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Kinetic aspects of aqueous aluminum chemistry: environmental implications

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Contents

Abstract

Aluminum is a common constituent of the earth's crust and is present in many rock and soil forming minerals. In spite of its abundance Al(III) usually is not very soluble in water. However, strong mineral acids, such as may be present in rainfall, can solubilize some of the aluminum. On becoming solubilized the Al(III) can be present in the natural water environment in a number of forms. The speciation of Al(III) is complex and depends not only on the aqueous environment itself (inorganic and organic ions present, the solids the water is in contact with, inorganic and organic) but also on the past history of the Al(III) containing water.

An attempt is made to predict the fate of Al(III) in water after it has been solubilized in some manner, such as through the precipitation of strong inorganic acid containing rain on various diverse landscapes. The past history of the Al(III) containing water, the effect of pH rise, the presence of inorganic and organic dissolved substances and the presence of various minerals and organic materials are considered in the predictions.

Keywords: Aluminium solubilization; Aluminium(III) speciation; Aluminium(III) fate

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1. Introduction

Al(III) present in surface and ground water can exist in a number of different forms. The presence or absence of the various species depends on the presence and

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concentrations of various other anions and cations, on the organic material (type, amount) present, the type of minerals present, the pH of the water and on the past history of the aqueous Al(III) [1–24]. In basic solution Al(III) will primarily be found in anionic form. In acidic solution the Al(III) will be found primarily in cationic form. The aqueous Al(III), when in cationic form, can react with many of the anions to form various Al(III) complexes. In the absence of significant concentrations of other anions the aqueous Al will form various hydroxy complexes, the relative amounts of which will depend on pH and on the past history and the initial concentration of the Al in solution [10,13–15,19,22–25]. Of importance is how the pH of the solution reached its present value (whether the pH has slowly risen over time from some lower pH value or has risen rapidly from some lower value or has lowered from some more basic value). If other anions such as fluoride, sulfate, phosphate are present these anions form complexes with Al(III) [8,17,26,27]; fluoride, especially, forms strong complexes and in some environmental water samples most of the Al is present in the form of these complexes [28–32]. The relative stability of hydroxy complexes and other anionic complexes will, of course, be a function of pH and the concentrations of the other anions. Obviously, changes in the pH of the water can cause all equilibria to shift in direction.

Organic substances, living and dead, such as humic materials, plant roots etc. can strongly sorb Al(III). Such sorption is strongly pH dependent and episodic additions of acids can cause desorption of sorbed Al(III) [33–36]. Aqueous Al in all forms can and will adsorb onto many rock and soil forming minerals [10–37]. The adsorption and desorption are also strongly pH dependent.

A consequence of rain containing significant amounts of sulfur or nitrogen oxyacids is likely to be increased geochemical mobility of Al(III) [38]. The increased mobility results from the interaction of the strong acids with aluminum containing minerals and/or with organic matter containing complexed and/or adsorbed aluminum [19]. The increased solubilization of aluminum is significant since aluminum toxicity has been implicated in fish loss in lakes and streams [28,38–41], forest damage [42,43] and plant damage in general [44–47]. There is some evidence, however, that all forms of aqueous Al are not equally toxic to living organisms [28].

2. Aluminum speciation

Aluminum hydrolysis is quite complex because of the apparent existence of polynuclear macro-ions. These ions are highly charged. They may exist only in metastable form [10,13,14] although there is substantial evidence for the existence of some stable forms [3,15,24,48–50]. Regardless of the existence of the stable aquo-aluminum polynuclear species, the metastable species often appear to exist for months or even years [10,13,14,24]. There is some evidence that the metastable species grow in size as a function of time and ultimately are converted to microcrystalline gibbsite [10,13,14].

Okura et al. [15] first introduced the concept that basic forms of aluminum in aqueous solution could be determined by observing the kinetics of reaction of Al(III)

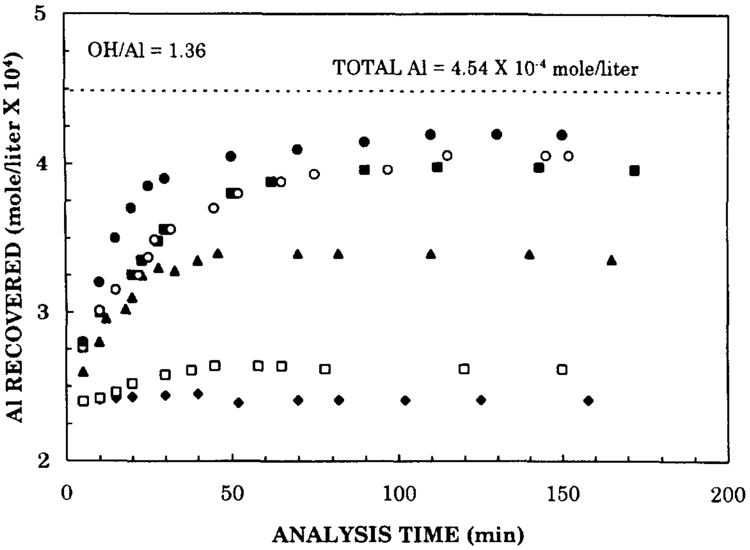

Fig. 1. Aluminum recovered by the reverse ferron method as a function of analysis time for several aging times (total Al(III), 4.54×10^{-4} m dm^{-3}; OH:Al = 1.36): ●, 23 h; ○, 96 h, ■, 625 h; ▲, 46 days; □, 82 days; ◆, 121 days. From Ref. [10].

species with the complexing reagent, 8-quinolinolate. In the method, after a timed reaction with the Al(III) solution, the complex formed was extracted into chloroform and read at 390–420 nm. The procedure was later used by Turner and coworkers [11,12,15] to determine that three major forms of Al(III), mononuclear, polynuclear and slow reacting material can exist in mildly acidic aqueous solution. Further, the effet of aging on the concentrations was also investigated.

The use of ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) reaction kinetics to study Al(III) speciation was introduced in 1969 by Smith [10,13]. The method is a variation of the analytical method of Rainwater and Thatcher [52] in which the order of reagent addition was altered in order to emphasize the relative rate of reaction of aluminum with ferron. The procedure has an advantage over the 8-quinolinolate method in that in the ferron method an extraction into chloroform is not required before spectrophotometric reading. In this work the three forms of Al(III) were denoted Al_a, Al_b and Al_c. Al_a was considered to be composed of mononuclear Al(III) species, Al_b was considered to be composed of polynuclear Al(III) species and Al_c was considered to be composed of microcrystalline gibbsite.

Fig. 1 illustrates the type of data obtained from the experimentation [10,13,14]. The Al(III) reacting (almost) instantaneously with ferron was considered to be, ignoring coordinated water molecules, the mononuclear species Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3(aq)$ and $Al(OH)_4^-$, the Al_a. Assuming the solid present in the system to be α-$Al(OH)_3$, the relationships among these species are indicated by the following relationships [10,13,14]:

$$\alpha\text{-Al(OH)}_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O, \quad K_{s0} = 10^{8.22} \qquad (1)$$

$$\alpha\text{-Al(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{AlOH}^{2+} + 2\text{H}_2\text{O}, \quad K_{s1} = 10^{3.22} \tag{2}$$

$$\alpha\text{-Al(OH)}_3 + \text{H}^+ \rightleftharpoons \text{Al(OH)}_2^+ + \text{H}_2\text{O}, \quad K_{s2} = 10^{-1.54} \tag{3}$$

$$\alpha\text{-Al(OH)}_3 \rightleftharpoons \text{Al(OH)}_3, \quad K_{s3} = 10^{-6.5} \tag{4}$$

$$\alpha\text{-Al(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + \text{H}^+, \quad K_4 = 10^{-5.00} \tag{5}$$

$$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+, \quad K_1 = 10^{-5.00} \tag{6}$$

$$\text{AlOH}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^+ + \text{H}^+, \quad K_2 = 10^{-4.76} \tag{7}$$

The Al(III) reacting over a period of up to about 2 h following a pseudo-first-order rate law was considered to be polynuclear aluminum, the Al_b. The remaining, very slowly reacting material, reacting with ferron following, apparently, a pseudo-zero-order rate law was considered to be a micro-solid, probably microcrystalline gibbsite, the Al_c.

The relationship derived for the reaction of an Al(III) solution with ferron is

$$[\text{Al}]^\text{T}(t) = [\text{Al}_\text{a}] + [\text{Al}_\text{b}]_0 - [\text{Al}_\text{b}]_0\,\text{e}^{-ik_\text{b}t} + k_\text{c}t \tag{8}$$

where $[\text{Al}]^\text{T}(t)$ is the total aluminum in the system that has reacted in time t, $[\text{Al}_\text{b}]_0$ is the amount of Al_b present at time 0, k_b is the pseudo-first-order rate constant for Al_b and k_c is the pseudo-zero-order rate constant for Al_c.

In the experimentation the solutions to be studied were prepared by partially neutralizing acidic aluminum solutions with addition of base solutions containing no aluminum. Solutions were prepared that had OH : Al ratios between 0.55 and 3.0. It was found that the amount of Al_b formed was a function of the rate of addition of the base to the aluminum solutions; the slower the addition the more Al_b formed. Fig. 2 shows the effect of rate of neutralization on the amount of Al_b present in solution.

After preparation of the solutions they were allowed to age. As a function of time the concentration of Al_b decreased and the concentration of Al_c increased. The progress of a typical solution is illustrated in Fig. 3 and the disappearance of Al_b as a function of time from solutions of different OH : Al ratios is illustrated in Fig. 4.

Hem [8,9], Smith [10,13] and Smith and Hem [14] concluded that the Al_b polymers increased in size with time starting with the formation of a six-member ring structure from aluminum hydroxy dimers. The rings then combined to form larger structures. Ultimately the rings grew to such a size and organization that they were converted to Al_c. Hsu [5,7] proposed a similar growth mechanism. Turner [15], however, while agreeing that the polymers were present presented evidence that the polymers were not directly converted to microcrystalline gibbsite, but rather to another polymeric form that reacted much more slowly with ferron (also according to a pseudo-first-order rate law, albeit exhibiting much smaller rate constants). Also, there is considerable evidence for the existence of a stable tridecamer aluminum hydroxy species possessing a Keggin-type structure [48,53–55].

Although there have been differing opinions about the form of Al_b and exactly

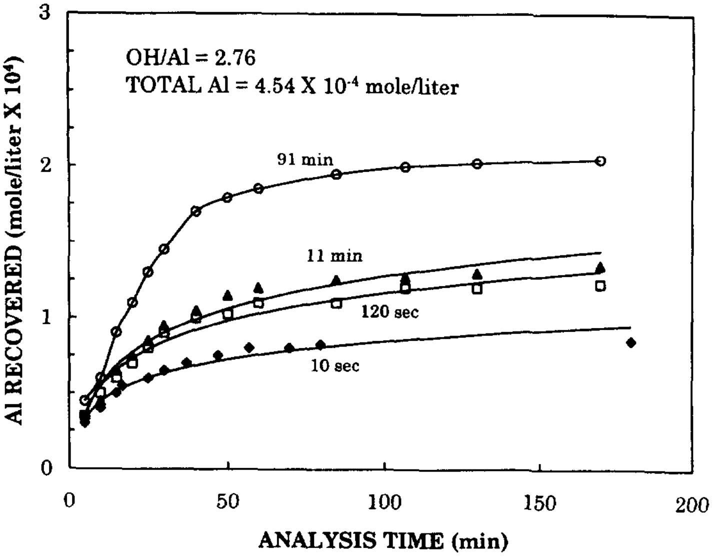

Fig. 2. Effect of length of time of adding base in preparing solutions on the amount of Al_b formed: total Al(III), 4.54×10^{-4} m dm^{-3}; OH:Al = 2.76. From Refs. [10,14].

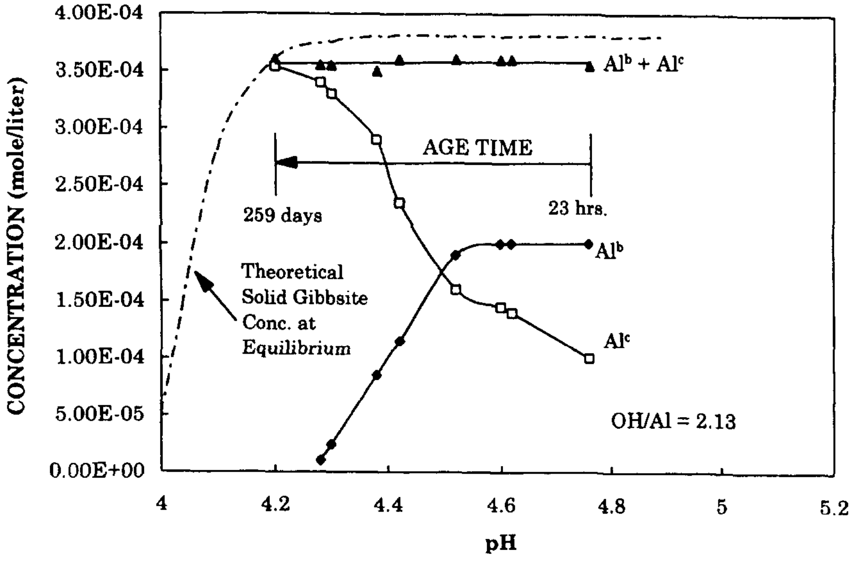

Fig. 3. Concentration of Al_b and Al_c as a function of pH and aging time; arrows indicate increasing aging time; total Al(III), 4.54×10^{-4} m dm^{-3}; OH:Al = 2.13. From Ref. [10].

what happens to it as a function of time, it is apparent that the kinetics of both the formation of this form of Al(III) and its disappearance or conversion to another form as a function of time must play an important role in the environmental fate of Al(III) and, hence, the effect of Al(III) on living organisms.

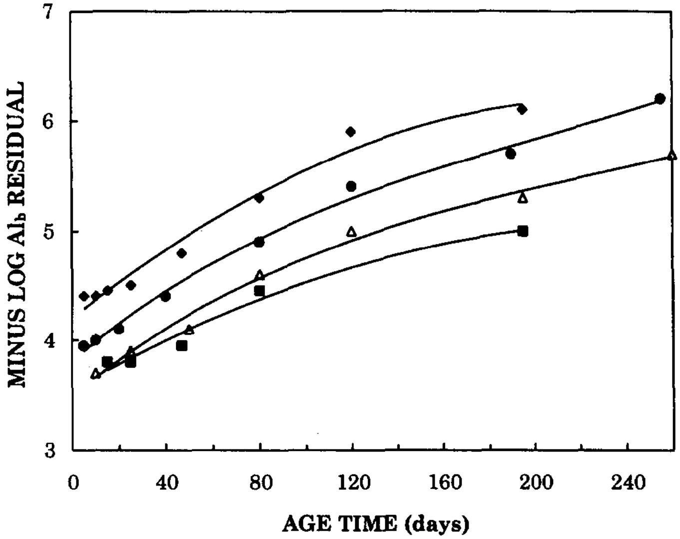

Fig. 4. Disappearance from solution of Al_b as a function of aging time for aluminum solutions containing various Al:OH ratios: ■, OH:Al = 1.36; △, OH:Al = 2.13; ●, OH:Al = 2.47; ◆, OH:Al = 2.76. From Ref. [10].

3. Reaction of Al(III) with other inorganic ions, organic materials and mineral surfaces

Competing with hydroxyl ion for formation of aluminum complexes are ligands such as F^- and SO_4^{2-}. Considering a pH value of pH 5 and the Al(III) present as fluoride complexes or Al^{3+} or $Al(OH)^{2+}$, from equilibrium data for aluminum hydroxy monomers and fluoride complexes, Fig. 5 from Hem [8] can be constructed.

From such data and similar data on aluminum sulfate complexes it can be concluded in acidic solutions containing more fluoride than aluminum that nearly all of the Al(III) will be present in the form of fluoride complexes. Further, it is likely that in acidic environmental solutions containing significant fluoride, unless there are very high concentrations of sulfate, the most important inorganic ligand complexing with aluminum will be fluoride [8].

Organic ligands can also be present in natural waters [33-36,56,57], particularly in heavily vegetated, forested, areas. Some ligands, such as salicylic, oxalic and malonic, can form strong complexes with Al(III) and may compete with inorganic ligands for the principal form of Al(III) present in solution. Some organic acids, such as citric, oxalic, tartaric and salicylic, solubilize aluminum from bauxite in amounts in excess of a simple lowering of pH by these acids. Fig. 6, from Lind and Hem [33], shows the effect of oxalate complexes on the equilibrium solubility of aluminum in the presence of halloysite. Humic substances, naturally occurring in waters, contain carboxyl and phenolic groups that strongly react with Al(III). In addition, many of these organic species can promote the formation of gibbsite from

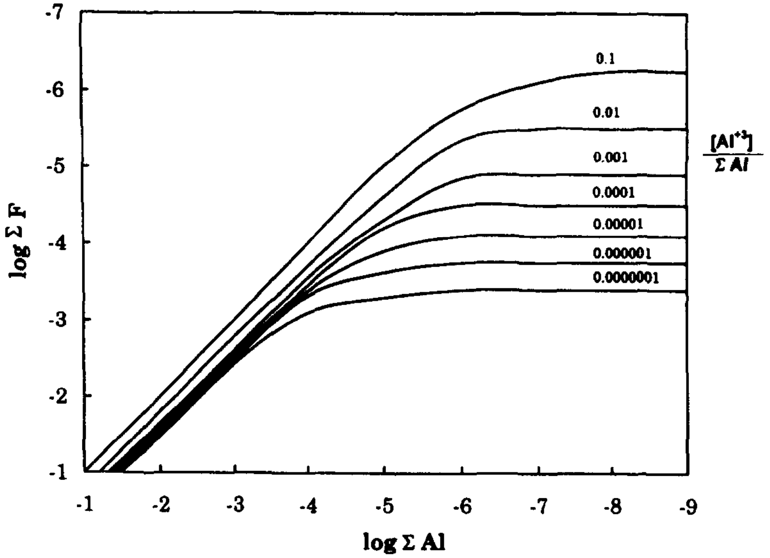

Fig. 5. Ratio of free aluminum activity [Al^{3+}] to total dissolved aluminum as a function of total dissolved fluoride and aluminum; pH 5.0. From Ref. [8].

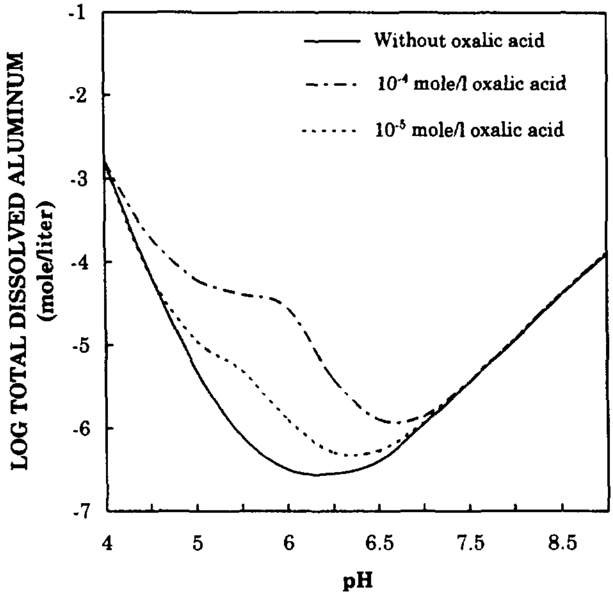

Fig. 6. Effects of oxalate complexes on the equilibrium solubility of aluminum in the presence of synthetic halloysite; dissolved silicic acid, $10^{-3.48}$ mole dm^{-3}. From Ref. [33].

supersaturated, aluminum containing waters [37]. Thus, their presence in natural waters may greatly control aluminum chemistry in such systems. Indeed, their presence in tropical and subtropical colored acidic rain forest waters may account for the relatively little effect of low pH in such systems as plant and animal life, in part, perhaps, because they remove Al(III) from solution.

Acidic rain can react with aluminum containing minerals to mobilize Al(III). At the same time, rock and soil forming minerals have the ability to sorb Al(III) species [10,37]. For example, montmorillonite, kaolinite, volcanic ash and feldspathic sand are able to adsorb mononuclear Al(III) readily from aqueous solution and such adsorption reactions are essentially complete after 1 h [37]. Rapid adsorption of polynuclear aluminum (Al_b) can also take place and the adsorption follows a Langmuir isotherm [37]. The adsorption is a function of the surface area of the solid. Note that in the absence of suitable surfaces such polynuclear species can remain in solution in metastable form for months or even years. Also, it appears that there is evidence of the presence of microcrystalline gibbsite on the solid surfaces. It has also been observed that polynuclear aluminum will adsorb onto α-Al_2O_3 [10]. It is, thus, apparent that the type, surface area and amount of mineral solids will influence the concentrations of both mononuclear and polynuclear Al(III) species. Therefore, the effect of solubilized Al(III) can be in part mitigated by the presence of various minerals that function as adsorbents.

4. Progress of aluminum in water after mobilization

The acidity of water falling on land will vary widely in pH. Were no sulfur oxides, nitrogen oxides or other acid forming oxides present in rain except for CO_2 the pH of the rain should be about 5.6–5.7, this pH resulting from equilibration of the rain with CO_2. However, because of the natural presence of some of these acids a more realistic pH for non-anthropogenic contaminated rain should be closer to pH 5.0 [58–60] unless the rain falls in very dry regions. In these cases, alkalis become air borne and may substantially raise the pH of the rain.

Ground waters, rising to the surface, will possess pH values which result from equilibration with the rocks through which the waters have been flowing. The waters should be of neutral to basic pH unless they contact hydrothermal fluids containing sulfur acids etc., in which case they can by quite acidic. Equilibration with carbonate rocks should result in an initial pH value (on arrival at the surface) greater than 8.0. Should the waters contact granitic rocks the waters are probably mildly basic [61]. In some cases, where ultrabasic rocks are present and contain minerals such as serpentine, the waters can be quite basic with pH values greater than 10.0 [62].

Anthropogenic introduced sulfur and nitrogen oxides from sulfide mineral smelters, coal burning power plants, internal combustion engines etc. can greatly lower the pH of rain striking the earth's surface to values well below 5.0, although the amount of pH lowering can vary widely [58–60,63–68].

In the subsequent discussion only acidic waters will be considered. As low pH rain water falls it will initially contact rocks, vegetation or soils. Such an encounter will, of course, greatly depend on the terrain onto which the rain falls. Should the rain fall in the high mountains, for example, of the western United States a great deal of the initial contact will be with rock minerals. Should the rain fall in a wet, heavily forested, area with much forest undergrowth the initial contact will be with plants and soil (an extreme example would be a tropical rain forest where most of the contact will be with vegetation).

Initially, as acidic rain reacts with aluminum containing minerals, such as feldspars, or with other aluminum containing materials, the pH will rise somewhat through the reaction [69,70] that mobilizes Al(III) and through the release of alkalis (Na^+, K^+) loosely held in the minerals' surface structure. The amount of mobilization will, in part, depend on whether considerable movement and breakage of the surface rocks has taken place through rock slides, freezing and thawing etc. Then, as the water flows to first-, second- and higher-order streams or to a nearby lake, further pH rise is likely because of dilution with less acidic water. Assuming an initial pH of the rain between 2 and pH 4 followed by slow dilution with other waters to an ultimate pH of about 5–6 a number of things can happen to the aqueous Al(III) depending on the absence or presence of various organic and inorganic substances.

Further, assume first that little organic material is present. Such conditions should obtain in a granitoid environment, particularly in places as the high altitude granitic mountains of the western United States or in many other subalpine, alpine or arctic environments. Inorganic ions likely to be present in waters in this environment include Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^-, NO_3^-, Cl^-, HCO_3^-, PO_4^{3-}, F^- and silicate [18,71–73]. If only Na^+, K^+, NO_3^-, Cl^- and HCO_3^- are present in significant quantities a reasonable history of the aqueous aluminum mobilized by acidic rain might be as follows.

(1) Al(III) species initially formed would be primarily monomeric aluminum (Al_a). The water pH at this point would depend on the initial rain pH.

(2) Then the Al_a should partially react evenly and slowly with hydroxyl ions present in dilution waters to form metastable hydroxy complexes (Al_b). These could be of several different forms as suggested by various researchers [10,13–16,22–24]. Thus, as pH rises the water becomes supersaturated with respect to solid aluminum oxide and hydroxide species [19]. The polymeric species are ultimately converted to microcrystalline gibbsite or some other solid.

(3) Alternatively, the monomeric and polymeric species may adsorb onto a number of minerals including alumina [10], various clay minerals and other minerals [2,34,37,74–76]. Adsorption of polynuclear aluminum onto certain minerals such as kaolinite is especially strong. This strong adsorption of Al_b onto minerals is not surprising since most of it probably is present in metastable form and should condense onto nucleation sites. In addition, the microscopic solid Al_c, being highly positively charged [10], should adhere strongly to negatively charged silicate mineral surfaces. Much of the precise progress of the system will depend on the pH values of the dilution waters which are likely to be determined by the rock minerals present and items such as the amount of rainfall; the drier the climatic sequence, the more residence time the water has in a lake and the more basic will be the pH of water

in lakes [77,78]. Of interest is evidence that the polynuclear form of aluminum is particularly toxic to plants [79].

(4) Both monomeric and polynuclear aluminum also can adsorb or complex with various organic substances should the water encounter these organics [33–36]. It appears that organic aluminum is less toxic to aquatic life than inorganic aluminum [57,80]. Thus, overall removal of aluminum will proceed as the water travels from a first-order to a second-order to a higher-order stream provided that minerals and organic matter encountered in the course of stream flow have not reached saturated adsorption. Most of the aqueous aluminum will have been removed before the water has traveled a great distance and usually only surface water high on a watershed should contain biologically significant concentrations of aqueous aluminum [81,82]. Of interest here is the damage spring acid precipitation as snow probably will do to fish eggs and fry when spawning grounds receive a sudden large charge of acidic Al(III) containing water derived from spring snow melt.

If, in addition to the inorganic ions, aqueous silica is also present some of the previously noted reactions can be hindered and other, additional, reactions can take place [83]. Gibbsite formation is hindered. Various types of cryptocrystalline and non-crystalline aluminum silicates can precipitate. Such colloidal substances can form more rapidly than gibbsite does in the absence or near absence of silicate [83]. The formation of some aluminum silicates may be catalyzed by the presence of organic material [33]. Paces [69,70] believes that it is a cryptocrystalline aluminosilicate that controls concentrations of alumina and silicate in natural waters. Overall, then, the presence of significant concentrations of soluble silicates should enhance the removal of inorganic aluminum from surface waters.

The presence of fluoride can produce marked changes in the progress of aluminum in water. Since fluoride ion forms strong complexes with aluminum it can considerably increase the solubility of aluminum [8,30]. Further, natural waters, at least in a head water stream environment, can contain substantial concentrations of F^- [30]. Overall, then, in the absence of significant amounts of organic material in lakes and streams which can tie up the fluoride, it appears that the effect of the presence of fluoride will be to increase the concentration of aluminum in solution. In many systems, thus, it is likely that aqueous aluminum is present mainly as fluoride complexes and these forms of aluminum may be the primary toxic entities causing fish egg and fry mortality.

It appears, from both field and theoretical studies, that sulfate in low order waters is not likely to be of significance in the progress of aqueous aluminum in these waters [8].

When substantial quantities of organic substances are present in the water the progress of the aluminum species should be greatly altered. Many field and experimental studies indicate that organic substances readily complex and, if solid, adsorb, Al(III) species [33–36]. In fact, polynuclear aluminum species have been studied and used in practice to coagulate and remove humic materials from water [84]. Evidence from acidic waters containing organic material suggests that the presence of humic acids decreases the toxic effect of aqueous aluminum toward animals and plants [57,85,86]. Thus, the presence of humic substances and other organics should greatly facilitate the removal of Al(III) from natural waters and reduce the toxicity of this aluminum.

It appears that most problems with toxic environmental aqueous aluminum occur in headwater, low-order waters, and that after the Al(III) travels very far most will either be removed from the aqueous solution by sorption or reaction or be rendered less toxic.

5. Summary

It is apparent that aluminum speciation is of great importance in determining not only the type and quantity of Al(III) in surface waters but also its toxicity. The further the water has traveled after having fallen as acidic rain the less likely is Al(III) to be present unless the water is still quite acidic (pH values well below 5). If such a very low pH is still present enormous amounts of mineral acids must be present in the rain or large amounts of organic acids produced by vegetation are present. The former might be the case for waters very close to where, for example, a sulfide mineral smelter or smelters operate that have little SO_2 control (as at one time in the Sudbury District in Canada). In this case the Al(III), primarily in some inorganic form, is likely to be quite toxic to plant and animal life. The latter case appears to exist in areas of very heavy rainfall such as in many tropical and subtropical parts of the world. This low pH water is not likely to contain significant amounts of aluminum because of reaction with and sorption onto organic substances. If, however, acidic rain falls directly onto forests or, especially, cultivated crops, Al(III) released through reaction with aluminum containing minerals or aluminum containing organic materials can react directly with the nearby growing plants causing aluminum intoxication of the plants.

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