SURFACE COMPLEXATION MODELING
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Gibbsite

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To Werner Stumm

Water chemist, surface chemist, and scientific leader
his insights and vision continue to inspire
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FOREWORD

Writing this foreword brings me several years back, when David Dzombak was a graduate student at MIT, a young man in whom one could already perceive the future eminent professor. This was a time when a great wave of experimental work on the adsorption of solutes on oxides had just peaked, the data being interpreted and reported with the help of a variety of models with multiple surface layers. Though differing from each other in the way they represented and parameterized the solid–water interface, all these models descended from Werner Stumm and Paul Schindler’s original insight that surface complexation—that is, the formation of chemical bonds between solutes and atoms at the surface of solids—dominate adsorption phenomena in nature and that the corresponding free energy can be added to a coulombic term calculated from some version of the Gouy–Chapman–Stern–Grahame theory.

But the different models used by different research groups resulted in parameters that had different meanings, and different values for fitting the same experimental data. This made comparison among data sets difficult and also limited their use. David Dzombak, who always had a keen interest in making use of scientific advances for practical applications, embarked on the daunting task of interpreting all published adsorption data on oxides with a unique model. Refusing to be intimidated by the formidable triple layers emanating from the West Coast, he chose the unassuming two-layer model, which could simply account for the experimental observations. It turned out, of course, that assembling critically and re-interpreting all published adsorption data on oxides was an enormous undertaking, one that tested David’s Augustinian patience and attention to details. (The truth be told, he found weekly solace with friends drinking in a louche bar on Massachusetts Avenue.) When it was time to graduate, he presented the first installment of his work, that on hydrous ferric oxide, as his doctoral thesis. It was accepted and published as a book.

Nearly 20 years later, in a demonstration of uncommon tenacity, David Dzombak and his postdoctoral associate Athanasios Karamalidis have brought to fruition another chapter of that original thesis idea; yet another book; this one on Gibbsite. This important addition to the available database on sorption reactions has great practical value, of course. Reactions at the solid–water interface play a key role in controlling the concentration and fate of solutes in natural and engineered aquatic systems. This book, like its predecessor, provides the means to quantify these reactions conveniently. But I believe that these books do more than reinterpreting
data and compiling coherent thermodynamic parameters. By enabling comparison among sorption parameters, they also give insight into the variety of physical and chemical mechanisms responsible for the adsorption of solutes on solid surfaces. For example, by exposing the effects of ionic strength, they bring to light the contrasting behaviors and roles of activity coefficients in the bulk solution and at surfaces (i.e., the “coulombic term”). More importantly perhaps, the remarkable Linear Free Energy Relationships obeyed by consistent adsorption constants demonstrate an important underlying chemical regularity; they also provide the means to effectively make predictions where no data are available. We can now begin to reflect on the question of what coherence we should or should not expect between stoichiometries that underpin average thermodynamic quantification of sorption reactions and spectroscopic information on the coordination environment of atoms at surfaces.

Whether interested in making practical thermodynamic calculations, or in reflecting on the fundamental nature of the interactions at interfaces, we should be thankful to Athanasios Karamalis and David Dzombak for this new opus.

François M. M. Morel

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The development of this thermodynamic database for surface complexation of inorganic ions on gibbsite builds on the effort initiated in 1990 by David Dzombak and François Morel for amorphous iron oxyhydroxide, or hydrous ferric oxide (HFO). A primary objective in the publication of *Surface Complexation Modeling: Hydrous Ferric Oxide* (Wiley Interscience, 1990) was to advance the practical application of surface-complexation modeling. From the start of the development of surface-complexation models in the 1960s, a variety of different models have been developed, each with a particular physical description of the solid–water interface and hence with a different formulation for the electrostatic interaction submodel. The variations in descriptions of the solid–water interface result in different model parameters and types of surface-complexation reactions used to fit the same ion-sorption data. As a result, surface-complexation reactions and equilibrium constants extracted from sorption data sets with different models cannot be used collectively as a database for modeling sorption reactions.

Dzombak and Morel used a surface-complexation model with a simple solid–water interface model to interpret available data for inorganic ion sorption on HFO and thereby develop an internally consistent thermodynamic database for modeling sorption on this important sorbent in natural systems. While the simple two-layer model (one surface layer and a diffuse layer of counterions in solution) has its limitations as a description of reality for a complex solid like HFO in complex aqueous solutions, it has the benefit of being able to fit data for equilibrium sorption of ions on oxide surfaces across a range of solution conditions usually as well as more complex models and with fewer fitting parameters. The comparable performance and relative simplicity of the two-layer model is what guided its selection for the initial work with HFO.

The extensive use that the HFO database and the two-layer model have received has been gratifying. The model and HFO database have been used to gain quantitative insight into the role of sorption in natural aquatic systems of all types as well as in water, soil, and waste-treatment systems. The use of the model and HFO database has been facilitated by the incorporation of both into widely used general chemical equilibrium models derived from the original MINEQL model (John Westall, Joseph Zachary, and François Morel, Massachusetts Institute of Technology, 1976): MINEQL+, developed by Environmental Research Software, Inc.
MINTEQ developed by the U.S. Environmental Protection Agency (http://www.epa.gov/ceampubl/mmedia/minteq/); MINTEQA2 for Windows developed by Allison Geoscience Consultants (http://www.allison-geoscience.com/); and VisualMINTEQ developed by the KTH Royal Institute of Technology in Sweden (http://www.lwr.kth.se/English/OurSoftware/vminteq/). While all models are subject to misuse and the HFO database and model no doubt have been applied inappropriately in some cases, the majority of applications have been appropriate and helpful to investigators. Results have been interpreted with consideration of the limitations associated with all applications of chemical-equilibrium models to complex aqueous systems encountered in natural and contaminated environments and treatment systems. The HFO model and database have certainly advanced the practical application of surface-complexation modeling.

Another goal in developing the HFO database was to provide the start of a larger database encompassing other important oxide sorbents for aqueous systems of interest in environmental science and engineering. Subsequent to the publication of the HFO database in 1990, the two-layer model and methodology used to develop the database were employed in follow-up database-development efforts for goethite (Samir Mathur and David Dzombak, 1995, 2006) and for hydrous manganese oxide (Jennifer Tonkin, Laurie Balistrieri, and James Murray, 2004). In this book, we present the fourth internally consistent database, for the very important natural sorbent, the aluminum hydroxide mineral gibbsite.

This book is organized based on the outline of the original HFO study. The first two chapters serve as a general introduction to aluminum (hydr)oxide chemistry, the following two chapters serve as the “materials and methods” section, and the final four are dedicated to surface complexation and modeling. In Chapter 1, we describe the importance of aluminum oxides and hydroxides in natural or engineered environments and their abundant occurrence. In Chapter 2, the formation and properties of gibbsite and its closely related minerals are presented. In this chapter, we try to clear the ambiguity in the various designations given for the aluminum (hydr)oxides and suggest a nomenclature. Chapters 3 and 4 describe the experimental data that constrain surface-complexation models and the systematic procedure followed to extract model constants from the data in the current and previous efforts. The historical development of surface-complexation modeling and the history and development of the generalized two-layer model are presented in detail by Dzombak and Morel (1990) and are not repeated in full here, but summarized information is provided. In addition, there is a discussion of surface spectroscopy constraints on surface-complexation modeling which has advanced since the initial work with HFO. In Chapter 5, we focus on potentiometric titration data fitting and surface acidity constant extraction for gibbsite. In this chapter, we also explore the influence of gibbsite dissolution on acid–base titration of gibbsite suspensions and the issue of accounting for the dissolution in formulating surface-complexation models for gibbsite. In Chapters 6 and 7, we present the available cation and anion sorption data for gibbsite and the results of fitting those data with the generalized two-layer model. In an attempt to constrain our model based on spectroscopic evidence, detailed information about available spectroscopic data for sorption of different ions on
gibbsite is presented. The manner in which spectroscopic data were considered in fitting the experimental sorption data for each ion is discussed. Chapter 8 presents an investigation of linear free energy relationships for identifying trends in sorption data and predicting surface-complexation constants for conditions not yet studied experimentally. This chapter also examines the relative reactivity of the surface hydroxyl groups of gibbsite, goethite, HFO, and hydrous manganese oxide, through the comparison of the two-layer model surface-complexation constants extracted using the methodology specified in Dzombak and Morel (1990).

We gratefully acknowledge support for this work from Carnegie Mellon University through the Walter J. Blenko, Sr. Professorship, and assistance from the Department of Civil and Environmental Engineering. We thank Sabine Goldberg of the U.S. Salinity Laboratory for her time and comments on our work. Her extensive knowledge of the surface chemistry of aluminum oxide and surface-complexation modeling, and her generosity in answering our questions and reviewing various portions of our work were most helpful. We also thank Antonio Violante of Università degli Studi di Napoli Federico II for discussing various issues related to the crystallography of gibbsite, for reviewing Chapter 2, and for sharing with us information and parts of his voluminous work on gibbsite. We are grateful to several anonymous reviewers arranged by Wiley, whose comments improved our manuscript. We thank François Morel for reading parts of the manuscript and writing the Foreword, and for his vision which initiated this effort almost 30 years ago. We express special thanks to our families, and especially to Thanasis’ family for putting up with the extended absences from home required to bring this effort to completion, particularly during the summer of 2009 when video conferences substituted for family travel!

Finally, we humbly thank all the experimentalists whose careful and diligent work was critical to the development of this gibbsite surface-complexation database.

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1.1 INTRODUCTION

In natural aqueous systems, reactions at the solid–water interface are among the key processes controlling the transport and fate of metals and other inorganic chemicals. Hydrous metal oxides are abundant minerals in soils and sediments and are also important sorbents for inorganic species in these systems (Dzombak and Morel, 1990; Alloway, 1995; Goldberg et al., 1996a; Martinez and McBride, 1999; Trivedi and Axe, 2000, 2001).

The sorption of metal ions and other inorganic species on hydrous metal oxides across a range of solution chemistry conditions can be described with surface complexation models. To use such models for predictive simulation in chemical equilibrium modeling, it is necessary to have a consistent surface complexation model and a database of reactions and equilibrium constants extracted from experimental data with the particular surface complexation model (Dzombak and Morel, 1990; Goldberg, 1992).

With use of the generalized two-layer surface complexation model, internally consistent databases have been developed for sorption of inorganic ions on hydrous ferric oxide (Dzombak and Morel, 1990), on the common crystalline iron oxide goethite (Mathur and Dzombak, 2006), and on hydrous manganese oxide (Tonkin et al., 2004). Another class of metal oxides equivalently common to hydrous iron oxides is gibbsite, which is the subject of this book. Iron, aluminum, and manganese oxides and hydroxides are the most ubiquitous of the hydrous metal oxides.
Aluminum (Al) occurs ubiquitously in the terrestrial environment. It is the most abundant metal in the lithosphere, comprising about 8.2 percent of the Earth’s crust (Bowen, 1979) and about 7.2 percent of soils (Schacklette and Boerngen, 1984; as reported by Sposito, 1989). Due to its reactivity, Al does not occur in elemental form in nature but is present predominantly in sparingly soluble oxides and aluminosilicates (Scancar and Milacic, 2006). Aluminum is a key component of clays, and also occurs in various oxide and hydroxide minerals as described below. Aluminum oxide and hydroxide solids are of great importance in the chemistry of soil, sediment, surface water, and groundwater systems because of their adsorptive role and dissolution properties.

When aluminum dissolves into water from clays and hydrous metal oxides, the liberated free aluminum ion $\text{Al}^{3+}$ reacts with water to form various hydroxy species including $\text{AlOH}^2^+$, $\text{Al(OH)}_2^+$, $\text{Al(OH)}_3^0$, and $\text{Al(OH)}_4^-$. The aqueous speciation of dissolved $\text{Al}$ strongly depends on pH. The released mononuclear ionic $\text{Al}$ species may undergo polymerization (Bi et al., 2004) or may be complexed by available organic or inorganic ligands (Martell et al., 1996; Smith, 1996; Exley et al., 2002; Scancar and Milacic, 2006). Polymerization of the ionic $\text{Al}$ species leads to precipitation of aluminum hydroxide or oxyhydroxide solids. Thus, the abundance and form of aluminum in soil and water systems is dependent on the dissolution–precipitation cycle of clays and aluminum oxides and hydroxides.

Aluminum oxides and hydroxides are also used in a variety of industrial and technological applications, including as adsorbents in water and wastewater treatment. Aluminum sulfate (alum) is widely employed in drinking water treatment systems across the world to precipitate aluminum hydroxide as a coagulation agent for particle removal (Licsko, 1997; Letterman et al., 1999) and as an adsorbent for contaminants such as arsenate (McNeill and Edwards, 1999). In addition, aluminum oxide is used as a fixed-bed adsorbent for removal of arsenate, fluoride, and other ionic contaminants in drinking water treatment (Chowdhury et al., 1991; Huang and Shiu, 1996; Martell et al., 1996; Clifford, 1999; Viraraghavan et al., 1999; Dayton and Basta, 2005; Ayoob et al., 2008) and industrial wastewater treatment (Karthikeyan et al., 1997; De-Bashan and Bashan, 2004).

### 1.2 Occurrence of Aluminum Oxides and Hydroxides in the Subsurface

The nonsilicate aluminum minerals that occur in soils and the shallow subsurface environment include the aluminum hydroxides, gibbsite $(\text{Al(OH)}_3(s))$, bayerite $(\text{Al(OH)}_3(s))$, nordstrandite $(\text{Al(OH)}_3(s))$, and the oxides or (oxy)hydroxides boehmite $(\text{AlO(OH)}(s))$, diaspore $(\text{AlO(OH)}(s))$, alunite $(\text{KA}_3(\text{SO}_4)_2(\text{OH})_6(s))$, and corundum $(\text{Al}_2\text{O}_3(s))$ (Eswaran et al., 1977). The most common aluminum hydroxides, oxyhydroxides, and oxides found in nature are shown in Table 1.1.

Weathering of minerals to form gibbsite occurs most intensely in humid tropic environments, but also in other environments. Gibbsite has been found in the clays of alpine soils (Reynolds, 1971), in volcanic ash soils in Japan (Wada and Aomine, 1966),
<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Occurrence in Nature</th>
<th>Frequency of Occurrence</th>
<th>Year Approved by IMA ( ^a )</th>
<th>Year of Discovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>Al(OH)(_3)</td>
<td>Occurs abundantly in humid tropical climates (usually in soils at high weathering stage, such as oxisols, ultisols, or ferrolsols). (^b) Occurs ubiquitously in soils and structures of clays</td>
<td>Very common ( ^c,d )</td>
<td>1822</td>
<td>1820 (Dewey)</td>
</tr>
<tr>
<td>Bayerite</td>
<td>Al(OH)(_3)</td>
<td>Precipitated from high aluminum concentration gels at pH ( &gt;5.8 ); as weathered crusts on amphiboles and pyroxenes; in bauxites</td>
<td>Very rare ( ^d,e )</td>
<td>1928</td>
<td>1925 (Böhm)</td>
</tr>
<tr>
<td>Nordstrandite</td>
<td>Al(OH)(_3)</td>
<td>Weathering product of bauxitic soils derived from limestone. Alteration product of aluminum carbonate minerals. Late-stage mineral in nepheline syenite pegmatites</td>
<td>Very rare ( ^c,d )</td>
<td>1958</td>
<td>1956 (Van Nordstrand)</td>
</tr>
<tr>
<td>Doyleite</td>
<td>Al(OH)(_3)</td>
<td>Occurs in albite veins in nepheline syenite and in silicocarbonatite sills</td>
<td>Very rare ( ^c )</td>
<td>1985</td>
<td>1985 (E.J. Doyle)</td>
</tr>
<tr>
<td>Boehmite</td>
<td>AlO(OH)</td>
<td>Occurs abundantly in subtropical areas of high rainfall and commonly in soils elsewhere</td>
<td>Very common ( ^c )</td>
<td>1927</td>
<td>1925 (Böhm and Niclassen)</td>
</tr>
<tr>
<td>Diaspore</td>
<td>AlO(OH)</td>
<td>Common in many environments</td>
<td>Very common ( ^c )</td>
<td>1801</td>
<td>1801 (Hauy)</td>
</tr>
<tr>
<td>Corundum</td>
<td>Al(_2)O(_3)</td>
<td>Corundum occurs as a mineral in mica schist, gneiss, and some marbles in metamorphic terranes. It also occurs in low silica igneous syenite and nepheline syenite intrusions. Because of its hardness and resistance to weathering, it commonly occurs as a detrital mineral in stream and beach sands</td>
<td>Common ( ^c )</td>
<td>1798</td>
<td>1798 (Greville)</td>
</tr>
</tbody>
</table>

\(^a\) The International Mineralogy Association, which maintains a public listing of all the approved mineral names for all minerals since 1959, where official determinations are on record.

\(^b\) USDA (1996); FAO (1998); Brady and Weil (2002).

\(^c\) Wefers and Misra (1987).

\(^d\) Hsu (1977).

\(^e\) Huneke et al. (1980).
in temperate areas in North Carolina (Cate and McCracken, 1972), France (Dejou et al., 1970), and Scotland (Wilson, 1970), and in hotter areas such as Zaire (Eswaran et al., 1977).

An accumulation of gibbsite with or without the other forms of aluminum hydroxides or oxides (e.g., diaspor) characterizes bauxite, the primary ore used for production of aluminum metal. Bauxite rich in gibbsite is usually found in areas characterized by a tropical climate with alternating rainy and dry periods. Bauxite with primarily boehmite appears to be more constrained to the subtropical areas (Mediterranean-type bauxite) (Kloprogge et al., 2006). In lateritic bauxites, gibbsite and boehmite are the most common minerals, diaspor occurs but not frequently, and corundum appears very rarely. In karst and sedimentary bauxites, diaspor is frequently found while corundum is occasionally observed (Trolard and Tardy, 1987). It has been shown (Bardossy, 1982; Trolard and Tardy, 1987) that the distribution of these minerals is a function of climate, petrographic organization, age of formation, degree of compaction, and, in some cases, temperature and degree of metamorphism.

Generally, bauxite is considered to have at least 45.5 percent by weight Al₂O₃ and less than 20 percent Fe₂O₃ and 3.5 percent combined silica (Valeton, 1972; Eswaran et al., 1977). Global bauxite resources are estimated to be 55–75 billion tons, located in Africa (33 percent), Oceania (24 percent), South America and the Caribbean (22 percent), Asia (15 percent), and elsewhere (6 percent) (U.S. Geological Survey, 2008).

In addition to its occurrence as a pure phase, gibbsite occurs ubiquitously as precipitates in the interlayer or as part of the structure of common clay minerals, especially the illite, kaolinite, chlorite, and montmorillonite/smectite groups (Barnishel and Rich, 1963; Weaver and Pollard, 1973; Violante and Jackson, 1981; Dixon et al., 1989; Bird et al., 1994; Sposito, 1996). The individual aluminum hydroxide layers in these clays are gibbsite. Gibbsite can be formed from the hydrolysis and desilication of clay minerals (Freeze and Cherry, 1979; Sposito, 1989; Bird et al., 1994).

The clay minerals are important constituents of soil and they are excellent sorbents (e.g., gibbsite) for toxic metals and natural scavengers for cations and anions as water flows over soil or penetrates underground. The high specific surface area, high cation exchange capacity, layered structure, chemical and mechanical stability, Brønsted and Lewis acidity, and so on have made them excellent materials for adsorption (Tanabe, 1981; Dubbin et al., 2000; Gupta and Bhattacharyya, 2006; 2008; Bhattacharyya and Gupta, 2008a; 2008b).

1.3 OCCURRENCE OF ALUMINUM OXIDES AND HYDROXIDES IN SURFACE WATER

Surface waters contain a wide range of total aluminum (dissolved and solid phase) concentrations, with the amount depending on watershed soil characteristics and chemistry of rainwater and runoff. Generally, more acidic waters contain the most
aluminum. Based upon data obtained in the northeastern United States, Canada, Sweden, Norway, and Germany, Cronan and Schofield (1979) concluded that one of the primary effects of acid deposition is increased mobilization of Al from soils to surface waters (Sullivan and Cosby, 1998). Acid rain has caused the aluminum level in many freshwater sources to increase (Schecher and Driscoll, 1988; Swistock et al., 1989). Al mobilization is now widely believed to be the most important ecological effect of surface water acidification (Sullivan and Cosby, 1998). Aqueous Al concentrations in acidified drainage waters are often an order of magnitude higher than those in circumneutral waters. Concentrations of Al in surface waters correspond reasonably well with the equilibrium solubility of Al(OH)₃(s), but at low pH are generally undersaturated with respect to gibbsite (Sullivan and Cosby, 1998; Gensemer and Playle, 1999).

In aquatic systems, the solubility of Al is often controlled by amorphous Al(OH)₃(s) or by microcrystalline gibbsite (Zänker et al., 2006), the latter being almost three orders of magnitude less soluble than the former. These solids exhibit solubility minima in the pH range 6–7. However, equilibrium conditions often do not exist because the Al hydroxo mono- and polynuclear complexes react slowly, and metastable polymorphs that form recrystallize slowly (Wesolowski, 1992; Zänker et al., 2006). The metastable species may exist for months or even years. There is some evidence that the metastable species grow in size as a function of time and ultimately are converted to microcrystalline gibbsite (Berkowitz et al., 2005). Gibbsite may form via different routes without hindrance in a short period of time varying from days to few weeks (May et al., 1979; Sposito, 1996).

Aluminosilicate minerals are formed when polysilicic acid reacts with dissolved aluminum species. Thus, the aluminosilicate secondary mineral kaolinite controls the equilibrium solubility of aluminum in natural waters as soon as the Si concentration exceeds about 1–3 ppm (Langmuir, 1997; Zänker et al., 2006). This condition is fulfilled by many natural water compositions. The dependence of kaolinite precipitation rates, which are slow, on pH under environmental conditions (at about 22°C) has not yet been determined. The rate of kaolinite precipitation could influence or even control the overall rate at which chemical weathering occurs (Yang and Steefel, 2008).

High aluminum concentrations have been reported in surface waters receiving large inputs of acid sulfate solution, such as acid rain and acid mine drainage, basically due to the enhanced dissolution kinetics of gibbsite (and by analogy, of other aluminum-containing minerals) (Ridley et al., 1997). Speciation calculations for aluminum in water samples taken from a basin imported by acid mine drainage demonstrate that above pH 4.9 dissolved Al is consistent with the equilibrium solubility of microcrystalline gibbsite or amorphous aluminum hydroxide (Nordstrom and Ball, 1986). Some investigators have reported that the activity of Al₃⁺ in high sulfate loading in groundwaters and soil solution appears to be regulated by the solubility of jurbanite (Al(OH)SO₄·5H₂O) (Karathanasis et al., 1988; Alvarez et al., 1993; Driscoll and Postek, 1996).

Particles bearing aluminum are common in surface waters. Clay and silt particles from erosion that are suspended in surface waters are sources of particulate Al.
In addition, aluminum hydroxide that is precipitated \textit{in situ} contributes to the Al suspended solids, either as a separate solid or as a coating on other particles. In surface water, Al(OH)\textsubscript{3} solids with dissolved substances sorbed to them are common.

### 1.4 USE OF ALUMINUM HYDROXIDE IN WATER TREATMENT

The use of aluminum-bearing compounds in drinking water treatment has been conducted since the late 1800s. Al-based coagulants such as aluminum sulfate (alum, Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}(s)) or polyaluminum chloride (PACl) are commonly used in drinking water treatment to enhance the removal of particulate and colloidal substances via coagulation processes (Srinivasan et al., 1999). Addition of the aluminum salts results in precipitation of voluminous Al(OH)\textsubscript{3}(s) particles that settle and remove finer particles. They are widely used because they are effective, readily available, and relatively inexpensive. The parallel processes that take place after aluminum sulfate addition to water to precipitate Al(OH)\textsubscript{3}(s) and form particle flocs during water treatment are depicted in Figure 1.1.

![Figure 1.1: Parallel processes leading to incorporation of colloids into Al(OH)\textsubscript{3} flocs.](image)

**FIGURE 1.1** Parallel processes leading to incorporation of colloids into Al(OH)\textsubscript{3} flocs. Arrows indicate possible pathways; dashed lines are secondary pathways. (Adapted from Chowdhury et al., 1991.)
Precipitated $\text{Al(OH)}_3(s)$ also serves as an adsorbent in drinking water treatment, for removal of ionic contaminants such as arsenate (McNeill and Edwards, 1999) and dissolved natural organic matter (Huang and Shiu, 1996). The major mechanisms of organic acid removal by alum coagulation involve complexation, charge neutralization, precipitation, and adsorption entrapment (Huang and Shiu, 1996).

Typically, a portion of the alum added to the raw water is not removed during treatment and remains as residual aluminum in the treated water. The use of alum as a coagulant for water treatment often leads to higher concentrations of dissolved aluminum in the treated water than in the raw water itself. There is considerable concern throughout the world over the levels of aluminum found in drinking water sources (raw water) and treated drinking water. A high (3.6–6 mg/L) concentration of aluminum in treated water gives rise to turbidity, reduces disinfection efficiency, and may precipitate as $\text{Al(OH)}_3$ during the course of distribution (Srinivasan et al., 1999; Snoeyink et al., 2003).

Aluminum deposits can form in distribution systems because aluminum particles are not completely removed by sedimentation, and because the water is supersaturated with solids such as $\text{Al(OH)}_3(\text{am})$ and $\text{Al}_2\text{O}_3(s)$, aluminosilicates, and aluminum phosphates. Supersaturation leading to Al precipitation may result because of (1) failure to reach equilibrium in the treatment plant during coagulation, flocculation, and sedimentation; (2) lowering of temperature during storage and transport; and (3) decreasing pH in the distribution system within the pH range of 6–10 (Snoeyink et al., 2003).

Granular aluminum oxide particles, typically granular activated alumina, are sometimes used in drinking water treatment and in treatment of industrial process water or wastewater via a fixed-bed configuration (Brattebo and Odegaard, 1986; Karthikeyan et al., 1997; Ghorai and Pant, 2004). Removal of fluoride has often been a target for such systems, but alumina has the ability to adsorb many other chemical contaminants, including oxyanions of arsenic and many dissolved metals (Manning and Goldberg, 1997; Paulson and Balistrieri, 1999; Lin and Wu, 2001; Goldberg, 2002; Singh and Pant, 2004; Ghorai and Pant, 2005; Violante et al., 2006).

1.5 SUMMARY

Gibbsite and amorphous aluminum hydroxide are the aluminum (hydr)oxide solids most commonly formed under environmental conditions in soils, sediments, surface waters, and shallow groundwaters. Gibbsite $\text{Al(OH)}_3(s)$ is the most common crystalline form of aluminum hydroxide in nature (Schoen and Robertson, 1970; Violante and Huang, 1993; Gale et al., 2001; Digne et al., 2002; Liu et al., 2004). The presence of gibbsite in soils is generally attributed to the action of weathering processes of high intensity and of long duration. It is especially abundant in highly weathered, acidic soils. It also occurs ubiquitously as part of the structure of common clay minerals, and can be liberated from weathering of clay minerals through hydrolysis and
desilication. Gibbsite is very stable under most earth surface conditions, but may alter under special conditions to clay minerals, such as the kaolin minerals.

As is the case with most of the hydrous metal oxides, gibbsite has the ability to adsorb metal ions and anions as well as ligands on its surface. Ion binding on gibbsite in soils and sediments is well documented. Because of its sorptive role in nature and in water treatment, this book and the database it contains is focused on gibbsite.
Aluminum oxides including gibbsite, boehmite, and diaspor are ubiquitous in soils in various crystalline and amorphous forms. Like the common oxides of iron, manganese, and silicon, aluminum oxides can sorb a host of chemical species and are important sorbents in natural systems.

Aluminum oxides with physical and surface properties engineered through thermal and other kinds of treatments are used in water treatment, catalysis, pharmaceuticals, separations, and other technology areas. Expansion of commercial applications has been driven by the increasing scientific understanding of the chemical, structural, and surface properties of aluminum hydroxides and oxides.

In this chapter, detailed descriptions of gibbsite and closely related aluminum oxide minerals and their properties under environmental conditions are provided. Nomenclature for gibbsite and its mineralogic neighbors is reviewed and clarified. Crystal properties that distinguish the various forms are explained and summarized.

2.1 Al POLYMERIZATION MODELS

The formation of aluminum hydroxides, such as gibbsite, is generally achieved by hydrolysis–polymerization of Al$^{3+}$. The hydrolysis–polymerization mechanisms and species conversions of Al$^{3+}$ have been extensively explored for over a century. These mechanisms are explained by three widely accepted models: the “Core-links” model, the “Cage-like” Keggin-Al$\text{_{13}}$ model, and the “Continuous” model (Bi et al., 2004). The three models are briefly described below.
2.1.1 The “Core-Links” Model

The model was initially introduced in 1954 by Brosset et al. who suggested a series of “Core-links” polymeric Al species whose form was Al(Al₂(OH)₅)ₙ³⁺ₙ (Brosset et al., 1954). The Core-links model gives a distribution of the continuously changing transient state species of Al in the hydrolysis–polymerization process. It provides a basis for interpreting the various possible transient polymeric Al species and for explaining the experimental facts about how the monomeric and polymeric Al are converted into Al(OH)₃(am). However, it lacks direct and unequivocal evidence to prove the existence of these transient species, and it works under the condition of moderate rate of base injection in titrating Al³⁺ salts (Bi et al., 2004). The hydroxyl Al species change from monomeric to polymeric following the hexameric ring model (Fig. 2.1). The structure of OH–Al polymer in solution is the same as that of Al(OH)₃(s), whose basic units are either Al₆(OH)₁₂(H₂O)₁₂⁶⁺ (single hexamer ring) or Al₁₀(OH)₂₂(H₂O)₁₆⁸⁺ (double hexamer rings).

The Core-links model is the most commonly invoked model for Al polymerization, especially in the field of geochemistry because it follows the crystallographic law of gibbsite. Many scholars remain strong supporters of the model, so it has been coexisting with the “Cage-like” Keggin-Al₁₃ model for more than 50 years (Bi et al., 2004).

2.1.2 The “Cage-Like” (Keggin-Al₁₃ Structure) Model

The model was initially proposed by Johansson (1960, 1962) and it was based on sulfate precipitation from partially neutralized Al³⁺ solutions that were heated for 30 min at 80℃ and aged for few days. The model considers that in Al solutions there are monomer, dimer, Keggin-Al₁₃ polymer, and larger polymerized Al species. These species can be transformed from one to another directly (Akitt et al., 1972; Bottero et al., 1980; 1987; Bi et al., 2004). The metastable Keggin-Al₁₃ polymer molecule is formed by the structural reordering of transient species after aging. Under the conditions of aging, heating, adding extra SO₄²⁻, and slow addition of base, transient polymeric Al species transform from a state of disorder to a more ordered state (Bi et al., 2004). The Cage-like model is widely used in studies of the aqueous chemistry of aluminum because the polynuclear species of Al³⁺ invoked in the model are those identified experimentally.

![FIGURE 2.1 The polymerization of Al³⁺ via coalescence of the hexamer units. (Source: Bi et al., 2004.)](image-url)
2.1.3 The “Continuous” Model

The model was introduced by Bi et al. (2004). Polynuclear Al species are considered to be a series of dynamic intermediates formed in the process of “hydrolysis–polymerization–flocculation–sedimentation.” The model considers that in aged polymeric Al solutions, under a fixed molar ratio of OH/Al, if prolonging the aging time properly, only one polymeric Al species may exist, and this is Keggin-Al13 (Bi et al., 2004). The metastable Keggin-Al13 is formed by the structural reordering of transient species after aging. Aging is one prerequisite for Keggin-Al13 formation; elevating temperature and addition of extra SO42− promote this conversion process. It is a combined model unifying the “Core-links” model and the “Cage-like” model. It can explain the entire course of hydrolysis–polymerization upon the addition of base to Al3+ solution (Bi et al., 2004). A conceptual representation of the “Continuous” model is shown in Figure 2.2.

![Figure 2.2: A conceptual representation of the “Continuous” model for Al3+ hydrolysis and polymerization, which builds on the “Core-links” model for evolution of transient polymeric Al species. Through self-assembly, the more stable species after aging are Al2, K-Al13, Al13, and [Al(OH)3]n(s). [Al(OH)3]n(s) can be characterized by solid-state 27Al NMR spectroscopy or X-ray diffraction. Other forms, including Al(OH)4−/C0, can be measured by solution 27Al NMR spectroscopy. Al2: Al2(OH)2(n(H2O))10−n6−n+ (n = 2–6); Al3: Al3(OH)3(n(H2O))14−n9−n+ (n = 4–9); Al13: Al13O4(OH)n(H2O)32−n31−n+ (n = 24–31); K-Al13: Keggin-Al13; C-Al13: Cage-Al13. (Source: Bi et al., 2004.)](image-url)
Gibbsite is one of the dominant forms of aluminum oxide resulting from precipitation and aging of aluminum hydroxide gels. Aluminum hydroxide gels are formed from solutions of aluminum salts by precipitation and aging. The relationship between the freshly precipitated amorphous aluminum hydroxide and the other forms has been summarized by several groups (Bye and Robinson, 1964; Schoen and Robertson, 1970; Alwitt, 1976). These groups document that in the environmental temperature range the amorphous aluminum hydroxide transforms first to pseudoboehmite, then to bayerite, and upon elevated pH to gibbsite (Alwitt, 1976). Norstrandite may also be present in the last two steps of the proposed transformation mechanism. Hsu (1966) proposed that the difference between the formation of the two polymorphs (gibbsite and bayerite) was in the source of the OH$^-$ groups. When a strong alkaline solution is used, OH$^-$ almost immediately couples with Al$^{3+}$ to form bayerite. When acid solution is used, then the OH$^-$ must come from the dissociation of water and gibbsite forms. Alwitt (1976) proposed that the transformation from pseudoboehmite can lead to any of the three forms of the aluminum trihydroxide, namely, gibbsite, bayerite, or norstrandite (Fig. 2.3), with the final product depending on aging conditions. In water, at temperatures up to 80°C and at a pH range of 7–11, the predominant product is bayerite (Alwitt, 1976). However, bayerite is considered a thermodynamically metastable phase and gibbsite is the stable phase below 90°C at 1 atm. It has been reported that upon aging bayerite can be transformed to gibbsite in several months (Pascal et al., 1963).

Bertsch and Parker (1996) proposed a mechanism for aluminum hydroxide solid formation similar to that in Figure 2.3, but which includes multiple reaction pathways as shown in Figure 2.4, many of which may occur simultaneously but in different relative proportions. Reaction pathway I occurs when solutions are brought to supersaturation through dilution or when samples are neutralized rapidly. Under these conditions, gibbsite crystals appear within days or weeks of aging. Reaction