



Quasi-quantitative determination of elemental relationships and surface properties in aqueous aluminium-silicon systems



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ABSTRACT

Interactions of aluminium (1 mM) and silicon (0.1–2 mM) in aqueous solutions were studied at a low ionic strength medium representing fresh water and water treatment process environments, attempting to quantify elemental relationships of the formed precipitates as well as their surface charge properties with a novel combination of analytical techniques. FESEM analyses showed that the Al:Si ratio in the obtained precipitates was clearly affected by the Al:Si ratio in the initial aqueous solution. According to XRD, the precipitates originated from the 1 mM Al and the 1 mM Al + 0.1 mM Si solutions were gibbsite, while for the initial Al:Si ratios equalling to 1:0.5 or higher, only amorphous material was precipitated. Zeta potential decreased as a function of the initial silicon content, and reached negative values at pH 6.2 with the initial concentrations of 1 mM Al + 2 mM Si. In contrast, for the total surface charge, a maximum value was found between pH 4.5 and 5, and it clearly decreased with the amount of silicon present. To conclude, the dissolved silicon had a significant effect on the formation of charged aluminium species. This may have considerable environmental and health effects. A reaction mechanism for the formation of hydroxyaluminosilicates from silicic acid and aluminium hydroxide was proposed.

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1. Introduction

Aqueous aluminium ions hydrolyze and polymerize into different species as a function of pH. At low pH (<3), aluminium is present in the form of the Al^{3+} ion. As the pH is increased above the value of 3, monomeric aluminium hydroxide species are formed (i.e., $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$). At pH 4.8, aluminium hydroxide species tend to polymerize to different polymeric species e.g. $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ [1]. These polymerized aluminium cations are believed to increase aluminium toxicity by increasing membrane rigidity [2]. On the other hand, they are effective charge neutralizers in the coagulation step in water treatment processes and may also utilize the patch and bridging mechanisms in coagulation [3]. At neutral pH values, however, major part of aluminium precipitates as hydroxides and

oxo-hydroxides [4]. In water treatment applications, this feature is utilized in sweep coagulation processes, in which the insoluble precipitate may adsorb and sweep down the suspended material while settling down. Due to its toxicity, in the EU-area, a quality recommendation of maximum 0.2 mg/l of Al (7.4 $\mu\text{mol/l}$) has been given on drinking water (98/83 EY). For this reason, its usage in water treatment needs to be carefully monitored.

Aluminium forms complexes with silicic acid ($\text{Si}(\text{OH})_4$) in neutral and slightly acidic solutions [5]. It has been proposed that these complexes have an important role in reducing the solubility of aluminium and thus decreasing its aquatic toxicity. A proposed reaction mechanism for hydroxyaluminosilicates (HAS) formation by Exley and Birchall [6] involves inhibition of the aluminium hydroxide polymerization mechanism by monomeric silicic acid. In this reaction scheme, $\text{Si}(\text{OH})_4$ attaches across adjacent hydroxyl groups on a framework of $\text{Al}(\text{OH})_3$, thus causing its precipitation. Two forms of HAS have been identified and characterized by solid state ^{29}Si and ^{27}Al -NMR combined with SEM-EDX (scanning electron microscopy energy dispersive

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X-ray analysis) [7] and atomic force microscopy (AFM) [8]. HAS_A (Al:Si = 2:1) was formed when there was excess or equal aluminium to silicon in the aqueous solution. The structure was dominated by Si coordinated through three Si–O–Al linkages to Al in an octahedral geometry (Al^{VI}) [7]. HAS_B (Al:Si = 1:1) was formed when the initial amount of silicon in the solution was significantly higher than the amount of aluminium. HAS_B contained approximately equal amounts of Al^{VI} and tetrahedrally coordinated Al (Al^{IV}). Moreover, AFM showed differences in morphologies of HAS_A and HAS_B.

Natural water supplies contain silicon in the dissolved form at about 0.8–15 mg/l in streams and 3.5–28 mg/l in groundwater [9]. In dilute neutral and acidic solutions, dissolved silicon is present as monomeric silicic acid [5]. It may have a tremendous impact on the interactions between aluminium and humic substances by reducing electrostatic attractive forces. In addition, the formation of the HAS structures may have a considerable effect on the biogeochemical cycle of aluminium by keeping it out of biota [10,11].

In addition to the natural systems, dissolved silicon may have an effect on water treatment processes. Already as early as 1937, Baylis reported that silica aided alum coagulation [12]. On the other hand, Duan and Gregory found that silicic acid can either promote or inhibit the coagulation of suspensions by aluminium salts [13]. At low concentration of silicic acid (0.3 mM, pH 7), the flocculation of a kaolin suspension by aluminium sulphate (0.06 mM) was enhanced due to the destabilization of particles. The surface charge of kaolin-aluminium hydroxide particles decreased with an increasing concentration of silicic acid [13]. Higher concentration of silicic acid hindered the flocculation, since restabilization of particles occurred. Silicon may also prevent the iron crystallization process and this effect is significant when iron-containing groundwaters are treated [14]. Mertens et al. reported that silica improved As(III) removal from arsenic-contaminated well water when treated with polyaluminium chloride [15]. In order to improve the coagulation efficiency of polyaluminium chlorides, Gao et al. developed polyaluminium silicate chloride coagulants [16,17]. The added silicon resulted in higher molecular weight polymers and a larger floc.

Despite of the multitude of techniques successfully used for the study of the aquatic aluminium silicate chemistry; there are still many phenomena that cannot be unambiguously resolved. In order to understand the effect of silicon on the growth of oxo-aluminium structures, we investigated interactions of aluminium (1 mM) and silicon (0.1–2 mM) in acidic to neutral pH range and in a low ionic strength medium, representing natural and water treatment plant conditions.

For the first time, these interactions were quantified in terms of the elemental relationships of the formed precipitates and their charge properties with a novel combination of analytical techniques. According to a computational thermodynamic speciation, in the conditions of this investigation, no aluminium-silicon compounds were present, but aluminium existed in its dehydrated form diaspore, AlO(OH). Correspondingly, silicon was present in the form of silicic acid and in its dehydrated form, SiO₂ (quartz). Only at the highest pH investigated, 9, a small fraction of the silicic acid, 3%, is deprotonated [4]. The specific aims of the study were to characterize elemental relationships (with Field Emission Scanning Electron Microscope (FESEM)), crystal structures (with X-ray diffraction (XRD)) and surface charge properties (with zeta potential (ZP) and total surface charge (TSC)) of the formed aluminium and silicon precipitates with the intent to deepen the knowledge on the role of silicon in aluminium hydroxide and oligomeric species formation. An additional focus was to evaluate the suitability of flow cytometry for studying reacting aluminium and silicon aqueous systems.

Table 1

Formation of precipitates (3 months duration).

Sample	Concentration	Conditions
S1	1 mM Al	Mixing, pH 6.2 ± 0.2
S2	1 mM Si	Mixing, pH 6.2 ± 0.2
S3	1 mM Al + 0.1 mM Si	Mixing, pH 6.2 ± 0.2
S4	1 mM Al + 0.5 mM Si	Mixing, pH 6.2 ± 0.2
S5	1 mM Al + 1 mM Si	Mixing, pH 6.2 ± 0.2
S6	1 mM Al + 2 mM Si	Mixing, pH 6.2 ± 0.2
S7	1 mM Al + 1 mM Si	Mixing, no pH adjustment after 1st day
S8	1 mM Al + 1 mM Si	No mixing, no pH adjustment after 1st day
S9	1 mM Al + 2 mM Si	Mixing, no pH adjustment after 1st day
S10	1 mM Al + 2 mM Si	No mixing, no pH adjustment after 1st day

2. Materials and methods

2.1. Elemental relationships and crystal structure characterization

Systems containing different initial Al:Si ratios were prepared in 10 l polyethylene beakers. The size of the system was chosen in order to guarantee adequate amounts solid material for FESEM and XRD investigations. The initial concentrations are shown in Table 1. No glass-made laboratory wares were used to prevent external silicon source when sodium silicate solution was handled. High quality ultrapure MilliQ water was used. First, a silicon solution was prepared by the dilution of commercially available Na₂SiO₃ solution (Merck). This was followed by an addition of 1 mM Al as a AlCl₃·6H₂O (Sigma–Aldrich). At this stage, the pH values of the systems were about four and those were elevated to the target value 6.2 ± 0.2 with NaOH (1 M or more diluted, BDH Prolabo). For the 1 mM Si system (S2), HCl (1 M or more diluted, Merck) was used to decrease the pH to 6.2 ± 0.2. Beakers were then covered and the solutions were left to age away from light at room temperature for 3 months in order to confirm stable conditions and adequate amount of precipitates for FESEM and XRD analyses. The conductivity of the systems was ~0.4 mS/cm, except for S2 it was 0.03 mS/cm.

Solutions S1–S7 and S9 were kept under a mild recirculation of 17 ml/min with ISMATEC MS-CA 4/640 tubing pump with four tubes that were placed approximately in the middle of the beakers in order to avoid disturbance in the precipitate forming. The solution pH values were measured approximately once a week and, for the samples S1–S6, the solution pH was adjusted with NaOH and HCl to the original value, if necessary. The pH values of the samples were measured using VWR pHenomenal pH 1000L device with an epoxy electrode (Cat. No. 662-1769, the same pH metre was used throughout the study). The electrode was calibrated in accordance with the instrument's manual using buffer solutions of pH 4 and pH 7 (BDH Prolabo).

After three months of ageing, samples were filtered using 0.2 µm Whatman Nuclepore polycarbonate membranes. Only part of the 10 l systems (1.5–3.9 l) was filtered by sampling from the bottom of the beaker containing higher solid concentrations. Sample S2 (i.e., 1 mM Si) did not contain any precipitates.

The Al:Si ratios of the precipitates were investigated using FESEM (Zeiss Ultraplus) equipped with EDS (Inca x-act Oxford Instruments). Before the samples were analyzed, they were coated with a thin carbon layer to achieve a conductive layer using a JEOL Jee-420 vacuum evaporator. The used acceleration voltage was 15 kV. For every sample, two measurements were made from different positions of the sample.

For the X-ray diffraction (XRD) measurements samples were finely ground and homogenized after a few months of storage at room temperature. The measurement itself was performed with a Bruker D8 Discover equipped with copper (Cu) X-ray tube, using a 40 kV voltage, and 40 mA current. The samples were measured in the 2-theta range from 15° or 20° to 80° with a step size of 0.010 and an integration time of 0.5 s.

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