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Deposition behavior of residual aluminum in drinking water distribution system: Effect of aluminum speciation

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ABSTRACT

Finished drinking water usually contains some residual aluminum. The deposition of residual aluminum in distribution systems and potential release back to the drinking water could significantly influence the water quality at consumer taps. A preliminary analysis of aluminum content in cast iron pipe corrosion scales and loose deposits demonstrated that aluminum deposition on distribution pipe surfaces could be excessive for water treated by aluminum coagulants including polyaluminum chloride (PACl). In this work, the deposition features of different aluminum species in PACl were investigated by simulated coil-pipe test, batch reactor test and quartz crystal microbalance with dissipation monitoring. The deposition amount of non-polymeric aluminum species was the least, and its deposition layer was soft and hydrated, which indicated the possible formation of amorphous $\text{Al}(\text{OH})_3$. Al_{13} had the highest deposition tendency, and the deposition layer was rigid and much less hydrated, which indicated that the deposited aluminum might possess regular structure and self-aggregation of Al_{13} could be the main deposition mechanism. While for Al_{30} , its deposition was relatively slower and deposited aluminum amount was relatively less compared with Al_{13} . However, the total deposited mass of Al_{30} was much higher than that of Al_{13} , which was attributed to the deposition of particulate aluminum matters with much higher hydration state. Compared with stationary condition, stirring could significantly enhance the deposition process, while the effect of pH on deposition was relatively weak in the near neutral range of 6.7 to 8.7.

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Introduction

Aluminum is one of the common metallic elements in natural water, and its concentration in drinking water is generally restricted by regulations all over the world. However, the factors influencing the concentration of aluminum in tap water are very complicated. Meeting the drinking water quality standards of aluminum is a great challenge for many

water utilities. Based on one investigation of drinking water quality in some cities of China, aluminum concentration collected from tap water could significantly exceed the standard limit of 0.2 mg/L (according to Chinese standards for drinking water quality, GB 5749-2006) (Li et al., 2013). Elevated levels of aluminum have been associated with health problems. For example, bone disorders were testified to be related with aluminum among dialysis dependent patients

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(Dahl et al., 2014). Additionally, aluminum accumulated in humans may cause severe nervous system diseases, such as Alzheimer's disease, amyotrophic lateral sclerosis and Parkinson's dementia (Dzulfakar et al., 2011).

The source of aluminum in finished drinking water may originate from raw water or be introduced from Al-based coagulants (Snoeyink et al., 2003). Previous investigations on residual aluminum conducted in China, the United States and the Europe, showed that aluminum salts used for coagulation could increase residual aluminum content significantly (Wang et al., 2010b). Polyaluminum chloride (PACl), has been widely applied as coagulants in drinking water treatment (Lin et al., 2014) due to its many advantages, such as being effective within a broader pH range, rapid aggregation and sedimentation of its flocs (Gao et al., 2002).

Various aluminum hydrolysis products exist in PACl, including Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Keggin- Al_{13} species), $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{24}]^{18+}$ (Al_{30} polymer) and $\text{Al}(\text{OH})_3$ (Xu et al., 2011). The coagulation efficiency of PACl is highly related to its aluminum speciation, and Al_{13} is claimed as the most efficient species for coagulation in PACl (Hu et al., 2006). The detrimental effects of aluminum on humans are also highly related to its specific species (Wang et al., 2010a). As dissolved aluminum could be assimilated immediately, it shows high cytotoxicity to both animal and plant (Szatanik-Kloc and Jozefaciuk, 2007). The mononuclear aluminum form is known to be severely neurotoxic because it can accelerate the formation of neurofibrillary tangles and senile plaques in the brain. While, the toxicity of polynuclear aluminum is relatively small as a result of its slow dissociation process (Wang et al., 2010c). However, it is currently not clear on the transformation and fate of residual aluminum with different speciation in finished water from the treatment plant to the consumer taps.

It has been reported that aluminum ubiquitously existed in corrosion scales and loose deposits within cast iron pipes, lead pipes, plastic pipes and cement-mortar lined pipes (Snoeyink et al., 2003). The aluminum accumulated in pipe scale and sediments may release back into bulk water once the water chemistry or hydraulic condition changes, which could result in relatively high aluminum content in tap water. Furthermore, severe deposition of aluminum might weaken disinfection efficiency, increase turbidity and interfere water transport capacity.

In order to control residual aluminum concentration in drinking water, many studies were conducted and different measures were proposed. However, most previous research focused on the optimization of coagulant dosage and coagulation condition, the investigation of aluminum transformation and deposition in drinking water distribution system was relatively rare. To our knowledge, study on the migration and transformation of different aluminum species in pipe distribution process has not been reported.

The main objective of this work was to understand the deposition features of different aluminum species on pipe surface, particularly on inert interface. Aluminum content in real distribution pipe corrosion scales and loose deposits, obtained from two cities with different source water types, was firstly analyzed. The deposition behavior of different aluminum species was systematically investigated using both simulated coil-pipe test and batch reactor test. QCM-D (Quartz

Crystal Microbalance with Dissipation Monitoring) technique was applied to explore the characteristics of deposition layer formed between different aluminum species and inert interface. The influence of hydraulic condition (stagnant vs. stirring) and pH (within neutral range) on the deposition behavior of different aluminum species were also observed. The deposition mechanism of different aluminum species was discussed.

1. Materials and methods

1.1. Analysis of aluminum content in real water distribution pipe scales and deposits

Cast iron pipe and plastic pipe sections were obtained from a northern and a southern city of China. Pipe corrosion scales and loose deposits were collected, respectively, where available. Totally 76 samples were collected from the northern city, among them 67 samples were hard iron corrosion scales, 9 samples were surficial loose deposits. Fifteen samples were collected from the southern city, 6 hard iron corrosion scale samples and 9 surficial loose deposit samples (including 3 from plastic pipes). Aluminum content in these two type scales were analyzed using XRF (X-ray Fluorescence, Advant' XP, Thermo Electron, Ecublens, Switzerland) and the pretreatment procedures were performed according to the report of Yang et al. (2012).

1.2. Preparation of stock solutions with different aluminum species

Three stock solutions Al_0 , Al_{13} and Al_{30} with different aluminum speciation were prepared as follows. Their total aluminum concentration and speciation are provided in Table 1. All reagents used were of analytical grade. Milli-Q water was used to rinse all reactors and to prepare all solutions.

For Al_0 solution, a measured amount of AlCl_3 was directly dissolved into 100 mL milli-Q water. Such solution was dominated by monomeric aluminum and some oligomeric aluminum species. For Al_{13} , firstly, PACl with basicity (OH/Al , molar ratio) 2.0 was prepared by base titration method. 0.5 mol/L NaOH was slowly titrated into a predetermined amount of AlCl_3 solution under magnetic stirring. The obtained PACl solution was mixed with Na_2SO_4 , settled for 24 hr, then filtered to obtain the precipitate. Then 0.1 mol/L BaCl_2 was added to the precipitate, rapid stirring for 3 hr. The supernatant was filtered by 0.45 μm membranes after 10 min settlement to obtain purified Al_{13} polymer (Xu et al., 2014). For Al_{30} solution, 1.0 mol/L AlCl_3 solution with a measured amount of Na_2CO_3 was mixed to obtain a molar ratio of $\text{Na}_2\text{CO}_3/\text{Al}^{3+} = 1.15$, then heated at 80°C till the precipitation dissolved. After settling for 12 hr the

Table 1 – Al concentration and speciation of stock solutions.

	Concentration (10^{-3} mol/L)	Al_a (%)	Al_b (%)	Al_c (%)
Al_0	50.00	92.68	7.06	0.26
Al_{13}	21.62	13.10	83.35	3.55
Al_{30}	28.67	7.07	7.05	85.88

solution was diluted 10 times to obtain PACl with basicity 2.3. Then the solution was heated again for 48 hr at 95°C. A measured amount of Na₂SO₄ was added with molar ratio of SO₄²⁻/Al³⁺ = 0.33 and settled for one week. The obtained precipitate was mixed with Ba(NO₃)₂ solution, and ultrasonically vibrated for 30 min, settled for 4 hr. Finally, the supernatant was filtered by 0.45-μm membranes to obtain purified Al₃₀ polymer (Duan et al., 2014).

1.3. Aluminum speciation characterization

In this work, for each collected water sample, total aluminum and dissolved aluminum concentrations were directly obtained through membrane separation, then the amount of deposited aluminum was calculated based on the initial dosage. The separation procedure is illustrated in Appendix A Fig. S1. Ferron timed complex-colorimetric method was applied to classify soluble aluminum as Al_a (reacted within 1 min with ferron; including monomeric and oligomeric aluminum (denoted as “Al₀” in this work)), Al_b (reacted from 1 min to 120 min; including medium polymeric aluminum, which is almost equivalent to Al₁₃), and Al_c (slow-reacting colloidal or unreacted species; in Al₃₀ stock solution, Al_c was the main constituent) (Wang et al., 2004).

1.4. Coil-pipe test

To examine aluminum species variation in drinking water distribution system (mainly on inert interface), coil-pipe test was operated using plastic pipes. The definition of inert interface presented in this work is material with charge neutral, chemically inactive, and hard to react with other substances (including plastic pipe in coil-pipe test, beaker in batch test, quartz crystal sensor with gold-coated surface in QCM-D characterization).

Synthetic test water was prepared by diluting Al₀, Al₁₃ and Al₃₀ stock solutions, respectively, using Milli-Q water to obtain initial total aluminum concentration of 0.2 mg/L according to WHO guidelines (2004). Besides, the test water contained 0.5 mmol/L NaHCO₃ and 0.5 mmol/L NaNO₃ to achieve certain buffer capacity and ionic strength. The pH of the test water was adjusted to 7.7 by adding HCl and NaOH solutions. Synthetic test water was stocked in the tank with 300 r/min magnetic stirring.

The plastic pipes were 10 m long, with 6 mm inner diameter. Peristaltic pump was used to drive Al₀, Al₁₃ and Al₃₀ containing test water into the coil pipe. The flow rate was adjusted to achieve 8 hr of hydraulic retention time (from the inlet to outlet) in the pipe. After running for 8 hr, water was kept stagnant in pipes for 16 hr. Water samples were collected each day after 16 hr stagnation during flowing period. Each operation cycle was 7 days. The schematic graph of coil-pipe test is shown in Appendix A Fig. S2.

1.5. Batch test

The aluminum variation for the coil-pipe test consisted of two parts, that is, variation in the feed solution tank and variation in the pipe. To further elucidate the deposition behavior of different aluminum species, and testify the findings of coil-pipe test, a well-controlled batch test was established and the

variation of different aluminum species was observed in glass beaker reactors. Additionally, stationary and magnetic stirring (300 r/min) conditions were applied to compare the effect of hydraulic condition.

Al₀, Al₁₃ and Al₃₀ stock solutions were dosed respectively into each reactor (which contained Milli-Q water) to obtain test water with 0.2 mg/L total aluminum (0.5 mmol/L NaHCO₃, 0.5 mmol/L NaNO₃, and pH 7.7, same as coil pipe test). 50 mL water samples were collected from each reactor at predetermined time intervals. One subsample was filtered with 0.45-μm membrane. Then the samples were digested with guaranteed grade HNO₃ at pH 1.0 for 2 hr. Total and dissolved aluminum concentrations were measured by Chrome Azurol S Spectrophotometry method.

1.6. Characterization by QCM-D

The deposition layer features of different aluminum species onto inert material were characterized using a QCM-D (Quartz Crystal Microbalance with Dissipation Monitoring) instrument (E4, Q-Sense, Gothenburg, Sweden). A 5-MHz AT-cut quartz crystal sensor with gold-coated surface (QX301, Q-Sense, Gothenburg, Sweden) was mounted in the flow module. Prior to measuring, crystal sensors were cleaned as described in protocols recommended by Q-Sense (SI).

QCM-D application for adsorption layer characterization has been previously described (Palmqvist and Holmberg, 2008). The general principle is to apply a voltage to the electrodes affixed to the quartz crystal which resulted in oscillations of piezoelectric quartz crystal. The QCM-D response is sensitive to any mass change of the quartz crystal. When deposition occurs, a shift in the vibrational frequency of the crystal takes place and the signal is recorded. The energy of dissipation is also simultaneously monitored to extract the viscoelastic properties of the deposited layer.

The experiments were performed at 20 ± 0.1°C. A peristaltic pump was used to obtain flow rate of 150 μL/min, which resulted in a laminar flow across the sensor, and avoided air bubbles (Isaacson et al., 2011). QCM-D measurements were initiated with flowing air to examine whether a steady state achieved, then a baseline was established with flowing Milli-Q water for appropriate background correction, and then each test solution was pumped in. The frequency and dissipation response of the crystal sensors at various overtones were simultaneously monitored throughout the experiment.

In the deposition experiments, the variation of frequency and dissipation were monitored at four overtones ($n = 3, 5, 7, 9$). For uniform flat and rigid layers, the deposited mass (Δm , kg) is proportional to the change in resonance frequency ($\Delta f = f - f_0$, Hz) as described by the Sauerbrey equation (Tammelin et al., 2004).

$$\Delta m = -\frac{C_{\text{QCM}}}{n} \Delta f$$

where, Δm (kg) is the change in deposited mass, C_{QCM} is the mass sensitivity constant (17.7 ng/(Hz cm²)), n is the overtone number (1, 3, 5, 7, ...; the number of resonance for output frequency of a quartz oscillator) and Δf (Hz) is the shift in resonance frequency. For soft and viscoelastic layers, the Vogit model was used (Rodahl et al., 1997) to fit the frequency change (Δf) and energy dissipation (ΔD) simultaneously at multiple overtones to

obtain the mass and physical properties (e.g., density, thickness, shear elastic modulus, and viscosity) of the deposited film. In Voigt model, fluid density and fluid viscosity were 1000 kg/m^3 , $0.001 \text{ kg/(m}\cdot\text{sec)}$, respectively. The deposited layer density was presumed to be 1000 kg/m^3 .

2. Results and discussion

2.1. Aluminum in corrosion scales and loose deposits of real distribution pipes

Aluminum content in pipe hard corrosion scales and loose deposits were analyzed through XRF and the cumulative aluminum occurrence profiles are illustrated in Fig. 1. Obviously, the profiles for surficial loose deposit and hard scale are distinct. The surficial deposit samples had much higher aluminum content across the entire range for both cities. The average aluminum content of hard scales in the northern city was $8975 \mu\text{g/g}$, significantly lower than that of surficial deposit ($32,714 \mu\text{g/g}$). For samples extracted from the southern city, average aluminum content of surficial deposit was $49,444 \mu\text{g/g}$, higher than $16,013 \mu\text{g/g}$ of hard scales. The much higher amount of aluminum presented in surficial deposit testified that aluminum deposition process occurred to a great extent in real distribution pipes.

Besides, for the southern city, raw water was surface water treated with PACl as coagulant. While for the northern city, raw water included surface water and ground water, PACl was also the coagulant applied to treat the surface water. Since different aluminum species co-existed in PACl, and dominant species may vary for different products, study on the deposition behavior of different aluminum species is crucial for aluminum control in drinking water distribution system.

2.2. Aluminum speciation variation in coil-pipe test

In order to observe the deposition behavior of different aluminum species, coil-pipe test was established to simulate a water distribution pipe. Aluminum concentration and speciation of samples collected from outlet of the coil-pipe were measured. It was observed that the concentration variation of different aluminum species exhibited different patterns

(Fig. 2). The aluminum concentration decrease for Al_0 system was rather limited (less than 0.03 mg/L), however for Al_{13} and Al_{30} systems, aluminum concentration decreased dramatically. For Al_0 system, total and dissolved aluminum decreased slightly at first four days, and then increased slowly in the following days, where the difference between total and dissolved aluminum was relatively small. It indicated that Al_0 did not tend to deposit during the experimental period. For Al_{13} systems, total aluminum concentration decreased in the first four days, then kept at 0.065 mg/L with little fluctuation in the following days. In addition, dissolved aluminum concentration showed similar variation trend. Particulate aluminum concentration was considerable in the first two days, and then nearly equal to zero in the following days. Such variation of particulate aluminum might be due to its deposition. Besides, deposited aluminum calculated by initial dosage minus measured total Al concentration, increased with time and accounted for the large decreased proportion in the solution after the third day.

Al_{13} ($[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) was characterized by relatively stable structure, nanometer molecular diameter and high self-aggregation tendency. It has been detected by ^{27}Al -NMR (Nuclear Magnetic Resonance) and small angle X-ray scattering that Al_{13} is a polycation with Keggin structure with the central AlO_4 surrounded by 12 aluminum atom in octahedral and with molecular diameter of 1.0 nm (Gao et al., 2009). It was investigated that pure Al_{13} species exhibited certain anti-hydrolysis stability, because the unique Keggin structure could interfere protons to access the AlO_4 kernel (Wang et al., 2011). Consequently, the interchange of structural aluminum with bulk-aluminum and structure rebuilding is rather slow. However, due to the high aggregation property of Al_{13} , it might easily become line or branch formed polymers by decreasing its charge and losing Cl^- in the hydration layer (Tang and Luan, 1997). The polymers were aggregated together with sizes ranging from tens to hundreds of nanometers (Tang, 1998). Additionally, Al_{13} might hydrolyze to bayerite $\alpha\text{-Al}(\text{OH})_3$ within solutions with higher pH (Wang and Muhammed, 1999). Consequently, Al_{13} was apt to deposit as a result of the increment of apparent molecular weight.

For the Al_{30} system, total and soluble Al decreased in the first three days and appeared slightly increment at the fifth day, then gradually stabilized at 0.070 mg/L in the last two days. Dissolved

Fig. 1 – Relative aluminum content in corrosion scale samples and loose deposit specimens extracted from a northern city and a southern city in China.

Fig. 2 – Aluminum speciation vs. time in coil test.

aluminum is at relatively lower level and the gap with total Al is large in the first two days, which also indicated that particulate Al occupied large proportion in the first two days. However, in the following days, dissolved aluminum was nearly equal to the amount of total aluminum, which indicated that the particulate Al was almost deposited. Besides, large amount of deposited aluminum appeared in the Al₃₀ system. Compared with Al₁₃ reaction system, particulate aluminum content of Al₃₀ system was obviously higher in the first two days and it could directly deposit. The higher concentration of particulate matter in Al₃₀ system might be explained by its higher molecular size. Al₃₀ ([Al₃₀O₈(OH)₅₆(H₂O)₂₄]¹⁸⁺) polymer is the largest Al polycation isolated and characterized in hydrolytic PACl solution. It also possesses Keggin structure, composed of two δ-Al₁₃ connected by four Al monomers (Chen et al., 2006). Al₃₀ has unique nanometer molecule dimension (2.0 nm in length) and eighteen positive charges (Allouche et al., 2000). However in Al₁₃ system, the large amount of deposited aluminum might be partly resulted from the gradual aggregation of dissolved Al₁₃ species. Consequently, the deposition behaviors that occurred in the Al₁₃ and Al₃₀ systems were significantly different.

Table 2 presents the pH variation before and after a week cycle in the coil-pipe test, and it shows that pH decreased in three systems, which indicated that Al₁₃ and Al₃₀ might gradually hydrolyze to higher polymer. The decreasing soluble aluminum could be partly due to its transformation into higher polymers, which was apt to deposit. The pH reduction barely differed in three systems, whereas reduction in Al₀ system was relatively lower, indicating that the hydrolysis was weak. Small amount of amorphous Al(OH)₃ could be formed in Al₀ system.

2.3. Aluminum speciation variation in batch test

2.3.1. Comparison of standing and stirring condition in batch test

The deposited aluminum that occurred in coil-pipe test included two parts, that is, the deposition in the feed solution tank (under stirring condition, 300 r/min) and the deposition in the pipe. Additionally, the variation of aluminum

concentration in the coil-pipe test was affected by hydraulic condition. Therefore, to further elucidate the deposition behavior of different aluminum species and testify the findings of coil-pipe test, a well-controlled batch test was established. Besides, stationary and magnetic stirring (300 r/min) conditions were applied to compare the effect of hydraulic condition.

In batch test, total and dissolved aluminum concentration exhibited similar trends with the aluminum variation in coil-pipe test (Fig. 3). Under stationary condition, for Al₀ reaction system, aluminum concentration had minimal reduction, which indicated that such aluminum species did not tend to deposit. For the system of Al₁₃, total aluminum concentration decreased continuously with time and stabilized at 0.11 mg/L after six days. Besides, particulate aluminum existed but decreased from 0.051 to 0.020 mg/L. Meanwhile, deposited aluminum increased from 0.015 to 0.090 mg/L, nearly half amount of aluminum deposited to the reactor surface. For Al₃₀ system, total aluminum content decreased from 0.178 on the first day to 0.148 mg/L at last. Meanwhile, deposited aluminum increased from 0.022 to 0.052 mg/L.

Compared with Al₃₀ system, total and dissolved aluminum reduction in Al₁₃ system was relatively higher, which indicated that Al₁₃ was more apt to deposit. The changing trend of aluminum species in Al₃₀ solution was more stable and exhibited less decrease with time, meanwhile, relatively higher level particulate aluminum existed and was hard to precipitate in stationary state.

Compared with stationary condition, it is apparent that deposited aluminum was much higher under stirring condition. Additionally, particulate aluminum barely existed in the last three days for all systems. These results verified that stirring condition enhanced the deposition process and accelerated the reaction to reach equilibrium.

2.3.2. Ferron timed complex-colorimetric characterization of Al speciation variation

Ferron timed complex-colorimetric method was applied to further determine the aluminum speciation changes in three systems under stationary condition. The comparison of aluminum speciation before and after a week is shown in Fig. 4. In the solution with Al₀, the proportion of Al_a increased, and the percentage of Al_b decreased. However, the changes of Al_a, Al_b and Al_c were relatively small. A possible explanation is that small percentage of particulate aluminum was deposited and part of Al_b aggregated which resulted in the increment of Al_a percentage. For Al₁₃ system, the proportion of Al_b increased

Table 2 – pH variation of test water with different Al speciation for coil-pipe test.

	Before	After	Reduction
Al ₀	7.70	7.28	0.42
Al ₁₃	7.70	7.24	0.46
Al ₃₀	7.70	7.22	0.48

Fig. 3 – Aluminum speciation vs. time in batch test under stationary and stirring condition.

from 61.49% to 76.22% with the decreasing Al_c . The increased Al_b percentage indicated that part of aluminum gradually hydrolyzed to higher polymers. Besides, the decreased Al_c could be due to the deposition. In Al_{30} system, the percentage of Al_c distinctly increased from 69.90% to 90.25%. Additionally, Al_a and Al_b proportions decreased to less than 10%. In Al_{30} stationary system, particulate aluminum was dominant and the gradual hydrolyzation resulted in the increment of Al_c proportion.

Based on the results obtained from the batch tests and the ferron timed complex-colorimetric characterization, it could be deduced that deposited aluminum in Al_{13} system might

mainly be due to its self-aggregation; while for Al_{30} system, particulate aluminum precipitation could be the dominant reason for the large amount of deposited aluminum. This hypothesis will be further discussed below.

2.3.3. Comparison of coil-pipe test and batch test

Compared with the initial aluminum concentration of test water, the decrement in aluminum concentration measured at the outlet of coil-pipe included the aluminum variations in both test water tank and coil-pipe. Therefore, the actual deposited aluminum in coil-pipe could be calculated by deducting the aluminum deposited in test water tank (stirring condition) (shown in Fig. 3) from the total deposited aluminum in both test water tank and coil pipe (shown in Fig. 2). The calculated variation of deposited aluminum concentration in coil-pipe is presented in Fig. 5. It is interesting to find that the deposited aluminum for Al_{13} and Al_{30} systems could be negative and positive values, which fluctuated around zero. Only Al_0 system exhibited positive values all the time. This phenomenon demonstrated that the aluminum deposition for Al_{13} and Al_{30} systems in the coil pipe test mainly occurred in test water tank. The negative value was due to the unstable state in coil-pipe under the changing flow condition, which could result in deposited aluminum release to solution. The findings of simulated coil-pipe test implicated that aluminum deposition behavior in real distribution system was more complicated and apt to be affected by the hydraulic condition, to which attention should be paid by water utilities.

2.3.4. Effect of pH on aluminum deposition

The pH effect on deposition behavior of different aluminum species was conducted and shown in Appendix A Figs. S3–S5. For Al_0 system, pH effect was relatively obvious. Total aluminum and dissolved aluminum concentration followed the pH sequence of $7.7 > 7.2 > 6.7 \approx 8.2 \approx 8.7$. High pH promoted Al_0 hydrolysis to high polymers, and the low pH might be inclined to the formation of amorphous $Al(OH)_3$.

For Al_{13} system, when $pH = 6.7$, total aluminum concentration was distinctly higher than that under other pH conditions. Besides, dissolved aluminum content followed the pH sequence of $6.7 > 7.2 > 7.7 \approx 8.2 \approx 8.7$, with minor gaps. With regard to Al_{30} system, when $pH = 8.7$, total aluminum and dissolved aluminum concentration were relatively lower. For Al_{13} and Al_{30} , total aluminum and dissolved aluminum concentration were relatively higher at lower pH and smaller at higher pH, which implied that higher pH promoted hydrolyzation. Generally, the pH effect on aluminum deposition was relatively small for Al_{13} and Al_{30} .

2.4. Deposition characterization of different aluminum species by QCM-D

To further investigate the deposition mechanism of different aluminum species, QCM-D technique was applied. The deposition behavior of Al_0 , Al_{13} and Al_{30} was characterized by QCM-D at pH of 7.7, temperature of 20°C with initial total aluminum concentration of 0.2 mg/L. Real-time recording of frequency shifts (Δf) and dissipation shifts (ΔD) at four overtones ($n = 3, 5, 7, 9$) are presented in Fig. 6 for Al_0 , Al_{13} and Al_{30} , respectively. The curves at the first overtone (5 MHz) were not included as a

Fig. 4 – Aluminum speciation before and after a week under stationary condition.

result of high scattering, which also observed by (Yan et al., 2011). A stable baseline was first established through injection of Milli-Q water. After introduction of 0.2 mg/L of Al_0 , Al_{13} , and Al_{30} solutions into QCM-D, respectively, Δf decreased to different extent along with increasing ΔD from the baseline. It took 3, 1.5 and 4 hr for Al_0 , Al_{13} , and Al_{30} systems to achieve near steady-state, respectively.

2.4.1. Deposition features

In Al_0 system (Fig. 6), only small Δf was detected, which indicated that the deposition mass was relatively small. The dissipation shifts increased significantly, which implied that the deposited layer was rather soft and hydrated.

Fig. 6 also shows the curves of Δf and ΔD versus time for the deposition of Al_{13} . When Al_{13} was introduced, Δf sharply decreased compared with the referred baseline, indicating that rapid deposition occurred on the surface. Relatively slight increments of dissipation shifts indicated that the deposition of Al_{13} formed a more rigid layer. Besides, when Al_{13} was bound, dissipation shifts at different overtones tended to get closer, which was extremely different from the distinct separated shifts of Al_0 and Al_{30} solutions. Such a weak sensitivity to overtone number is typical for a rigid film (Sun et al., 2014), which further verified that Al_{13} layer was

Fig. 5 – Deposited aluminum concentration vs. time in coil-pipe for different aluminum species.

Fig. 6 – Performances of deposition behavior of different aluminum species monitored by QCM-D (Quartz Crystal Microbalance with Dissipation Monitoring). (a) Al_0 ; (b) Al_{13} ; (c) Al_{30} .

Fig. 7 – Characteristics of deposited layers (a) $\Delta D/\Delta f$ at $n = 5$ overtone for Al_0 , Al_{13} and Al_{30} ; (b) deposition mass calculated by the Voigt model.

more rigid, while layers formed by Al_0 and Al_{30} were rather soft and hydrated (Mohan et al., 2014).

The deposition of Al_{30} on the gold surface was characterized by relatively high rate and high amount, as determined by the significant decrease in Δf values, shown in Fig. 6. In addition, dissipation shifts exhibited a considerable increment compared with the baseline, indicating that a rather viscoelastic film was formed on the surface (Wang et al., 2014).

2.4.2. Deposited layer characteristics

The viscoelastic properties and conformational changes of the deposited layers could be evaluated by the ΔD – Δf plot, as shown in Fig. 7a (Li et al., 2014). The slope of ΔD to Δf was steepest with Al_0 , followed by Al_{30} and Al_{13} , which indicated that the deposited layer of Al_{13} was the most rigid and a most soft dissipative film was formed for Al_0 . For Al_{13} and Al_{30} , with direct inspection, the slope of ΔD to Δf exhibited a linear relationship, which meant that no conformational alternation occurred during the deposition process (Che et al., 2014). With respect to Al_0 , the slope became larger with increasing $|\Delta f|$, which meant that the film became more loosely attached to the surface (Li et al., 2014).

The soft hydrated deposited layer formed by Al_0 might be related with the amorphous $Al(OH)_3$ formed by Al_0 hydrolyzation. However, Al_{13} might form substance with more ordered structure, as a result of its self-aggregation characteristics. And such deposition layer was relatively rigid. For the deposition layer formed by Al_{30} , its properties lie between Al_0 and Al_{13} films. Combined with the findings in batch test, that is, particulate aluminum accounted for high proportion. It could be deduced that the deposition layer of Al_{30} was mainly formed by particulate aluminum deposition.

2.4.3. Deposited mass

Since the deposited Al_0 and Al_{30} exhibited characteristics of a viscoelastic layer, as determined by the relatively higher $\Delta D/\Delta f$ ratio (Mohan et al., 2014), Voigt-based model was applied, instead of the Sauerbrey equation. For Al_{13} deposited layer, it was more rigid than Al_0 and Al_{30} deposited films, however, it might not be rigid enough to fit the Sauerbrey equation. Therefore, the deposited mass calculated by Sauerbrey equation

was compared with the mass by Voigt model. Model fitting results are summarized in Table 3. In Voigt viscoelastic model, the frequency shifts and dissipation shifts at three overtones ($n = 3, 5, 9$ for Al_0 , $n = 7, 9, 11$ for Al_{13} , $n = 5, 7, 9$ for Al_{30}) were fitted with changeable parameters of layer viscosity, shear and thick. Constant parameters were used for layer density of 1000 kg/m^3 , fluid density of 1000 kg/m^3 , and fluid viscosity of 0.001 kg/(m·sec) (Sun et al., 2014).

The comparison results showed that the Voigt mass values were higher than the Sauerbrey mass values, where for Al_0 and Al_{30} , mass values were two times higher. However, Δm_{voigt} of Al_{13} was 603 ng/cm^2 and $\Delta m_{\text{Sauerbrey}}$ was 500 ng/cm^2 , with relatively small gap. For a viscoelastic, non-rigid layer, deposited mass calculated by Sauerbrey equation would result in an underestimation compared with the mass based on Voigt mass (Suhr et al., 2014). Consequently, it was inappropriate to use Sauerbrey equation due to the viscoelastic properties of the deposited layers. It has been reported that when materials are deposited to the crystal, water could be coupled into the deposited molecular as an additional dynamic mass via entrapment and/or direct hydration within the deposited layer (Dixon, 2008). This could be the explanation for the elastic properties of deposited layers. Besides, the influence of coupled water was not included in Sauerbrey equation, only deposited dry mass was considered (Suhr et al., 2014).

Fig. 7b illustrates the deposited mass calculated through Voigt model plotted with time. It is demonstrated that the near steady state deposition mass were $168, 603$ and 2683 ng/cm^2 for Al_0 , Al_{13} and Al_{30} , respectively. The maximum deposition occurred when Al_{30} was introduced, while the deposition of Al_0 was the minimal.

Table 3 – Fitting results of deposition mass by Sauerbrey equation and Voigt model.

Solution	$\Delta m_{\text{Sauerbrey}} (\text{ng/cm}^2)$					$\Delta m_{\text{voigt}} (\text{ng/cm}^2)$
	Average	$n = 3$	$n = 5$	$n = 7$	$n = 9$	
Al_0	95	119	135	60	66	168
Al_{13}	500	539	505	492	464	603
Al_{30}	1386	1726	1450	1254	1114	2683

Fig. 8 – Schematic deposition features of residual aluminum with different speciation characteristics.

2.5. General discussion

Based on the above results, Al_0 was difficult to deposit, and the small deposition might be due to the formation of amorphous $\text{Al}(\text{OH})_3$. Al_{13} was most apt to deposit due to self-aggregation. For Al_{30} , particulate aluminum occupied large proportion and easily deposited under stirring. The deposited mass estimated by QCM-D included the mass of coupled water, and the deposited Al_0 layer exhibited highly soft, hydrated property. Therefore, though the result of QCM-D experiment showed that 168 ng/cm^2 Al_0 deposited to the gold surface, the actual dry mass of deposited Al_0 was much smaller.

For Al_{13} , the result of QCM-D demonstrated that the deposited film was rather rigid. Besides, the deposition was fastest and deposition mass per unit time was the largest. Such characteristics were in accordance with the batch test. Al_{13} was most apt to deposit. Additionally, based on the rigid deposition layer and characteristics of Al_{13} , Al_{13} deposition may mainly be attributed to its self-aggregation.

With regard to Al_{30} , the deposited mass was massive, however the deposited film was rather soft and hydrated, deposition process was slow. Such behavior was also consistent with the findings in batch test that particulate aluminum slowly deposited with time. Since the hydrated or entrapped water might account for large proportion of the deposited mass, the deposition amount (in terms of elemental aluminum) of Al_{30} was less than Al_{13} during the same period. Based on the deposition properties of Al_{30} , it could be conjectured that the deposition of particulate aluminum be the main mechanism of Al_{30} deposition. A schematic graph to express the characteristic deposition behaviors of different aluminum species is presented in Fig. 8.

3. Conclusions

In this work, coil-pipe test, batch test and QCM-D technique were used to understand the deposition behavior of different aluminum species (Al_0 , Al_{13} and Al_{30}), some main conclusions were obtained as below: the Al deposition rate and mass (as elemental Al) followed the order: $\text{Al}_{13} > \text{Al}_{30} > \text{Al}_0$. Al_{13} was most inclined to deposit, and Al_0 hardly deposit. The deposition layer formed by Al_{13} was rigid and compact, but those formed by Al_{30} and Al_0 were rather soft and loose. Compared with the stationary system, stirring enhanced the interaction between solution and interface, therefore, the process of deposition was accelerated. For aluminum species

with higher deposition tendency, more proportion of aluminum might accumulate in the pipe surface under stirring condition. Within the neutral pH range of 6.7–8.7, the pH effect on deposition behavior was relatively small for Al_{13} and Al_{30} . However, for Al_0 , the effect was relatively larger.

The main deposition mechanism of Al_{13} was self-aggregation. The deposition of Al_{30} was mainly due to the particulate aluminum deposition. The observed aluminum deposition of Al_0 might be mainly due to the formation of amorphous $\text{Al}(\text{OH})_3$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in online version at <http://dx.doi.org/10.1016/j.jes.2015.05.010>.

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