ascorbate and oxalate; from Banwart *et al.*[44]

3.1.2 Reductive Dissolution in the Presence of Fe(II) and Oxalate

Although oxalate alone dissolves iron(III) (hydr)oxides at a considerable rate, in the presence of small concentrations of iron(II) and the same concentrations of oxalate, the dissolution rate is increased remarkably. The combination of ferrous iron and oxalate is a special case of a dissolution with a reductant and a complex former. Fe(II) complexes are better reductants than Fe^{2+}. The enhancement of the dissolution by Fe(II) in the presence of a suitable ligand, however, must be explained kinetically in terms of an electron transfer through a bridging ligand:



(10)



(11)

The surface iron(II) thus formed is detached from the surface of the oxide as the rate determining step,[46] Figure 6b. As also illustrated in Figure 6b, there is no net reduction although the reduction of the surface iron(III) has a strong effect on the kinetics of the reaction, thus, indicating that Fe(II) acts as a catalyst for the dissolution of iron(III) (hydr)oxides. At a given oxalate concentration the rate of this Fe(II) catalyzed dissolution is first order with respect to the surface concentration of the adsorbed iron(II).[46] The interpretation given here is a variation of that given by Blesa *et al.*[47].

3.1.3. Photochemical Reductive Dissolution in the Presence of Oxalate

Figure 7 (top) shows the various elementary steps involed in the surface photoredox reaction, leading to dissolution of hematite. Electron transfer occurs *via* an electronically excited state (indicated with a star) which is either a ligand to metal charge transfer transition of the surface complex and/or $Fe^{III} \leftarrow O^{-II}$ charge transfer transition of hematite. In a ligand to metal charge transfer transition, electron densitiy is shifted from the ligand to the metal (Fe^{III}) or from the lattice O^{-II} to the Fe^{III} central ion, respectively, thus leading to a reduced surface iron and the oxidized ligand. In analogy to the mechanism proposed for the photolysis of dissolved trioxalato ferric iron, the oxalate radical, or after decarboxylation the CO_2^- radical, may undergo further redox reactions, such that two surface iron(II) and two CO_2 may theoretically be formed per absorbed photon. However, the quantum yield of this surface redox reaction is less than two[41] because of loss reactions such as thermal deactivation from the excited state. For the sake of simplicity these thermal reactions of the oxalate radical are omitted in Figure 7. The reduced surface site is rehydrated prior to being detached from the surface. After detachment of the surface group, the surface of hematite is reconverted into its original configuration, hence, the surface concentration of active sites and of adsorbed oxalate does not change throughout the experiment

Under nitrogen, the photochemical reductive dissolution of hematite in the presence of oxalate occurs according to the following stoichiometry, Figure 7 (middle):

$$\alpha\text{-}Fe_2O_3 + C_2O_4^{2-}(\text{ads.}) + 6\,H^+ \xrightarrow[N_2]{h\nu} 2\,Fe^{2+} + 2\,CO_2 + 3\,H_2O \qquad (12)$$

The rate of this photochemical reductive dissolution depends upon the surface concentration of the adsorbed oxalate, Figure 7 (bottom). The rate constant, k_{hv}, depends on the incident light intensity and on several variables that can be taken to be constant for a given reacting species (such as the wavelengths integrated extinction coefficents of the primary chromophore, the quantum efficiency of surface iron(II) formation, and the efficiency of detachment of reduced surface iron from crystal lattice[27]).

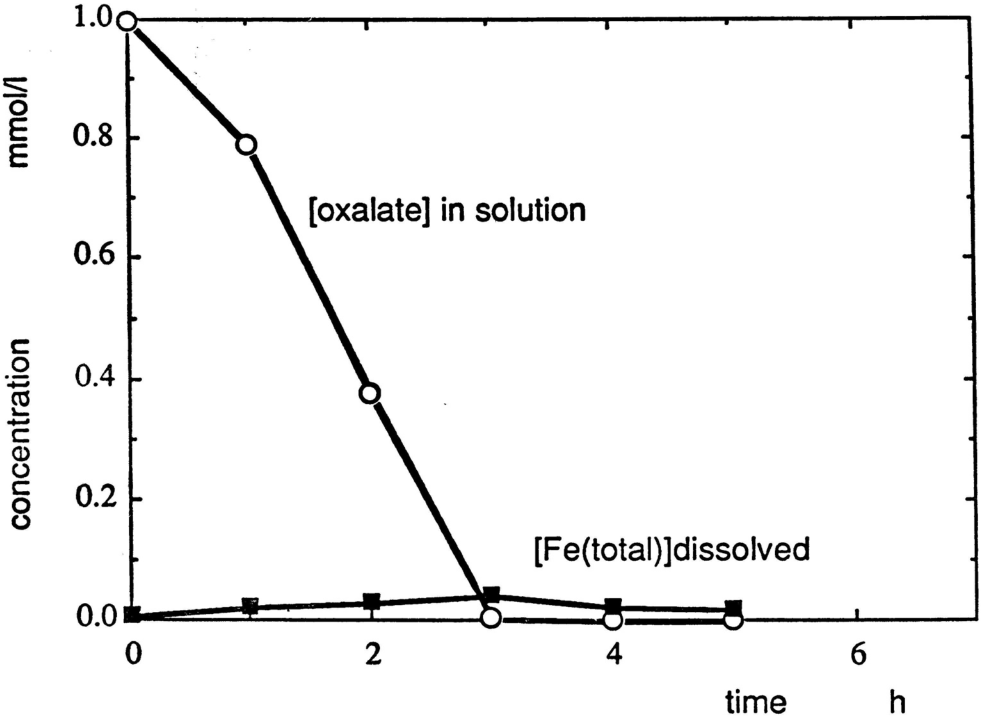


Figure 9. Photocatalytic oxidation of oxalate in an irradiated hematite suspension. Experimental conditions: 0.5 g/l hematite; initial oxalate concentration: 1 mmol l^{-1}; pH = 3 $I_o \cong 4$ kW/m^2; white light from a high pressure xenon lamp after passing a pyrex glass filter; irradiated surface $\cong 50$ cm^2, reaction volume: 250 ml; oxygen atmosphere. From. Siffert and Sulzberger, in preparation[41].

In the presence of oxygen, the stoichiometry given in equation (12) is no longer valid. In this case, oxalate is oxidized much faster than under nitrogen and the dissolution of hematite is inhibited, Figure 9. (Since this experiment, was carried out at low pH, the difference in dissolved iron under nitrogen and oxygen cannot be explained in terms of reprecipitation of iron(III) in an oxygen environment). Obviously a reaction takes place which competes with the reduction and subsequent detachment of iron(II) groups from the surface. Plausibly, adsorbed molecular oxygen reacts with the photoelectrons, e^-_{ss}, trapped on the iron sites at the hematite surface:

$$O_2(\text{ads.}) + e^-_{ss} \xrightarrow[\text{hematite}]{h\nu} O_2^- \qquad (13)$$

To what extent reaction (13) occurs instead od detachment of reduced surface sites from the crystal lattice depends on the crystallinity of the iron(III) (hydr)oxide phase and is less probable with a hydrous iron(III) oxide less crystalline than hematite. The inhibition of the photochemical reductive dissolution of iron(III) (hydr)oxides by oxygen provides further experimental evidence that detachment of iron(II) from the surface is the rate-determining step of the dissolution reaction.

3.1.4 pH Dependence of the Rate of Reductive Dissolution

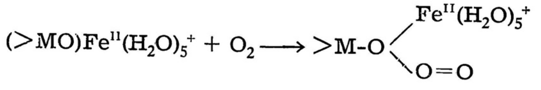
Reductive dissolution is often faster at low pH because a certain degree of surface protonation is necessary for the polarization of the crystal bonds and the detachment of a Fe(II) surface group into solution. Furthermore, the adsorption of the reductant to the oxide surface is pH dependent. But usually above pH 4.5 the rate of dissolution in all reductive pathways appears to be inhibited. One plausible explanation[48] is that Fe(II) that becomes adsorbed to hydrous oxide surfaces above pH = 4 blocks surface sites, either as $>\text{Fe}^{\text{III}}$--O-Fe^{II} or after oxygenation as $>\text{Fe}^{\text{III}}\text{-O-Fe}^{\text{III}}\text{-(OH)}_n$ and prevents further dissolution. In natural waters where such dissolution reactions are anyhow rather slow, the effects of Fe(II) adsorption may be — because of low concentrations of Fe(II) — less important. Less inhibition should be observed in the presence of any complex former that keeps free $[\text{Fe}^{2+}]$ low. This is the case if EDTA is used as a complex former. In the presence of EDTA substantial dissolution rates with ascorbate at pH = 6 are observed.[44]

4. SURFACE CATALYZED REDOX REACTIONS

Specific interactions of oxidants and reductants with the functional groups of hydrous oxide surfaces may catalyze redox processes in various ways. Two cases of interest in the geochemistry of natural waters will be illustrated: 1) the oxygenation of surface coordinated transition metal ions; and 2) photocatalysis.

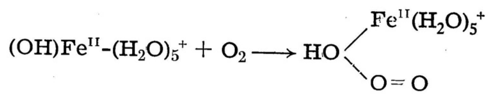
4.1 Oxidation of Transition Metal Ions by O_2

Surface ligands play an active role in the redox kinetics of adsorbed trasition metal ions[33]. Oxygen may become attached (inner- or outer spherically) simultaneously with the transition metal ion to be oxidized; *e. g.*



$$(>\text{MO})\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5^+ + \text{O}_2 \longrightarrow >\text{M-O}\begin{cases}\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5^+ \\ \text{O=O}\end{cases} \tag{14}$$

similar to its attachment to a hydrolyzed transition metal ion



$$(\text{OH})\text{Fe}^{\text{II}}\text{-}(\text{H}_2\text{O})_5^+ + \text{O}_2 \longrightarrow \text{HO}\begin{cases}\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5^+ \\ \text{O=O}\end{cases} \tag{15}$$

where the lone electron pairs of the hydroxo group may interact with the π orbitals of the dioxygen molecule. In general, the binding of Cu(I), Fe(II), V(IV) and Mn(II) to surface O-ligands enhances the oxidation by O_2 to a similar extent as hydrolysis, *i. e.* complex formation with OH^- in solution. We exemplify here the oxidation of Fe(II).

The rate law commonly used for the oxygenation of Fe(II) in solution (valid for PH>A5)[48]

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]\,[OH^-]^2\,[O_2] \qquad (16)$$

can be interpreted in the sense that, within the pH-range of interest, the hydrolyzed Fe^{2+}, $Fe(OH)_2$ is the species that is being oxidized

$$-\frac{d[Fe(II)]}{dt} = k'\,[Fe(OH)_2]\,[O_2] \qquad (17)$$

Similarly the Fe(II) bound to the hydroxo-groups of a hydrous oxide is oxidized with O_2 as[37,38]

$$-\frac{d[Fe(II)]}{dt} = k''\,\{Fe(OM<)_2\}\,[O_2] \qquad (18)$$

Over the entire range of pH values the rate of Fe(II) oxidation can be expressed more generally as[49]

$$-d[Fe(II)]/dt = (k_o[Fe^{2+}] + k_1[Fe(OH)^+] + k_2[Fe(OH)_2])\,[O_2] \qquad (16a)$$

The $Fe(OH)_2$ species, similar to the surface complex $Fe^{II}(OM<)_2$, has an electron arrangement that can associate with O_2, thus, facilitating the electron transfer to O_2.

It is well known that bacteria can mediate the oxidation of Fe(II) and Mn(II). Even with heterotrophic bacteria (*i. e.* bacteria that are not chemoautotrophic) oxidation catalysis is possible because their surfaces can serve as a template to bind Fe(II) on Mn(II) enabling the heterogeneous oxidation by O_2.

In Figure 10 homogeneous and heterogeneous oxidation of Fe(II) is compared. Wehrli[50] has shown that the oxygenation rate of many transition element species can be predicted in a linear Marcus type relationship, in which the rate constant k is ploted *versus* the free energy ΔG of the redox reaction step:

$$\begin{aligned} &\text{species} + O_2 = \text{oxidized species} + O_2^- \\ e.g.\ &Cu^+ + O_2 = Cu^{2+} + O_2^- \\ &Fe(OH)_2 + O_2 = Fe(OH)_2^+ + O_2^- \end{aligned}$$

Figure 11 compares the half lives of V(IV), Fe(II) and Mn(II) towards oxidation by oxygen $P_{O_2} = 0.2$ atm). In each case, the relative effect of hydrolysis and adsorption is significant and similar. Deprotonation of the aquo ion causes an acceleration of the oxidation rate by more than 10^4.

4.2 *Photocatalysis*

In natural waters various redox pairs are often not in equilibrium with each other, *e. g.* O_2 in the presence of Fe(II), or HSO_3^-, or an organic solute. In the presence of a hydrous metal oxide, acting as a photocatalyst, redox equilibrium in solution may be restored. A photocatalyst, PC, is a light-ab-

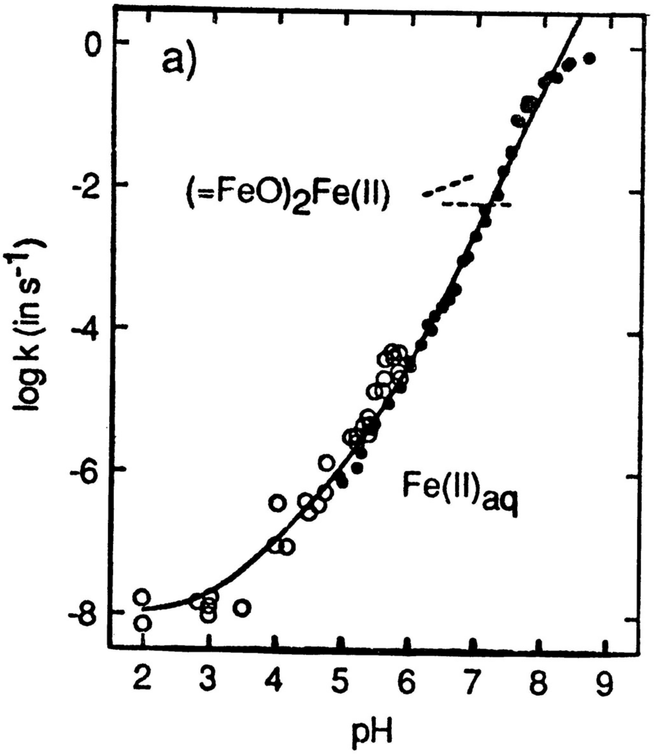


Figure 10. Oxygenation kinetics for 1 atm O_2. a) Oxidation of Fe(II). Open circles represent data by Singer and Stumm (1970), dots are data from Millero *et al.* (1987). The solid line was calculated. Small dotted lines represent heterogeneous rate constants for Fe(II) adsorbed to $Fe(OH)_3$ (uper line) and α-FeOOH (lower); data from Tamura *et al.*[37]; from Wehrli[50].

sorbing species that enables the redox reaction but which remains unchanged after the overall process:

$$PC \xrightarrow{h\nu} PC^* \qquad (19)$$
$$PC^* + A \longrightarrow PC + B$$

The term »photocatalyst« is used independent of the sign of the free energy change of the overall process. For heterogeneous systems it is convenient to distinguish beween »heterogeneous photocatalysis«, where the rate of a thermodynamically favorable reaction ($\Delta G < 0$) is increased by the presence of the illuminated solid, and »heterogeneous photosynthesis«, where a thermodynamically unfavorable reaction ($\Delta G > 0$) is caused to occur by the presence of an illuminated solid, leading to conversion of radiant to chemical energy[51].

An example of a photocatalytic reaction where hematite is involved as a photocatalyst is given in equation (13). For photocatalytic reactions the semiconduction properties of metal oxides are of particular interest. Hematite is

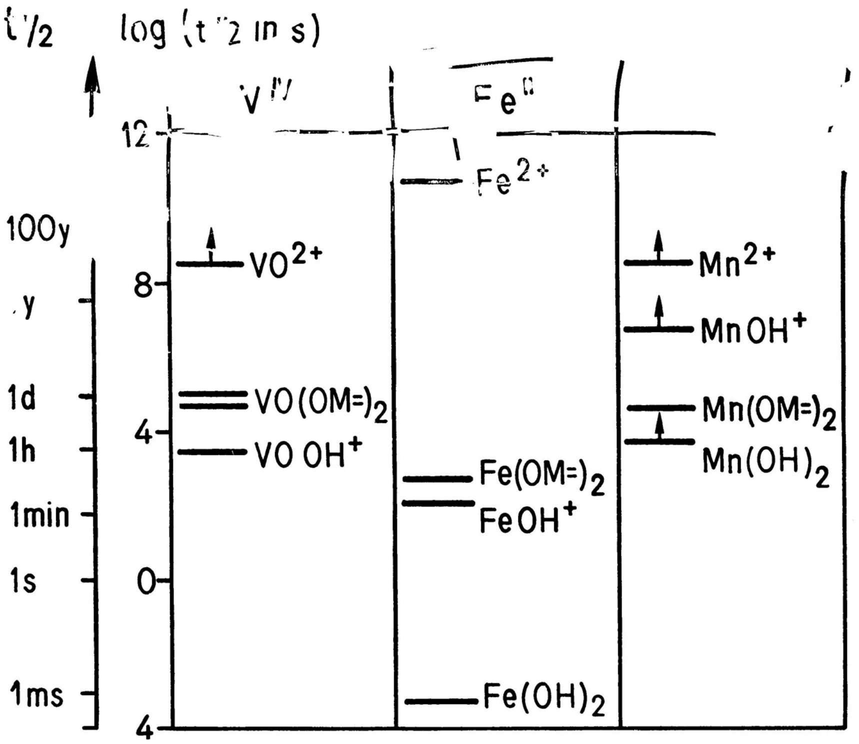


Figure 11. Effects of hydrolysis and adsorption on the oxygenation of transition metal ions. Arrows indicate lower limit. Data represent order of magnitude because surface area concentrations were not detarmined; from Wehrli and Stumm[68].

a semiconductor with different band gaps. Electronic excitation with light energy higher or equal the 2.2 eV band gap energy corresponds to a d-d transition whereas excitation of the 3.5 eV band gap corresponds to a $Fe^{III} \leftarrow O^{-II}$ charge transfer transition (Goodenough)[52]. For the photocatalytic oxidation of refractory organic pollutants, TiO_2 is usually being investigated as a photocatalyst because of its relative inertness with regard to dissolution. The activity of an adsorbed electron donor for the interfacial electron transfer depends on both, its ability to be oxidized by the photogenerated hole and its adsorption properties. The first is a thermodynamic, the second a kinetic requirement. Kinetic experiments performed at various concentrations of the electron donor can give information on its adsorption properties. Different authors have reported, that the rate of the photocatalytic oxidation of an electron donor such as oxalate or 4-chlorophenol, respectively, at the TiO_2-surface varied as a function of the dissolved concentration of the electron donor according to a Langmuir-type isotherm (Herrmann *et al.*[53], Al-Ekabi *et al.*[64]). These findings are in agreement with the assumption of an inner-spherically bound electron donor, since a Langmuir-type adsorption is consistent with the formation of a surface complex by surface ligand exchange:

$$>\mathrm{MOH} + \mathrm{HL}^- \overset{\text{fast}}{\rightleftarrows} >\mathrm{ML}^- + \mathrm{H_2O}; \tag{20}$$

$$\mathrm{K^s} = \{>\mathrm{ML}^-\}/(\{>\mathrm{MOH}\} \cdot [\mathrm{HL}^-])$$

$$\{>\mathrm{ML}^-\} = \frac{K^s S[\mathrm{HL}^-]}{1 + K^s[\mathrm{HL}^-]} \quad \text{(in mole m}^{-2}\text{)} \tag{21}$$

K^s is the conditional microscopic equilibrium constant of the adsorption equilibria, and S the concentration of the total surface sites that are available for the adsorption of the anion HL^-, $S = \{>\mathrm{MOH}\} + \{\mathrm{ML}^-\}$. Equation (21) follows thus directly from equation (20). This means that also in these photocatalytic reactions — as for the dissolution reactions — the rate is linearly dependent on the concentration of the adsorbed electron donor, $R = k\{>\mathrm{ML}^-\}$.

The efficiency of interfacial electron transfer depends also on the type of surface complex formed between a specifically adsorbed electron donor and a surface metal center. Using methylviologen (MV^{2+}) as electron acceptor, Darwent and Lepre[55] have reported, that the yield of photochemical MV^+ formation was much higher in the presence of an electron donor, where two functional groups are likely to be bound to the $\mathrm{TiO_2}$ surface, compared to an electron donor that can only from a monodentate surface complex.

The photocatalytic oxidation of adsorbed reductants such as $\mathrm{HSO_3}^-$ or of (refractory) organic compounds is of interest in atmosphere and surface waters. For example, it has been shown that iron(III) oxide can catalyze reaction of $\mathrm{O_2}$ with sulfite[56].

5. APPLICATION TO NATURAL AND TECHNICAL SYSTEMS

5.1. *Cycling of Electrons as Exemplified by the Cycling of Iron*

The geochemical cycling of electrons is believed to be dominated by microbiological mediation. We will ilustrate that surfaces, by catalyzing electron transfer, can provide abiotic redox processes. Such cycling of electrons occur to a larger extent where deep redox gradients and large concentrations of surfaces (*e. g.* sediment-water interface, oxic-anoxic boundaries in waters and soils) prevail or by photocatalysis in the photic zones of surface waters. The redox transformations of ubiquitous iron and managanese, although influenced by biological mediation can occur abiotically.

Figure 12 illustrates and exemplifies the various redox processes that are often mediated by surfaces in the cycling of iron, above all: i) the reductive dissolution of iron(III) oxides by organic ligands, ractions that may, if they occur in surface waters, be photocatalyzed; and ii) the surface catalyzed oxidation of Fe(II) by oxygen.

The cycling of iron in natural environments, in soils, waters and sediments is of great importance in the weathering processes and in the geochemical cycling of other reactive elements. The oxidation of Fe(II) to Fe(III) (hydr)oxides is accompanied by the binding of reactive compounds (heavy metals, silicates, phosphates and other oxyanions of metalloids such as As(III,V) and Se(III,V) to the hydrous Fe(III) oxide surface, and the reduction of the hydrous Fe(III) oxides to dissolved Fe(II) is accompanied by the re-

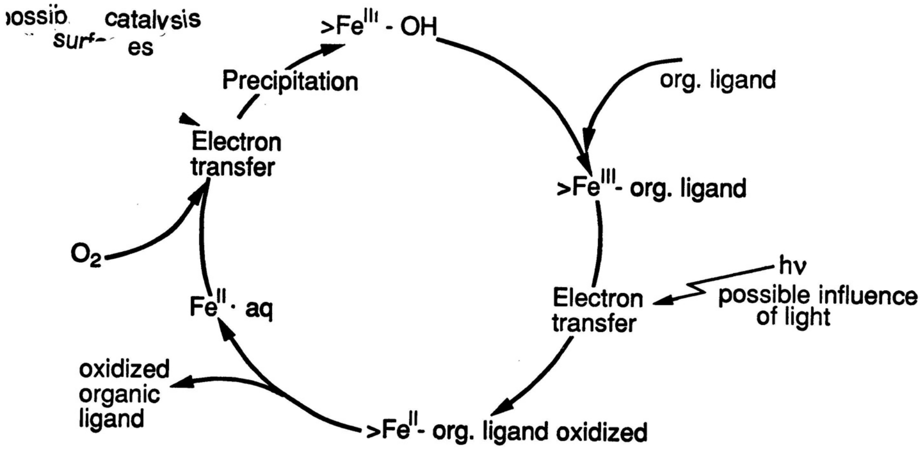


Figure 12. The dissolution of Fe(III) (hydr)oxides promoted by reductive organic ligands and the subsequent reoxidation of Fe(II) by O_2 plays an important role in soils and sediment water systems and causes relatively rapid cycling of electrons and of reactive elements (*e.g.* organic carbon, oxygen, trace metals phosphate) at the oxic-anoxic boundary. This cycle can also occur, photochemically induced, in oxic surface waters. On overall balance, the iron cycle mediates the progressive oxidation: O_2 + organic matter → oxidized organic matter.

lease of these substances. On overall balance the turnover cycle given in Figure 12 represents a mediation of the oxidation of organic matter by oxygen. This oxidation may be an important part, both in the degradation and the polymerization ractions of organic matter in soils and in waters.

5.1.1 Light-induced Release of Fe(II) in the the Photic Zone of Surface Waters

In oxic surface waters Fe is present, from a thermodynamic point of view, as Fe(III) (hydr)oxide. In the photic zone light may induce the release of soluble Fe(II), thus modifying the iron cycle and possibly rendering the iron more bioavailable (see chapter 3.1.3. and Figure 7). In natural waters the reductants (whose electron transfer with the iron(III) (hydr)oxide is photochemically catalyzed) is usually an organic ligand that may have been released by exudation from algae or from decomposition of organic matter. The rate of reductive dissolution depends on the extent of surface complex formation, on the light intensity and its energy and increases with decreasing pH. The reduced iron is reoxidyzed by oxygen, a reaction which is also strongly dependent on pH. In ideal cases a steady state concentration of soluble Fe(II) results which is dependent on pH, on light intensity and on the concentration of suitable photolytic surface complexes.

In surface waters diurnal variations in dissolved Fe(II) have been observed.[57,68] Figure 13 shows such a dial variation of the concentration of dissolved Fe(II) in a slightly acidic alpine lake (Lake Cristallina) of Switzerland. The net concentration of Fe(II) at any day time reflects the balance of the reductive dissolution and the oxidation/precipitation reactions and parallels the light intensity, leading to a diurnal variation in the Fe(II) concentration. It is believed that this photochemical reductive dissolution of Fe(III) (hydr)oxides is also of importance in marine systems; however, around pH = 8 the reductive dissolution may be much smaller than at lower pH-values. In the photic zone of ocean waters the concentration of H_2O_2 may be sufficiently high so that oxidation of Fe(II) with H_2O_2 may compete with oxygenation.

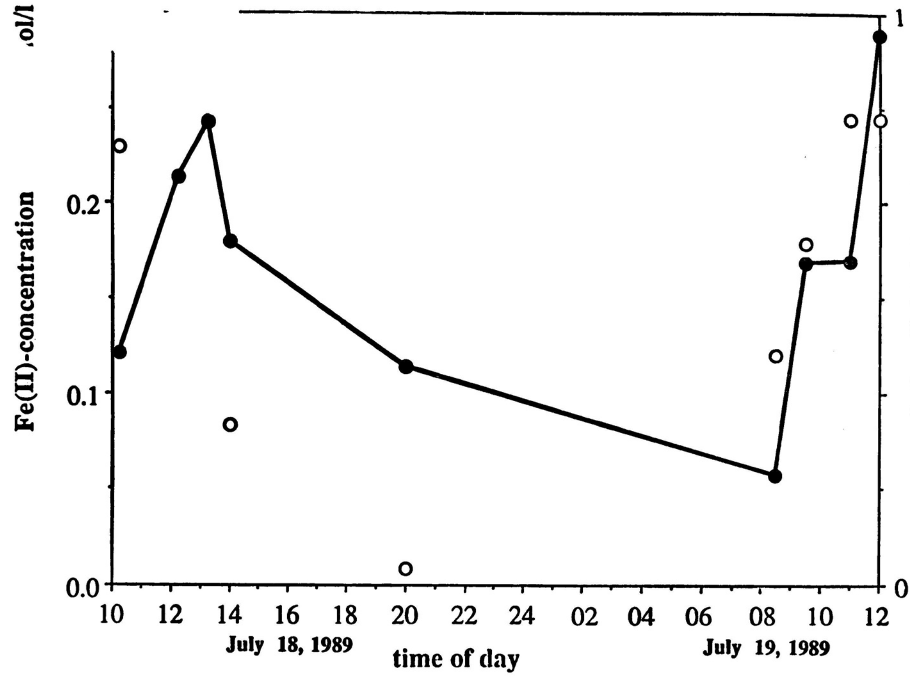


Figure 13. Diurnal variation of concentration of dissolved Fe(II) in Lake Cristallina.

The photoredox cycling of iron in surface waters may enhance the oxidative degradation and the recycling of organic matter and produce less refractory substances that can serve as organic nutrients. It was shown recently[48] that pyruvic acid is produced in surface water photochemically. Furthermore, it has been suggested[63] that Fe is a limiting nutrient in the oceans. Thus, the reactions discussed here may be of relevance for the photosynthetic productivity of marine systems.

5.1.2 Significance of Iron Cycling at the Oxic-anoxic Boundary in Waters and Soils

The reductive dissolution of Fe(III) (hydr)oxides occurs readily in the absence of light in anoxic reducing environments. A rapid turnover of iron takes place at the oxic-anoxic boundary of waters. This is schematically shown in Figure 14. The important items are: (1) The principal reductant is the biodegradable biogenic material that settles in the deeper portions of the water column. (2) Electron transfer becomes more readily feasible if, as a consequence of fermentation processes — typically occurring around redox potentials of 0 to — 0.200 V — molecules with reactive functional groups such as hydroxy and carboxyl groups are formed. (3) Within the depth-dependent redox gradient, concentration peaks of solid Fe(III) and of dissolved Fe(II) develop[58], the peak of Fe(III) overlying the peak of Fe(II). (4) As illustrated in Figure 14, the Fe(II), forming complexes with these hydroxy and carboxy ligands, encounter in their upward diffusion the settling of Fe(III) (hydr)-oxides and interact with these according to the catalytic mechanism, thereby dissolving rapidly the Fe(III) (hydr)oxides. The sequence of diffusional transport of Fe(II), oxidation to insoluble $Fe(OH)_3$ and subsequent settling and reduction to dissolved Fe(II) typically occurs within a relatively narrow redox-cline.

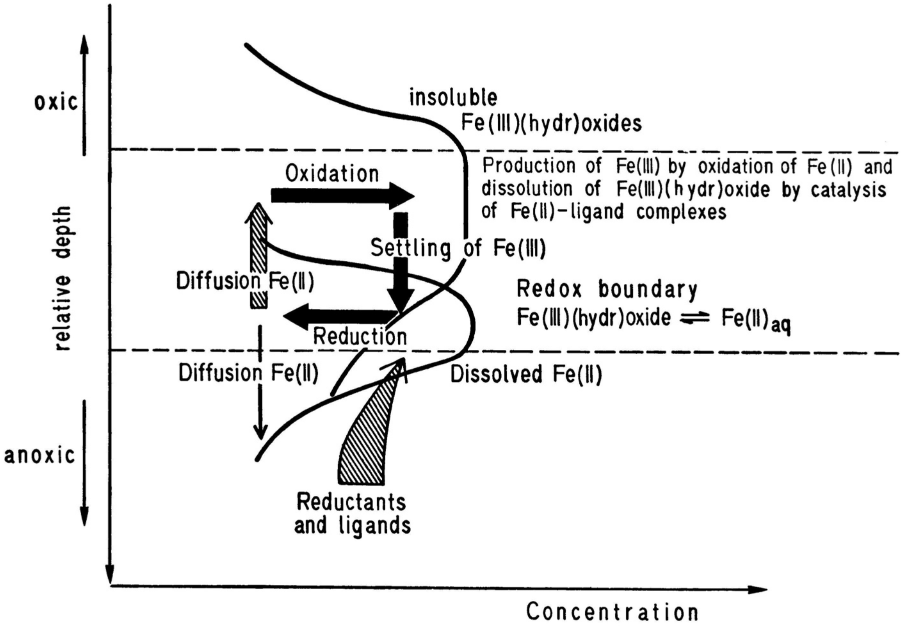


Figure 14. Transformation of Fe(II, III) at an oxic-anoxic boundary in the wate or sediment column. Peaks in the concentration of solid Fe(III) (hydr)oxides ar of dissolved Fe(II) are observed at locations of maximum Fe(III) and Fe(II) production, respectively. The combination of ligands and Fe(II) produced in underlying anoxic regions are most efficient in dissolving Fe(III) (hydr)oxides. Redox reactions of iron — oxidation accompanied by precipitation, reduction accompanied by dissolution — constitute an important cycle at the oxic-anoxic boundary that is often coupled with transformations (adsorption and desorption) of reactive elements such as heavy metals, metalloids and phosphates. Davison[58] has illustrated the depth concentration profiles of Fe(III) and Fe(II) at the oxic-anoxic boundary.

Some of the processes, mentioned above occur also in soils. Microorganisms and plants produce a larger number of biogenic acids. Oxalic, maleic, acetic, succinic, tartaric, ketogluconic and p-hydroxybenzonic acids have been demonstrated in top soils with oxalic acids, the most abundant in concentrations as high as $10^{-5} — 10^{-4}$ M. The downward vertical displacement of Al and Fe observed in the podsolidation of soils can be accounted for by considering the effect of pH and of complex formers on both the solubility and the dissolution rates.

The reductive dissolution of Fe(III) (hydr)oxides is also of importance in the iron uptake by higher plants. According to Brown and Ambler[59] iron defiency causes a release of reducing exudates from the roots. These substances cause the reductive dissolution of Fe(III) in the proximity of the roots. This reduction is followed by uptake of Fe(II) into the root cells.

5.1.3 Iron Transformation in the Atmosphere

Redox reactions in gigantic dimensions, above all the oxidation of SO_2, NO, and reduced C-compounds occur in the atmosphere. Although liquid water is present with less than 10^{-6} % in the troposhere, the aqueous phase (clouds, fog, rain) chemical processes, especially the oxidation of S(IV), (SO_2, HSO_3^-, SO_3^{2-}) are of great relevance. Transition metals such as Fe, Mn and Cu and their redox pairs Fe(III)/Fe(II), Mn(1V,III)/Mn(II) and Cu(II)/Cu(I) are important as catalysts and reductants. Jacob *et al.*[60] and Jacob and Hoffmann[61] suggest that Fe(III) acts either as a catalyst or as a direct oxidant for S(IV), Behra and Sigg[62] report on measurements of Fe in atmospheric water. A large fraction of the total Fe is present as dissolved Fe(II) (up to 0.2 mM in fog water, pH 3-7). The concentration of Fe(II) increases both with decreasing pH and exposure to light. These authors[62] assume that Fe(III) (hydr)oxide is reduced by sulfite, organic compounds and also by free radicals formed photochemically during day time. These pH- and light-dependent reduction reactions can be fast enough to outcompete reoxidation of Fe(II) by O_2. At night the reaction of Fe(III) with sulfite is the main source for Fe(II) with concommitant formation of the strong acid H_2SO_4. Thus atmospheric depositions may be a source of dissolved Fe(II) to surface waters which would influence the availability of iron to aquatic biota.

5.2 Corrosion; Passive Films

To what extent is our know-how on the reactivity of oxides useful for the understanding of corrosion reactions and passivity. The corrosive behaviour of a few metals is essentially determined by the kinetics of the dissolution of the corrosion products. This seems to be the case for Zn in HCO_3^- solutions, for passive iron in acids and passive Al in alkaline solutions.[64] The mechanism of the dissolution of iron and of the passivation of this dissolution is extremely complex. We may not know exactly the composition of the passive film; but it has been suggested that it consists of an oxide of $Fe_{3-x}O_4$ with a spiral structure. The passive layer seems to vary in composition from Fe_3O_4 (magnetite), in oxygen-free solutions, to $Fe_{2.67}O_4$ in presence of oxygen. It may also consist of a duplex layer consisting of an inner layer of Fe_3O_4 and an outer layer of γ—Fe_2O_3. The Coulombic reduction of the passive layer gives two waves which are interpreted either by the reduction of two different layers, Fe_2O_3 and Fe_3O_4, or by successive reduction of Fe_3O_4 to lower valence oxides and its further reduction to metallic iron. Figure 15 represents a schematic model of the hydrated passive film on iron as proposed by Bockris and colaborators[65]. Obviously the hydrated passive film on iron displays the coordinative properties of the surface hydroxyl groups (Figure 1) which contain complex forming oxygen donor atoms which can coordinate with H^+ and metal ions; furthermore the surface OH^- ions can be exhanged against ligands (ligand exchange).

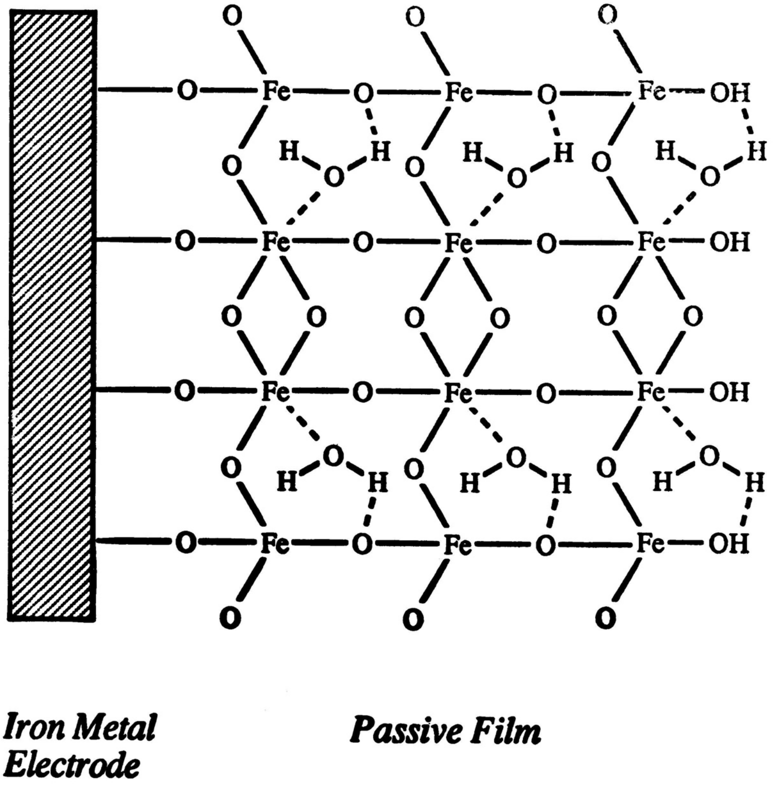


Figure 15. Schematic representation of the hydrated passive film on iron; from Pou *et al.*[65]

As illustrated in Figure 1b, the extent of adsorption (surface binding) of cations, and anions (or weak acids) to the hydrated passive film is pH-dependent; it can be quantified by surface coordination equilibria (mass action equations) and can be explained by considering the affinity of the surface sites for metal ions or ligands and the pH-dependence of the adsorption reactions. This is in line with recent conclusions of Sato[63] which show that hydrated iron oxides are anion-selective in acidic or neutral solutions, and cation-selective in alkaline solutions (Figure 1b).

Since the dissolution rate of passive metals is apparently related to the dissolution rate of the passive film, some of our informations on the effect of solution variables on the dissolution reactivity of such type of oxides appear applicable to the interpretion of some of the factors that enhance or reduce passivity. i) *Protons.* Obviously surface protonation will enhance dissolution. For the passivation of iron, critical current density must be exceeded which increases with decreasing pH. ii) *Fluoride and chloride.* These ions form surface complexes and presumbly permeate into the crystalline lattice; they destroy especially at low pH the passivity of iron oxides films. iii) *Reductants* not only tend to lower the electrode potential and may reduce O_2 but also favour the reductive dissolution of passive iron oxide films; if these reductants are able to form surface complexes, especially surface chelates, they can facilitate the electron transfer to the oxide. Presence of Fe(II) in solution can catalyze this reductive dissolution. *Oxidants* added to the water as an inhibitor may prevent this reductive dissolution and restore high electrode potential. iv) Surface complex forming *ligands* like oxalate, salicylate and phenols, especially at low pH, tend to dissolve the passive film. v) *Cations* like Zn^{2+}, Al^{3+}, Cr^{3+}, block surface sites and thus stabilize the passive film. vi) *Phosphates*, silicates, polyphosphates or polymeric ligands may have different effects at low pH and at neutral or alkaline pH values; they enhance the dissolution at low pH; they may form mononuclear surface complexes that assist the detachment of the Fe into solution. At higher pH values, these ligands may form bi- or multinuclear surface complexes. Presumably these would tend to act as inhibitors of dissolution because a high activation energy is necessary to detach simultaneously two or more metal centers from the crystalline lattice into solution. It is also possible that these ions form new surface phases on top of the oxides.

Figure 16 shows a typical polarization curve (cyclic voltametry) of pure iron in a borate buffer of pH = 8.4. In the anodic step the iron dissolution peak at the electrode potential of — 0.4 V (*vs.* NHE) corresponds to the for-

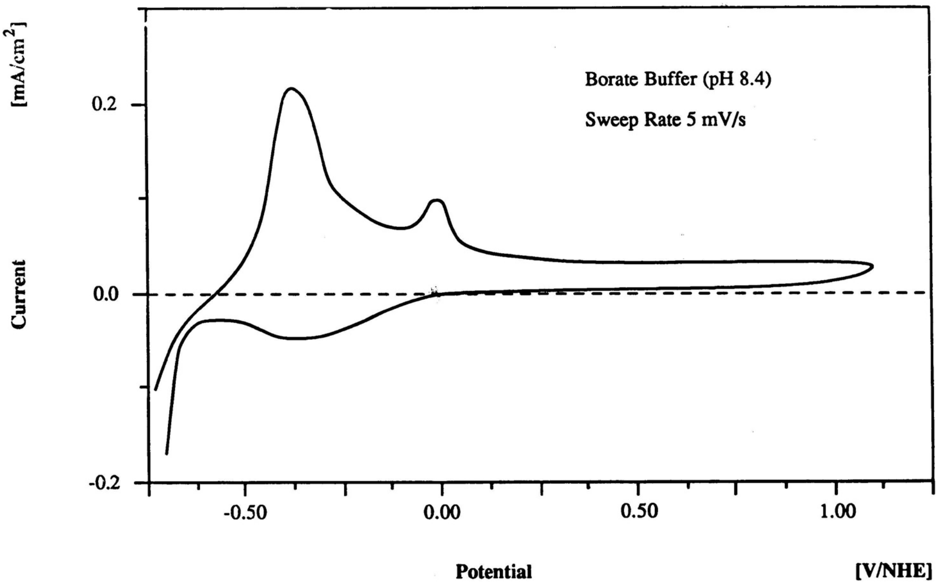


Figure 16. Typical cyclic voltammogram of pure iron in borate buffer solution obtained at a sweep rate of 5 mV/s. In the anodic sweep, the iron dissolution peak at -0,4 V/NHE corresponds to the formation of a monolayer of the passive film.

mation of the passive film. The current necessary to passivate the metal anodically corresponds to that which is able to form a layer of corrosion products preventing further dissolution by blocking the metal surface. The anodic current observed above 0.2 V is the passive current which reflects the minimal corrosion rate (which may under certain simplifying steady state assumptions be equivalent to the dissolution rate of the oxide film).

We were able to show that in ClO_4^- media (without borate buffer) in nearly neutral solutions, bidentate surface complex formers such as oxalate tend to increase the passive current while the monodentate ligand benzoate tends to reduce the passive current. Such observations are in accordance with those observed in experiments on the dissolution of dispersed Fe(III) oxide colloids, where oxalate enhances the dissolution rate and benzoate, although strongly bound to the hydrous oxide surface is inert, *i.e.*, benzoate may reduce the surface reactivity by blocking surface functional groups.

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SAŽETAK

Kemijska koordinacija na granici faza oksid-elektrolit; ovisnost reaktivnosti površine (otapanje, redoks reakcije) o površinskoj strukturi.

W. Stumm, B. Sulzberger i J. Sinniger

Prikazani su bitni elementi koncepta kemijske koordinacije u procesima na granici faza oksid-elektrolit. Osnovni pristup počiva na paradigmi da hidratizirana površina oksida sadrži funkcionalne OH-grupe čija asocijacija sa H^+ i OH^- ionima te ionima metala i različitim ligandima uveliko ovisi o strukturnom identitetu površinskih specija a što je opet određeno kemijskim reakcijama koordinacije na granici faza čvrsto-tekuće.

Naglašava se važnost tzv. generičkih (termičko gibanje i elektrostatske interakcije) i specifičnih interakcija (stvaranje površinskih kompleksa) na granici faza.

Procesi na granici faza kao što su otapanje, redoks i fotoredoks procesi, diskutiraju se na teuelju općenitog zakona brzine reakcije $R = k\, x_a P_j S$, gdje je R, brzina reakcije (mol m^{-2} s^{-1}); /, konstanta brzine reakcije (s^{-1}); x_a, molarni udio reaktivnih površinskih mjesta; P_j, vjerojatnost nalaženja aktivnog mjesta u povoljnoj koordinativnoj formi; i S, koncentracija površinskih mjesta (mol m^{-2}). Smatra se da je površinska kemijska koordinacija najčešće brzi proces dok je transformacija površinske specije (npr. redukcija metalnog iona-konstituenta čvrste rešetke) i prelaz u otopinu, spori proces.

Na primjeru kruženja željeza, Fe(III) / Fe(II) u prirodnom sistemu (voda, sediment, atmosfera) prikazani su mogući paralelni ili sukcesivni procesi uz koorinativno djelovanje organskih liganada i katalitičko djelovanje svjetlosti.

Koncept površinske kemijske reaktivnosti primjenjen je i u interpretaciji korozije metala, posebno pasivnosti sloja željeznog oksida