Aluminium in Groundwater
Possible Solution Equilibria

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Recent investigations in the west coast region of Sweden has revealed the occurrence of groundwaters with a pH of around 4 and, further, alarmingly high concentrations of soluble aluminium. The reason for the occurrence of acid groundwater is, of course, the acid precipitation falling over this area of Sweden in combination with coarse soils on resistant types of granites and gneisses. The »resistance« against acidification of groundwater offered in the soil profile by aluminium and iron hydroxides must obviously have been partly broken. It seems therefore relevant to examine the solubility conditions of aluminium compounds in soils and rocks. From this we may reconstruct the process which led to the present state and we may also be able to tell what information on soils is needed in order to predict the future acidification of groundwater.

The Chemistry of Inorganic Aluminium Compounds in Soils and Rocks below pH 7.5

Aluminium occurs in primary minerals (e.g. feldspars, micas, hornblendes). Considering the pH-range 3-6 the aluminium released will be found either in hydroxides or in secondary so called clay minerals of kaolinite or montmorillonite type, possibly also as basic salts.

a) *Hydroxides*
A number of studies has been made on precipitates from aluminium solutions. Qualitatively they can be summarized following Petrović (1976) as in Fig. 1. There
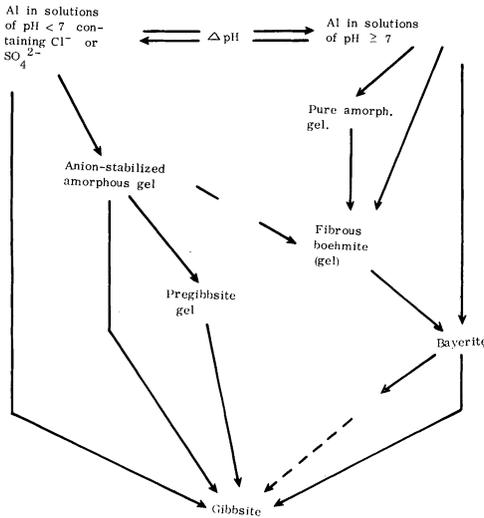
Fig. 1. Precipitation and phase transformation pattern of aluminium hydroxides and oxyhydroxides.
From Petrovic (1976).

are quite a considerable number of paths and forms which can occur. However, on the acid side we need only consider amorphous $Al(OH)_3$ and gibbsite. Gibbsite seems to form by polymerization of aluminium ions complexed by 6 molecules of either water or hydroxyls (Hem and Roberson 1967), a process which proceeds at a reasonable speed. A pre-gibbsite has been identified.

For aluminium hydroxydes we have the reaction

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$
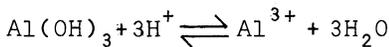
with the equilibrium condition (p = – log)

$$p[Al^{3+}] = pK + 3 pH$$

brackets indicating active concentrations. For pK the are three values of interest

Amorphous $Al(OH)_3$ (Sillén and Martell 1964)	pK = -9.7
Gibbsite, microcrystalline (Hem and Roberson 1967)	pK = -9.36
Gibbsite (Robie and Waldbaum 1968)	pK = -9.23

There is another value for gibbsite given by Smith and Hem (1972) as pK = -8.22 the determinations being carried out on well-crystallized material. From this figure it appears to be much more stable than shown in previous investigations. Tardy and Garrels (1974) adopted the solubility value given by Robie and Waldbaum, referring to a redetermination of the free energy of formation of gibbsite done by R.A. Robie. One may take this to mean that they rejected the Smith and Hem value.

In Fig. 2 the activities of Al^{3+} are shown as a function of pH for the three cases listed (the lines 1,2 and 3).
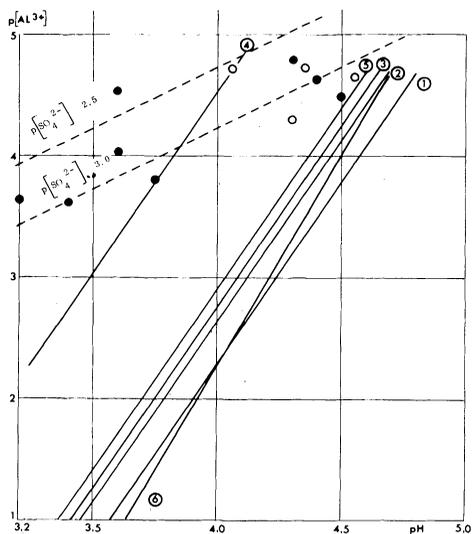
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Fig. 2. The activity of aluminium ion as function the pH in solutions in equilibrium with different solid aluminium compounds.

Solid lines

① with amorphous aluminium hydroxide

② with micro-crystalline gibbsite

③ with gibbsite

④ with kaolinite, $p[SiO_2] = 3.5$

⑤ with halloysite, $p[SiO_2] = 3.5$

⑥ with amorphous aluminium silicate according to Paces (1978), $p[SiO_2] = 3.5$

Broken lines refer to a postulated basic aluminium sulphate $AlOHSO_4$ (van Breemen 1973) at the sulphate ion activities indicated.

Filled circles, aluminium activity data from Stenunge (Hultberg and Johansson 1978). Open circles, same from Bredvatten/Lysevatten (Johansson 1977).

b) *Al-silicate minerals*

There are three minerals of interest: dickite, kaolinite and halloysite of the composition $Al_2Si_2O_5(OH)_4$. The data by Robie and Waldbaum (corrected according to Tardy and Garrels) can be used to compute the equilibria for the reaction

$$\tfrac{1}{2}Al_2Si_2O_5(OH)_4 + 3H^+ \rightleftharpoons Al^{3+} + H_4SiO_4 + \tfrac{1}{2}H_2O$$
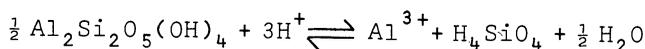
the equilibrium being given by

$$p[Al^{3+}] + p[H_4SiO_4] = pK - 3\,pH$$

We obtain

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kaolinite    pK = -3.97         halloysite    pK = -5.60
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Dickite is very close to kaolinite.

The Al^{3+} activity hence depends both on pH and the concentration of soluble silica, SiO_2. Since this corresponds to $p[H_4SiO_4] \sim 3.5$ with variations from 2.7 (saturated amorphous SiO_2) to 4 (solubility of quarts) we can enter the following relations in Fig. 2.

④ $p[Al^{3+}] = -7.47 + 3\,pH$ (kaolinite)

⑤ $p[Al^{3+}] = -9.10 + 3\,pH$ (halloysite)

It is seen in Fig. 2 that with a silica concentration of 19 mg/1 (as SiO_2) equivalent to $p[H_4SiO_4] = 3.5$ none of the aluminium hydroxides are stable. Halloysite and,

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ultimately, kaolinite would be formed. Even if the concentration of silica was decreased to 6 mg SiO_2/l (p H_4SiO_4 = 4) which is the solubility of quarts at 25 C, kaolinite would still be the most stable of the compounds.

c) »Amorphous« aluminium silicates

Recently Paces (1978) put forward a hypothesis about the existence in natural waters of solid compounds representing reversible metastable states in the chain of breakdown of primary minerals into thermodynamically stable secondary minerals. These metastable reversible solids determine the apparent equilibrium states in solution, the irreversible reactions being too slow to influence the metastable equilibrium to any noticeable degree. Considering the breakdown of e.g. feldspars Paces postulates an x-ray amorphous aluminium silicate as a metastable reversible solid. He refers to an early work by Mattson (1928) on studies of the charge properties of precipitated amorphous aluminium silicates and the elaborations of this work done much later by Parks (1967). The important point here is that the proportions of $Al(OH)_3$ and SiO_2 in the precipitate varies regularly with the pH as to attain the least possible net charge in the colloidal state. Paces writes the reaction

$$[Al(OH)_3]_{(1-x)}[SiO_2]_x + 3(1-x)H^+ \rightleftharpoons (1-x)Al^{3+} + x\, H_4SiO_4 + (3-5x)H_2O$$
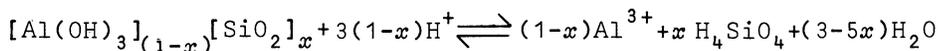
From Mattson's experiment Parks obtains

$$x = 1.24 - 0.135\, pH$$

Since the activity coefficient of the reaction can be written

$$(1-x)\, p[Al^{3+}] + x\, p[H_4SiO_4] = pK + 3(1-x)pH$$

pK can be evaluated by assuming the metastable phase to be an ideal solid solution between amorphous silica and alumina. This assumption leads to

$$pK = -9.7 + 12.4\, x$$

since the solubility of amorphous silica is $10^{-2.7}$ moles/l and the

$$p[Al^{3+}] = -9.7 + 3\, pH$$

for amorphous aluminium hydroxide. With this pH or x can be eliminated.

There are, of course, two crucial assumptions involed. One is the ideal solid solution of the amorphous aluminium silicate. This is doubtful in the acid range where the gibbsite lattice seems to form far more easier than tetrahedral silica layers as Paces is well aware of. The other weakness is the relation between x and pH which probably deserves some more careful studies under well controlled conditions. In view of the way dissolution of feldspars takes place (cf. Busenberg and Clemency 1976 and Petrovic 1976) the precipitation of aluminium by silica must, at best, be extremely slow whereas in Mattson's experiment precipitation was fast.

Using the relations referred to with pK = 5.89 – 1.59 pH as suggested by Paces

one can compute p [Al^{3+}] for various pH-values and different silica activities. Choosing p[SiO_2] = 3.5 (i.e. 19 mg SiO_2/l) one arrives at the line labelled 6 in Fig. 2. It is seen that it does not differ much from the amorphous hydroxide. If p[SiO_2] = 3 had been chosen the line would appear somewhere between the halloysite and kaolinite lines.
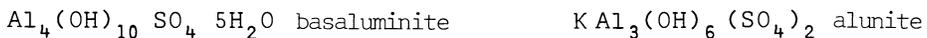
d) *»Basic« aluminium sulphate*

van Breemen (1973) discovered that in acid sulphate waters a nearly perfect relation reading

$$p[Al^{3+}] + p[SO_4^{2-}] - pH = 3.23$$

which suggests a solid phase of the composition $AlOHSO_4$. This is of great interest in acid groundwaters since the acid part comes from sulphate. The activities of sulphate in the samples to be discussed later vary, most of them being in the range p[SO_4^{2-}] = 2.5 to 3.0. The p[Al^{3+}] = 3.23 + pH – p[SO_4^{2-}] is shown in Fig. 2 for p[SO_4^{2-}] = 2.5 and 3.0. We can note immediately that at pH-values below 4 the postulated aluminium sulphate is likely to precipitate, thus controlling the activity of aluminium. In the absence of kaolinite the »basic«sulphate control extends to between pH 4.5 and 5 where the hydroxides take control.

Basic aluminium sulphates of different compositions are known. Adams and Hajek (1978) studied basaluminite and alunite of the compositions

$$Al_4(OH)_{10} SO_4 \ 5H_2O \ \text{basaluminite} \qquad K \, Al_3(OH)_6 (SO_4)_2 \ \text{alunite}$$

If we compare the slope of the [Al^{3+}] – pH relations for the basic aluminium sulphates we will have for

$$AlOHSO_4 \ p[Al^{3+}] \propto pH \, ; \quad \text{alunite } p[Al^{3+}] \propto 2\,pH \, ; \quad \text{basaluminite } p[Al^{3+}] \propto 2.5\,pH$$

Hence, the slope of the basaluminite solubility would be fairly close to that of the hydroxides and the silicates in Fig. 2.

Experimental Data

Two sets of chemical analysis of acid groundwaters were available. One set was taken from a report by Johansson (1977) from investigations around two small lakes, Bredvatten and Lysevatten on the west coast of Sweden. The other is from a report by Hultberg and Johansson (1978) on an investigation of acid groundwater in the vicinity of a small river, Stenunge å, also on the west coast. Only analysis which included aluminium were selected but these included mostly sulphate and silica as well. pH measured in the field was used in the computation. Whenever some of the major constituents were lacking ionic strength was estimated from the electrical conductivity using an empirical relation. Since ionic strengths did not exceed 0.05 the simple formula.

$$\log \gamma_z = 0.5z \ \frac{\sqrt{I}}{1+\sqrt{I}} \qquad (I = \text{ionic strength})$$

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was used to compute activity coefficients. The equation is recommended by Stumm and Morgan (1970) for mixed electrolytes.

Table 1 lists computed activities of the aluminium ion, the sulphate ion and silicic acid. When computing the activity of the aluminium ion consideration was given to the species $AlOH^{2+}$. It was computed from the equation

$$p[AlOH^{2+}] + pH = 4.84 + p[Al^{3+}]$$

(Latimer 1956, p 281).

Activities are expressed by their negative logaritm. The $p[Al^{3+}]$ data have been entered in Fig. 2 plotted against pH. Filled circles are data from Stenunge, open circles from Bredvatten/Lysevatten. One can almost immediately conclude that the simple basic aluminium sulphate seems to be the major control practically in the whole range. The way the points are spreading is significantly along the direction of the lines setting the conditions for sulphate control of aluminium. In Table 1 the last column displays $p[Al^{3+}]$ values computed from the equation

$$p[Al^{3+}] = 3.23 + pH - p[SO_4^{2-}]$$

For the Stenunge area the agreement between these and those computed from aluminium analysis is sometimes remarkably good.

The discrepancy between actual and computed $p[Al^{3+}]$ values is in general greater at pH-values below 4 where most of the samples appear supersaturated with respect to the postulated $AlOHSO_4$. Between pH 4 and 4.5 the agreement is better. This may mean that kaolinite is not present or at least is not in equilibrium with aluminium. Nor are any of the hydroxides of aluminium.

So all the evidence at present indicates that the aluminium concentration in acid groundwater is by and large determined by the sulphate concentration at least for pH<4.5, thus in the range where it is of environmental concern.

Table 1 – Selected data on groundwater

| Sample location		pH	$p[Al^{3+}]$	$p[SO_4^{2-}]$	$p[SiO_2]$	$p[Al^{3+}]$ comp. fr sulphate equil.
Stenunge å, pit 1A		3.75	3.81	2.49	3.23	4.49
»	1A	3.80	3.71	2.44	3.12	4.59
»	2C	4.40	4.62	3.09	3.50	4.54
»	3A	4.30	4.88	2.85	–	4.68
»	1B	3.60	4.03	2.72	3.25	4.11
»	pkt 2, 05-07	4.50	4.48	2.83	3.44	4.92
»	2A, 1 m	3.20	3.65	2.39	–	4.04
»	2A	3.40	3.60	2.23	3.05	4.40
»	1C	4.30	4.78	2.90	3.57	4.63
»	pkt 2, 04-11	4.20	4.63	3.09	3.70	4.34
»	3C	3.60	4.55	3.07	3.50	3.76
Bredvatten B4		4.30	4.29	3.65	–	3.88
Lysevatten L1		5.30	6.21	3.60	–	4.93
»	L2	4.55	4.64	3.76	–	3.82
»	L3	4.35	4.72	3.96	–	3.62
»	L5	4.06	4.72	3.84	–	3.45

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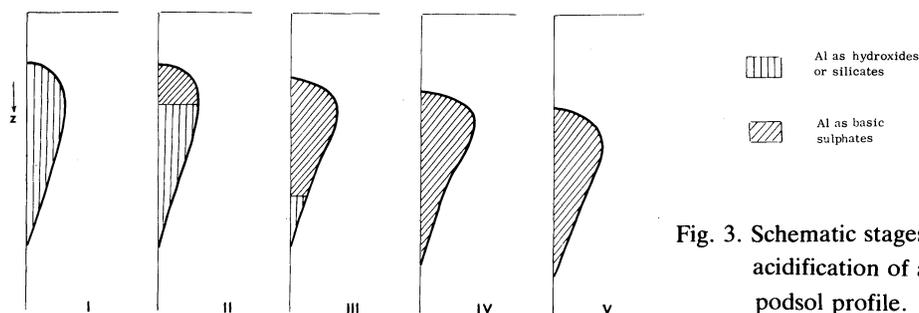
Fig. 3. Schematic stages of acidification of a podsol profile.

The Acidification Process in the Soil Profile and in the Ground

The appearance of acid groundwater marks a far reaching change in the soil profile where maybe the largest resistance, i.e. buffering, against acidity is expected in the B-horizon. One can picture the time development as follows. When the precipitation turns acid this will first attack the cation exchange reservoir in the soil. Once this is depleted aluminium hydroxides in the B-horizon are attacked. When sulphate concentrations are high enough the aluminium oxides are transformed into basic sulphates probably the simple $AlOHSO_4$. The reaction is thus

$$Al(OH)_3 + 2H^+ + SO_4^{2-} \longrightarrow AlOHSO_4 + 2H_2O$$
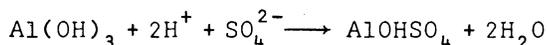
the transformation requiring 2 moles of hydrogen per mole aluminium hydroxide. Some aluminium has to go into solution, however, which eventually will shift the basic aluminium sulphate downwards along the path of the water. The course of events can, in a very simplified way, be pictured as in Fig. 3, the different stages being assigned roman numerals. Stage I picture the distribution of aluminium as secondary silicates or hydroxides in a soil profile before the onset of acidification, this particular distribution being typical of a podsolic soil. In stage II acidification has proceeded to such an extent that the upper part of the aluminium storage is converted into basic sulphates. Not much aluminium is actually lost at this stage because of the more neutral conditions of the lower end of the profile.

In stage III the conversion into basic sulphate is nearly complete and a downward shift of the aluminium at the top end can be noted. In the following stages the downward shifts continue. When the process has continued long enough the aluminium »front« will reach the groundwater table.

Although the reasoning may appear extremely hypothetical it is not improbable, much less impossible. Much of it can be verified in nature.

Andersson and Eriksson (1978) noted when computing balances of common constituents in forested catchments that less sulfur left the catchments than was brought down by precipitation. It is not unlikely, since precipitation is at present acid, that this depends on formation of basic aluminium sulphates in the podsolic soils in the catchments.

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