
ALUMINUM OXIDES AND HYDROXIDES UNDER ENVIRONMENTAL CONDITIONS

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 Al^{3+} reacts with water to form various hydroxy species including AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, and $\text{Al}(\text{OH})_4^-$. The aqueous speciation of dissolved Al strongly depends on pH. The released mononuclear ionic 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 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 (Licisko, 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 ($\text{Al}(\text{OH})_3(\text{s})$), bayerite ($\text{Al}(\text{OH})_3(\text{s})$), nordstrandite ($\text{Al}(\text{OH})_3(\text{s})$), and the oxides or (oxy)hydroxides boehmite ($\text{AlO}(\text{OH})(\text{s})$), diaspore ($\text{AlO}(\text{OH})(\text{s})$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6(\text{s})$), and corundum ($\text{Al}_2\text{O}_3(\text{s})$) (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 1.1 Aluminum oxides and hydroxides occurring under environmental (surface and near-surface, low-temperature) conditions

Name	Chemical Formula	Occurrence in Nature	Frequency of Occurrence	Year Approved by IMA ^a	Year of Discovery
Gibbsite	Al(OH) ₃	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	Very common ^{c,d}	1822	1820 (Dewey)
Bayerite	Al(OH) ₃	Precipitated from high aluminum concentration gels at pH >5.8; as weathered crusts on amphiboles and pyroxenes; in bauxites	Very rare ^{d,e}	1928	1925 (Böhm)
Nordstrandite	Al(OH) ₃	Weathering product of bauxitic soils derived from limestone. Alteration product of aluminum carbonate minerals. Late-stage mineral in nepheline syenite pegmatites	Very rare ^{c,d}	1958	1956 (Van Nordstrand)
Doyleite	Al(OH) ₃	Occurs in albitite veins in nepheline syenite and in silicocarbonatite sills	Very rare ^c	1985	1985 (E.J. Doyle)
Boehmite	AlO(OH)	Occurs abundantly in subtropical areas of high rainfall and commonly in soils elsewhere	Very common ^c	1927	1925 (Böhm and Niclassen)
Diaspore	AlO(OH)	Common in many environments	Very common ^c	1801	1801 (Haüy)
Corundum	Al ₂ O ₃	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	Common ^c		1798 (Greville)

^aThe 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.

^bUSDA (1996); FAO (1998); Brady and Weil (2002).

^cWefers and Misra (1987).

^dHsu (1977).

^eHuneke 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., diaspore) 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, diaspore occurs but not frequently, and corundum appears very rarely. In karst and sedimentary bauxites, diaspore 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 Al_2O_3 and less than 20 percent Fe_2O_3 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, Brönsted 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 $\text{Al}(\text{OH})_3(\text{s})$, 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 $\text{Al}(\text{OH})_3(\text{s})$ 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 Al^{3+} in high sulfate loading in groundwaters and soil solution appears to be regulated by the solubility of jurbanite ($\text{Al}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$) (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 *in situ* contributes to the Al suspended solids, either as a separate solid or as a coating on other particles. In surface water, $\text{Al}(\text{OH})_3$ 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, $\text{Al}_2(\text{SO}_4)_3(\text{s})$) 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 $\text{Al}(\text{OH})_3(\text{s})$ 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 $\text{Al}(\text{OH})_3(\text{s})$ and form particle flocs during water treatment are depicted in Figure 1.1.

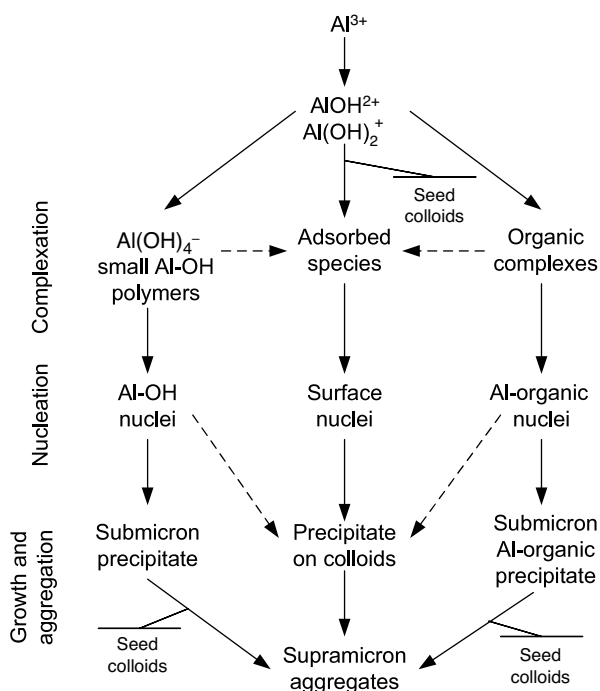


FIGURE 1.1 Parallel processes leading to incorporation of colloids into $\text{Al}(\text{OH})_3$ flocs. Arrows indicate possible pathways; dashed lines are secondary pathways. (Adapted from Chowdhury et al., 1991.)

Precipitated $\text{Al}(\text{OH})_3(\text{s})$ 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 $\text{Al}(\text{OH})_3$ 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 $\text{Al}(\text{OH})_3(\text{am})$ and $\text{Al}_2\text{O}_3(\text{s})$, 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 $\text{Al}(\text{OH})_3(\text{s})$ 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.