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UNIVERSITATIS OULUENSIS

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THE HYDROLYSIS OF ALUMINIUM, A MASS SPECTROMETRIC STUDY

FACULTY OF TECHNOLOGY,
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ARJA SARPOLA

**THE HYDROLYSIS OF ALUMINIUM,
A MASS SPECTROMETRIC STUDY**

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Abstract

This thesis is focused on the hydrolysis of aluminium, the polymerisation of the hydrolysis products, and how these can be monitored by mass spectrometric methods. The main aim of this research is to figure out how the aqueous speciation of aluminium changes as a function of pH (3.2–10), concentration (1–100 mM), reaction time (1s–14d), and counter anion (Cl^- , SO_4^{2-} , HCOO^-). The method used was electrospray mass spectrometry. The results showed more variable speciation than those suggested earlier. The main species were Al_2 , Al_3 , and Al_{13} , which were found in all of the conditions under scrutiny. The effect of pH was the most remarkable of all the parameters researched. The formation of large highly charged complexes was strongly dependent on it. Also the Al-concentration in the bulk solution had a clear effect on speciation: in dilute solutions there were more protonated ligands and less attached counter anions. This could mean that the species in more diluted bulk solutions had fewer different states of charge. Reaction time caused only minor changes to speciation in the initial pH: there was slightly more variation of a certain sized species in the aged solution. In elevated pH, the birth of important Al_{13} oligomers was time dependent. The effect of the counter anion was tremendous. In a chloride environment the speciation was rich and diversified. With sulphate the speciation was limited to solid-like compounds, and the variation of single-sized species was almost lacking. The formate as a counter anion caused most surprising results; the charge of aluminium in some studied complexes was lowered from the common $3+$ to $1+$. If this reaction also occurs in natural circumstances, the uses of aluminium formate would be wide. The results can be utilised in following the progress of dissolution, the mobilization and toxicity of aluminium in natural waters, as well as in water purification, and in reaching minimal chemical contamination levels in sludge as well as in aqueous waste.

Keywords: aluminium, coagulation, electrospray, mass spectrometry, speciation, water treatment

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At Muhos, 13 September 2006

Arja Sarpola

Table of acronyms and symbols

Al_n^z	n aluminium containing oxo hydroxo complex with the charge z e.g. $[\text{Al}_{13}\text{O}_4(\text{OH})_{29}]^{2+} = \text{Al}_{13}^{2+}$
$\alpha\text{-AlO}(\text{OH})$	diaspore, an aluminium mineral
$\gamma\text{-AlO}(\text{OH})$	boehmite, an aluminium mineral
$\alpha\text{-Al}(\text{OH})_3$	bayerite, an aluminium mineral
$\text{Al}(\text{OH})_3$	gibbsite, an aluminium mineral
Al_2O_3	corundum, an aluminium mineral
Bauxite	rock, a mixture of boehmite, gibbsite, and diaspore
ESI	electrospray ionisation
FT-ICR	Fourier-transform ion cyclotron resonance mass spectrometry
IR	infra-red spectroscopy
MS	mass spectrometer
MS/MS	tandem mass spectrometry
MS-Q	quadrupole mass spectrometer
m/z	mass-to-charge ratio
M	unit of concentration; mol/L, mol dm^{-3}
mM	unit of concentration; mill mol/L, $10^{-3} \text{ mol dm}^{-3}$
μM	unit of concentration; micro mol/L, $10^{-6} \text{ mol dm}^{-3}$
$\mu\text{-OH}$	terminal OH-ligand
$\mu_2\text{-OH}$	bridging OH-ligand
$\mu_3\text{-OH}$	central OH-ligand, e.g., in a trimeric ring structure
NMR	nuclear magnetic resonance
TIC	total ion count in a mass spectrometer
TOF	time of flight detection
XRD	X-ray diffraction

List of original papers

- I Sarpola A, Hietapelto V, Jalonen J, Jokela J & Laitinen RS (2004) Identification of the hydrolysis products of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ by electrospray ionization mass spectrometry. *Journal of Mass Spectrometry* 39: 423. DOI: 10.1002/jms.607.
- II Sarpola A, Hietapelto V, Jalonen J, Jokela J, Laitinen RS & Rämö J (2004) Identification and fragmentation of hydrolysed aluminum species by electrospray ionization tandem mass spectrometry. *Journal of Mass Spectrometry* 39: 1209. DOI: 10.1002/jms.722.
- III Sarpola A, Hietapelto V, Jalonen J, Jokela J & Rämö J (2006) Comparison of the hydrolysis products of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in different concentrations by electrospray ionization time of flying mass spectrometer. *International Journal of Environmental Analytical Chemistry* 86: 1007. DOI: 10.1080/03067310600687583.
- IV Sarpola A, Hellman H, Hietapelto V, Jalonen J, Jokela J, Rämö J & Saukkoriipi J (2007) Hydrolysis products of water treatment chemical aluminium sulfate octadecahydrate by electrospray ionization mass spectrometry; connection with mineral compositions. *Polyhedron* 26: 2581-2588. DOI:10.1016/j.poly.2007.01.035.
- V Sarpola A, Saukkoriipi J, Hietapelto V, Jalonen J, Jokela J, Laasonen K & Rämö J (2007) Identification of hydrolysis products of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with presence of sulphate by electrospray ionization time of flight mass spectrometry and computational methods. *Physical Chemistry Chemical Physics* 9: 377-388. DOI: 10.1039/b614814j.

Table of contents

Abstract	
Acknowledgements	5
Table of acronyms and symbols	7
List of original papers	9
Table of contents	11
1 Introduction	13
2 Water treatment	17
3 Hydrolysis of aluminium	19
4 Traditional methods of studying of hydrolysis of aluminium	25
4.1 Potentiometric titration and calculated speciation.....	25
4.2 The ²⁷ Al-NMR	27
4.3 The spectrophotometric detection	27
4.4 The surface analysis	28
4.5 Computational chemistry	30
5 The mass spectrometric method	31
5.1 Electrospray ionization (ESI).....	32
5.2 Time of flight analyser (TOF)	36
5.3 MS/MS with triple quadrupoles	37
6 Speciation of aluminium detected by mass spectrometer	40
6.1 Anionic aluminium species	42
6.2 Monomers	43
6.3 Dimers	45
6.4 Trimers	47
6.5 Small oligomers	51
6.6 Ten aluminium containing complexes.....	54
6.7 Aluminium 13	56
6.8 Other polyaluminium species.....	59
6.9 Effect of concentration	61
6.10 Effect of pH.....	63
6.11 Effect of time	64
6.11.1 Ageing	65
6.11.2 Kinetics: Distribution diagramme by mass spectrometer	65
6.12 Effect of counter anion.....	70
6.12.1 Chloride	70
6.12.2 Sulphate	71
	11

6.12.3 Formate.....	73
6.12.4 Phosphate.....	74
7 Conclusions	77
References	81
Original papers	99

1 Introduction

Purified water is by far the most precious chemical for mankind. In the industrialised world, the use of this irreplaceable product can be several hundred liters per person per day. Meanwhile, billions of people live either with no access to a water source, or have an insufficient supply of drinking water which, for example, is a major reason for high infant death rates. [1] In this light as well as taking into account a variety of industrial purposes, the amount of research focused on water treatment should be much higher.

Coagulation is an important and widely used unit operation in water and wastewater treatment, which chemically binds colloid materials and small suspended particles into larger aggregates, thereby facilitating their removal in the subsequent sedimentation or flotation and filtration stages. Dissolved organic matter is generally adsorbed on these aggregates. The chemicals used for coagulation are mainly aluminium- or iron-based salts, including different types of prepolymerised aluminium products, chlorides and as the most frequently used application, aluminium sulphate, more commonly known as alum. Even though they are widely used, their aqueous structure and behaviour is still under investigation. [2-4] Aluminium has a rich and dynamic speciation, which is very sensitive to changes in the surrounding environment (e.g. pH, temperature, etc.). Therefore, the coagulation and flocculation mechanisms of Al particles are largely unknown.

More focused unit operations would remarkably reduce unnecessary chemical loading, material streams and energy consumption, as illustrated in Fig. 1. This is becoming increasingly important in cities and in geographical areas that are difficult to reach. An essential part of the people who have an insufficient supply of drinking water (today about 3 billion) live in such areas. [1] A general understanding of aqueous aluminium structures can be utilised in evaluating its toxicity for humans and the environment as well as its synergistic effects with other toxic compounds. [5] Interactions with microbes also play an outstanding role in water treatment processes. [6]

Furthermore, deeper knowledge can be utilised in many practical applications such as sludge recycling, the evaluation of the mobility of aluminium in soils exposed to acids or earth dust, the development of nitrifying wetlands preceded or followed by chemical treatment, the assessment of phosphate binding and precipitation as well as liberation from soil, as well as investigations on the other detrimental or beneficial ions or compounds by aluminium.

The global usage of aluminium chemicals for different kinds of water treatment processes amounts to millions of tons annually. Considering the entire life cycle of these products, health issues, as well as environmental and technical impacts, the effects of their usage are thus tremendous.

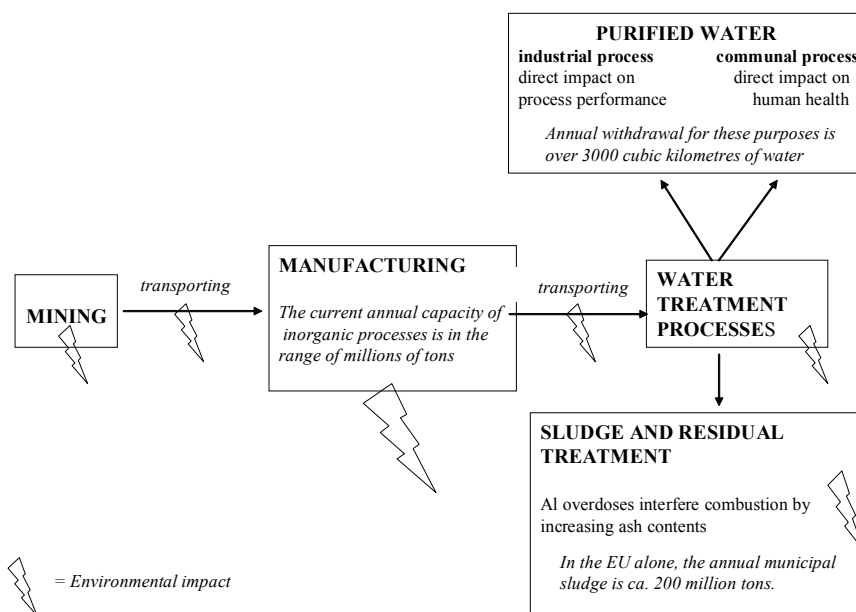


Fig. 1. The environmental impacts of Al as a water treatment chemical.

In the last decades, a lot of attention has been paid to aluminium and its distribution in nature and the environment. Aluminium is one of the most abundant elements in the earth's crust, and by far the most abundant metal. [7] It is therefore not surprising that aluminium is one of the major components of atmospheric aerosol particles from natural sources, i.e. volcanic activity and Aeolian dust. [8,9] Aluminium occurs mainly in aluminosilicates, the most common minerals of the crust – like the feldspars Na or $K(AlSi_3O_8)$ and $CaAl_2Si_2O_8$. [10] Also, several species are crystallised in sulphate rich environments forming various sulphate containing minerals. [11–16]

The total concentration of solvated species of aluminium in most natural waters is generally considered to be at the micromolar level, because minerals containing aluminium have relatively low solubility. However, near solid/aqueous

boundaries concentrations can be much higher. Moreover, due to the increased input of acids into the environment and, more recently, dust originating from an increased level of land use, a considerable release of this element has occurred in the streaming waters of Finland. [17] These elevated levels of total aluminium concentration in natural waters and soils have been reported to be toxic to freshwater fish[18] as well as plants. [19]

However, the different forms of aluminium such as that obtained by chemical speciation or by binding to particles (physical speciation), define its important features in nature, i.e. toxicity, bioavailability and transportation of aluminium. In the surface waters of Ostrobothnia, which are mainly slowly flowing river waters, the investigation of speciation and fractions of aluminium is exceptionally interesting, since the area includes humic substance containing waters with low metal concentration and acidic metal rich waters. [20]

The monomeric and dimeric thermodynamic stable aluminium hydrolysis complexes are well established, but the metastable and polymeric complexes are not so known. [21] The monomeric, positive charged hydroxyl-complex-ions ($[\text{AlOH}]^{2+}$, $[\text{Al}(\text{OH})_2]^+$) have been observed to be the most toxic components of aluminium in water environments, although polymeric species existing in the same pH range may considerably enhance the toxicity by decreasing the fluidity of membranes as well as crosslinking biomolecules. [22,23] Certain human ailments may also be connected to aluminium, although the molecular basis of the toxicity is still not clear. [24,25] The Al_{13} -complex has been observed to be the most significant species in acidified soils, [26] and polynuclear aluminium species have been reported to be involved in plant toxicity as well. [27–29] Generally, it can be said that the speciation of the aluminium fraction in water is more significant than the total content when evaluating the conditions of natural waters. The release and interactions of aluminium are widely being studied by modern methods. [30–32]

To obtain the complete distribution of aluminium in a water sample is very difficult because all species take part in the dynamic equilibrium. An interaction with one species will lead to a rearrangement among the other species. The complexity of the problem has necessitated the development of fractionation procedures in order to distinguish between broad groups of aluminium species. The exact speciation and structure of polyaluminium complexes is a much-debated topic: opinions differ according to the measuring method used. [33,34] Potentiometric titration has been used most widely. In addition, ^{27}Al -NMR and different spectrophotometric measurements have been done. This thesis focuses on the hydrolysis of inorganic aluminium salts and the polymerisation of the

hydrolysis products. In these studies MS spectrometry was utilised to open a new window into speciation research.

The main challenge in this research was to obtain more detailed information about the speciation of Al chlorides and sulphates mainly in acidic conditions, and to characterise the aqueous structures of polymeric aluminium coagulants. The structure and characteristics of aluminium formulations depend on many factors, such as aluminium concentration, the type of anions, the type and concentration of base added, the aging temperature and time, and the rate and method of the base additions. [7] Furthermore, the exact role of the chloride or sulphate in water purification systems is not understood. This needs further investigation with the objective to predict the optimal coagulation and coagulant production conditions. The understanding of the aquatic chemistry of aluminium increase the knowledge base concerning the optimal utilisation of aluminium minerals as well as their usage in high volume processes, while providing improvement opportunities to human health at a global scale.

2 Water treatment

Egyptian paintings depict sedimentation apparatuses and wick siphons as early as the 13th–15th centuries BCE, and it is speculated that the ancient times alum was utilised to remove suspended solids. [35] The use of aluminium sulphate as a coagulant in water purification systems was started in the 1930's in Finland [36]. Nowadays it is the most widely used water treatment chemical all over the world. Hence, water purification processes with aluminium have a long tradition. These traditions have been the base for practise instead of novel scientific information. This has been leading to unoptimised processes causing inadequate purification results, unnecessary chemical loading and thr worsening of sludge properties. Variations in the composition of raw water cause problems, which could be managed much better were most efficiently functioning species and particles known. The separation of aluminium from sludge, which is the end product in water treatment, can offer good possibilities to be utilised as a raw material for new Al-coagulants. An improved understanding of the impact of process parameters on purification results will provide a key to enhance the material efficiency of processes and create better possibilities for recycling.

In water purification systems, the removal of organic matters is very important and the aim is to obtain aluminium ions having high charge due to the extensive coagulating power of the ions. Coagulation/flocculation is an essential stage of industrial and domestic water treatment processes aiming to aggregate colloid material and small suspended particles (minerals, humic substance) into a removable form. In the disinfection stage the removal of microbes [37] and even protozoan [38] can be improved by aluminium treatment. The major chemical coagulation/flocculation mechanisms are surface charge reduction with a condensation of the double layer, inter-particle bridging, patch adsorption and, because aluminium oxo hydroxo polymers form large three-dimensional nets, sweeping. Solid precipitated aluminium hydroxide as well as the soluble polyions and nanoparticles thus play thus an essential role in the process, but detailed information about aqueous structures and the progress of hydrolysis of the polyions is still unclear. [39] The unit operation itself is straightforward, but yhe management of versatile chemistry involved in it is still insufficient.

If added directly into the raw water, aluminium salts cause extremely rapid hydrolysis, and frequently, very rapid precipitation. A major drawback in the use of aluminium salts is that it has not been possible to control the nature of the coagulant species formed. When the coagulating salts are partially hydrolysed

they are much more efficient. Examples of these partially hydrolysed chemicals are polyaluminium chlorides and sulphates. [40-43] These more basic coagulants make the water purification process possible at a higher pH. Although a number of published studies have dealt with the use of Al(III) in water and wastewater treatment, [44,45] few of them have detailed the preparation and characterisation of the polymeric coagulating species. Moreover, the published results are inconsistent. The anionic part of the coagulant (chloride, sulphate, formate) is also an important parameter affecting the coagulation and formation of different Al(III) species [46]. Further investigation is needed in order to be able to predict optimal coagulation or coagulant production conditions.

It could be said that the current comprehension of the nanoscale structures of polyaluminium complexes in an aquatic environment and the progress of hydrolysis of the polyions is insufficient. More specific information about the reaction conditions compared with speciation is useful in water treatment processes. More specific information is also helpful in terms of understanding the environmental behaviour of aluminium in water.

In the pulp industry aluminium chemicals are extensively used to produce chemically purified water. Additionally, the management of increasing system closures calls for the usage of coagulation agents such as aluminium and polyaluminium products. Keeping in mind diminished water intakes, these facts also set new requirements on the material efficiency of the aluminium used.

3 Hydrolysis of aluminium

The interaction between ion and solvate increases when the size of the ion decreases. Aluminium presents itself in a normal environment as the Al^{3+} -cation. Its first energy of ionisation is 577 kJ/mol, second 1820 kJ/mol and third 2740 kJ/mol. The radius of the Al-atom ($1s^22s^22p^63s^23p^1$) is 143 pm: that of the Al^{3+} -cation ($1s^22s^22p^6$) 50 pm, [47] which means that the aluminium-ion has great density of charge, and that is a hard Lewis acid (small, compact, not very polarisable). The aluminium cation takes six ligands into the inner coordination sphere, forming an octahedral complex in water. (Fig. 2) This has been confirmed by e.g. a proton nuclear magnetic resonance (^1H NMR) method. [48] To the outer, secondary, solvate sphere, it can bind twelve water molecules, the positions of which are directed by the inner sphere. [7] The same octahedral structure can also be found also in a solid state: even though aluminium chloride with six crystal waters is usually written as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, the more accurate way to write it would be $\text{Al}(\text{OH}_2)_6 \cdot 3\text{Cl}$. [49] The bond strength between aluminium and oxygen in a diatomic molecule is 507.5 ± 10.5 kJ/mol, [50,51] and between aluminium and chlorine it is 494 ± 13 kJ/mol. [52] Even though the difference is not big, it is remarkable enough to prefer the hydration of aluminium even in a solid state. [53] Hence, Al^{3+} can be hydrolysed strongly, forming polynuclear hydroxo complexes.

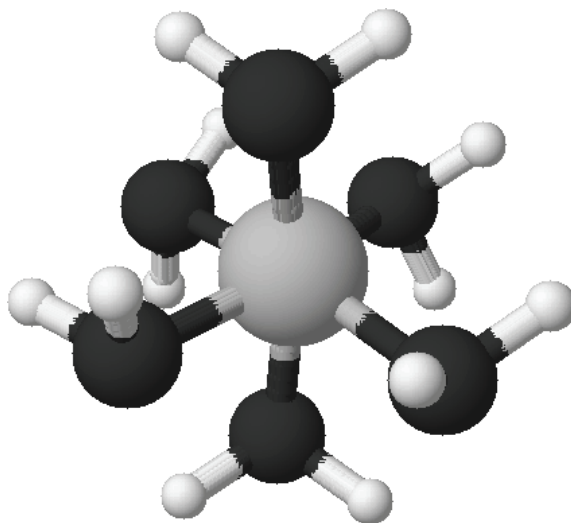
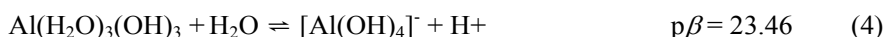
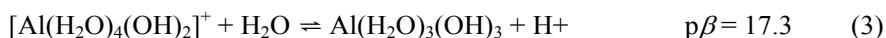
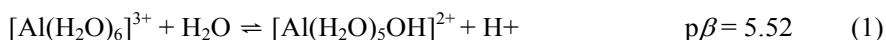


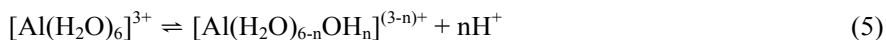
Fig. 2. Solvated aluminium cation $[\text{Al}(\text{OH}_2)_6]^{3+}$.

Fundamental investigations on the hydrolysis of aluminium were made already at the beginning of the last century, mainly in Czechoslovakia. The most widely used method was potentiometric titration, which was supported by voltammetric and conductivity measurements. [54-74] It was already known then that the aluminate-ion $[\text{Al}(\text{OH})_4]^-$ forms other complex ions [60] and that hydrolysis is independent of time [64]. Since the 1980s there has been wide consensus about the speciation of aluminium in water, based on potentiometric data and calculated concentrations. The species agreed on were $[\text{Al}(\text{OH})]^{2+}$, $[\text{Al}(\text{OH})_2]^+$, $[\text{Al}(\text{OH})_3]^0$, $[\text{Al}(\text{OH})_4]^-$, $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$, $[\text{Al}_3(\text{OH})_4]^{5+}$ and $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The ratio $n = (\text{OH})/(\text{Al})$ was limited in calculations to 2.5. [75]

According to this model, when pH is below three, Al^{3+} is the dominant species. Above this pH, the $[\text{OH}]^-$ anion is joined to the inner coordination sphere as a ligand of aluminium. The complex $[\text{Al}(\text{OH})]^{2+}$ is predominantly present at the pH range 4–5. The formation of polymeric aluminium species begins approximately at pH 4.5. Above pH 8, aluminate anion $[\text{Al}(\text{OH})_4]^-$ is the dominating species. In addition to the polymeric species mentioned above, certain oligomeric complexes, such as $[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{6+}$ and $[\text{Al}_8(\text{OH})_{20}]^{4+}$ were also identified but rarely used in calculations. [7,75-79] The hydrolysis reaction chain is usually written as a bare series of mononuclear complexes [7]:



Thus the common form for the formula of the hydrolysis is:



According to formula 5, in which $pK_a = 4.7$, the water solutions of aluminium compounds are usually acidic, unless the counter anion of the compound does not make the solution basic. Aluminium hydroxide $\text{Al}(\text{OH})_3$ precipitated eagerly (solubility constant $pK_{s(\text{am})}(25^\circ\text{C})$ 31.5) [39] at a neutral pH range as colourless gel. The thermodynamic stable speciation of a very dilute (10^{-9}M) aluminium chloride solution is illustrated In Fig. 3. The calculation was performed with the MINEQL+ programme. [80] This was the most concentrated solution, in which there were still species other than Al^{3+} , $[\text{Al}(\text{OH})_4]^-$ and a precipitating diaspor (logK -6.8730, ΔH 24.630). In higher concentrations the solid phase dominated

the diagramme. The fresh solid precipitation is usually considered to be the amorphous $\text{Al}(\text{OH})_3$, which is amphoteric. It dissolves in a basic solution having excess of hydroxo-ions as aluminate-anion, or in acidic solutions as a cationic mono- or dihydroxo complex.

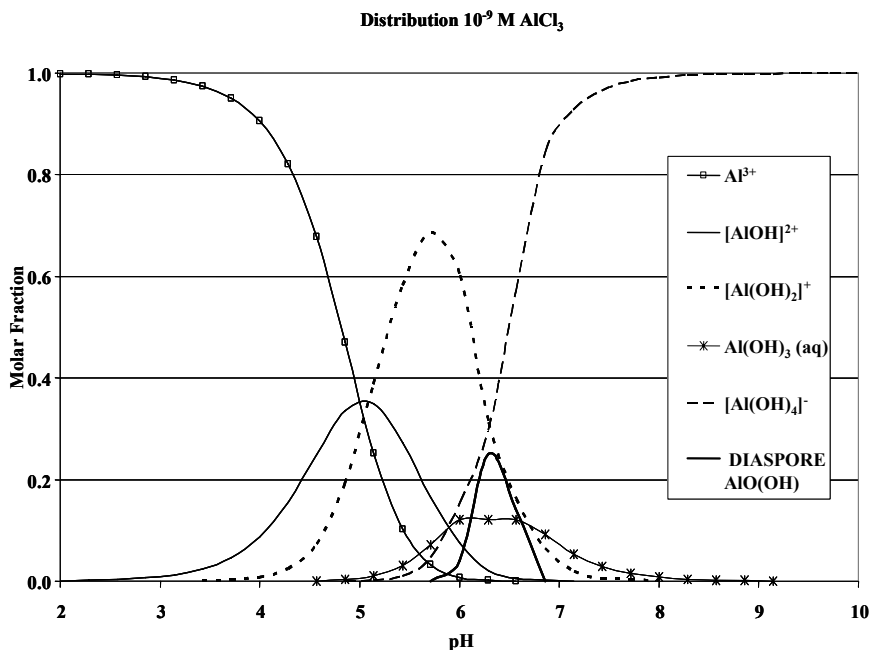


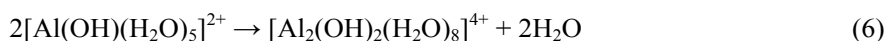
Fig. 3. An example of the distribution diagramme of an aluminium solution.

According to this classical distribution aluminium-ions present themselves in water solutions mainly as monomeric $[\text{Al}(\text{OH})_2]^+$, $\text{Al}(\text{OH})_3$ and $[\text{Al}(\text{OH})_4]^-$ forms. The structure of the cations is octahedral with hydroxo and aqua ligands, but the structure of the anion is tetrahedral without any involved aqua ligands. [81] The putative soluble $\text{Al}(\text{OH})_3$ might only be a temporary species, a precursor of insoluble gibbsite and diaspore ($\text{AlO}(\text{OH})$), but the kinetics of the precipitation remain uncharted.

In many studies it has been proved that Al-hydrolysis is not simply a mononuclear process. Those monomers polymerise by bridging to dimers, trimers, etc. In the pH area 4.0–5.5 the most of the hydrolysis products are polynuclear. [82,83] The structure and amount of these complexes depend strongly on time, temperature and the total concentration of aluminium. The

standard hypothesis is that hydrolysed aluminium complexes contain bridged μ -OH and terminal hydroxides and terminal water molecules. [7,64,84,85] However, the speciation is strongly dependent on counter anions. When there are significant amounts of organic ligands available, the speciation and precipitation of Al(III) could be quite different, as in humic soils where they are pronouncedly present. [86]

The precipitation of the polymeric aluminium hydroxide sol is considered to be a stepwise process, and there are several schemas about the process. One of the possibilities is given in equation, in which two partly hydrolysed aluminium cations react together eliminating two aqua ligands, producing a dinuclear hydroxo-bridging entity. [87]



Computational chemistry gives an alternative path, where the starting molecule is $\text{Al}(\text{OH})_3$ as illustrated in Figure 4. [85]

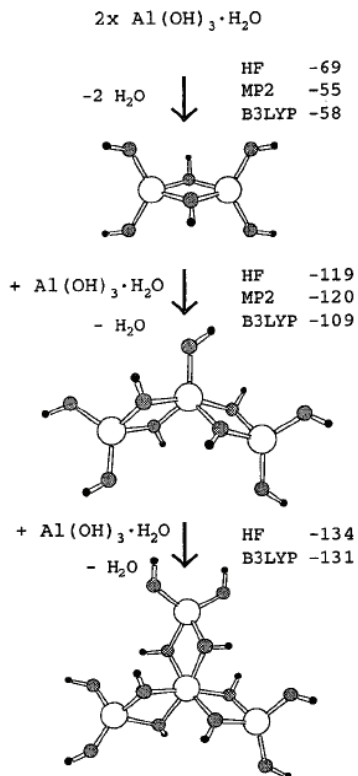


Fig. 4. One possible reaction path for the formation of $\text{Al}_4(\text{OH})_{12}$. [85]

It is possible that aluminium forms a series of polymeric oxo hydroxo cations, in which the monomer is an Al^{3+} -central atom surrounded by four oxygen atoms [AlO_4]. Several different schemas concentrating the complexes and precipitating agglomerates were born, have been introduced in earlier literature. [84,87,88] Usually, one of the intermediate products suggested is the six member ring system; [87,88] the final products have a corresponding structure to gibbsite, boehmite or other aluminium minerals. This process can also be written as a condensation of octahedral aluminium hexa aqua cations producing polyaluminium complexes, which is illustrated in Figure 5.

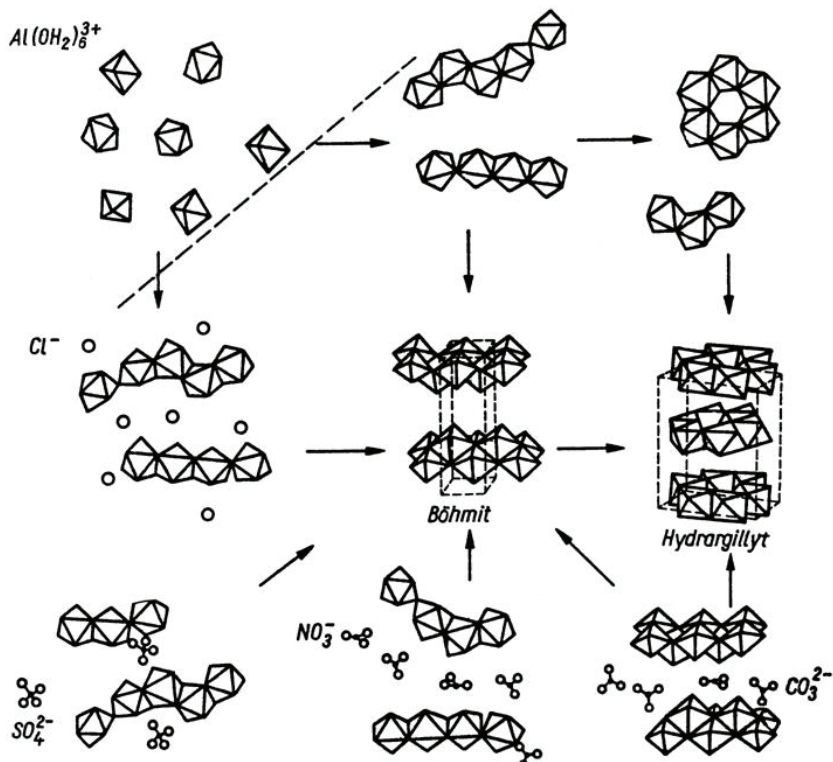


Fig. 5. Possible formation routes of polyaluminium complexes. [87]

As said earlier, the exact structure of polyaluminium complexes is a much-debated topic. The opinions differ according to method of analysis applied. Before mass spectrometric studies, the most convincing evidence had been obtained from studies done on dimers and Al_{13} -structures. [89,90] Only some individual studies included other oligomers, such as $[Al_8(OH)_{20}]^{4+}$. [91]

4 Traditional methods of studying of hydrolysis of aluminium

4.1 Potentiometric titration and calculated speciation

The hydrolysis of Al^{3+} has been investigated by potentiometric methods for approximately 70 years. At different times, different laboratories have suggested hydrolysis profiles based on a very wide range of polyhydroxo species. [7] Despite of its imperfections, the method is still the best and almost only method to get information on the concentrations of the species formed. The data achieved is usually handled by software that calculate the best fit of the titration curve for a suggested speciation as well as gives β -values of the selected species. The values are usually indicated as distribution diagrammes. The programmes select the simplest compounds if there are several n-values $[\text{Al}_x(\text{OH})_y]_n^{3x-y}$ available at the same time, preferring prime number solutions. In addition, the oxo-ligand with a charge (-2) is treated as to two hydroxo-ligands with the charge (-1) in these calculations.

The species used for calculations have to be selected by chemical intuition based on knowledge of the initial material, such as crystallographic data before running a programme. [7] Since the speciation is deduced on the basis of a sum response, no structural details about the species can be obtained. Hitherto, the only evidence on the structure of the polynuclear complexes has been obtained in the solid state by X-ray diffraction, as exemplified by $[\text{AlO}_4(\text{Al}(\text{OH})_2)_{12}]^{7+}$, the Keggin Al_{13}^{7+} -cation. [92] However, the molecular structure of the crystals does not necessarily reflect the nature of the main species present in the solution, [93] especially when the counter anion in the solution differs from the one in the solid phase.

The achieved results provide stability constants in thermodynamically stable conditions. The observed solution state is always only an average, where the changes of conformations and proton transfers occur constantly. [23] Some reactions are very slow in room temperature, and are often related to the forming of very big metastable polymeric or colloid species, the structure -or even the combustion – of which is not known. Hence calculation programmes do not necessarily include them. However, several numerical equilibrium constants for the formation of aluminium polynuclear ions have been reported in the literature. [94,95]

A distribution diagram is presented in Fig. 6, which is based on the potentiometric titration of an 1mM aluminium chloride solution. For the pH measurement, the matrix was 2.5M NaCl, which is quite often used because, according to the hypothesis, would not interfere in the speciation. In the results the hexa aqua cation is the dominating species in the pH-range of below 5, and the aluminate anion is dominant in the pH range above 7. The calculation programme omitted the inserted soluble dimeric species. Also, the precipitating $\text{Al}(\text{OH})_3$ was left out of the figure. These calculations were performed by Dr. Hietapelto with the computer programme Letagrop. [96] This kind of calculations could be more accurate, if all species found in MS investigations could be involved in calculations.

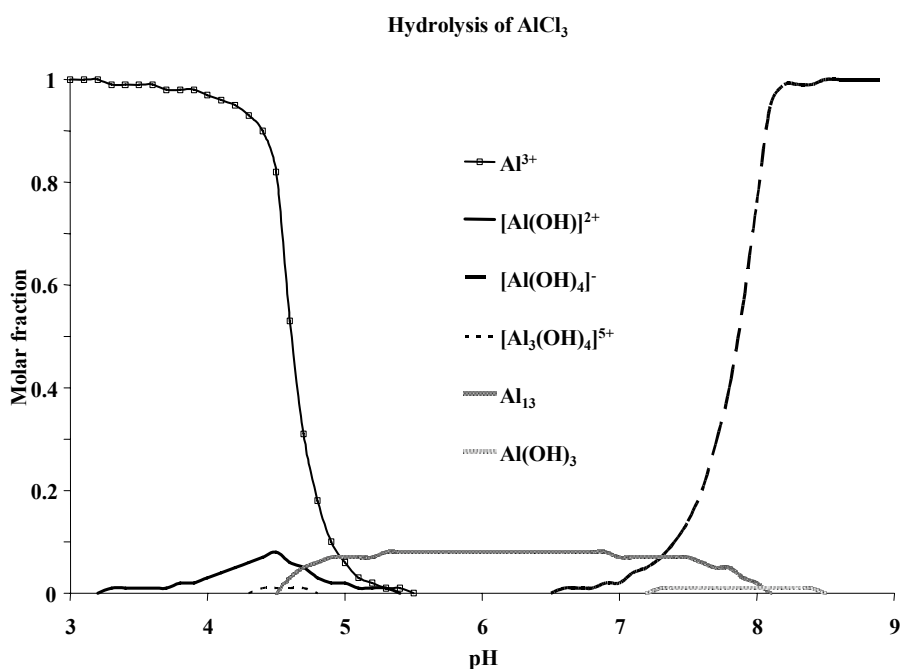


Fig. 6. Soluble hydrolysis products of aluminium chloride.

There are commercial programmes [80,97] that calculate the speciation of aqueous solutions based on the equilibrium constants and the activities of the species (Fig.3.). Generally, the programmes use only monomeric species for calculations and also, these calculations ignore kinetics completely: Hence, for example at the calculated thermodynamic equilibrium of 1 mM AlCl_3 at a pH of 4.5, all the aluminium should be precipitated as $\text{Al}(\text{OH})_3$ but in this study the test

solution remained clear for a period of two weeks. Furthermore, the equilibrium was calculated against mineral forms of aluminium, such as diaspore, which are highly organised. The formation of crystals involve always time. [98,99]

4.2 The ^{27}Al -NMR

^{27}Al NMR offers information from the stage of hydrolysis in a solution. The method was founded in 1969 by Akitt et al. [100,101] and the main tetrahedral, octahedral and Keggin structures of aluminium were investigated in the 1980s. [89] The method has been used together with potentiometric data to recognise monomeric, dimeric and polymeric species and the changes of their relative concentrations during the hydrolysis. [21,102-114] However, the method being rather slow, it requires relatively concentrated solutions. Furthermore, detecting unsymmetrical aluminium-units, such as five coordinated aluminium hydroxide is quite challenging. [115]

There are usually three major signals. The first corresponds to aluminium ions in octahedral coordinations such as the monomeric ions $[\text{Al}(\text{H}_2\text{O})]^{3+}$, $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$. The same signal can also be attributed to the dimeric complex $[\text{Al}_2(\text{OH})_x(\text{H}_2\text{O})_{10-x}]^{(6-x)+}$. The scale is usually normalised selecting this signal to 0 ppm. Then the signal at 62.5 ppm is assigned to the Keggin cation $[\text{AlO}_4(\text{Al}(\text{OH})_2)_{12}]^{7+}$ or otherwise written $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$. The tetrahedral AlO_4 -unit in the middle of the cation with a symmetrical environment is the main reason why this cation can be detected by ^{27}Al NMR. The third signal is at 80 ppm, corresponding to ions of tetrahedral coordination such as $[\text{Al}(\text{OH})_4]^-$. Research is usually focused on minor signals at new transitions, as well as the comparative intensities of known signals in the same spectra at a different time. Identification of new species has hardly been done. [116]

4.3 The spectrophotometric detection

By kinetic spectrophotometric measurements, total aluminium concentration can be determined through several complexing agents, such as Ferron, aluminone, or quinolinic acid. [117] Combining these complex formation reactions with different cation exchange procedures it is possible to analyse “reactive” or “labile” and “non-labile” fractions of total aluminium from water samples. [118,119] These fractions are important when evaluating the toxicity of natural waters but only reflect the availability of aluminium to plants and other organisms.

In preparing of aluminium water purification products, the fractions are mainly obtained by the Ferron test, because it has proven to be the preferred method based on its simplicity, its level of precision, and its moderate reaction rate with Al. [120] Combined with other analytical methods, it gives useful information for following the production process. [121] Ferron (8-hydroxy-7-iodo-5-quinoline-sulphonic acid) reacts with aluminium by forming a complex that absorbs light at the wavelength of 370 nm. The three classes of species (Al_{mono} , Al_{13} and Al_{poly}) react with Ferron at a different rate. [122] When measuring the absorption as a function of time and plotting the results, the shape of the curve can be used to evaluate the distribution of different Al fractions as illustrated in Fig. 7. [119] The hypothesis of the test is that monomeric aluminium reacts immediately, small polymers (Al_{13}) slowly, and larger polymers as well as $Al(OH)_3$ hardly at all with Ferron. Thus, this speciation achieved by spectrophotometric methods is only a classifying tool, not an exact characterisation. [123]

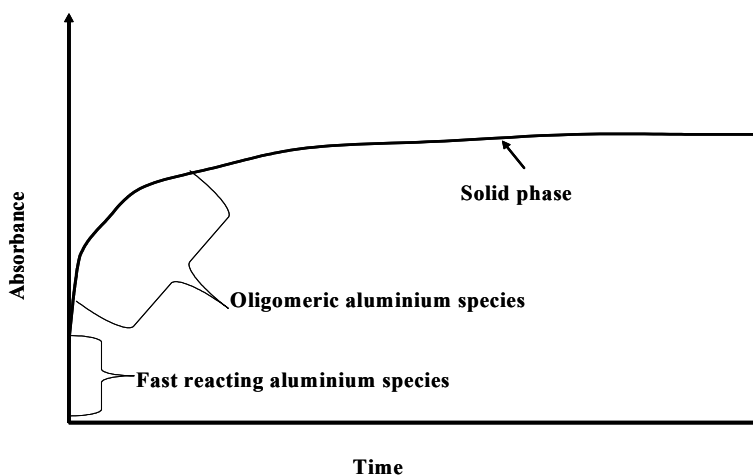


Fig. 7. Common interpretation of the slope of the ferron reaction.

4.4 The surface analysis

The formation and break-up of alum flocs during coagulation have conventionally been investigated using the jar-test procedure, as well as by applying continuous optical monitoring of the turbidity. [124] This tells only a little of the size and charge of those flocs. More exact information could be amassed if the size distribution, zeta potential and total surface charge were measured.

Floc size distribution can be measured by different techniques, that are widely used in investigating the properties of activated sludge. [125] Zeta potential is a measure of the magnitude of the repulsion between particles and it gives an indication of the potential stability of the colloidal system. Thus, the larger the intrinsic value of the zeta potential, the more stable the suspension generally is. When it is near zero, the particles and colloids tend to agglomerate and precipitate. [126] Its measurement brings detailed insight into the dispersion mechanism, and is the key to electrostatic dispersion control. The electrical double layer and zeta potential of the suspension particle is illustrated in Figure 8. (Figure courtesy of Malvern Instruments Nordic Ltd.) [127] Aluminium solutions usually have positive zeta potential in the acidic pH range. [2,3]

The streaming current (or streaming potential) titrations reveal the total surface charge of the colloidal dissolved substances. [128] The effect occurs when a particle is mechanically being moved through the fluid, or the fluid moves past the particle, resulting in a separation of charges that causes potential differences in solution. Practically, these parameters characterise the final hydrolysis products in suspension in a much more accurate way than plain turbidity. With these parameters, larger species, – that would otherwise remain invisible with electrospray mass spectrometric methods – can be described. Combining such results to those obtained through mass spectrometry, a continuum of speciation from the small fresh born dimers to huge polynuclear clusters can be achieved.

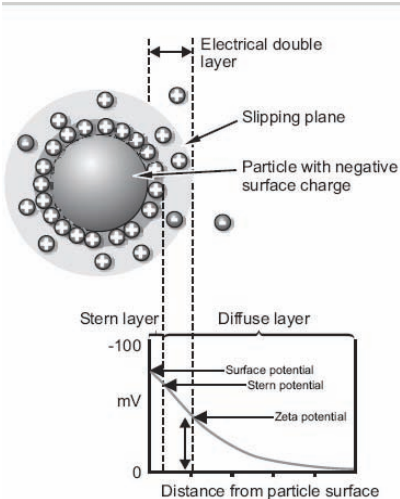


Fig. 8. The double layer and zeta potential of the suspension particle. [127]

4.5 Computational chemistry

Computational chemistry is a state of expertise to investigate the structures of the aluminium oxo hydroxide species. In our mass spectrometric research computational chemistry has been a great support. Without its help many questions concerning the protonation order or $(\text{OH})_2 - \text{O}(\text{H}_2\text{O})$ variations would have been left without answers. [129] The calculating capacity increases annually and the absolute energies of larger complexes can be reached. Gaining a clearer picture of the energy differences of various isomers in the complexes and the ways of binding concerning the counter anions has been even more of importance for us. These calculations have given the answer to many structural questions and sometimes even unexpected ones. [130] Furthermore, different calculations for the solvolysis of the aluminium species are more than welcome. [85,131]

There is an increasing number of articles dealing with computed relative energy minimums and even absolute energies of aluminium oxohydroxo complexes. [132] Also, even the models have limitations concerning the amount of the atoms in a complex, the ligand exchange at the surface of larger species has been examined by computational methods. [133,134] With experimental arrangements several interesting molecules can be produced and their structures and energies computed. [135-137] Even though those species could not survive in ordinary manufacturing process conditions or in nature, their properties might possibly correspond to those of spontaneously born species, too.

5 The mass spectrometric method

The mass spectrometric method is based on detection of mass-to-charge ratio, m/z , of atoms and complexes. It is the only method known, where one can obtain direct experimental evidence of the sizes of the species. The IR and Raman studies give us a good view-point to functional groups attached to complexes. NMR (Chapter 4.2) tells us the coordination of complexes, whether the aluminium is four or six coordinated as well as even the coordination state of the environment near the measured atom. However, neither can give the information if e.g. the six coordinate aluminium groups are on the surface of a large complex.

Mass spectrometry, especially electrospray ionisation mass spectrometry, (ESI MS), is a well established as a semi-quantitative analysis method for organic substances and proteins. More novel application for it is to gain snapshot information about the speciation of hydrolysed metal ions in solutions. [138] It is very suitable for extensive identification of new species not discovered by other methods, and it gives direct information on the structure of the elemental cores even from water- and salt cluster ions. [139-142]

It has been shown that in almost every case where the identity of ions in a solution has been established by some other technique, such as NMR spectroscopy or electrochemistry, the intact ions observed by ESI MS agree with prior identification. [143-145] It has been reported that oxoanions of W, V, and Rh detected by ESI were consistent with reported speciation in aqueous solutions. [147] Even though the species identified from the solutions were not exactly the same as those found in the spectra, the identification was possible because the core was intact, and all changes were limited to outer sphere protonation and solvation.

In this study two detection systems with electrospray ionisation were used. The instruments had been tested before studying aluminium by repeating the speciation investigation of molybdenum. [141] The running parameters for aluminium were optimised with the MODDE-software. [147] The first equipment, Micromass LCT, with which most of the experiments were made was fitted up with a time of flight detector (TOF, Chapter 5.2). The other apparatus was a tandem mass spectrometer, Micromass Quattro, equipped with three quadrupoles (Chapter 5.3). Both equipments had Z-spray electrospray interfaces (Chapter 5.1). These instruments had high resolution capabilities and an accurate mass analysis can be achieved with them. However, in our study we could not find suitable calibration materials (lock mass), not even from our own spectra. After some tests

we had to ignore the usually very informative capabilities provided by this equipment.

5.1 Electrospray ionization (ESI)

Electrosprays transfer relatively softly pre-existing ions through a capillary from solution to the gas phase, where the ions can be examined semi-quantitatively by conventional mass spectrometric techniques. [148] A mandatory condition in working with electrospraying is that the compound of interest must be ionised in the solution. [149] In our studies this demand was seen clearly, when the pH of the aluminium solution was raised to reach dominance of $\text{Al}(\text{OH})_3$: The liquid was still visibly clear, but no signal was obtained by mass spectrometry. Most probably, the hydrolysis products were colloid, yet not precipitated. This strongly supports the assumption that the species found were not fragments that evolved during ionisation or detection.

For standard electrospray ionisation [138] the sample is usually dissolved in a polar, volatile solvent and pumped through a narrow, stainless steel capillary. A voltage is applied to the tip of the capillary, which is situated within the ionisation source of the mass spectrometer. This strong electric field forces the sample to emerge from the tip, dispersing into an aerosol of highly charged droplets. Due to the solvent evaporation, the size of the droplet diminishes. Consequently, the density of misbalanced charges at the droplet surface increases. The repulsion forces between the charges increase causing a series of explosions until analyte ions evaporate from the droplet. This is a quite violent procedure, and even if the ESI is much softer than other ionisation methods, some outer sphere reactions occur during evaporation, which could change the initial charge of the solvated species. [I,II,IV] For labile equilibrium, the ratio of the initial-to-final droplet volume could be critical, changing the pH of the environment in the droplet. [150] The kinetics of aluminium polymerisation is slow. [75,76] Hem and Robertson [81] have measured the reaction rates of dissolution of aluminium hydroxide polymers and found the k level to be 10^{-5} . This means that the half-life of the species is ca. one day. Also in those studies, the pH was found to need over two hundred hours to stabilise. Of course, the speed of degradation of the compound is not simply the same as formation, but could nevertheless give a clue as to what kind of reactions we are dealing with. Since it is not probable that the equilibrium of the hydrolysis is affected during the nebulation and desolvation, which happen in less than one second.

With the ESI technique, multiply charged ions can be obtained especially in aqueous solutions because water has high polarity (dielectric constant, ϵ_r 78.54) [151] which is a parameter that stabilises high charges in solutions. [152] However, there is a possibility to charge reduction, which can take place during the evaporation. [153-156] For example, the hydrolysis of aluminium described in reactions (1)–(4) is a spontaneous reaction in a solution and it is very probable that it occurs to a pronounced extent during nebulation. It might be one reason why the hexa aqua aluminium cation has never been observed in any of our studies. [157]

The other possible charge reductions process is ion pairing of the aluminium oxo hydroxide species with an outer sphere counter anion during evaporation. [158-160] This phenomenon explains our findings quite well: almost all species found contained chloride or sulphate. Also the fact that in dilute solutions, where the amount of free counter anions is diminished, more pure oxo hydroxo species were found than in more concentrated solutions. All the phenomena involved in the ESI process are still under intensive investigations. [161-164]

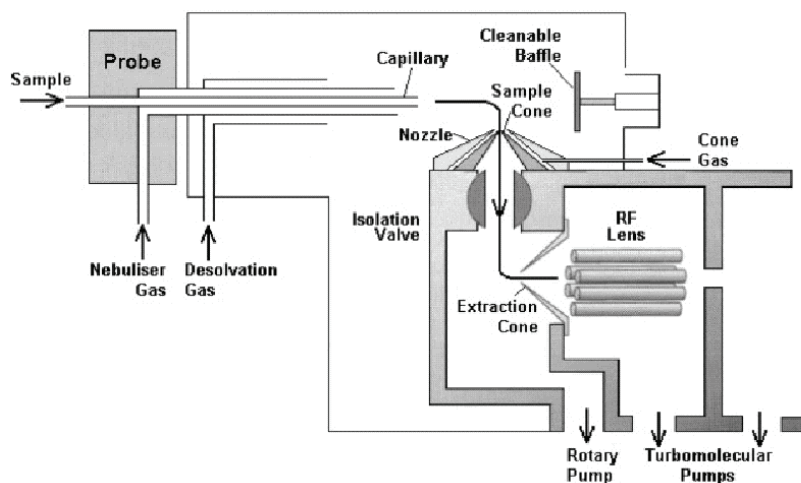


Fig. 9. Z-Spray ionisation source used in this study. [165]. Courtesy of Waters Micromass UK.

Table 1 lists some typical ions produced by electrospray ionisation. In our study, the sodium adducts were the only detrimental impurities. Especially in a chloride environment, they carried an excess of chlorine atoms so that the charge and

structure of the original species were thus impossible to figure out. An example of this kind of species is $[Al_5(OH)_5NaCl_{10}(H_2O)_{1.5}]^-$. Sodium-containing complexes were found mainly at initial pH, and with a higher sample cone voltage in A_1 , Al_3 , Al_4 , Al_5 , Al_6 , Al_7 and Al_{13} cores. Contrary to monoisotopic sodium, potassium, ^{39}K and ^{41}K , were very informative, having their own isotopic patterns, which made the interpretation of the spectra easier.

Table 1. Typical ions produced by electrospray ionisation.

Mode	Ions
Positive	$[M+H]^+$, protonated molecule (M) $[M+Na]^+$, $[M+K]^+$, adducts $[M+H_2O+H]^+$ protonated, + solvent adducts
Negative	$[M-H]^-$ deprotonated molecule $[M+HCOO]^-$, adducts

Aqua adducts were even more informative in our study than potassium isotopes: in pure monocharged aluminium oxo hydroxide systems, the Gaussian distribution of signals with the mutual distances ($\Delta m/z$) of 18u suggests how many aqua ligands were attached to one species. They helped to confirm the charge of the species, and gave a hint of the structure by showing how many free coordination places there were in the core. Similar water cluster series have been found e.g. with nickel (II) cations up to 10 water ligands. [153] When hydroxo-ion was replaced in the same $[Al_x(OH)_{3x-y}Cl_y(H_2O)_n]$ complex with a chloride-ion, almost similar $\Delta m/z$ 18u series were observed. However, isotope patterns changed according to the amount of chlorides. Both of these phenomena are revealed in Fig.10. This measurement was done with MS-Q equipment (5.3), and the solution was a fresh 10 mM $AlCl_3$ at pH 3.88. [II] In higher pH ranges the separation of 9u, 6u, and 4.5u were observed corresponding to double-charged, triple-charged, and quadruple-charged complexes, respectively. To conclude, the shape of the isotopic patterns unveiled whether the signal was part of the water series or born by hydroxide chloride competition.

In our study the infusion pump was directly connected to the electrospray probe, which consisted of a metallic capillary surrounded by a nitrogen flow. Four different electric fields were used to direct the species to be detected: capillary voltage (3.5–4 kV) smaller sample cone voltage (40–70 V), extraction cone voltage (5 V) and RF lens (200 V). This part of the Z-spray interface is illustrated

in Fig.9. The capillary and extraction voltages only had a little effect on the spectra: the noise mostly increased with very high voltages and the smallest signals vanished when the voltage was very low. The parameter that had the biggest effect was the sample cone voltage, which effected tremendously on the shape of the spectra: even the base signal could vanish, and a new arise, when this parameter was changed.

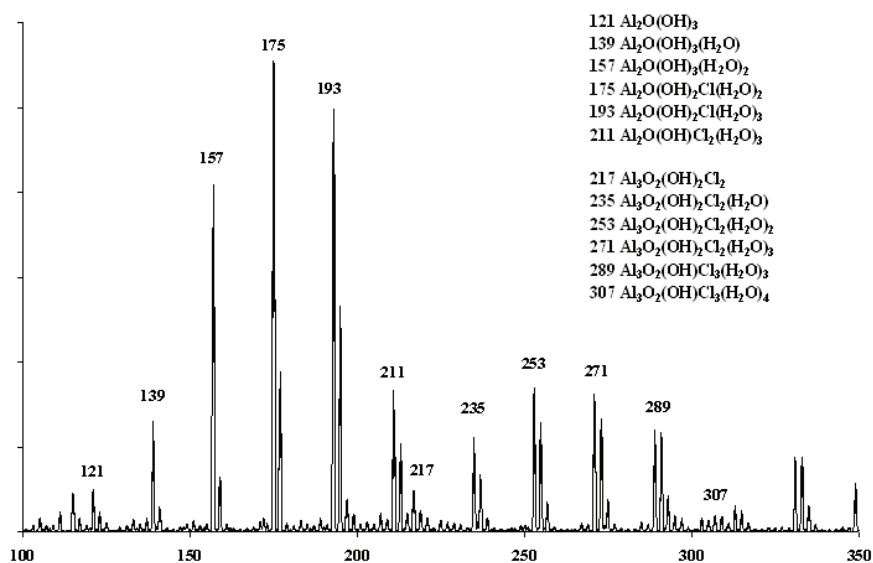


Fig. 10. Water series and hydroxide-chloride competition. All species are monocharged cations.

With the correct combination of the voltage parameters in a chloride environment the water series showed symmetrical bell-shaped distributions. The long pattern of signals with the same intensity at the beginning of the water series could indicate the fragmentation of two hydroxide ligands as one water molecule leaves one unprotonated oxygen atom in the complex. This phenomenon was clearly seen in our MS/MS study (Chapter 5.3), where the complexes were collated to investigate their substructures. [II] If the water series continued without a clear start- and endpoint, the simplest core composition was hard to determine. In the sulphate environment, 40 V was observed to be the most suitable sample cone voltage because there the shape of the mass spectra showed only one signal with a relative intensity of 100%. Increasing the voltage, the amount of signals

multiplied, and several signals reached 100% intensity. Decreasing the voltage diminished the total ion count to a level too low to be able to draw exact conclusions.

With a fourth parameter, the RF lens, the size of the species was selected. In this research the range 70–1000 was studied in detail. The lower m/z values would also have been very interesting, but the equipment always showed a huge signal pattern around m/z 60, probably originating from some organic solvent from earlier measurements, and thus the m/z 45 from $[\text{Al}(\text{OH}_2)_6]^{3+}$ was out of our reach.

5.2 Time of flight analyser (TOF)

Time-of-flight (TOF) mass spectrometers are technically quite old inventions [166] that nowadays combine a relatively simple mechanical setup with modern data handling. By measuring the time which the ions spend for travelling a fixed distance [167] the mass - charge ratio of the ions can be calculated. The ions are introduced from the ion source (ESI) of the instrument as a pulse, after which they are extracted and accelerated to a high velocity (v) by an electric field (E) into an analyser. The pulse results in equal initial kinetic energy ($\frac{1}{2}mv^2$) for all ions. As they subsequently pass along, they are separated by their masses (m), lighter ions traveling faster. The ions pass along the field free drift zone (d , meters) until they reach a detector, so that all ions of the same m/z arrive at the detector at the same time. This enables the instrument to record all ions as they arrive and therefore accounts for high sensitivity of the technique. If the distance from the ion source to the detector is d and the time (t) an ion needs to traverse the length of the drift tube, the equation (7) follows:

$$\frac{1}{2}mv^2 = \frac{1}{2}m(d/t)^2 = zeE, \quad (7)$$

where:

m = mass of the ion (kg)

v = velocity of the particle (m/s)

d = length of the field-free drift zone (m)

t = measured time-of-flight of the ion (s)

z = charge of the ion

e = the charge on an electron ($1.60217733 \times 10^{-19}$ coulomb)

E = electric field, extraction pulse potential (V).

Typically the length of the flight path in commercially available TOF spectrometer systems is about 1-2 m. The kinetic energies typically used are ca.

2000 eV, the flight times are 5...100 μs , hence the width of individual TOF peaks is in a few nanoseconds. Therefore, when in equation (7), d is fixed, E is held constant in the instrument, and e is a universal constant, the flight time of an ion t is directly proportional to the square root of m/z :

$$t = \text{constant } (m/z)^{1/2}. \quad (8)$$

Equation (8) shows that an ion of m/z 400 will take twice as long to reach the detector as an ion of m/z 100. The above description of a time-of-flight mass spectrometer is very simplified, and there is usually e.g. a magnetic reflector for minimising the dispersion of ions with the same m/z value. [168] Also, the method requires a very high vacuum in the detection chamber, as well as extremely fast electronic data acquisition, both of which are costly demands. In theory there is no upper mass limitation but in practice it becomes increasingly difficult to discriminate between the times of arrival at the detector, as the m/z value becomes high. When the shape of the molecule is very long or arborescent, it could reach the detector gradually “splashing”, i.e. not as a one single shot, which might broaden the signals.

5.3 MS/MS with triple quadrupoles

The analyser of a “triple quad” instrument consists of two quadrupoles MS1 and MS2, separated by a collision chamber. This is illustrated in Fig.11. Such a configuration is often referred to as a “tandem in space” instrument. Although the ion signal is reduced during the transmission, the chemical noise, which is a major limitation for complex samples is also largely decreased, leading to an improvement of the signal-to-noise ratio.

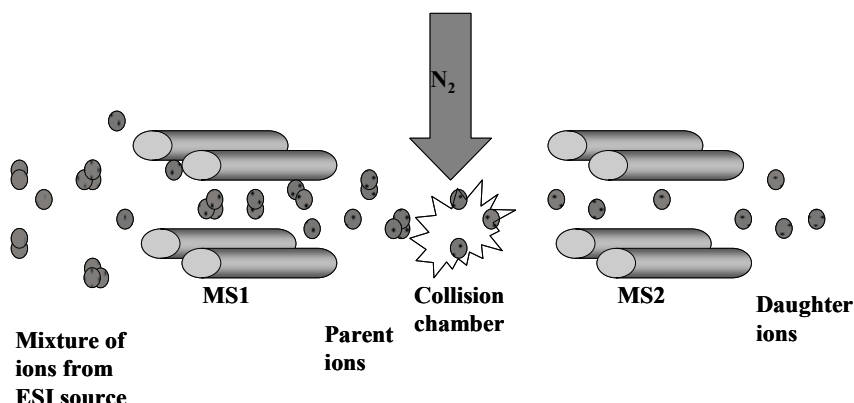


Fig. 11. Triple quadrupole analyser.

In Full Scan mode the equipment brings all precursor ions directly to the detector. Thus the presence or absence of ions is assured. In the Single Ion Mode (SIM) mode only one certain precursor ion is selected after the MS1 quadrupole and directed to the detector. With these kinds of research experiments the intensity changes of certain ions could be monitored e.g. in terms of kinetics. In these studies, it has to be remembered that the selection is done with m/z values. Depending on the resolution of the first MS1 scan, different kinds of species with the same m/z value could reach the detector. As in our study, the fragmenting ligands $[(OH)(H_2O)]^-$ and Cl^- had the same mass and charge. [II] These kinds of investigations are also possible with TOF-equipment.

Table 2. A triple quad instrument can be used in various ways.

Experiment	MS1	C	MS2
Full Scan Spectrum	Scanning	No collision	Scanning
Single Ion Mode, SIM	Parent Mass Selection	No collision	Scanning
Daughter Ion Spectrum	Parent Mass Selection	Collision	Scanning, (SIM)
Parent Ion Spectrum	Scanning	Collision	Daughter Mass Selection

The third mode is the actual MS/MS investigation. Also, in this mode the first quadrupole MS1 is used to select a precursor, or as it is usually called, a parent ion, but now is fragmented in the collision cell C. A study on mass spectral fragments can provide structural information. This is typically achieved in the collision cell by accelerating the ions in the presence of a collision gas. In our study we used ultra pure argon (99.9999%). [II] The energy of the collision with

the gas can be regulated to allow different degrees of fragmentation. The resulting fragments, so called daughter ions, are analysed by the second quadrupole MS2, used either in SIM or more commonly in the scan mode. The fourth mode is used for studying the parents, the molecules from which the detected fragments are born. Then analysis is subsequently made upstream: the on fragment is selected from amongst scanned MS2 spectra and its parents are detected from amongst MS1 spectra. [169]

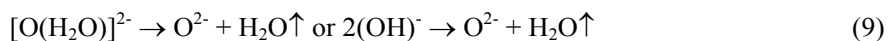
6 Speciation of aluminium detected by mass spectrometer

In this section observed species are described on the basis of size (Chapters 6.1–6.8) and factors affecting on speciation (Chapters 6.9–6.12) are presented. At the beginning, however, several general observations are briefly discussed.

In our study we found a series of species ranging from monomeric aluminium complexes to quite large, 26 aluminium containing oxo hydroxide complexes, by using the electrospray mass spectrometer. Although the concentration of aluminium is at the micromolar level in natural waters, the millimolar level used in these studies is relevant to water purification processes, as well as in terms of solid-liquid-phase boundaries.

In some cases in this study, the identified complex could have several possibilities of a formula. For example the peak at m/z 295 could be written as $[\text{Al}_4\text{O}(\text{OH})_8\text{Cl}]^+$, $[\text{Al}_4\text{O}_2(\text{OH})_6\text{Cl}(\text{H}_2\text{O})]^+$, $[\text{Al}_4\text{O}_3(\text{OH})_4\text{Cl}(\text{H}_2\text{O})_2]^+$, $[\text{Al}_4\text{O}_4(\text{OH})_2\text{Cl}(\text{H}_2\text{O})_3]^+$, and $[\text{Al}_4\text{O}_5\text{Cl}(\text{H}_2\text{O})_4]^+$. Mainly because $[(\text{OH})_2]^{2-}$ and $[\text{O}(\text{H}_2\text{O})]^{2-}$ produced identical m/z values and showed identical isotopic distributions, the assignments were not always definite without computational assurance. The hypothesis used was that the first signal with the lowest m/z value of the water series was a dry species such as for example $[\text{Al}_4\text{O}(\text{OH})_8\text{Cl}]^+$, without any aqua ligands. In several cases it was obvious, because no alternative assignment could be made.

In few cases, MS/MS collision spectra investigations showed fragmentation of aqua ligands from the first signal of water series, observed in the scan mode spectra. [II] However, this did not change the prior identification because, as seen through the mass spectra, direct fragmentation of aqua ligands did not differ from a reaction in which two hydroxo ligands react with each other producing a fragmenting water molecule and an oxo ligand. (Eq. 9)



All changes in the complexes were limited to protonation and solvation. Neither condensation nor fragmentation was observed. Because aluminium always appears as Al^{3+} , and when O^{2-} and OH^- are involved, protonation equilibrium rather than redox reactions occur. Despite many investigations of sulphuric acid, $[\text{SO}_4]^{2-}/[\text{SO}_3]^{2-}$ redox reactions have not been observed in mass spectrometric studies. [170-175] Therefore, no redox reactions were expected during these MS-measurements. The fact that almost all major signals were assigned to

stoichiometric compounds and no evidence of free or protonated sulphites ($[\text{SO}_3]^{2-}$ or $[\text{HSO}_3^-]$) were found, also supports this hypothesis. [IV,V] Therefore, the assignment of polyaluminum formate was a surprise, there were signals that had to be assigned to unstoichiometric complexes. (Subchapter 3.12.3) However, this phenomenon was not observed with other counter anions [I-V].

Also the sulphate containing complex such as $[\text{Al}_4\text{H}_{11}\text{O}_{10}(\text{SO}_4)]^+$ had several structural alternatives. In this case the computed minimum energy structure was $[\text{Al}_4\text{O}(\text{OH})_7(\text{SO}_4)(\text{H}_2\text{O})_2]^+$, and the structure next closest in energy $[\text{Al}_4\text{O}(\text{OH})_8(\text{HSO}_4)(\text{H}_2\text{O})]^+$. The cores of the suggested complexes were similar; the differences emerged from the protonation of the sulphate. Even though, it cannot be ruled out that these compact structures open in water, the minimum energy of the conventional chain structure variation was calculated to be considerably higher than these ones. [IV,V] Without the help of computational structure analysis the choice between different structures would only have been done according to the structural possibilities of free coordination places for water and counter anions and the possible protonation of sulphate would have to be ignored.

For very large complexes containing over 17 hydroxo- or 13 oxo ligands there were several choices for different identifications. E.g. four signals m/z 474.5–476 with mutual distance of $\frac{1}{2}$ units could be assigned to species with mass 1898u and the shape of the pattern unveiled four chlorine atoms. This could be formulated as $[\text{Al}_{32}\text{O}_{41}(\text{OH})_{14}\text{Cl}_4]^{4+}$, $[\text{Al}_{29}\text{O}_{28}(\text{OH})_{31}\text{Cl}_4]^{4+}$, $[\text{Al}_{26}\text{O}_{15}(\text{OH})_{48}\text{Cl}_4]^{4+}$ or $[\text{Al}_{23}\text{O}_2(\text{OH})_{65}\text{Cl}_4]^{4+}$. At the beginning the $[\text{Al}_{32}\text{O}_{41}(\text{OH})_{14}\text{Cl}_4]^{4+}$ was chosen as the best candidate because as an anion it contained the most oxo ligands out of the suggested complexes. The Al_{29} and Al_{26} structures were also considered proper candidates but the $\text{Al}_{23}\text{O}_2(\text{OH})_{65}$ core carried too many hydroxo ligands to be a δ - Al_{13} -Keggin core variant containing a tetrahedral AlO_4 central unit. [I,92] Later the Al_{26} formula seemed the most convincing because it could be formed from two Keggin structures. [III,176] When the multiply charged complexes did not contain chloride, sulphur, potassium or carbon (isotopic signals) nor had they any water series, the identification became impossible. For example, the single peak in chloride environment, m/z 350, found in many aged solutions, had no explanation because no evidence of its original charge could be acquired. [I,II,III] Tetramethylammonium (TMA) clusters, originating from the pH adjusting chemical, were observed in a chloride environment. [I,II,III,V] They were identified with chlorine and carbon isotope patterns, and they usually had even m/z -values. Usually their signals dominated the spectra with the cationic main

signal m/z 183 $[\text{TMA}_2\text{Cl}]^+$ or as in anionic spectra with intense TMA - chloride patterns up to m/z 1016 $[\text{TMA}_9\text{Cl}_{10}]^-$. The complexes were not only pure $[\text{TMA}_n\text{Cl}_{n-1}]^+$ or $[\text{TMA}_{n-1}\text{Cl}_n]^-$ ($n=1-10$), but there were often combinations with sodium, such as $[\text{NaTMA}_3\text{Cl}_3]^+$ or $[\text{Na}_2\text{TMA}_7\text{Cl}_8]^+$. Some anionic assignments were TMA - sodium hydroxide derivates. An interesting phenomenon was that very few TMA adducts were identified in sulphate environment, and their intensity was low. Only one signal assigned to a TMA complex had an intensity of over 5%, which was m/z 521 $[\text{TMA}_3(\text{HSO}_4)_2(\text{SO}_4)]^-$. [IV] All these TMA variants could cause ion suppression of aluminium complexes. [177]

Table 3. Observed Al TMA clusters.

$[\text{Al}_2\text{O}(\text{OH})_2\text{TMA}_4\text{Cl}_{15}]^+$	$[\text{Al}_2(\text{OH})_4\text{TMA}_3\text{Cl}_6]^-$	$[\text{Al}_3\text{O}_2(\text{OH})_2\text{TMA}_2\text{Cl}_6]^-$
$[\text{NaAl}_3(\text{OH})_8(\text{H}_2\text{O})\text{TMACl}_2]^+$	$[\text{Al}_2(\text{OH})_4\text{TMACl}_4]^-$	$[\text{Al}_3(\text{OH})_7\text{TMA}_2\text{Cl}_5]^-$
$[\text{NaAl}_3\text{O}(\text{OH})_4\text{TMACl}_4]^+$	$[\text{Al}_2(\text{OH})_4\text{TMACl}_4(\text{H}_2\text{O})]^-$	$[\text{Al}_3\text{O}_2(\text{OH})\text{TMA}_2\text{Cl}_7]^-$
$[\text{Al}_5(\text{OH})_3\text{TMA}_2\text{Cl}_{13}]^+$	$[\text{Al}_2(\text{OH})_3\text{TMA}_2\text{Cl}_5]^-$	$[\text{Al}_3\text{O}(\text{OH})_3\text{TMA}_2\text{Cl}_7]^-$
$[\text{Al}_5\text{O}_3(\text{OH})_9\text{TMA}_6\text{Cl}_5]^+$	$[\text{Al}_2(\text{OH})_4\text{TMA}_3\text{Cl}_6]^-$	$[\text{Al}_4\text{O}_4(\text{OH})_4\text{TMA}_3\text{Cl}_4]^-$
$[\text{NaAl}_7\text{O}(\text{OH})_{12}\text{TMA}_3\text{Cl}_{10}]^+$	$[\text{Al}_2(\text{OH})_4\text{TMA}_6\text{Cl}_9]^-$	

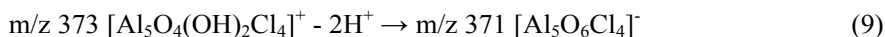
Furthermore, some TMA-adducts formed various combined complexes with small aluminium hydrolyse products as shown in Table 3. This phenomenon was not observed in fresh solutions. These clusters could give us a hint of the intact speciation in water, since these clusters most probably were generated in the bulk solution during the ageing process. [I,III]

6.1 Anionic aluminium species

The detected complex anions contained more oxo ligands than the corresponding cations and the water series were hardly observed. Generally, they contained Al_2O_3 , AlOCl and $[\text{AlCl}_4]^-$ or $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}_2\text{O}(\text{SO}_4)_2$, $\text{Al}_2\text{O}_2(\text{SO}_4)$, and $[\text{Al}(\text{SO}_4)_2]^-$ units. In the chloride environment the assignment consisted of modified hydrolysis products with Al_xO_y -cores ($y \geq x$). [I,II,III] Similar simple aluminium oxo chlorides have been found in organic chloroaluminate melts by secondary ion mass spectrometry. [178] The structures, such as $[(\text{AlCl}_3)_n\text{Cl}]^-$, which are common e.g. iron solutions [179], were not observed. The sulphate containing anions were not exactly hydrolysis products: there were some adducts or partly undissociated alum such as $[\text{Al}_9\text{O}_5(\text{SO}_4)_{10}]^{3-}$ {e.g. $3\text{Al}_2(\text{SO}_4)_3 + [\text{Al}_3\text{O}_5(\text{SO}_4)]^{3-}$ }. [IV] In pure sulphate environment, even the small anionic species were often multiply charged.

[IV] When both anions, Cl^- and SO_4^{2-} , were present, mixed complexes such as $[\text{AlCl}_2(\text{SO}_4)]^-$ were also observed to form. [V]

In many cases, it was possible to find a pair of an anion and a cation with the same amount of Al and chloride, in which the anion was the deprotonated cation (Eq.9). This deprotonation reaction is commonly called “Wrong-way-round” electrospray ionisation. [180]



The competition between water and chloride ligands together with deprotonation or/and dehydration during the nebulation process could be another explanation. E.g., the m/z value 349 could be identified as $[\text{Al}_4\text{O}_3(\text{OH})_2\text{Cl}_3(\text{H}_2\text{O})_3]^+$, and the corresponding anion has been discovered to be m/z 401 $[\text{Al}_4\text{O}_4\text{Cl}_5(\text{H}_2\text{O})_3]^-$. These kinds of pairs were lacking in sulphate environment probably because sulphate binds strongly with protons. There was only one cation - anion pair with different amounts of sulphate ($[\text{Al}_2(\text{OH})_3(\text{SO}_4)]^+$, $[\text{Al}_2\text{O}(\text{OH})(\text{SO}_4)_2]^-$).

The trimeric species, which were very common as cations were missing as anions in sulphate environment. Also Al_{13} was found as an anion in very low pH. It is possible that these changes occur already in bulk solution but it could also mean that sulphate changes the speciation strongly in anionic mode, driving it closer to solid state combustions and structures. [IV]

Hence, one should be careful when iterating solution state speciation with a presence of sulphate, according the anionic MS results. Because the anions are probably formed during the measuring via outer sphere reactions, the investigations should be made with several different parameters to obtain all the information the anions could give. On the contrary, the information could be quite far from the solution state, because the generation of the anions is still ambiguous.

6.2 Monomers

In conventional aluminium speciation by potentiometry, monomeric complexes are usually considered the major ones. Also in our investigations with the quadrupole detector (Q), signals at m/z values 61, 79, 97, and 115 dominated all spectra. [III] These signals were assigned to the complexes $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_{0-3}]^+$. The six-coordinated member m/z 133 $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ of this water series was not observed, although according to the NMR and potentiometric investigations, this species should be present in water. In literature, there are several $p\beta$ values for this monocharged dihydroxide: 7.7–11.3. [7,75,181,182] These were the only

direct observations of cationic monomeric species in chloride environment. With the TOF detector there were no observations of monomers, although they would have been in measuring range. Because both equipments had the identical ESI interfaces, there either has to be some reactions in the vacuum chamber of TOF that polymerise those species. Alternatively, the harsh environment in quadrupoles causes fragmentation and they are therefore not true species in solution.

All monomeric species found are collected In Table 4. The column “Fully protonised” expresses the species as they are written when used in potentiometric calculations. The unprotonised oxygen atoms are replaced with two hydroxide ligands and all other anions are ignored.

In a chloride environment with an anionic mode the very intense signal of $[\text{AlCl}_4]^-$ was found in the ESI-TOF measurements. It may indicate that the major monoaluminum species is the octahedral $[\text{Al}(\text{OH})_6]^{3+}$ (m/z 45) surrounded by outer sphere chloride counter anions. Because of the low m/z value, the cation itself was not observed. During nebulation aqua ligands evaporated and the counter anions react with the aluminium cation to form the tetrahedral $[\text{AlCl}_4]^-$. This could also be the reaction path for the forming of the larger anions found in the ESI-TOF experiments (Chapter 6.1).

There were several different monomeric ions in a sulphate environment. The reasons and circumstances behind the birth of these species probably vary and at least three explanations can be found. They could be partly undissociated alum such as $[\text{Al}(\text{SO}_4)_2]^-$. On the other hand, in the ion pairing reaction, sulphate and hydroxide anions may have attached to the aluminium cation during the nebulation as it could be in the case of $[\text{Al}(\text{OH})(\text{HSO}_4)(\text{H}_2\text{O})_{0-2}]^+$, $[\text{AlO}(\text{SO}_4)]^-$, and $[\text{Al}(\text{OH})_2(\text{SO}_4)]^-$. Also attachment of hydrogen sulphate on to completely hydrolysed $\text{Al}(\text{OH})_3$ ($p\beta$ values 15.6–17.3 [7,75,183]) could have been possible, as in the case of $[\text{Al}(\text{OH})_3(\text{HSO}_4)(\text{H}_2\text{O})]^-$, and $[\text{Al}(\text{OH})_3(\text{HSO}_4)_2(\text{H}_2\text{O})_4]^{2-}$. In a chloride environment, a similar ionisation was not detected. The formation of these species could be an interesting topic for computational chemistry.

The aluminate ion $[\text{Al}(\text{OH})_4]^-$ was detected in our study only once at pH 7.05 and only as a minor signal at m/z 99. The conventional distribution diagramme shows, that it should be the major species above pH 7, but in those a few MS measurements we did at higher pH, no evidence of it was detected. [III] It is given $p\beta$ values 22.20–23.75 in various literature sources. [7,75,91,184]

Table 4. The observed monomeric species.

Species	Al ³⁺ mM	pH-range	Env.*	Detector	Sample cone voltage, V	Fully protonised
[AlCl ₂] ⁺	10	3.88	I	Q	70	Al ³⁺
[AlCl ₄] ⁻	100,10,1	3.27–4.72	I, II	TOF	70,150,200	Al ³⁺
[AlCl ₂ (SO ₄)] ⁻	10	3.74–4.03	III	TOF	70	Al ³⁺
[Al(SO ₄) ₂] ⁻	10	3.76–4.03	II, III	TOF	40,70	Al ³⁺
[Al(OH)Cl] ⁺	10	3.88	I	Q	70	[Al(OH)] ²⁺
[Al(OH)Cl ₃] ⁻	100,10,1	3.72–4.72	I, II	TOF	70,150,200	[Al(OH)] ²⁺
[Al(OH)Cl(SO ₄)] ⁻	10	3.74–4.03	III	TOF	70	[Al(OH)] ²⁺
[Al(OH)(HSO ₄)] ⁺	10	3.76–3.92	II	TOF	40	[Al(OH)] ²⁺
[Al(OH) ₂] ⁺	10	3.88	I	Q	70	[Al(OH) ₂] ⁺
[Al(OH) ₂ Cl ₂] ⁻	10,1	3.72–4.72	I, II	TOF	70	[Al(OH) ₂] ⁺
[AlOCl ₂] ⁻	100,10	3.72–4.50	I	TOF	70	[Al(OH) ₂] ⁺
[Al(OH) ₂ (SO ₄)] ⁻	10	3.76–3.92	II	TOF	40	[Al(OH) ₂] ⁺
[AlO(SO ₄)] ⁻	10	3.76–3.92	II, III	TOF	40,70	[Al(OH) ₂] ⁺
[Al(OH) ₃ (HSO ₄)] ⁻	10	3.76–3.92	II	TOF	40	[Al(OH) ₃] ⁰
[Al(OH) ₃ (HSO ₄) ₂] ²⁻	10	3.76–3.92	II	TOF	40	[Al(OH) ₃] ⁰
[Al(OH) ₄] ⁻	10	7.05	I	TOF	70	[Al(OH) ₄] ⁻

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.3 Dimers

In fresh solutions, signals assigned to dimers dominated the spectra observed by ESI-TOF, indicating that the dimer aluminium complexes were stable in aqueous solution. When the solutions were aged, more stable trimers took over. No dimers were observed in prehydrolysed polyaluminium chlorides. [185]

Also, dimers are first species, which have been identified by crystal studies, [11] and by NMR. [79] In literature sources $p\beta$ values have been reported for [Al₂(OH)₄]²⁺ (16.00) [76], [Al₂(OH)₃]³⁺ (1.44–11.55) [76], and for [Al₂(OH)₂]⁴⁺ (7.25–8.00) [7,76,186]. Nowadays their structures have been computed using different kind of density functions. [85,129] Dimers seem to favour two octahedral Al centres connected by a common edge (di- μ -OH- bridge) in aquatic environment. [187] With low charges (+1 – +3), dimeric species have a tendency to form a five-coordinate trigonal bipyramidal configuration. However, the energy

differences among many configurational isomers are so small that they may coexist and convert into each other easily at room temperature. [188] Those dimeric species that we found by mass spectrometric methods seemed to prefer tetrahedral structure. However it is apparent, that in water they complete their coordination with aqua ligands, which evaporate during nebulation.

Dimers are considered the first polymeric species born during the hydrolysis. It has been thought that the polymerisation continues via these dimers. [189,190] Our preliminary results considering kinetics, also indicate this (Subchapter 6.11.2).

Table 5. The dimeric species.

Species	Al ³⁺ mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
[Al ₂ (OH) ₅] ⁺	100,10	3.27–4.50	I, II, III	TOF	40,70	[Al ₂ (OH) ₅] ⁺
[Al ₂ O(OH) ₃] ⁺	100,10,1	3.72–4.98	I, III, V	Q, TOF	70	[Al ₂ (OH) ₅] ⁺
[Al ₂ (OH) ₅ Cl] ⁻	10	3.72–4.50	I	TOF	70	[Al ₂ (OH) ₅] ⁺
[Al ₂ (OH) ₄ Cl] ⁺	100,10,1	3.27–4.72	I, III	TOF	70,150,200	[Al ₂ (OH) ₄] ²⁺
[Al ₂ O(OH) ₂ Cl] ⁺	100,10,1	3.27–4.72	I, III	Q, TOF	70	[Al ₂ (OH) ₄] ²⁺
[Al ₂ O(OH) ₂ Cl ₃] ⁻	10	3.74–4.03	III	TOF	70	[Al ₂ (OH) ₄] ²⁺
[Al ₂ O ₂ Cl ₃] ⁻	100,10,1	3.27–4.72	I, III	TOF	70,150,200	[Al ₂ (OH) ₄] ²⁺
[Al ₂ (OH) ₄ (HSO ₄)] ⁺	10	3.76–3.92	II	TOF	40	[Al ₂ (OH) ₄] ²⁺
[Al ₂ O(OH) ₂ (HSO ₄)] ⁺	10	3.74–4.03	II, III	TOF	40, 70	[Al ₂ (OH) ₄] ²⁺
[Al ₂ O ₂ (SO ₄) ₂] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₂ (OH) ₄] ²⁺
[Al ₂ (OH) ₃ Cl ₂] ⁺	100,10	3.74–4.20	I, III	Q, TOF	70	[Al ₂ (OH) ₃] ³⁺
[Al ₂ O(OH)Cl ₄] ⁻	100,10,1	3.74–4.72	I, III	TOF	70,150,200	[Al ₂ (OH) ₃] ³⁺
[Al ₂ (OH) ₃ (HSO ₄) ₂] ⁺	10	3.76–3.92	II	TOF	40	[Al ₂ (OH) ₃] ³⁺
[Al ₂ (OH) ₃ (SO ₄) ₂] ⁻	10	3.74–4.03	II, III	TOF	40, 70	[Al ₂ (OH) ₃] ³⁺
[Al ₂ O(OH)(SO ₄) ₂] ⁻	10	3.76–3.92	II	TOF	40	[Al ₂ (OH) ₃] ³⁺
[Al ₂ OCl ₅] ⁻	100,10,1	3.27–4.72	I, III	TOF	70,150,200	[Al ₂ (OH) ₂] ⁴⁺
[Al ₂ OCl ₃ (SO ₄)] ⁻	10	3.74–4.03	III	TOF	70	[Al ₂ (OH) ₂] ⁴⁺
[Al ₂ O(SO ₄) ₃] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₂ (OH) ₂] ⁴⁺
[Al ₂ (OH)Cl ₄] ⁺	10	3.88	I	Q	70	[Al ₂ (OH)] ⁵⁺

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.4 Trimers

The trimeric species had the most stable structure since they had the greatest variation, increasing as a function of time. In prehydrolysed polyaluminium solutions the very dry $[Al_3O_4]^+$ species was always present in the spectra (m/z 163). [185] Even in rising pH when the larger oligomers vanished, this pattern had the most intense signal. The trimers also usually carried chlorine or sulphate ligands, which means that their charge in the bulk solution could have been higher, since the anions attached to the core during the measurement. For some reason trimeric species have never yet been found as anions in sulphate environment.

In literature sources trimeric species are well known. The $p\beta$ values have been measured for two species: $[Al_3(OH)_4]^{5+}$, 13.13–13.88 [7,75,76,182,184] and $[Al_3(OH)_3]^{6+}$, 9.78 [76]. These two complexes were also found in our MS studies, although not as major complexes. In sulphate environment they were mainly found without a water series.

One of the most stable species seemed to be $[Al_3O(OH)_6]^+$, since it was found with both counter anions (Cl^- , SO_4^{2-}), even with wide range of sample cone voltages and concentrations. It carried no aqua ligands itself but the series continued with a hydroxide exchange into chloride or bisulphate. These species are indicated in bold in Table 6. The series ends in $[Al_3O(OH)_3Cl_3]^-$ and $[Al_3O(OH)_3(HSO_4)_3]^+$, which refers to structure, in which there is a central oxygen, three bridging hydroxide ligands, and counter anions as terminal ligands. The structure of these kinds of species could be the compact *sompa*¹- structure, where three aluminium atoms are connected by μ_2 -OH-bridges forming six-membered ring with one common central oxygen μ_3 -O ligand or its open variant, in which the central oxygen is attached only to two aluminium atoms instead of three. [III,129] These structures are illustrated in Fig.12. The central oxygen ligand is acidic, and a proton could not attach to it easily. [191] There are four such ring systems as a substructure of the Keggin cation, and they could also be the precursors of precipitating boehmite. [189,190]

¹ “*Sompa*” is Finnish word for part of cross country skiing equipment, which prevents the poles sinking in the snow. Traditionally they were rattan rings tied with three leather ribbons to wand. There is no corresponding word in English.

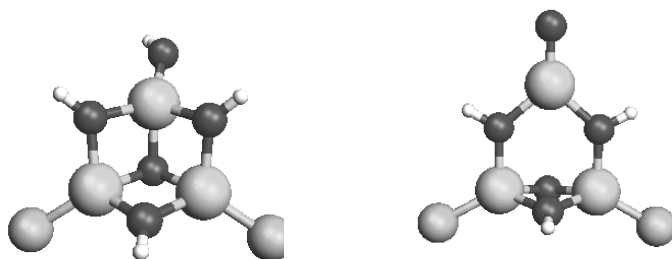


Fig. 12. The alternative structures of $[Al_3O(OH)_4Cl_2]^+$. *Sompa* structure left, open variant right.

The anionic $[Al_3(OH)_{10}]^-$ and cationic $[Al_3(OH)_8]^+$ could be a linear chain formed species, (Fig. 13) as the structures have been conventionally described. The anion seems to be more like three aluminate anions sharing hydroxide ligands and it could be a cluster ion. The cation may have conventional chain structure with double hydroxide bridges. This chain cation core also has a series, in which the terminal hydroxides are replaced with chloride or bisulphate up to $[Al_3(OH)_4Cl_4]^+$ in which all terminal hydroxides have been exchanged to chlorides.

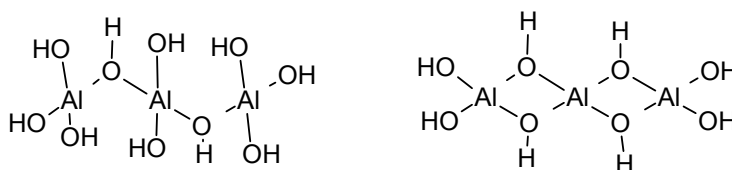


Fig. 13. Chain formed trimeric aluminium oxo hydroxides. Anion left, cation right.

There is solid NMR evidence about other compact trimeric complex, in which two oxygen atoms are unprotonated: $[Al_3O_2(OH)_4(H_2O)_8]^+$. In this cyclic complex was two aluminium atoms bonded by two bridging oxo groups, and the third aluminium atom was connected to both other aluminium atoms with two bridging OH groups. (Fig. 12) The aluminiums with three bridging ligands had also terminal OH groups. Each aluminium atom completed an octahedral coordination with aqua ligands. [192] In these mass spectrometric studies these complexes were also found. Only the several aqua ligands were now missing changing the coordination of the aluminium to tetrahedral, while some of the terminal hydroxides and aqua ligands were replaced with available chloride. There are

computational results on one chloride attaching willingly to inner coordination sphere of small aluminium oxo hydroxides in gas phase, stabilising the polymers. This also bends the linear complexes to curve. [193]

There are also crystallographic results of trinuclear citrate complex: $[\text{Al}(\text{H}_2\text{O})_6][(\text{Al}_3-(\text{C}_6\text{H}_4\text{O}_7)_2(\text{OH})_2(\text{H}_2\text{O})_4)_2(\text{NO}_3)\cdot 6\text{H}_2\text{O}]$. It has been precipitated at very low pH (1.66), where no polymeric species should exist, according conventional speciation methods. Eventough the formula of this complex seems quite different to most of the aqueous species, a similar core structure as the compact $[\text{Al}_3\text{O}_2(\text{OH})_4]^+$ can be found in the middle of the complex. In this case, the bridging oxygen atoms are part of the citric ligand. [194]

The prehydrolysed aluminium chloride chemicals showed interesting mass spectra. In these investigations no chloride containing complexes were identified. Even the smallest ones were pure aluminium oxo hydroxides. At initial pH, a diversity of small species was lacking and only very dry trimeric complex was recognised in the spectra: $[\text{Al}_3\text{O}_4(\text{H}_2\text{O})_{0-2}]^+$. Despite this, the spectra showed several series of signals in area 250–550, assigned to Al_{13} - Al_{16} . When pH was raised, those signals dominated the spectra. When the pH was raised close to 7, these signals assigned to larger species reduced and the trimeric complexes emerged again. [185]

All this indicates that trimers are very stabile and soluble species, which can have several conformations and state of charges even in circumstances where the larger complexes form colloids and coagulate.

Table 6. The trimeric species.

Species	Al ³⁺ mM	pH-range	Env. [*]	Detector	Sample cone voltage, V	Fully protonised
[Al ₃ (OH) ₁₀] ⁻	1	3.92	I	TOF	70	[Al ₃ (OH) ₁₀] ⁻
[Al ₃ (OH) ₈] ⁺	10,1	3.72–4.72	I	TOF	70	[Al ₃ (OH) ₈] ⁺
[Al₃O(OH)₆]⁺	100,10	3.27–4.20	I, II, III	TOF	40,70,150	[Al ₃ (OH) ₈] ⁺
[Al ₃ O ₄] ⁺	1,0.1	4.94–6.95	IV	TOF	70	[Al ₃ (OH) ₈] ⁺
[Al ₃ (OH) ₇ Cl] ⁺	100,10,1	3.27–4.50	I	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al₃O(OH)₅Cl]⁺	100	4.20	I	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al ₃ O ₂ (OH) ₃ Cl] ⁺	10	3.74–4.03	III	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al ₃ O ₂ (OH) ₃ Cl ₃] ⁻	10	4.50	I	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al ₃ O ₃ (OH)Cl ₃] ⁻	100	3.27	I	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al ₃ (OH) ₇ (HSO ₄) ⁺	10	3.74–4.03	III	TOF	70	[Al ₃ (OH) ₇] ²⁺
[Al₃O(OH)₅(HSO₄)⁺	10	3.74–4.03	II, III	TOF	40,70	[Al ₃ (OH) ₇] ²⁺
[Al ₃ (OH) ₆ Cl ₂] ⁺	100,10,1	3.72–4.20	I, III	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al₃O(OH)₄Cl₂]⁺	100,10,1	3.27–4.72	I, III	Q, TOF	70,150	[Al ₃ (OH) ₆] ³⁺
[Al ₃ O ₂ (OH) ₂ Cl ₂] ⁺	10	3.74–4.03	III	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al ₃ (OH) ₆ Cl ₄] ⁻	10	3.72	I	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al ₃ O ₂ (OH) ₂ Cl ₄] ⁻	1	4.72	I	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al ₃ O ₃ Cl ₄] ⁻	100,10,1	3.27–4.72	I, III	TOF	70,150,200	[Al ₃ (OH) ₆] ³⁺
[Al ₃ (OH) ₆ (HSO ₄) ₂] ²⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₆] ³⁺
[Al ₃ (OH) ₆ (HSO ₄) ₂] ⁺	10	3.74–4.03	III	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al₃O(OH)₄(HSO₄)₂]⁺	10	3.74–4.03	III	TOF	70	[Al ₃ (OH) ₆] ³⁺
[Al ₃ (OH) ₅ Cl ₃] ⁺	100,10,1	3.47–4.72	I, III	Q, TOF	70,150	[Al ₃ (OH) ₅] ⁴⁺
[Al₃O(OH)₃Cl₃]⁺	10	3.72–4.50	I	Q, TOF	70	[Al ₃ (OH) ₅] ⁴⁺
[Al ₃ O ₂ (OH)Cl ₃] ⁺	10	3.72–4.50	I	TOF	70	[Al ₃ (OH) ₅] ⁴⁺
[Al₃O(OH)₃Cl₃]⁻	100,10	3.27–4.20	I	TOF	70	[Al ₃ (OH) ₅] ⁴⁺
[Al ₃ O ₂ (OH)Cl ₃] ⁻	10	3.74–4.50	I, III	TOF	70	[Al ₃ (OH) ₅] ⁴⁺
[Al ₃ (OH) ₅ (HSO ₄) ₃] ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₅] ⁴⁺
[Al ₃ (OH) ₄ Cl ₄] ⁺	100,10	3.27–4.20	I	Q, TOF	70	[Al ₃ (OH) ₄] ⁵⁺
[Al ₃ (OH) ₄ (SO ₄) ₂] ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₄] ⁵⁺
[Al ₃ O(OH) ₃ (HSO ₄) ₃] ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₄] ⁵⁺
[Al ₃ (OH) ₄ (HSO ₄) ₄] ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₄] ⁵⁺
[Al ₃ (OH) ₃ Cl ₅] ⁺	10	3.88	I	Q	70	[Al ₃ (OH) ₃] ⁶⁺
[Al ₃ (OH) ₃ (HSO ₄)(SO ₄) ₂] ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₃] ⁶⁺
[Al ₃ (OH) ₃ (HSO ₄) ₃ (SO ₄) ⁺	10	3.76–3.92	II	TOF	40	[Al ₃ (OH) ₃] ⁶⁺
[Al ₃ (OH) ₂ Cl ₈] ⁻	100	4.20	I	TOF	150,200	[Al ₃ (OH) ₂] ⁷⁺

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.5 Small oligomers

Tetramers proved to be almost as common as dimers and trimers (Table 7.). The calculation of the structure showed an adamantine-like core structure. No β -values were found for these tetrameric species in literature. They might have been ignored because the conventional speciation calculations can suppress them to dimers, if the numbers of hydroxide ligands in fully hydrolysed species – and thus also the charges – are even. Although the tetramers are not found as individual species with other methods, there is indirect evidence about their existence. A tetrameric subunit connects two Al_{13} Keggin structures together to form a large Al_{30} polyoxohydroxo cation. [176,195,196] There are also tetrameric substructures in gibbsite [197], which resemble the species calculated by Sillanpää et al. [85] (Fig.4.). Also, a very similar species as the compact structure calculated by Saukkoriipi et al. [129] is suggested to be the precursor of precipitating boehmite. [191]

In this study twenty different Al_5 -species were observed, indicating a great diversity of pentameric species in the bulk solutions. Almost all the Al_5 -species had at least one unprotonated oxo ligand, which could correlate to the structure in which there is a shielded oxo group that is unable to capture proton (Table 7.). The only exceptions were $[\text{Al}_5(\text{OH})_6\text{Cl}_8]^+$ and $[\text{Al}_5(\text{OH})_5\text{Cl}_9]^+$, which were found with very high sample cone voltages. Therefore it is a question if they were merely fragments or clusters rather than real species in the bulk solution. The extremely high number of chlorine atoms also suggests the existence of a disordered structure. In contrast to Al_5 , smaller species with exclusively hydroxide ligands were found using moderate parameters. The β -value of $[\text{Al}_5(\text{OH})_{12}]^{3+}$ is 43.41. [91] Corresponding species were found in our measurements with chlorine and sulphate. To conclude, the pentameric species seem to have a surprisingly stable structure and it could cause crystallisation of aluminium in water purification systems. [198] Similar results concerning the deviant structures of Al_5 -complexes have been found by Groenewold et al. [199] by a different mass spectrometric approach. Their results include observations from monomeric to decameric aluminium oxo hydroxo complexes.

Potentiometric experiments indicate that a polymer form $[\text{Al}_6(\text{OH})_{15}]^{3+}$ exists in a solution with β -value 53.78. [77] A corresponding species was found in our studies too, but only once with higher measuring parameters. Hexamers have been believed to be ring structures consisting of six octahedral units. [87] (Fig.5.) Also, the ring structure of $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}\text{Cl}_6$ molecule has been optimised by

computational methods. [193] There it was found as partly unprotonated species. In these measurements all hexamers contained unprotonated oxygen ligands, which would reflect a compact structure (Table 7.).

Table 7. The tetra-, penta-, and hexameric species.

Species	Al ³⁺ mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
[Al ₄ (OH) ₁₁] ⁺	100,10	3.72–4.20	I, III	TOF	70,150	[Al ₄ (OH) ₁₁] ⁺
[Al ₄ O(OH) ₉ (SO ₄)] ⁻	10	3.74–4.03	III	TOF	70	[Al ₄ (OH) ₁₁] ⁺
[Al ₄ O ₂ (OH) ₆ Cl ₃] ⁻	10	3.74–4.03	III	TOF	70	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O ₄ (OH) ₂ Cl] ⁺	100	3.72–3.92	I	TOF	150	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O ₃ (OH) ₄ Cl ₃] ⁻	100	3.27–4.20	I	TOF	70	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O ₄ (OH) ₂ Cl ₃] ⁻	10	4.50	I	TOF	70	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O ₅ Cl ₃] ⁻	100	3.27–4.20	I	TOF	150,200	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O(OH) ₈ (HSO ₄)] ⁺	10	3.74–4.03	III	TOF	70	[Al ₄ (OH) ₁₀] ²⁺
[Al ₄ O ₃ (OH) ₃ Cl ₂] ⁺	100	3.27–4.20	I	TOF	70,150	[Al ₄ (OH) ₉] ³⁺
[Al ₄ (OH) ₉ Cl] ⁻	10	3.72	I	TOF	70	[Al ₄ (OH) ₉] ³⁺
[Al ₄ O ₃ (OH) ₃ Cl ₄] ⁻	10	3.72	I	TOF	70	[Al ₄ (OH) ₉] ³⁺
[Al ₄ O ₄ (OH)Cl ₄] ⁻	10	3.72	I	TOF	70	[Al ₄ (OH) ₉] ³⁺
[Al ₄ O(OH) ₇ (SO ₄)] ⁺	10	3.74–4.03	III	TOF	70	[Al ₄ (OH) ₉] ³⁺
[Al ₄ O ₃ (OH) ₂ Cl ₃] ⁺	100,10,1	3.72–4.20	I	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O(OH) ₆ Cl ₃] ⁺	10	3.74–4.03	I, III	Q, TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O ₂ (OH) ₄ Cl ₃] ⁺	100,10	3.27–4.03	I, III	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O ₃ (OH) ₂ Cl ₃] ⁺	100,10,1	3.72–4.20	I	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O ₂ (OH) ₄ Cl ₅] ⁻	10	3.72	I	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O ₄ Cl ₃] ⁻	100,10	3.27–3.92	I	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ O ₄ Cl ₃ (SO ₄)] ⁻	10	3.74–4.03	III	TOF	70	[Al ₄ (OH) ₈] ⁴⁺
[Al ₄ (OH) ₇ Cl ₄] ⁺	10	3.88	I	Q	70	[Al ₄ (OH) ₇] ⁵⁺
[Al ₄ O(OH) ₅ Cl ₄] ⁺	100, 100	3.88–3.92	I	Q, TOF	70,150	[Al ₄ (OH) ₇] ⁵⁺
[Al ₄ O ₃ (OH)Cl ₄] ⁺	10	3.72	I	TOF	70	[Al ₄ (OH) ₇] ⁵⁺
[Al ₄ (OH) ₆ Cl ₅] ⁺	10	3.88	I	Q	70	[Al ₄ (OH) ₆] ⁶⁺
[Al ₄ O ₂ (OH) ₂ Cl ₇] ⁻	1	3.92	I	TOF	70	[Al ₄ (OH) ₆] ⁶⁺
[Al ₄ O ₃ (SO ₄) ₄] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₄ (OH) ₆] ⁶⁺
[Al ₄ (OH) ₅ Cl ₆] ⁺	10	3.88	I	Q	70	[Al ₄ (OH) ₅] ⁷⁺
[Al ₄ (OH) ₅ (HSO ₄) ₂ (SO ₄) ₂] ⁺	10	3.76–3.92	II	TOF	40	[Al ₄ (OH) ₅] ⁷⁺
[Al ₄ (OH) ₄ Cl ₇] ⁺	10	3.88	I	Q	70	[Al ₄ (OH) ₄] ⁸⁺
[Al ₄ (OH) ₄ (HSO ₄) ₃ (SO ₄) ₃] ⁺	10	3.76–3.92	II	TOF	40	[Al ₄ (OH) ₄] ⁸⁺
[Al ₄ O ₂ (SO ₄) ₃] ²⁻	10	3.76–3.92	II	TOF	40	cluster
[Al ₄ H ₁₃ O ₁₁ (SO ₄)] ⁺	10	3.74–4.03	III	TOF	70	
[Al ₄ H ₉ O ₈ (SO ₄) ₂] ⁺	10	3.74–4.03	III	TOF	70	
[Al ₄ H ₇ O ₅ (SO ₄) ₄] ⁺	10	3.74–4.03	III	TOF	70	

Species	Al ³⁺ mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
[Al ₅ O ₂ (OH) ₁₀] ⁺	100,10,1	4.20–4.72	I	TOF	70	[Al ₅ (OH) ₁₄] ⁺
[Al ₅ O ₆ (OH) ₂] ⁺	100	3.27–4.20	I	TOF	200	[Al ₅ (OH) ₁₄] ⁺
[Al ₅ O ₂ (OH) ₁₀ (SO ₄) ⁻	10	3.74–4.03	III	TOF	70	[Al ₅ (OH) ₁₄] ⁺
[Al ₅ O ₅ (OH)3Cl] ⁺	100	3.27–4.20	I	TOF	150,200	[Al ₅ (OH) ₁₃] ²⁺
[Al ₅ O ₄ (OH) ₄ Cl ₄] ⁻	100,10	3.27–4.20	I	TOF	70	[Al ₅ (OH) ₁₂] ³⁺
[Al ₅ O ₆ Cl ₄] ⁻	100	3.27–4.20	I	TOF	150,200	[Al ₅ (OH) ₁₂] ³⁺
[Al ₅ O ₂ (OH) ₈ Cl ₂] ⁺	100	3.27–3.92	I	TOF	150,200	[Al ₅ (OH) ₁₂] ³⁺
[Al ₅ O ₃ (OH) ₆ Cl ₂] ⁺	100	3.27	I	TOF	70	[Al ₅ (OH) ₁₂] ³⁺
[Al ₅ O ₅ (OH) ₂ (SO ₄) ₂] ⁻	10	3.76–3.92	II	TOF	40	[Al ₅ (OH) ₁₂] ³⁺
[Al ₅ O ₄ (OH) ₃ Cl ₅] ⁻	10	3.72	I	TOF	70	[Al ₅ (OH) ₁₁] ⁴⁺
[Al ₅ O ₂ (OH) ₆ Cl ₄] ⁺	10	3.72	I	TOF	70	[Al ₅ (OH) ₁₀] ⁵⁺
[Al ₅ O ₃ (OH) ₄ Cl ₄] ⁺	100,10,1	3.27–3.92	I	TOF	70	[Al ₅ (OH) ₁₀] ⁵⁺
[Al ₅ O ₄ (OH) ₂ Cl ₄] ⁺	100	3.27–3.92	I	TOF	70	[Al ₅ (OH) ₁₀] ⁵⁺
[Al ₅ O(OH) ₇ Cl ₅] ⁺	10	3.72	I	TOF	70	[Al ₅ (OH) ₉] ⁶⁺
[Al ₅ O ₄ Cl ₈] ⁻	100	3.27–4.20	I	TOF	70,200	[Al ₅ (OH) ₈] ⁷⁺
[Al ₅ O ₃ (OH)(SO ₄) ₅] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₅ (OH) ₇] ⁸⁺
[Al ₅ (OH) ₆ Cl ₈] ⁺	100	3.27	I	TOF	150,200	[Al ₅ (OH) ₆] ⁹⁺
[Al ₅ (OH) ₅ Cl ₉] ⁺	100	3.92	I	TOF	150	[Al ₅ (OH) ₅] ¹⁰⁺
[Al ₅ O ₂ (OH)(SO ₄) ₆] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₅ (OH) ₅] ¹⁰⁺
[Al ₆ O ₇ (OH) ₅] ⁻	10	3.76–3.92	II	TOF	40	[Al ₆ (OH) ₁₉] ⁻
[Al ₆ O ₃ (OH) ₁₁] ⁺	1	4.94	IV	TOF	70	[Al ₆ (OH) ₁₇] ⁺
[Al ₆ O ₆ Cl ₃] ⁻	100	3.27–3.92	I	TOF	150,200	[Al ₆ (OH) ₁₆] ²⁺
[Al ₆ O ₆ (OH) ₃ Cl ₂] ⁺	100	3.92	I	TOF	150	[Al ₆ (OH) ₁₅] ³⁺
[Al ₆ O ₂ (OH) ₁₀ Cl ₅] ⁻	100,10	3.27–4.50	I	TOF	70	[Al ₆ (OH) ₁₄] ⁴⁺
[Al ₆ O ₄ (OH) ₈ Cl ₅] ⁻	10	3.72	I	TOF	70	[Al ₆ (OH) ₁₄] ⁴⁺
[Al ₆ O ₇ Cl ₃] ⁺	100	3.27	I	TOF	70,150	[Al ₆ (OH) ₁₄] ⁴⁺
[Al ₆ O ₇ Cl ₅] ⁻	100	3.27–4.20	I	TOF	150,200	[Al ₆ (OH) ₁₄] ⁴⁺
[Al ₆ O ₄ (OH) ₆ Cl ₅] ⁻	100	3.27	I	TOF	70	[Al ₆ (OH) ₁₄] ⁴⁺
[Al ₆ O ₄ (OH) ₅ Cl ₄] ⁺	10,1	3.72–3.92	I	TOF	70	[Al ₆ (OH) ₁₃] ⁵⁺
[Al ₆ O ₂ (OH) ₉ Cl ₄] ⁺	100	3.27	I	TOF	70	[Al ₆ (OH) ₁₃] ⁵⁺
[Al ₆ O ₂ (OH) ₈ Cl ₅] ⁺	100	3.27	I	TOF	70	[Al ₆ (OH) ₁₂] ⁶⁺
[Al ₆ O ₅ (OH) ₂ Cl ₅] ⁺	100	3.27–3.92	I	TOF	70	[Al ₆ (OH) ₁₂] ⁶⁺
[Al ₆ O ₄ (SO ₄) ₆] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₆ (OH) ₈] ¹⁰⁺
[Al ₆ O ₃ (SO ₄) ₇] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₆ (OH) ₆] ¹²⁺

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.6 Ten aluminium containing complexes

The ten aluminium containing species were difficult to identify unequivocally. The signal distributions of potential decamers and Al_{13} were normally overlapping. Series assigned to Al_{10} were rarely seen individually in an aluminium chloride environment. Usually, there were two maximums of the double-charged water series in the m/z range 328–460. In these cases there was no unambiguous evidence that would suggest whether the first maximum (in 328–382) should be assigned to Al_{10} or Al_{13} . Only one β -value was found in literature: for $[\text{Al}_{10}(\text{OH})_{24}]^{6+}$ 81.18. [7] This variant was not found in our studies.

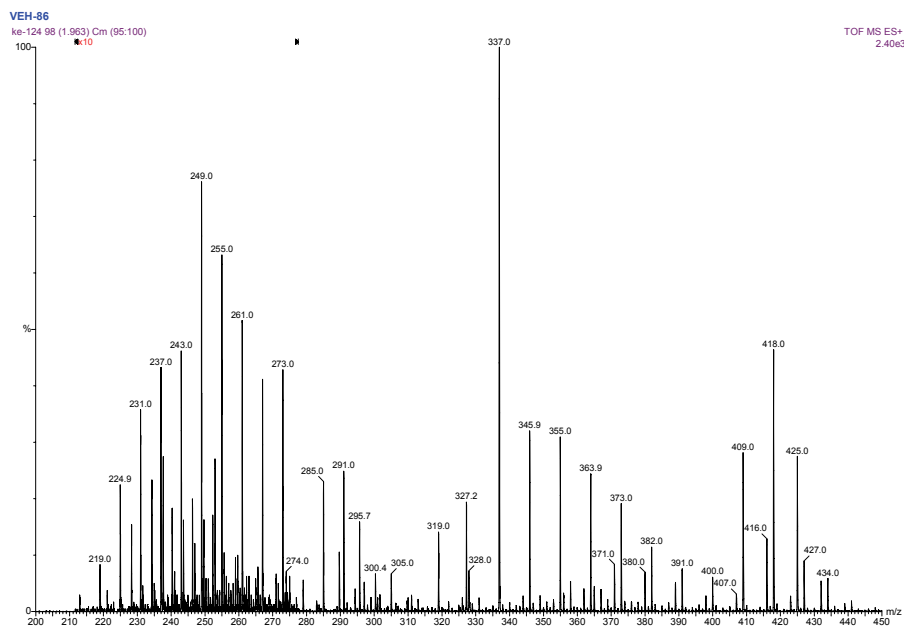


Fig. 14. Cationic spectra of the water series of Al_{10}^{2+} .

Since the m/z 328 was assigned to the dry $[\text{Al}_{13}\text{O}_{18}(\text{OH})]^{2+}$ without any aqua ligands, [II] the continuing double-charged water series below this m/z value (319, 310, 301, ... 247) would be an individual Al_{10}^{2+} series. However, such a series was observed only in one spectrum among the hundreds of measured spectra. (Fig. 14.) Considering the triple-charged series, in which the signal m/z 213 was assigned to the dry $[\text{Al}_{13}\text{O}_{18}]^{3+}$, [II] this kind of water series was completely absent. The

individual Al_{10}^{3+} series would have been found at the range 165–213 with mutual distances of 6u. [II]

The double-charged water series mentioned above emerged with a very specific aluminium chemical. The decameric species seemed to be only a temporal oligomer with a very short lifespan of only a few minutes. The spectrum, in which it could be observed, is presented in Fig.14. The water series begin at m/z 301, and the highest signal is m/z 337. The signal m/z 400 is probably an overlapping signal, and can be assigned to both Al_{10} and Al_{13} . The form of the distribution is not pure Gaussian, because the signal m/z 328 is quite low and the signal m/z 327, assigned to $[\text{Al}_2(\text{OH})_4(\text{HSO}_4)(\text{H}_2\text{O})_6]^+$ almost overlaps it. Also the signals 319, 337, and 355, assigned to pentameric $[\text{Al}_5\text{O}_3(\text{OH})_8(\text{H}_2\text{O})_{0.2}]^+$, can overlap with the Al_{10} series.

Table 8. The possible Al_{10} species.

Species	Al^{3+} mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
$[\text{Al}_7\text{O}_4(\text{OH})_{20}]^{2+}$	10	4.200	I	TOF	150	$[\text{Al}_{10}(\text{OH})_{28}]^{2+}$
$[\text{Al}_{10}\text{O}_6(\text{OH})_{16}]^{2+}$	100	4.50	I	TOF	70	$[\text{Al}_{10}(\text{OH})_{28}]^{2+}$
$[\text{Al}_{10}\text{O}_{12}(\text{OH})_4\text{Cl}_4]^{2-}$	100	4.20	I	TOF	70	$[\text{Al}_{10}(\text{OH})_{28}]^{2+}$
$[\text{Al}_{10}\text{O}_7(\text{OH})_{13}\text{Cl}]^{2+}$	100	4.20	I	TOF	70,200	$[\text{Al}_{10}(\text{OH})_{27}]^{3+}$
$[\text{Al}_{10}\text{O}_3(\text{OH})_{21}\text{Cl}_5]^{2-}$	10	4.50	I	TOF	70	$[\text{Al}_{10}(\text{OH})_{27}]^{3+}$
$[\text{Al}_{10}\text{O}_6(\text{OH})_{15}\text{Cl}_5]^{2-}$	100	4.20	I	TOF	70	$[\text{Al}_{10}(\text{OH})_{27}]^{3+}$
$[\text{Al}_{10}\text{O}_{11}(\text{OH})_3\text{Cl}_6]^-$	100	3.27–4.20	I	TOF	150,200	$[\text{Al}_{10}(\text{OH})_{25}]^{5+}$
$[\text{Al}_{10}\text{O}_9(\text{OH})_4(\text{SO}_4)_5]^{2-}$	10	3.76–3.92	II	TOF	40	$[\text{Al}_{10}(\text{OH})_{22}]^{8+}$
$[\text{Al}_{10}(\text{OH})_{20}\text{Cl}_9]^+$	100	3.27	I	TOF	150	$[\text{Al}_{10}(\text{OH})_{20}]^{10+}$

*I: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. [I,II,III]

II: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. [IV,185]

III: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{SO}_4$. [V]

I V: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

To sum up these observations, an absolute conclusion whether the Al_{10} species indeed exist can not be drawn due to overlapping signals with Al_{13} . The water series with several maximums could be explained with various potential structural conformations of Al_{13} .

6.7 Aluminium 13

The most agreed polymeric form of aluminium is Al_{13} . Its dominance was also observed during this research. The most important polynuclear cation of aluminium is the Keggin Al_{13}^{7+} -cation, $[\text{AlO}_4(\text{Al}(\text{OH})_2)_{12}]^{7+}$ or $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$ where the tetrahedral AlO_4 central unit is surrounded by twelve octahedral AlO_6 -units, in which hydroxo groups are attached to the vertexes of the octahedras. In solid precipitations, the Keggin structure of other elements has five isomers: α , β , γ , δ , and ϵ . The differences arise from the rotation of the Al_3O_{13} units at 60° as illustrated in Fig 15. [200] Only the ϵ isomer is well identified in aluminium: in the solid state with XRD [10,92] and in a solution with NMR. [89] The Keggin cation is considered the main unit in bigger precipitated and soluble complexes. With XRD, $[\text{Al}^{30}\text{O}^8(\text{OH})^{56}(\text{H}_2\text{O})^{24}]^{18+}$ has been observed to consist of two δ - Al_{13} -Keggin units bonded by four AlO_6 octahedras. [176,195] Other conformations of the Keggin structure are yet not found with aluminium. The structure and chemistry of these larger Al_{13} species is comprehensively described by Casey. [201]

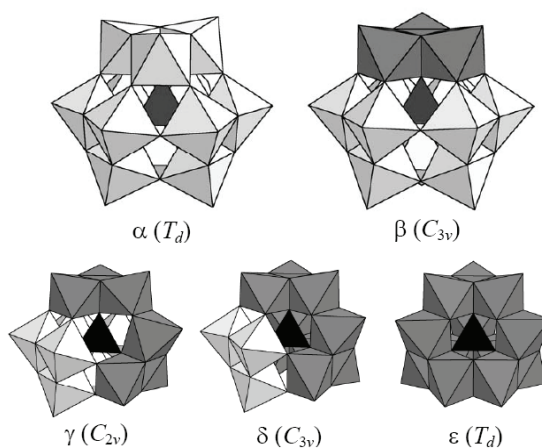


Fig. 15. The five rotational isomers of the Keggin cation according to Fernández. [202]

It is important to point out, that even the biggest structures may exist as genuine ions in a solution. When an aluminium solution has been aged for two years, the largest complexes found consisted of 20–400 aluminium atoms per structure. [203] Usually it is thought that polynuclear complexes are metastable intermediates in a slow process, where the solvated metal ion changes into a solid precipitation. [204]

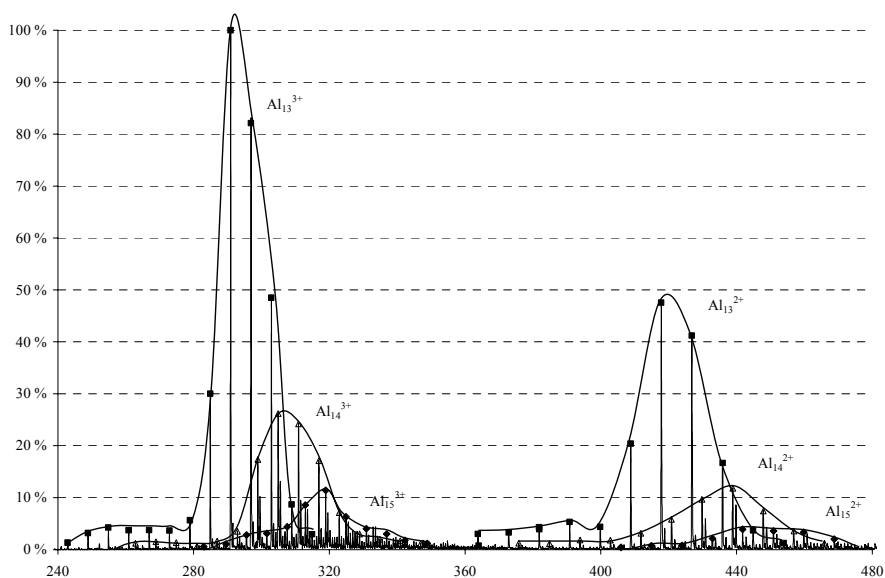


Fig. 16. Water series of double- and triple charged Al_{13} , Al_{14} , and Al_{15} .

Even the Al_{13}^{7+} cation is well known, and there are several β -values for it (100.40–109.50), [7,75,76,205] we did not find it at the charge of 7+. There were observations of six times charged Al_{13} species, but this high charge was always reduced by counter anions. Usually, the complexes were found at elevated pH double- or triple-charged in a chloride environment, with long water series. The triple-charged series were dependent on time. During a period of two weeks they vanished and appeared again in the spectra if the measurement was repeated several times during the ageing. The double-charged series was always present, but only with minor intensity when it existed together with the triple-charged one. [I,III] In MS/MS studies the Al_{13}^{3+} slightly changed its structure by releasing a proton during collisions and was thus also found in the daughter spectra as Al_{13}^{2+} . [II] A reaction occurring in the opposite direction was not observed. All this reveals structural differences between these complexes. With prehydrolysed polyaluminiums, both double- and triple-charged Al_{13} were found. In these investigations no chloride containing complexes were identified. [185]

A structure completely different from Keggin has been determined by Seichter et al. [206] They found a flat $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]\text{Cl}_{15}\cdot 13\text{H}_2\text{O}$, which was a net-like

structure. It is easier to discern how the extra aluminium units could be bounded to such a surface, as compared to the surface of a highly symmetrical, compact Keggin structure. Furthermore, when fragmenting such a flat structure, no special kinds of fragments could be expected. This flat form could be the reason for the coagulation efficiency of polyaluminium chlorides. It is important to notice that the $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15} \cdot 13H_2O$ [206] was precipitated in a chloride environment, while the Keggin structures were found with sulphate. [12,13,14,IV]

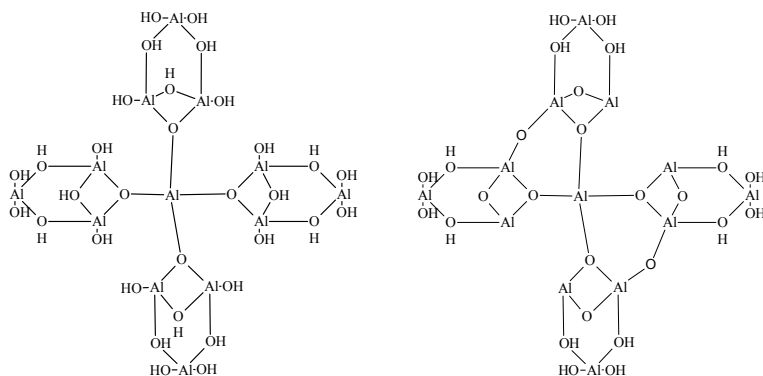


Fig. 17. Speculated open structures of two different Al_{13}^{3+} .

When present in solutions, the structure has much more freedom to form different isomers and conformations. It is possible that in solutions the tetrahedral AlO_4 central unit is surrounded not only by the octahedral AlO_6 -units, but also by open chains or ring substructures (Fig.17.). These drawn structures of $[Al_{13}O_4(OH)_{28}]^{3+}$ and $[Al_{13}O_{10}(OH)_{16}]^{3+}$ are in line with our MS results, according to the free coordination places unveiled by aqua ligands. [I,II,III,185] The formation of oxo bridges, when collating these species in a tandem mass spectrometer, referred also to this. [II] However, these forms are purely speculative. When the chains differ in the length, e.g. the Al_{14} and Al_{15} -cores can evolve.

Table 9. The observed Al₁₃ species.

Species	Al ³⁺ mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
[Al ₁₃ O ₁₀ (OH) ₁₇] ²⁺	10,1	4.50–4.72	I	TOF	70	[Al ₁₃ O ₄ (OH) ₂₉] ²⁺
[Al ₁₃ O ₁₁ (OH) ₁₅] ²⁺	100	4.20	I	TOF	70,150,200	[Al ₁₃ O ₄ (OH) ₂₉] ²⁺
[Al ₁₃ O ₁₄ (OH) ₉] ²⁺	100,1, 0.1	4.20–6.46	I, IV, V	TOF	70	[Al ₁₃ O ₄ (OH) ₂₉] ²⁺
[Al ₁₃ O ₆ (OH) ₂₅ (SO ₄) ₂] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₁₃ O ₄ (OH) ₂₉] ²⁺
[Al ₁₃ O ₇ (OH) ₂₂] ³⁺	10,1	4.50–4.72	I	TOF	70	[Al ₁₃ O ₄ (OH) ₂₈] ³⁺
[Al ₁₃ O ₁₀ (OH) ₁₆] ³⁺	100,10	4.20–4.50	I	TOF	70,150	[Al ₁₃ O ₄ (OH) ₂₈] ³⁺
[Al ₁₃ O ₁₄ (OH) ₈] ³⁺	1, 0.1	4.65–6.46	IV,V	TOF	70	[Al ₁₃ O ₄ (OH) ₂₉] ²⁺
[Al ₁₃ O ₁₀ (OH) ₁₆ Cl] ²⁺	100	4.20	I	TOF	70	[Al ₁₃ O ₄ (OH) ₂₈] ³⁺
[Al ₁₃ O ₁₆ (OH) ₄ Cl ₅] ²⁻	100	4.20	I	TOF	70	[Al ₁₃ O ₄ (OH) ₂₈] ³⁺
[Al ₁₃ O ₅ (OH) ₂₅ (SO ₄) ₃] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₁₃ O ₄ (OH) ₂₇] ⁴⁺
[Al ₁₃ O ₁₆ (OH)Cl ₈] ²⁻	100,10	4.20–4.50	I	TOF	70	[Al ₁₃ O ₄ (OH) ₂₅] ⁶⁺
[Al ₁₃ O ₄ (OH) ₂₅ (SO ₄) ₄] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₁₃ O ₄ (OH) ₂₅] ⁶⁺

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.8 Other polyaluminium species

Eight and nine aluminium containing variants, which had even several calculated β -values, were not observed at the time: [Al₈(OH)₂₀]⁴⁺, 68.70–69.82 [60,75,76] and [Al₉(OH)₂₃]⁴⁺, 80.14 [75]. Instead, Al₈ and Al₉ were found to have a lower charge due to the neutralising effect of the outer sphere chlorido and hydroxido ligands. The abundance of the outer sphere chlorido ligands refers to highly charged cores (Table 10.). The octamer found in an alum solution has also been found with other methods. [207] Intensities of signals of all these medium-sized (Al₇–Al₉) species were very low.

Al₁₄ was always present, whereas Al₁₃ was found in a chloride environment. This indicates that in this matrix aluminium formed more flexible structures than in a sulphate environment, where no Al₁₄ was found. [I–IV] Another evidence of Al₁₄ arises from potentiometric titrations: for the species [Al₁₄(OH)₃₄]⁸⁺ there is an equilibrium constant 113.14. [7] Also, the heptameric species [Al₇(OH)₁₇]⁴⁺ have a calculated equilibrium constant 59.48. [78] As mentioned before, the calculation programmes used to find the best fit for the titration curves for the speciation entered, favour prime number solutions. When entering several species such as

$[\text{Al}_2(\text{OH})_4]^{2+}$, $[\text{Al}_3(\text{OH})_6]^{3+}$, $[\text{Al}_4(\text{OH})_8]^{4+}$ etc., the programme selects only the simplest one and ignores the other species. Hence, if the $[\text{Al}_{14}\text{O}_{10}(\text{OH})_{20}]^{2+}$ is in the solution, the equilibrium calculations give a better fit for the species $[\text{Al}_7\text{O}_5(\text{OH})_{10}]^+$, or in fact for the species $[\text{Al}_7(\text{OH})_{20}]^+$. This is because the programmes generally do not take unprotonated oxo ligands into account. (Chapter 4.1)

Al_{15} was found almost as often as Al_{14} . However, several times it could be seen in spectra with such a low intensity that no intensive characterisation was performed. The larger Al_{16} was observed rarely, and its existence was not so obvious because if there were several Al_{13} variants, these were overlapping with the water series. All of them were accompanied by Al_{13} , and never seen individually. [I,III]

Al_{26} was an interesting observation. The same water series with the same amount of chloride ligands were observed in two different concentrations. Its formulation was not unambiguous. For instance, m/z 474.5 (= 1898 u, charge -4) could be formulated as $[\text{Al}_{32}\text{O}_{41}(\text{OH})_{14}\text{Cl}_4]^{4-}$, $[\text{Al}_{29}\text{O}_{28}(\text{OH})_{31}\text{Cl}_4]^{4-}$, $[\text{Al}_{26}\text{O}_{15}(\text{OH})_{48}\text{Cl}_4]^{4-}$ or $[\text{Al}_{23}\text{O}_2(\text{OH})_{65}\text{Cl}_4]^{4-}$. Only the Al_{23} was not as possible as the others, because there were not enough unprotonated oxygen to form Keggin like substructures.

Table 10. The larger oligomeric species.

Species	Al^{3+} mM	pH-range	Env. *	Detector	Sample cone voltage, V	Fully protonised
$[\text{Al}_7\text{O}_2(\text{OH})_{15}\text{Cl}]^+$	100	3.92	I	TOF	200	$[\text{Al}_7(\text{OH})_{19}]^{2+}$
$[\text{Al}_7\text{O}_4(\text{OH})_{10}\text{Cl}_2]^+$	100	4.20	I	TOF	200	$[\text{Al}_7(\text{OH})_{18}]^{3+}$
$[\text{Al}_7\text{O}_6(\text{OH})_6\text{Cl}_2]^+$	100	3.92	I	TOF	200	$[\text{Al}_7(\text{OH})_{18}]^{3+}$
$[\text{Al}_7\text{O}_9\text{Cl}_4]^-$	100	3.27–4.20	I	TOF	150,200	$[\text{Al}_7(\text{OH})_{18}]^{3+}$
$[\text{Al}_7\text{O}_6(\text{OH})_5\text{Cl}_3]^+$	100	3.92	I	TOF	150	$[\text{Al}_7(\text{OH})_{17}]^{4+}$
$[\text{Al}_7\text{O}_3(\text{OH})_{11}\text{Cl}_3]^+$	100	3.27	I	TOF	70	$[\text{Al}_7(\text{OH})_{17}]^{4+}$
$[\text{Al}_7\text{O}_8\text{Cl}_4]^+$	100	3.27	I	TOF	150	$[\text{Al}_7(\text{OH})_{16}]^{5+}$
$[\text{Al}_7\text{O}_8\text{Cl}_6]^-$	100	3.27–4.20	I	TOF	150,200	$[\text{Al}_7(\text{OH})_{16}]^{5+}$
$[\text{Al}_7\text{O}_4(\text{OH})_7\text{Cl}_5]^+$	100	3.27	I	TOF	70	$[\text{Al}_7(\text{OH})_{15}]^{6+}$
$[\text{Al}_7\text{O}_6(\text{OH})_3\text{Cl}_5]^+$	100	3.27–3.92	I	TOF	70	$[\text{Al}_7(\text{OH})_{15}]^{6+}$
$[\text{Al}_7\text{O}_2(\text{OH})_{11}\text{Cl}_5]^+$	100	3.27	I	TOF	70	$[\text{Al}_7(\text{OH})_{15}]^{6+}$
$[\text{Al}_7\text{O}_5(\text{SO}_4)_7]^{3-}$	10	3.76–3.92	II	TOF	40	$[\text{Al}_7(\text{OH})_{10}]^{11+}$
$[\text{Al}_8\text{O}_8(\text{OH})_7]^+$	1	4.94	IV	TOF	70	$[\text{Al}_8(\text{OH})_{23}]^+$
$[\text{Al}_8\text{O}_{11}\text{Cl}_3]^-$	100	3.27–4.20	I	TOF	200	$[\text{Al}_8(\text{OH})_{22}]^{2+}$
$[\text{Al}_8\text{O}_9(\text{OH})_3\text{Cl}_4]^-$	100	3.27–4.20	I	TOF	150,200	$[\text{Al}_8(\text{OH})_{21}]^{3+}$
$[\text{Al}_8\text{O}_7(\text{OH})_2\text{Cl}_7]^+$	100	3.27–3.92	I	TOF	70	$[\text{Al}_8(\text{OH})_{16}]^{8+}$

Species	Al ³⁺ mM	pH-range	Env. [*]	Detector	Sample cone voltage, V	Fully protonised
[Al ₈ O ₈ Cl ₇] ⁺	100	3.27–3.92	I	TOF	150,200	[Al ₈ (OH) ₁₆] ⁸⁺
[Al ₈ (OH) ₁₆ (SO ₄) ₅] ²⁻	10	3.76–3.92	II	TOF	40	[Al ₈ (OH) ₁₆] ⁸⁺
[Al ₈ (OH) ₁₄ Cl ₉] ⁺	100	3.27	I	TOF	150	[Al ₈ (OH) ₁₄] ¹⁰⁺
[Al ₉ O ₁₂ Cl ₄] ⁻	100	3.27–4.20	I	TOF	200	[Al ₉ (OH) ₂₄] ³⁺
[Al ₉ O ₇ (OH) ₅ Cl ₇] ⁺	100	3.27	I	TOF	70	[Al ₉ (OH) ₁₉] ⁸⁺
[Al ₉ O ₉ (OH)Cl ₇] ⁺	100	3.27	I	TOF	70	[Al ₉ (OH) ₁₉] ⁸⁺
[Al ₉ O ₆ (OH) ₆ Cl ₈] ⁺	100	3.27	I	TOF	70	[Al ₉ (OH) ₁₈] ⁹⁺
[Al ₉ (OH) ₇ Cl ₉] ⁺	100	3.27	I	TOF	150	[Al ₉ (OH) ₁₇] ¹⁰⁺
[Al ₉ O(OH) ₁₅ Cl ₉] ⁺	100	3.27	I	TOF	70	[Al ₉ (OH) ₁₇] ¹⁰⁺
[Al ₉ O ₆ (OH) ₉ Cl ₉] ⁺	100	3.27	I	TOF	70	[Al ₉ (OH) ₁₇] ¹⁰⁺
[Al ₁₁ O ₈ (OH) ₁₆] ⁺	100	4.20	I	TOF	70	[Al ₁₁ (OH) ₃₂] ⁺
[Al ₁₁ O ₁₄ Cl ₄] ⁻	100	3.27–4.20	I	TOF	200	[Al ₁₁ (OH) ₂₈] ³⁺
[Al ₁₂ O ₁₂ (OH) ₉ Cl ₄] ⁻	100	4.20	I	TOF	150	[Al ₁₂ (OH) ₂₁] ³⁺
[Al ₁₄ O ₁₀ (OH) ₂₀] ²⁺	100	4.20	I	TOF	50	[Al ₁₄ (OH) ₄₀] ²⁺
[Al ₁₄ O ₁₈ (OH) ₄] ²⁺	0.1	5.50	IV	TOF	70	[Al ₁₄ (OH) ₄₀] ²⁺
[Al ₁₄ O ₇ (OH) ₂₅] ³⁺	100, 10, 1	4.20–4.72	I	TOF	70	[Al ₁₄ (OH) ₃₉] ³⁺
[Al ₁₄ O ₁₆ (OH) ₇] ³⁺	1, 0.1	4.65–6.46	IV, V	TOF	70	[Al ₁₄ (OH) ₃₉] ³⁺
[Al ₁₄ O ₁₀ (OH) ₁₉ Cl] ²⁺	100	4.20	I	TOF	70	[Al ₁₄ (OH) ₃₉] ³⁺
[Al ₁₄ O ₁₇ (OH) ₂ Cl ₆] ²⁻	10	4.50	I	TOF	70	[Al ₁₄ (OH) ₃₆] ⁶⁺
[Al ₁₄ O ₁₈ Cl ₆] ²⁻	100	4.20	I	TOF	70	[Al ₁₄ (OH) ₃₆] ⁶⁺
[Al ₁₅ O ₁₀ (OH) ₂₃] ²⁺	100	4.20	I	TOF	150	[Al ₁₅ (OH) ₄₃] ²⁺
[Al ₁₅ O ₁₉ (OH) ₅] ²⁺	0.1	5.50	IV	TOF	70	[Al ₁₅ (OH) ₄₃] ²⁺
[Al ₁₅ O ₁₆ (OH) ₁₀] ³⁺	0.1	4.98–6.10	IV, V	TOF	70	[Al ₁₅ (OH) ₄₂] ³⁺
[Al ₁₅ O ₁₂ (OH) ₁₇ Cl ₂] ²⁺	100	4.20	I	TOF	70	[Al ₁₅ (OH) ₄₁] ⁴⁺
[Al ₁₆ O ₁₁ (OH) ₂₄] ²⁺	100	4.20	I	TOF	150	[Al ₁₆ (OH) ₄₆] ²⁺
[Al ₁₆ O ₁₅ (OH) ₁₅] ³⁺	1	4.20	V	TOF	70	[Al ₁₆ (OH) ₄₅] ³⁺
[Al ₂₀ O ₁₈ (OH) ₂₁] ³⁺	0.1	4.98	V	TOF	70	[Al ₂₀ (OH) ₅₇] ³⁺
[Al ₂₆ O ₁₅ (OH) ₄₈ Cl ₄] ⁴⁻	100, 10	4.20–4.50	I	TOF	70	[Al ₂₆ (OH) ₇₈] ⁰
[Al ₃₀ O ₃₅ (OH) ₁₇] ³⁺	100	4.20	I	TOF	150	[Al ₃₀ (OH) ₈₇] ³⁺

*I: AlCl₃·6H₂O. [I,II,III]

II: Al₂(SO₄)₃·18H₂O. [IV,185]

III: AlCl₃·6H₂O + H₂SO₄. [V]

IV: Highly basic polyaluminium chloride. [185]

V: Moderately basic polyaluminium chloride. [185]

6.9 Effect of concentration

The concentration comparison done with several spectra in an aluminium chloride environment revealed that the hydrolysis profiles were clearly dependent on the concentration. [III] The total concentration has earlier been thought to only have

an effect on the precipitation, and sliding the distribution diagramme towards acidic pH, not to the relative abundance of different species. [208]

Small complexes, containing one to six aluminium atoms, were found in all inspected concentrations. However, while the trimeric complexes were the most varying complexes in 100 mM solutions, in more dilute solutions the dimeric ones had the greatest diversity. Signals of these small complexes were always only monocharged. (Chapters 6.1–6.5) With diminishing concentrations the water series were short and the intensity of signals assigned to middle sized complexes were low. Also the noise to signal ratio kept increasing. The effect of the concentration is illustrated in Fig. 18, in which the relative intensity spectra of the 14 d aged 1, 10 and 100 mM solutions are given in their initial pH: 3.9, 3.7, and 3.3, respectively.

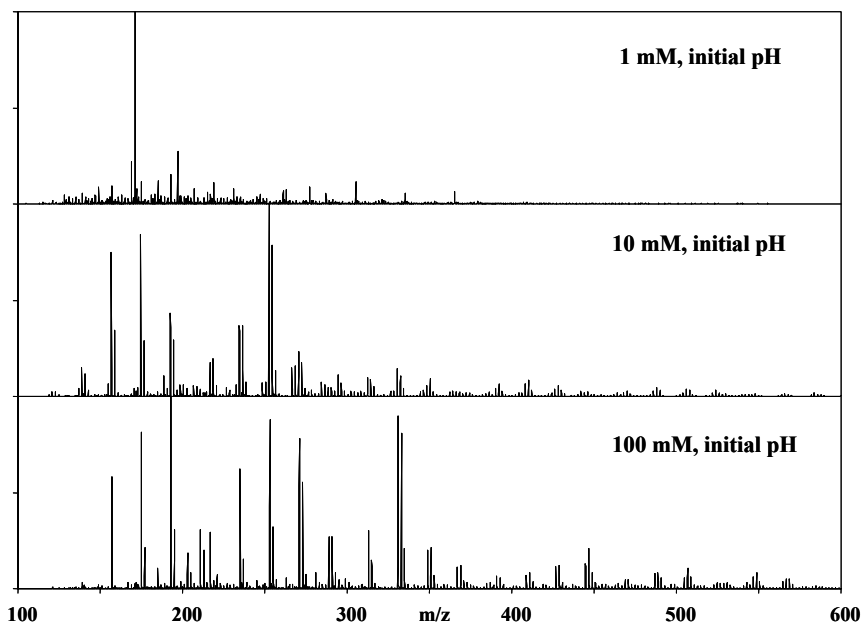


Fig. 18. The cationic mass spectra of the aged AlCl_3 solutions at initial pH.

Seven, eight and nine aluminium containing complexes existed only in the highest concentration studied, 100 mM. All of those signals were also monocharged. (Chapter 6.8) Ten and eleven aluminium containing oxo hydroxo complexes were seen in the spectra of the 100 mM and 10 mM solutions, and only when the pH was elevated approximately to 4.5 or above. Al_{13} and Al_{14} complexes were found

in all concentrations, and Al_{15} was found only in the highest concentration. In addition, Al_{26} complexes were observed in the spectra of the 100 mM and 10 mM solutions.

There were more protonated oxo ligands and less attached counter anions (Cl^- , SO_4^{2-}) in complexes as a function of decreasing concentration. This could mean that the species in more diluted bulk solutions have fewer different states of charge.

This reveals that concentration indeed had effect on speciation at initial pH, where the variation on single species was wider and more middle-size complexes could be found. In elevated pHs the effect of the concentration was not so apparent, only the water series of Al_{13} and its companions narrowed as a function of dilution. [III] This same phenomenon was observed with polyaluminium products. [185]

6.10 Effect of pH

As expected, the effect of pH on speciation was great. In a chloride environment four pH ranges could be found which clearly differed from each other. The first range was acidic. In the spectra of the 100 mM $AlCl_3$ solution at the initial pH of 3.3, only monocharged complexes were assigned. Signals that had intensities of over 10% originated from the $Al_2 - Al_6$ -cores. The most intensive series were assigned to the dimeric $[Al_2O(OH)_2Cl(H_2O)_{0-3}]^+$ and the trimeric $[Al_3O(OH)_4Cl_2(H_2O)_{0-3}]^+$. [I,III] In a sulphate environment, when the pH was raised only one unit, almost all aluminium vanished from the spectra. [IV,185] Thus, the exact border values depended also on concentration and the counter anion, which calls for major systematic tests to be made in the future.

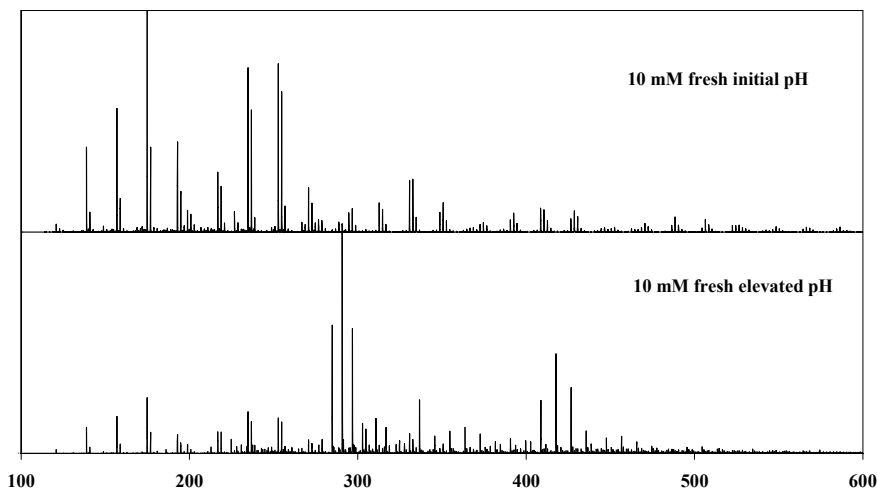


Fig. 19. The cationic mass spectra of AlCl_3 at initial and elevated pH.

In the second pH range, large but still soluble species were born. Multi-charged Al_{13} complex series with its accompanies had the most intensive signal series. In most cases, dimeric and trimeric monocharged complexes as well were observed. Very similar spectra were achieved with prepolymerised polyaluminium products. [185] The pH range with polymeric complexes was quite narrow.

The next ranges were near a neutral pH area, where aluminium first formed colloids, and then precipitated. This could be seen in the mass spectra, as indicated by the loss of all signals, even though the solution was still clear and transparent. The last range was in the basic pH range, and as measured with other methods, [79] the negative $[\text{Al}(\text{OH})_4]^-$ should be the major species. For reasons unknown to us, we have detected it only once.

6.11 Effect of time

The kinetics of aluminium in water is investigated with potentiometric and NMR methods. Earlier, the hydrolysis has been shown to be dependent on the reaction rate of the inner sphere ligands. [209] The formation of smaller, Al_2 - Al_6 species is quite fast, but the polymerisation of larger oligomers such as tridecameric species is obviously a slower process, and perhaps a second step reaction, whereas the smaller dimeric or trimeric complexes are the reactants. [190,191]

6.11.1 Ageing

In our experiments we let the “fresh” solutions equilibrate for one to four hours, which is thought to be enough for the smaller species to equilibrate. [210] The aged solutions were the same solutions measured after two weeks. In total, the amount of hydrolysed species increased at all pH values as a function of time. The shape of the spectra changed; the maximum of the intensities moved to greater m/z values.

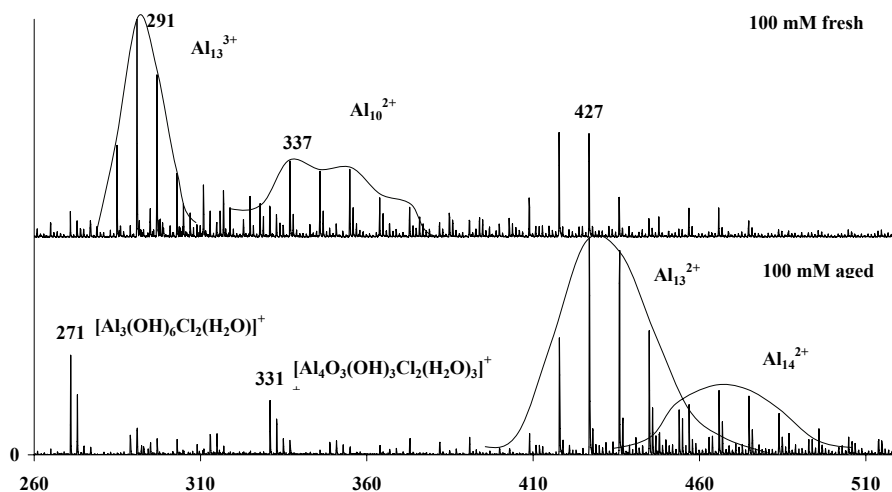


Fig. 20. The cationic mass spectra of fresh and aged solutions at elevated pH.

An interesting phenomenon was the time dependence of Al_{13}^{3+} series (maximum m/z 291), which had almost disappeared after two weeks when the double-charged Al_{13}^{2+} complex had increased its share (maximum m/z 427), as illustrated in Figure 20. Also, the putative Al_{10} species existed only temporarily; this could be observed in the fresh spectrum (maximum m/z 337). The behaviour of these species is not straightforward, [203] hence more systematic studies are needed to identify all the factors affecting their presence.

6.11.2 Kinetics: Distribution diagramme by mass spectrometer

With the mass spectrometer apparatus it is possible to monitor not only the spectra, but also the changes of intensities of selected signals as a function of time.

Monitoring the reaction products and their reaction rate is a handy tool for kinetical investigations. The experiments concerning how to use the mass spectrometry for monitoring the hydrolysis of aluminium described here are based on preliminary results.

For example, when absolute intensities of the four major signals assigned to trimeric aluminium complexes were monitored as a function of time, the shapes of the curves agreed quite well with the total ion count graph. The signals that were followed were m/z 199, 217, 235, and 253 respectively, assigned to the water series of $[Al_3O_2(OH)_3Cl(H_2O)_{0-3}]^+$. In Fig.21. the arrows point out the fact that when the abundance of the complex containing no aqua ligands (m/z 199) decreases the abundance of three aqua ligands carrying complex (m/z 253) increases. Therefore, the total abundance of this trimeric complex did not change during the time observed; only the amount of the aqua ligands carried changes.

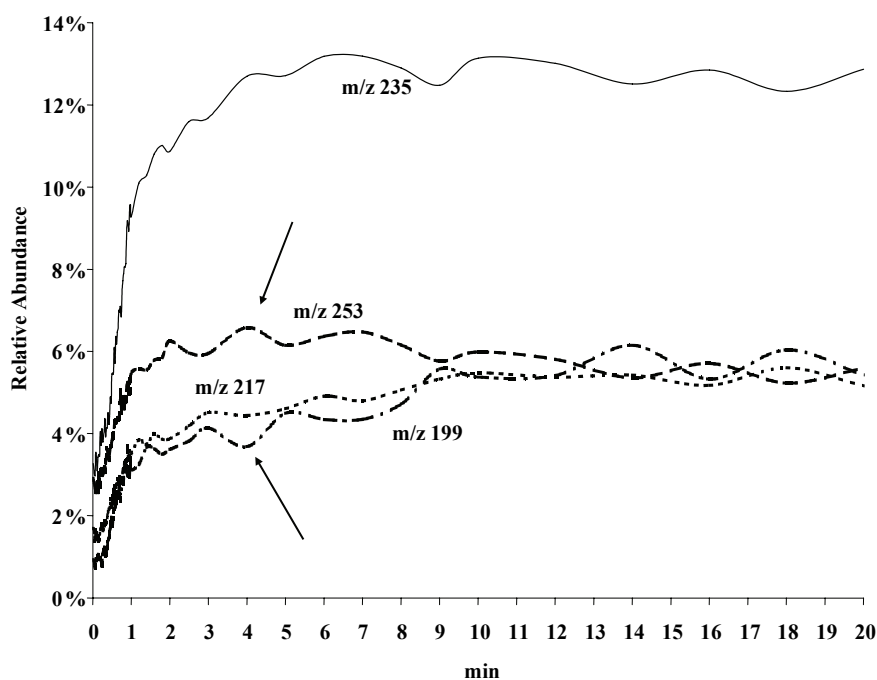


Fig. 21. Relative ion count of signals assigned to trimeric aluminium complex.

All the main species of trimeric aluminium studied contained chlorido ligands. The isotopic patterns had to be calculated together as one signal, because they are assigned to chemically identically complexes, although to different isotopes.

Also, there were a lot of minor signals, which in the earlier studies have been assigned to some aluminium complexes. However, they were now so small that monitoring them did not produce any information. Therefore, the mass spectrum was divided into m/z ranges, where the signals are mainly assigned to aluminium complexes of a certain size. All the signals were summed as “total” abundance of aluminium complex of that size. The ranges were slightly overlapping, but the errors considerably eliminated each other. The ranges were as follows: for dimeric aluminium complexes Al_2 m/z 100–196, and for trimeric aluminium complexes Al_3 m/z 197–276, Al_4 m/z 277–360, Al_5 m/z 361–440, Al_6 m/z 441–519, and Al_7 m/z 520–600. There were only minor signals of intensity at less than 1% at the range of over 600. No calculations were done in that range, although the patterns were identified. The sums of the intensities were calculated for every range at each point in time used and presented as graphs. In the range m/z 197–276 there were some signals assigned to known sodium adducts, which were omitted from the calculations. When the effect of the total ion count was abated by calculating the relative abundance of every ion at every point in time, the shapes of the curves did not change radically. Only the raise of curves during the first minute was steeper.

The initial pH distributions were measured twice, first with a 100 mM $AlCl_3$ solution. Then the experiment was repeated using a 10 mM solution in order to avoid contamination of the apparatus. The first distribution diagramme measured by mass spectrometer confirmed the rapid formation of small complexes in acidic environments. The major changes were observed during the first minute. All complexes were born almost simultaneously. For example, Al_6 were born at the same time with Al_3 -complexes, and no formation from one to another could be seen. In the second test the main results remained the same: the major changes occurred in the first minutes. The first monitoring lasted 0 to 20 minutes and after that two minutes of data were gathered at the time points 30, 40, 50, 60, and 100 minutes. In this experiment there was more noise in the curves because the ion count in the beginning was only about 100 ion counts per second, while, in the 100 mM solution the ion count was over 8000 ion counts per second.

The main difference between these two concentrations was that in the dilute concentration dimeric complexes were the major species, whereas trimeric complexes were the main species in the 100 mM concentration. This is in line

with our experience on the effect of the concentration. [III] Also, the distribution seemed to be very stable at 100 mM, which could be a consequence of the long period of exposure of the solid aluminium chloride to moisture. Fig.22. illustrates the 10 mM experiment at initial pH, in which some definite ups and downs were observed, indicating that some kind of a process towards equilibrium was taking place at the beginning of the monitoring. The formation of small complexes was completed after three minutes and their mutual abundances were stabilised after nine minutes. Only one disturbance occurred at 17 minutes, after which the lines were almost linear.

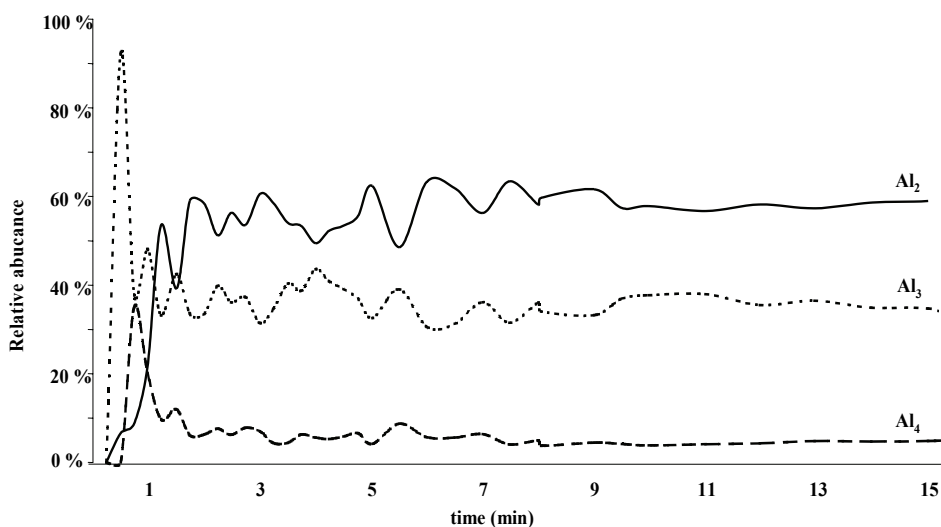


Fig. 22. Summated signals of the complexes classified by the size.

The third experiment was done at a higher pH. The pH was adjusted to 4.3 with TMA. This time, dividing the mass spectrum to simple m/z ranges did not work. The TMA also formed various minor signals, and recognising and removing them was impossible. Instead, the main signals of aluminium complexes of a certain size were summed. Some monocharged and multi-charged complexes had the same m/z values. Because all monocharged complexes contained chlorido ligands, they also have an isotopic pattern. The multi-charged complexes contained no chlorine and thus had only single signal. These overlapping multiple patterns were separated by simple simulating calculations by subtracting the overlapping signals.

The slower developing of the Al_{13} complexes was clearly seen as illustrated in Fig.23. During the first half an hour the concentrations of this oligomer increased, while the relative abundance of the dimeric species was diminishing. At 35 minutes the curve of the dimeric species was noticed to be rising again, but in a very swaying manner, while the Al_{13} line was continuing its course. At the same time as the dimeric species stopped diminishing, the trimeric curve seemed to be decreasing its level from a 12% towards a 9%, but the trends were not so obvious as that of the tridecameric. Stabilisation of the speciation was not reached in one hour.

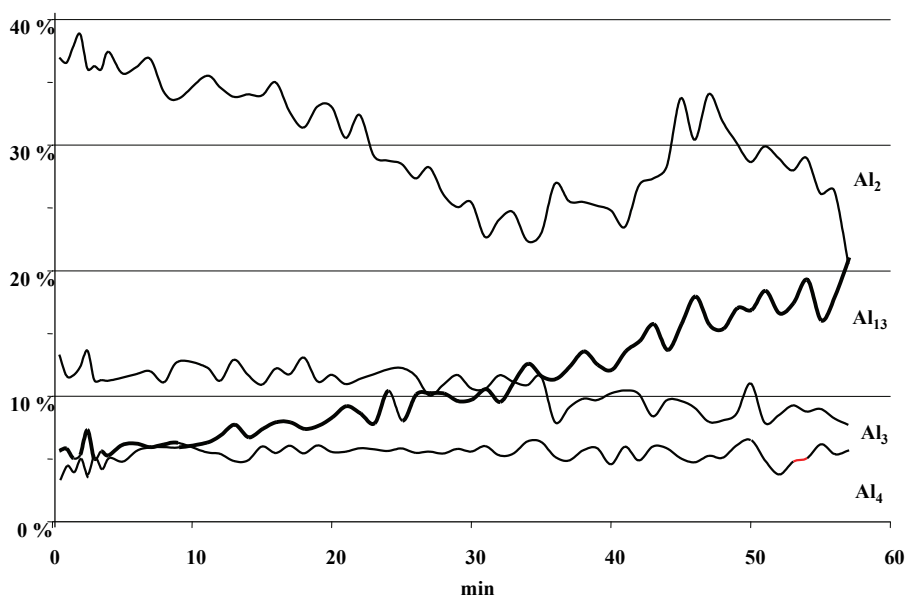
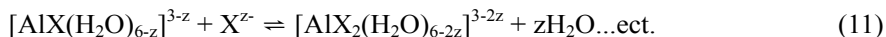
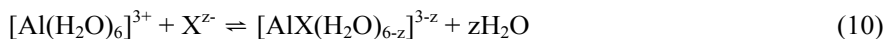


Fig. 23. Relative ion count of some aluminium complexes at elevated pH.

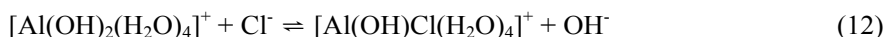
This kind of analysis will provide important information when considering the precursors of precipitating minerals and substructures of larger species. Also, interactions amongst certain species can be monitored with this procedure.

6.12 Effect of counter anion

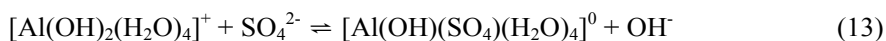
The role of the counter anion is remarkable for the speciation of hydrolysis products of aluminium. They take an active role in the stepwise hydrolysis process competing with hydroxide groups in the first coordination sphere of the aluminium. This competitive stepwise reaction can be shown by the equations [211]:



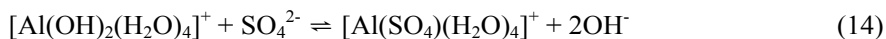
If the aluminium has already hydrolysed, competition takes place and changes the equation radically.



If sulphate is competing with hydroxide, attaching only monodentate way, the formulation is:



But if the sulphate acts as bidentate ligand, it replaces two hydroxides or one hydroxide and one aqua ligand:



The displacement of hydroxide depends on the intrinsic ability of the ligand X to form complexes with aluminium. Especially multivalent anions can complex aluminium strongly and even define how the hydrolysis and precipitation will continue. [190,211] The importance of counter anions in the chemistry of oligomers is discussed below.

6.12.1 Chloride

The common aluminium trichloride hexahydrate was the first chemical that we used in our studies. Chloride is quite an inert anion and it should not have an effect concerning the aquatic chemistry of aluminium. Only a few aluminium chlorides are known as minerals: chloraluminite $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as it is called in mineralogy [49], lesukite $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$ [212], and cadwaladerite $\text{Al}(\text{OH})_2\text{Cl} \cdot 4\text{H}_2\text{O}$ [213]. They are found in acidic fumaroles, volcanoes, and

burning mine dumps on terrestrial environment and in lunar soil [214]. Hence, attaching this anion to inner cores of hydrolysed aluminium species may require quite exotic circumstances. In our ESI TOF MS studies, the chloride anions of aluminium chloride seem to willingly attach to the aluminium oxo hydroxo core born in the hydrolysis. However, in our MS/MS studies chlorido ligands were eliminated quite easily as hydrochloric acid with relatively low collision energies, without breaking the structure of the hydrolysis product. Thus, it could be assumed that chlorido ligands were not bridging structures, but terminal ligands. [II] In our studies with prehydrolysed polyaluminium products no chloride containing complexes were identified. [185] There should therefore be a sufficient number of free chloride ions available at nebulation in order for chlorido complexes to be formed. Furthermore, in aqueous solutions they are hardly bonded to complexes.

6.12.2 Sulphate

The mass spectrometric study with a conventional aluminium sulphate, alum, revealed many new species, and the presence of sulphate in them was evident. [IV,185] Sulphate binds strongly to aluminium. Also, the binding of protons to hydrolysis products changed significantly when sulphate was present in the solution: the aluminium oxo hydroxide cores were less protonated than in a chloride environment. Many complexes identified had the same composition as minerals. These kinds of small polymeric complexes could be the precursor ions of precipitating crystals. [IV]

In these studies sulphate acted as a ligand in two different ways. Sulphate could be a terminal ligand as chlorine, attached either in a mono- or bidentate way to the hydrolysis product of aluminium or a bridging ligand, connecting unhydrolysed aluminium atoms. This is illustrated in Fig. 24. where aluminium atoms are marked grey, oxygen black, hydrogen white and small, while sulphur atoms are gray and marked by symbols. On the left a trimeric species can be seen, where all aluminium atoms are connected by three bridging sulphate ligands as well as central oxygen, $\mu_3\text{-O}$. The two upper aluminium atoms also have the common bridging hydroxide ligand $\mu\text{-OH}$. The lowest aluminium atom has also an aqua ligand, and the highest sulphate group is protonated.

On the right can be seen a trimeric *sompa* structure with bridging hydroxide groups and a central oxygen atom, and sulphate groups as terminal ligands

(compare to Fig.12.). To conclude, sulphate can strongly interfere in the hydrolysis and participate in evolving structures of hydrolysis products.

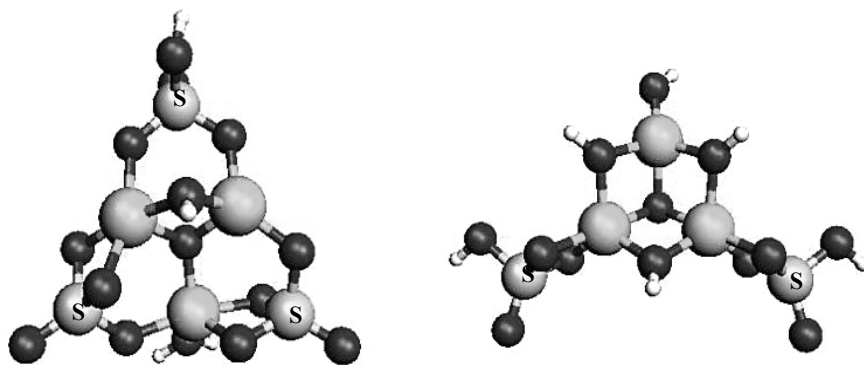


Fig. 24. Different trimeric aluminium species with sulphate. [IV]

Only minor signals of Al_{13} species were obtained without pH elevation and their high charges were reduced with several sulphate ligands. The Al_{14} and Al_{15} complexes, common escorts of Al_{13} in chloride environment, were lacking in a sulphate environment, which revealed that the chloride systems preferred more flexible speciation, in which hydroxo and chlorido ligands competed on free coordination places and polymerisation had a higher degree of freedoms. Therefore, in sulphate environment the high ratio of unhydrolysed oxygen ligands and the poor variation of species could indicate that this anion forces aluminium to form more organised, compressed, and solid like species even in aqueous environments.

When the pH was raised, the signals of aluminium compounds vanished quickly, indicating colloidal speciation and the beginning of precipitation. Unlike in the chloride environment no considerable change in the spectra could be seen just before this. The pH range where Al_{13} and its escorts would have been the dominant species was not found with sulphate. Either the range was so narrow that our investigations did not hit in it, or there really was no such range with sulphate.[185]

The lack of TMA-sulphate adducts also indicates that sulphate may play an unexpectedly active role in water purification processes, if they form colloids

with amine-containing impurities such as biological decomposition products. These observations also indicate that the coagulation principle of alum is different than that of the aluminium chlorides, due to the remarkable role of the sulphate anion. [185,IV]

Preliminary tests with commercial prehydrolysed polyaluminium sulphate have not yet been a great success, because the solid substance did not dissolve properly, and the MS spectra were very noisy due the low total ion counts. Those few identified species were either dimeric oxo hydroxides or an undissociated aluminium sulphate $[Al_x(SO_4)_y]^{3x-2y}$ cluster ions.

6.12.3 Formate

Because chloride is a very corrosive anion, there is growing need for other counter anions in aluminium products. Formic acid and its salts, formates, are compounds that degrade into carbon dioxide or monoxide and hydrogen or water. Although they have been known for a long time, the equilibrium and spontaneous photodissociation of formates are still under intensive investigation. [215,216]

The studied solutions were pilot products of polyaluminium formate. When interpreting the spectra, very interesting phenomena could be seen: not only the familiar oxo hydroxide complexes and those with a different amount of formate, but also unstoichiometric species. Because this result was so unexpected, the investigation was repeated three times with different production lots and the conclusions were unchanged. The beginning of the assignation is collected in Table 11. The unstoichiometric species are bolded.

In some cases when formate was complexed with aluminium the reaction possibly involved the elimination of two negative ligands: OH^- and $HCOO^-$, as neutral CO_2 and H_2O . This left the aluminium oxo hydroxo core undercharged: e.g., normally the species should have a charge of +3, but in the spectra it was assigned to a monocharged cation. This unstoichiometric species had to be quite stable, because it was found with different amounts of aqua ligands. The signals were intensive (>20%), so it was present with a large amount in the bulk solution, or the reaction in nebulation was energetically favourable.

If real unstoichiometric stable species are born in the solution, it possible, that polyaluminum formate can act as a redox-buffer with two excess electrons. Therefore, polyaluminium formate might not only be a water purification chemical but also a corrosion inhibitor.

Table 11. The unstoichiometric polyaluminum formate cations.

m/z	Species	Reaction
133	$[\text{Al}_2(\text{OH})_2(\text{HCOO})]^{1+}$	$[\text{Al}_2(\text{OH})_3(\text{HCOO})_2]^{1+} - [\text{OH}]^- - [\text{HCOO}]^- \rightleftharpoons [\text{Al}_2(\text{OH})_2(\text{HCOO})]^{3+} + 2\text{e}^- + \text{CO}_2\uparrow + 2\text{H}_2\text{O}\uparrow$
149	$[\text{Al}_2\text{O}(\text{OH})_2(\text{HCOO})]^+$	
151	$[\text{Al}_2(\text{OH})_2(\text{HCOO})(\text{H}_2\text{O})]^{1+}$	$[\text{Al}_2(\text{OH})_2(\text{HCOO})(\text{H}_2\text{O})]^{1+} + \text{H}_2\text{O}$
161	$[\text{Al}_2(\text{OH})(\text{HCOO})_2]^{1+}$	$[\text{Al}_2(\text{OH})_2(\text{HCOO})_3]^{1+} - [\text{OH}]^- - [\text{HCOO}]^- \rightleftharpoons [\text{Al}_2(\text{OH})(\text{HCOO})_2]^{3+} + 2\text{e}^- + \text{CO}_2\uparrow + 2\text{H}_2\text{O}\uparrow$
167	$[\text{Al}_2\text{O}(\text{OH})_2(\text{HCOO})(\text{H}_2\text{O})]^+$	
177	$[\text{Al}_2\text{O}(\text{OH})(\text{HCOO})_2]^+$	
179	$[\text{Al}_2(\text{OH})(\text{HCOO})_2(\text{H}_2\text{O})]^{1+}$	$[\text{Al}_2(\text{OH})(\text{HCOO})_2]^{1+} + \text{H}_2\text{O}$
195	$[\text{Al}_2(\text{OH})_3(\text{HCOO})_2]^+$	
205	$[\text{Al}_2\text{O}(\text{HCOO})_3]^+$	
223	$[\text{Al}_2(\text{OH})_2(\text{HCOO})_3]^+$	
255	$[\text{Al}_3\text{O}_2(\text{OH})_2(\text{HCOO})_2(\text{H}_2\text{O})]^+$	
265	$[\text{Al}_3\text{O}_2(\text{OH})(\text{HCOO})_3]^+$	
283	$[\text{Al}_3\text{O}_2(\text{OH})(\text{HCOO})_3(\text{H}_2\text{O})]^+$	

The reaction of monocharged Al^+ with water has been examined by theoretical modelling methods. [217] Also, measurements have been made with $\text{Al}^+(\text{H}_2\text{O})_n$, ($n = 3-50$) ion clusters with a Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR). [218] The Al^{2+} , Al_2^+ and even Al_2^- ions also have calculated properties, but all these states are accomplished in circumstances of pure metallic clusters, and as such the results are hardly useful considering aqueous natural environments. [219,220]

Another explanation rises from within the biochemistry of aluminium: this non-redox-active metal shows strong pro-oxidant activity. [221] It has been shown to promote biological oxidation both in vitro and in vivo. [222-226] Central to this mechanism could be the formation of an aluminium superoxide semireduced radical ion, $\text{AlO}_2^{\bullet 2+}$. [227] The charge of the radical cation is still too high to explain the observed phenomenon completely, but suggests a possible path to follow in order to exam these unstoichiometric complexes.

6.12.4 Phosphate

In various literature sources [94,228] in which the principles of water chemistry is described, the interaction between aluminium and phosphate anion is described simply in this manner: "Aluminium precipitates phosphate." The exact reaction between aluminium and phosphoric acid in an aqueous environment is not

specified. Furthermore, this is an important reaction when dealing with water purification systems. There is also no AlPO_4 available on sale; I searched for it in studies and the only solid commercial aluminium phosphates were powdered mixtures of Al_2O_3 and P_2O_5 . [229] Why is that? The reason to this is that perhaps because the unhydrolysed aluminium cation exists only at the low pH range of below 3 (see Fig.3. and 6.), while free phosphate exists only at higher pH range of above 12, as illustrated in Fig.25. In natural environments it is very unlike that these species would ever meet and react with each other.

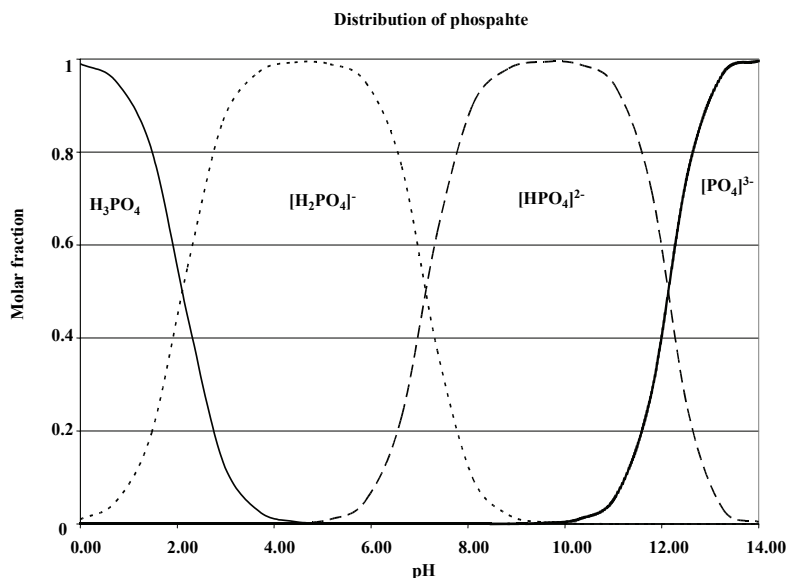


Fig. 25. The distribution diagramme of phosphoric acid.

For the significance of the fact that the presence of aluminium causes a diminishing of phosphate concentration in water, the reaction is certainly worth studying. But the methods this far have been either measurements of total concentration, [230] or the matrix is not water, [231] or the phosphoric acid has been modified. [232] Interesting studies made on modelling the behaviour of aluminium in serum shows also that the interactions between these ions do not only involve the simple precipitation of AlPO_4 . [233–235] The topic is also under keen investigations in China, and alas a few of the reports have been translated into other languages. Perhaps in the future, mass spectrometric methods could give us new and more accurate information on these reactions.

7 Conclusions

This research set a new stage for investigation of aluminium in aquatic environments and the results could be exploited for the benefit of environmental research and water purification processes. ESI MS indicated a much more complicated model for the speciation of aluminium in aqueous solutions than did the traditional methods. The cationic and anionic ESI MS spectra of aluminium solutions produced strong evidence of the presence of a variety of monomeric and polymeric complexes. The main species were Al_2 , Al_3 , and Al_{13} , which were found in all the conditions investigated. The chemical compositions observed with ESI-MS could be developed into structural information with the aid of computational chemistry. Combined, these methods together opened a new window of research for the solution chemistry of aluminium species.

ESI MS results also revealed that counter ions had a dominant role, since the speciation of aluminium changed strongly as a function of sulphate concentration. The highly positive charges of the complexes found through X-ray crystallography methods in solid states were reduced in the solutions with counter ions, which were possibly directly bonded to Al cores. According to these experiments it could be assumed that chlorido ligands were not bridging structures but terminal ligands. Instead, some compositions of aluminium sulphate revealed that sulphate formed bridging structures and the complex could be merely an aluminium sulphate core rather than oxo hydroxide produced by hydrolysis.

The diversity profile of hydrolysed aluminium complexes varied strongly as a function of concentration and pH. The effect of ageing time was slighter, but the abundance of Al_{13} increased gradually as a function of time. Several species with the same aluminium amount could be identified differently, depending on the charges as well as their structures. Signals assigned to polynuclear multi-charged aluminium complexes ($Al_{10} - Al_{15}$) were found in a narrow pH range preceding precipitation. This observation, as well as the remarkable role of sulphate and the eccentric behaviour of formate, could be of high importance in the development of coagulation processes. But the question still remained whether the stable Al_{13} in solutions was the best coagulating agent, or whether there were still more charged species or colloids that were not found with MS spectroscopy. However, the applications now created for ESI MS were proven to be a very useful tool in acquiring new information on the hydrolysis products of aluminium.

As shown in this study, the chemical distribution of aluminium in water is very sensitive to its environment, and one of the key challenges of future research is to choose parameters that model the real environment, and to understand the role of these parameters. This requires systematic experimental series studies with respect to at least pH, formation times, concentrations, adsorbents, temperature and mixing conditions. Beside the effect of the control parameters, the chemistry of aluminium will have many other unknown factors. These investigations showed that different counter ions, such as Cl^- , SO_4^{2-} etc. will have a big effect on Al cluster forming. The effect of the counter ions should be studied further in much deeper detail both experimentally and computationally. Another challenge for future studies is to resolve the large variety of oligomers that exist in the system. The third challenge is to understand the interactions of the Al oligomers and the dirt particles, as well as the flocculation and coagulation in water treatment processes. Also in this respect very detailed experiments and models are needed.

This study has produced a deeper knowledge on the hydrolysis products of polyaluminium chemicals. Improved knowledge about aluminium hydrolysis in the coagulation/flocculation units of water purification processes requires focusing on the functioning of chemicals. Current process optimisations of coagulating/flocculating units are based predominantly on single jar-test experiments, not on scientific information. Variations in the composition of raw water cause problems, which could be managed much better, if the most efficiently functioning species and particles were all known. In general, an improved understanding on the impact of process parameters on purification results will provide a key to enhance the material efficiency of processes. This can be achieved by combining the new information on the aluminium speciation of water treatment chemicals into different case studies with real waters. Research will continue with extended experiments on pure and real water types revealing what the really functioning species are, making the tailored use of chemicals possible.

Enhancing the effect of coagulation against microbes is necessary to support latter disinfection stages. Further, enhancing microbe inactivation by aluminium species (by stiffening cell membranes and cross-linking biomolecules in addition to conventional mechanisms) calls for an improved understanding of aluminium speciation.

The more focused unit operations achieved by this study will remarkably reduce unnecessary chemical loading, material streams and energy consumption

as illustrated in Fig. 26. This is becoming increasingly important in cities and in geographical areas beyond easy access. An essential part of the people who have an insufficient supply of drinking water (today about 3 billion) live in such areas. Also, it has become more and more important to reduce sludge productions. In the field of pulp and paper industry, an improved water quality not only means an enhanced product quality but also helps in developing water recycling and closed circulations.

In addition to water treatment processes, a general understanding of aqueous aluminium structures can be utilised in evaluating their human and environmental toxicity, as well as evaluating their synergistic effects with other detrimental or beneficial ions or compounds. Furthermore, knowledge obtained in this research can be utilised in many industrial and process applications such as sludge recycling. Also the environmental research can use the results in the evaluation of the mobility of aluminium in soils exposed to acids or earth dust, the development of nitrifying wetlands followed by chemical treatment, the assessment of phosphate binding and precipitation, as well as their exclusion from soil.

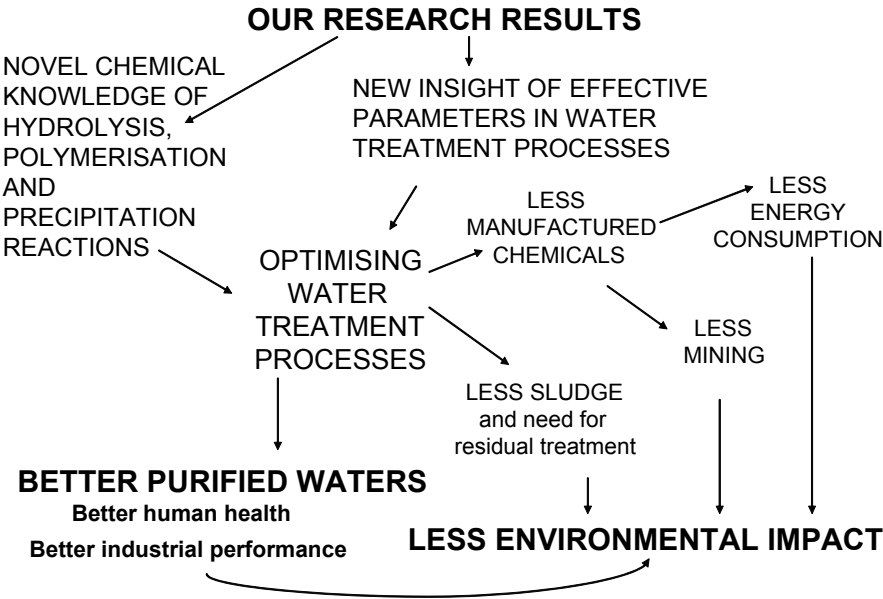


Fig. 26. Outcomes of the study.

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