Aluminium in drinking water: An overview

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Abstract

Aluminium (Al) is one of the trace inorganic metals present in drinking water. In addition to the naturally occurring Al in raw waters, use of Al-based coagulants especially $Al_2(SO_4)_3$ (alum) often leads to an increase in treated water Al concentrations. A high (3.6 to 6 mg/ℓ) concentration of Al may precipitate as aluminium hydroxide giving rise to consumer complaints. Al is also a suspected causative agent of neurological disorders such as Alzheimer's disease and presenile dementia. During conventional water treatment processes, Al undergoes various transformations (also called 'speciation' of Al) which are influenced by factors such as pH, turbidity, temperature of water source, and the organic and inorganic ligands present in water. Chemical precipitation, reverse osmosis, electrodialysis and cation exchange methods are efficient in Al removal from water. This paper gives an overview of the presence of Al in drinking water with reference to its speciation, removal (treatment methods), water supply and health problems, and the regulation of its levels in drinking water.

Introduction

Al-based coagulants such as aluminium sulphate ($Al_2(SO_4)_3$) (better known as alum) or polyaluminium chloride (PACl) are commonly used in drinking water treatment to enhance the removal of particulate, colloidal, and dissolved substances via coagulation processes. The treatment of surface water with aluminium sulphate has been in operation for over a hundred years all over the world. The use of alum as a coagulant for water treatment often leads to higher concentrations of aluminium in the treated water than in the raw water itself.

Typically, a portion of the alum added to the raw water is not removed during treatment and remains as residual aluminium in the treated water. The occurrence of aluminium in treated water has been considered for many years to be an undesirable aspect of treatment practice (Driscoll and Letterman, 1988; Van Benschoten and Edzwald, 1990). There is considerable concern throughout the world over the levels of aluminium found in drinking water sources (raw water) and treated drinking water. This has arisen mainly for two reasons. First, acid rain has caused the aluminium level in many freshwater sources to increase (Schecher and Driscoll, 1988). A high (3.6 to 6 mg/ℓ) concentration of aluminium in treated water gives rise to turbidity, reduces disinfection efficiency, and may precipitate as $Al(OH)_3$ during the course of distribution (Rahman, 1992). Secondly, the possibility of an association between aluminium and neuropathological diseases including presenile dementia and Alzheimer's disease is frequently hypothesised (Schecher and Driscoll, 1988; Crapper and Boni, 1980; Davidson et al., 1982; Martyn et al., 1989; Gardner and Gunn, 1991; Jekel, 1991).

This paper reviews the presence of aluminium in drinking water with an emphasis on its speciation, removal, health problems, and regulation.

Aluminium speciation studies in drinking water

This section will focus on the methods available for the speciation of Al, including speciation terminology and the variables affecting speciation. Literature indicates that the use of any coagulant containing Al may either increase or decrease the Al concentration in the finished water depending on its speciation in the source water and conditions of treatment. However, for many water supplies (particularly where alum is used as coagulant), the total Al increases after treatment. The fate of Al during the water treatment process is not clearly understood since the majority of the water treatment plants measure either total or dissolved Al only. These data alone cannot explain the observed increase in Al levels, and there is a need to study the various transformations (speciation) of Al present in water to address this issue.

A review of the literature relating to Al speciation studies in drinking water indicates that there is no uniformity in defining the terms relating to various fractions of Al. However, there is general agreement on the following definitions to differentiate between the various Al fractions (Letterman and Driscoll, 1994). Total Al is the sum of suspended, colloidal and monomeric forms of Al. Particulate Al is the sum of suspended and colloidal Al. Monomeric Al can be divided into two forms: non-labile, and labile. Non-labile Al is Al associated with dissolved organic carbon. Labile Al includes aquo (Al^{3+}), and hydroxide, fluoride, and sulphate complexes of Al. Fig. 1 shows a block diagram of various forms of Al.

Three different approaches for fractionating Al in drinking water at ambient temperature have been described in the literature. Table 1 summarises these approaches and the Al species (or forms) they characterise. As can be seen from Table 1, the principal procedural differences among the methods are as follows:

- Organically bound Al was fractionated out separately by Van Benschoten and Edzwald (1990) and Driscoll and Letterman (1988) but not by Gardner and Gunn (1991).
- Gardner and Gunn (1991) measured reactivity and particle or molecule size, whereas Van Benschoten and Edzwald (1990) and Driscoll and Letterman (1988) attempted to determine chemical associations of Al present.
- Driscoll and Letterman (1988) did not include a filtering step to eliminate the problem of Al absorption on filters as their speciation method (acid digestion followed by oxine extraction) is sensitive only to dissolved Al.

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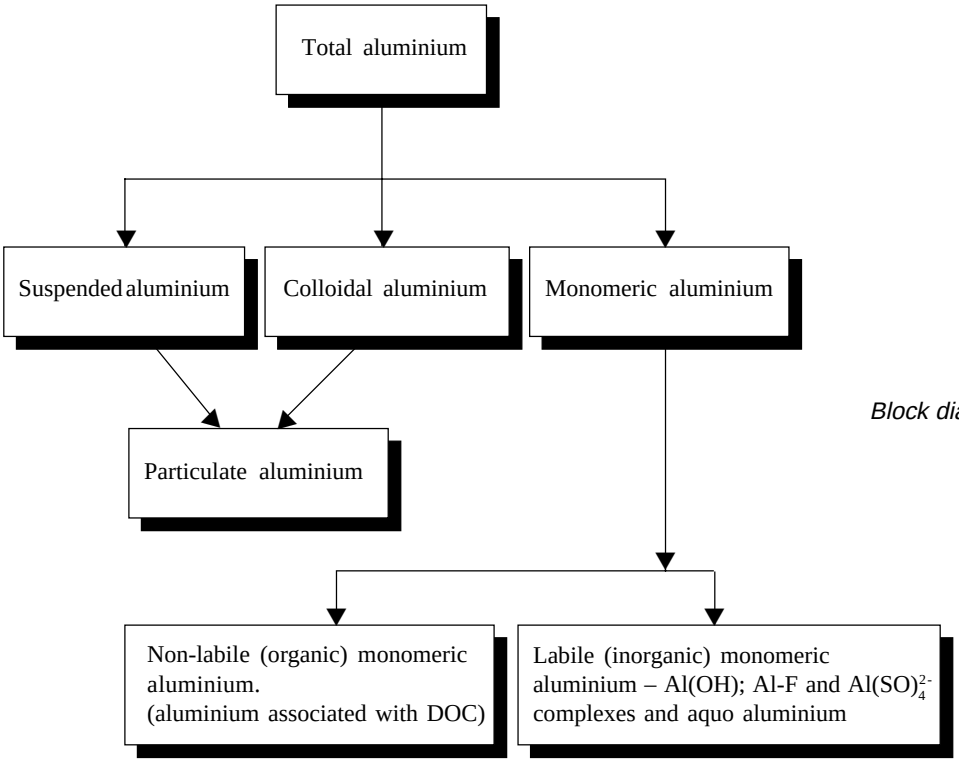

Figure 1
Block diagram showing various fractions of Al

All three studies recognised that Al in drinking water can exist in a mononuclear form as free Al (Al^{3+}) or can be complexed by other dissolved inorganic constituents (such as OH^-, F^-, SO_4^{2-}). It was also recognised that Al can be chemically bound to organic ligands or inorganic colloids. Al fractions, however, are quite different in raw water than in $Al_2(SO_4)_3$ - treated and filtered water. Much of the Al in raw water is associated with inorganic colloids or is bound to large organic molecules; the water contains only a small mononuclear fraction. Water treatment changes this distribution because of its emphasis on particle aggregation and filtration producing a treated water that is proportionately higher in mononuclear species.

Gardner and Gunn (1991) tested their Al speciation methodology in three water treatment plants. In one treatment plant, the raw water total Al concentration of 467 µg/ℓ was reduced to 120 µg/ℓ after treatment. In this plant the raw water total Al concentration was predominantly in particulate form and the treatment increased the concentration of low-molecular-mass chemically reactive species. In the second plant, Gardner and Gunn (1991) showed that treatment, applied to a relatively acid upland water (which had a relatively high proportion of a labile Al species) reduced all fractions of raw water Al. In treated water, the majority of the Al present, was in the form of low-molecular-mass chemically labile species. In the third case, Gardner and Gunn (1991) reported that there was little change in total Al concentration during treatment, but raw water particulate forms were replaced by low-molecular-mass forms of Al after treatment. Speciation studies of Gardner and Gunn (1991) showed that Al in water after treatment was often in a more chemically labile form than the more thermodynamically stable Al particles (minerals) found in raw waters. The organic fraction of Al is mostly associated with naturally occurring organic matter and is negatively charged. The inorganic or labile fraction of Al is positively charged. It can easily pass through a cell membrane and is also toxic. As the key issue of the study is to decide about the bioavailability and toxicity of Al, Gardner and Gunn (1991) did not separate out the organic fraction of Al.

Shovlin et al. (1993) reported that the significance of molecular mass and chemical lability to Al absorption is not known. But increased absorption of low-molecular-mass chemically labile forms as reported by Gardner and Gunn (1991) (in test humans) appears to be correct in the context of metal toxicity (Shovlin et al. 1993). Definite conclusions could not be drawn from this study about Al absorption as the study did not consider whether Al was associated with silicic acid or with fluoride. This is very important to decide the bioavailability of Al. Silicic acid may reduce the bioavailability and toxicity of Al by forming hydroxyaluminosilicate species with aqueous Al species. Fluoride may also reduce the bioavailability of Al by competing for absorption in the gut (Shovlin et al., 1993).

Driscoll and Letterman (1988) applied their speciation methodology at the Onondaga County Metropolitan Water Board treatment plant at Oswego, New York. The raw water source was Lake Ontario and the coagulant used at the plant was alum. In this method Al was fractionated into three groups:

- labile (inorganic) monomeric Al, which included aquo (Al^{3+}), and hydroxide, fluoride and sulphate complexes of monomeric Al;
- non-labile (organic) monomeric Al which was an estimate of Al that was associated with organic solutes (i.e. variety of organic acids of aquatic humic substances); and
- acid soluble Al which included particulate or very strongly bound Al-organic materials.

Raw water total Al concentration increased from 10±9 µg/ℓ to 49 ±9 µg/ℓ in filtered water. This showed a fivefold enrichment of the total Al after the addition of $Al_2(SO_4)_3$. Approximately 11% of the influent Al (present in raw water + Al contributed by $Al_2(SO_4)_3$ addition) was not removed during treatment and this residual Al was carried over through the distribution system. Raw water Al was mostly present in the particulate (3± 6 µg/ℓ) or non-

TABLE 1
ALUMINIUM FRACTIONATION IN DRINKING WATER (REIBER ET AL., 1995)*

Investigators	Al Fraction Group	Procedure	Fraction groups determined by difference
Driscoll and Letterman (1988)	1. Total reactive Al	Acid digested (HNO_3) at pH 1 for 1 h	Fraction 1 – fraction 2 is the concentration of acid soluble Al, including colloidal, polymeric Al, strong alumino-organic complexes
	2. Total monomeric Al	No acid digestion, extraction with 8-hydroxyquinoline	Fraction 2 – fraction 3 is labile monomeric Al, including free Al, monomeric aluminum sulfate, fluoride and hydroxide complexes
	3. Cation exchange treated monomeric Al	Passed through a strongly acidic cation exchange resin	Fraction 3 represents the non labile monomeric Al; also called monomeric alumino-organic complexes
Van Benschoten and Edzwald (1990)	4. Total reactive Al	Soluble Al after 1 h digestion (HNO_3) at pH 2	Particulate Al: fraction 4 – fraction 5
	5. Total dissolved Al	Acid soluble Al in a filtered sample, 0.22 µ-pore size	Polymeric and colloidal and strongly bound organic fraction: fraction 5 – fraction 6
	6. Dissolved monomeric Al	Filtered sample, no acidification, rapidly extracted with 8-hydroxyquinoline	Fraction 6 measures labile monomeric Al species such as free Al, monomeric aluminum hydroxide, fluoride, sulphate and monomeric organically bound Al
	7. Dissolved organically bound Al	Filtered sample passed through a column with a strongly acidic cation exchange resin and acidified before analysis	Dissolved inorganic: fraction 5 - fraction 7
	8. Dissolved organic monomeric Al	Filtered sample passed through same resin described in fraction 7 and analyzed without acidification	Dissolved inorganic monomeric fraction: fraction 6 - fraction 8
Gardner and Gunn (1991)	9. Total Al	Acid digestible	
	10. Dissolved Al	Filterable through a 0.45 µ-pore size filter	
	11. Low-molecular weight aluminum	Dialysis through a 1000 molecular mass - cutoff membrane	
	12. Chemically labile Al	Measured by speed of reaction with an Al binding agent	

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labile (organic) monomeric (7±6 μg/ℓ) form and concentrations of labile (inorganic) monomeric Al were insignificant. A shift in the distribution of Al fractions occurred due to water treatment. The treated water contained only a small amount (7±7 μg/ℓ) of particulate Al. Of the remaining Al, 71% was inorganic monomeric Al [out of which 52% was monomeric alumino-hydroxide complexes (21.8±10 μg/ℓ); and 19% was alumino-fluoride complexes (8±4 μg/ℓ)] and 29% was (non-labile) organic Al complexes (12 ± 8 μg/ℓ)]. Fluoridation and sulphuric acid addition used by the water treatment plant as part of the water treatment, coupled with seasonal variations in water temperature were largely responsible for the shift in the speciation of Al between raw and treated water (Driscoll and Letterman 1988).

Van Benschoten and Edzwald (1990) applied their speciation methodology at two water treatment plants; one at Denvers, Massachusetts and another at Burlington, Vermont. The authors purposefully selected these plants as they had different raw water characteristics and used different coagulants. The raw water source for Denvers plant was Middleton Pond which had low turbidity (< 2 NTU) and high natural organic matter (10 mg/ℓ). $Al_2(SO_4)_3$ was used for coagulation. The raw water source for the Burlington plant was Lake Champlain, which had moderate alkalinity (48 mg/ℓ), low turbidity (< 2NTU) and low concentrations of dissolved organic carbon (3 mg/ℓ). The coagulant used was Ultrion, an aluminium chloride and organic cationic polyeletrolyte mixture. Five different forms of Al were determined in this method. These included:

- total reactive Al
- total dissolved Al
- dissolved monomeric Al
- dissolved organically bound Al and
- dissolved organic monomeric Al (Table 1 shows details of Al groups).

Raw and treated water Al at both the plants were largely present as dissolved Al. Speciation results showed that the organically bound Al accounted for 75% and 90% of the dissolved Al in the raw water of the Denver and Burlington plants respectively. In treated water, these percentages decreased to 45% and 67% respectively. At the Denvers plant most of the dissolved Al (present in raw, clarified, filtered and treated waters) was in organic form, due to high raw water dissolved organic carbon, whereas the organically bound Al fraction at the Burlington plant at all stages (raw, clarified, filtered, and treated waters) was low due to low dissolved organic carbon levels of the raw water. The pH of coagulation, pH of the treated water and temperature were important factors influencing the residual Al concentrations. Review indicates that all the three speciation methods are equally suitable and can be applied to water treatment plants treating different raw waters.

Lazerte (1984) studied the speciation of Al in some Ontario (Canada) surface waters using dialysis and batch chelating resin techniques. In these waters, pH values were in the range of 6.5 to 7.0 (minimum solubility of Al) and hence Al concentrations were generally lower (20 μg/ℓ) and largely in an organic form. However, as surface water pH decreased, the distribution of Al shifted with increasing predominance of inorganic forms. Lazerte (1984) reported that inorganic Al in Ontario waters was predominantly complexed with fluoride (F).

Residual aluminium

This section deals with the components of residual Al (Al leaving the treatment plant in treated water and entering into the distribution system) and the factors influencing its distribution. Residual Al consists of dissolved and particulate species. Particulate Al can be easily removed by efficient operation of solid liquid separation facilities such as clarifiers and filters. Dissolved Al species are complex, and can include complexes with natural organic matter, fluoride, phosphate, sulphate, and hydroxyl ion. At acidic pH (pH = 5.8) and high F concentrations ($F \geq 0.23$ mg/ℓ), complexation reactions between Al and F are quite efficient (Roberson and Hem, 1969). Al-F complexes are soluble and could potentially increase residual Al concentrations. However in practice, F is added to the water following filtration and pH adjustment to a slightly alkaline pH (pH = 7.5 to 7.7). At alkaline pH, hydroxyl ion outcompetes F for Al and this should theoretically minimise the impact of F on residual Al. Natural organic matter (NOM) is also known to form strong complexes with Al, but it may also be a parameter affecting residual Al in treated waters, depending on raw water NOM levels and % removal of NOM by plants.

Temperature, pH and turbidity of the water are important factors in determining Al solubility and consequently residual Al. Al being an amphoteric element, is soluble at extremely acidic (pH < 6) and alkaline (pH > 8.5) conditions, but is insoluble at near neutral pH values (7.0 to 7.5). At lower temperature (4°C), the pH of minimum solubility increases, resulting in alum coagulation and hence resulting in higher residual Al levels. Jekel (1991) reported a correlation between residual Al and effluent turbidity. Specifically, residual Al concentrations were less than 0.1 mg/ℓ when the effluent turbidity was less than 0.15 NTU. This shows that low effluent turbidity would yield low particulate Al, leading to a reduction in residual Al.

Effects of type of filters on dissolved aluminium

Rezania (1985) investigated the effects of membrane filter material and pore size on the dissolved Al concentration using Millipore 0.45 micron (cellulose acetate), Nalgene 0.2 micron (cellulose acetate) and Nuclepore 0.2 micron (polycarbonate) filters. He conducted jar test experiments using three water samples (artificially prepared water which had 80 colour units on the platinum-cobalt scale) at acidic (4.6), neutral (6.9) and basic pHs (9.0). The filtration of the samples showed that the 0.2 μ cellulose acetate membrane filter (Nalgene) exhibited the most adsorption compared to the other filters (namely Millipore 0.45 μ cellulose acetate and Nalgene 1.2 μ cellulose acetate, while the 0.2 μ polycarbonate membrane filter (Nuclepore) showed the least adsorption regardless of the pH variation. Due to adsorption, the filter pore sizes of the Nalgene cellulose acetate membranes were reduced and hence they showed lower amounts of Al in the filtered portion compared to the Nuclepore polycarbonate filter. It can be concluded that delineation between dissolved and particulate Al is operational, and filter type and pore size significantly influence dissolved Al measurements.

Aluminium in water supplies

The presence of Al in water for domestic supplies is due either to the addition of Al salts in the course of coagulation and flocculation treatment, or is caused by a low pH (pH = 5.5± 0.5) value of either surface or groundwaters (Jekel, 1991).

Barnett et al. (1968) reported that the use of $Al_2(SO_4)_3$ as a coagulant in the treatment of drinking water increased the Al concentration in finished water. According to Kopp (1969), a five-year survey of 1 577 raw surface waters of the USA showed a 31.2% frequency of detection for Al, with ranges from 1 to 2 760 µg/ℓ and a mean of 74 µg/ℓ. The same survey on 380 finished waters showed a 47.8% frequency of detection for Al, with ranges from 3 to 1 600 µg/ℓ and a mean of 179.1 µg/ℓ. Bodek et al. (1988) found that, in US surface waters, the mean concentrations of suspended and dissolved Al were 3 860 µg/ℓ and 74 µg/ℓ respectively. The suspended form was observed in 97% of the samples, while dissolved Al was detected in only 31% of the samples. This showed that the raw water Al was predominantly in particulate form.

Sorenson et al. (1974) reported that the levels of Al found in groundwater were low (0.2 to 100 µg/ℓ) and were negligible when compared to surface water concentrations. The levels found naturally in raw surface water ranged from about 10 to 2 000 µg/ℓ (Sorenson et al., 1974). Al levels in areas where surface waters have become acidified (pH ~ 4.0 to 5.0) were in excess of 40 000 µg/ℓ. The maximum Al level found in treated water was 1 029 µg Al/ℓ (Schenk et al., 1989).

Driscoll and Letterman (1988) reported that approximately 11% of the Al input (through raw water and $Al_2(SO_4)_3$) remained in the finished water as residual Al and was transported through the distribution system without any significant loss. Letterman and Driscoll (1988) also found that high concentrations of Al in drinking water were related to both raw water concentrations and high treated-water turbidity. Surveys of residual Al in the United States (Miller et al., 1984; Letterman and Driscoll 1988) and in Europe (Sollars et al., 1989) have also shown similar results. The major findings of the studies were that $Al_2(SO_4)_3$ increased treated-water concentrations of Al, with the mean concentration values of Al from facilities using $Al_2(SO_4)_3$ as a coagulant being approximately 0.1 mg/ℓ; the Al concentrations in treated waters were, however, highly variable (0.05 to 0.25 mg/ℓ).

There is reported to be a 40 to 50% chance of increase in Al concentrations in drinking water over the concentrations in the raw water in plants using Al-based coagulants (Miller et al., 1984). In a USEPA survey of 186 water utilities, Miller et al. (1984) found that after coagulation with Al salts, the Al concentration in the treated water varied from 0.01 to 2.37 mg/ℓ. It can be concluded that $Al_2(SO_4)_3$ - treated waters generally contain more Al than raw surface waters.

Water supply problems

There has been concern over the use of Al salts as coagulants in the treatment of potable water, since elevated concentrations of Al in treated water may result in a variety of water supply problems. Water supply problems associated with increased Al concentration in treated water include the formation of a hydrous Al precipitate in the distribution system which may increase turbidity and the number of complaints about clarity (Costello, 1984). Hoff (1974) reported that Al floc in the system may interfere with the disinfection process by enmeshing and protecting micro-organisms. Another problem attributed to increased Al concentration is deposition of Al hydrolysis products on pipe walls, which decreases carrying capacity. Hudson (1966) noted that even thin coatings may result in a significant pressure drop and Costello (1984) reported that deposition of hydrous Al on pipes was a serious and widespread problem.

Health effects of aluminium

The presence of Al in drinking water has given rise to discussions on possible health effects, because of its suspected connection with Alzheimer's diseases or dialysis encephelopathy (Jekel, 1991). As early as 1942 Kopeloff et al. (1942) and Later Klatzo et al. (1965) indicated that studies in which animals were exposed to Al under controlled conditions demonstrated a correlation between neuropathological disorders and Al intake. Crapper and Boni (1980) observed a relationship between Al and both Alzheimer's disease and dialysis encephalopathy in humans. Davidson et al. (1982) found that kidney dialysis patients suffered dementia when their dialysis fluid contained an Al concentration of 80 µg/ℓ. Removal of Al from the fluid prior to dialysis decreased symptoms of dementia in patients.

Driscoll and Letterman (1988) reported that dialysis patients exposed to elevated Al may exhibit dialysis enchepholopathy, and/or bone mineralisation disorders such as dialysis osteodystrophy. Martyn et al. (1989) based on a survey of 88 county districts in England and Wales reported that rate of Alzheimer's disease was 1.5 times higher in districts where the mean Al concentration exceeded 0.11 mg/ℓ than in districts where concentrations were less than 0.01 mg/ℓ.

Al shows low acute toxicity. Chronic exposure data are limited, but indicate that Al likely interferes with phosphorus absorption, and causes weakness, bone pain and anorexia. Carcinogenecity, mutagenicity and teratogenicity tests have all been negative (Carol and Arnold, 1990). Baker and Schofield (1982) reported that the OH and F complexes of Al are highly labile (inorganic) and may be more bioavailable and harmful than organic or particulate forms of Al. Driscoll (1984) also confirmed, based on Al toxicity studies, that positively charged Al hydroxy species are much more toxic to fish than organic complexes. Nevertheless the bioavailability of Al species to humans is not known and hence definite conclusions cannot be drawn from these studies.

Aluminium removal from drinking water

In nature, Al exists in the trivalent oxidation state, i.e. Al^{3+}. Its electric charge and the small ionic radius (0.51Å) give Al^{3+} a strong polarising effect on adjacent atoms; therefore the element is too reactive to be found free in nature. As a strongly hydrolysing element, Al is practically insoluble in the pH range of 6.5 to 8.5; the solubility is enhanced under acidic pH (pH < 6) or alkaline pH (pH > 8.5) conditions, and/or in the presence of complexing ligands.

The transformation of the Al ions into $Al(OH)_3$ one of the mechanisms for Al removal, (hydrolysis) is a complex process involving several steps. But Licsko and Szakal (1988) gave a simplified version as shown below:

$$[Al(H_2O)_6] + H_2O \rightarrow [Al(H_2O)_5OH]^{2+} + H_3O^+$$
$$[Al(H_2O)_5OH]^{2+} + H_2O \rightarrow [Al(H_2O)_4(OH)_2]^+ + H_3O^+$$
$$[Al(H_2O)_4(OH)_2]^+ + H_2O \rightarrow [Al(OH)_3.3H_2O] + H_3O^+$$

The H_3O^+ ions formed above during the hydrolysis of the Al ions have to be removed from the system in order to facilitate formation of $Al(OH)_3.3H_2O$. This is generally accomplished in surface waters because of the presence of HCO_3^- anions as shown below:

$$H_3O^+ + HCO_3^- \rightarrow H_2CO_3 + H_2O$$

The poorly dissociating weak carbonic acid formed above does not impede the formation of the poorly water soluble aluminium hydroxide. The above equations show that the extent of change in pH caused by the $Al_2(SO_4)_3$ mainly depends on the buffering capacity [HCO_3^-(bicarbonate) concentration of the raw water] and type of $Al(OH)_3$ formed. In other words, the formation of $Al(OH)_3$ species, which is important from the point of view of the residual Al concentration, depends on both the pH and the HCO_3^- concentration of the raw water.

Based on the chemistry of Al removal, Licsko and Szakal (1988) conducted pilot-plant as well as bench-scale experiments to examine the possibility of reducing the Al concentrations in drinking water from waterworks drawing on surface water in Hungary. The objectives of the experiments were to compare the model system developed with a number of surface waters in Hungary as regards change in pH and the concentration of Al persisting in the dissolved condition at different $Al_2(SO_4)_3$ feed rates.

Model and surface waters tested, containing 1.62 to 8.1 mg/ℓ Al, showed that low initial alkalinity (0.66 meq/ℓ of $CaCO_3$) and high feed rates of $Al_2(SO_4)_3$ (80 to 120 mg/ℓ) as well as high initial alkalinity (3.7 meq/ℓ of $CaCO_3$) and low feed rates of $Al_2(SO_4)_3$ produced dissolved Al concentration levels higher than 0.2 mg/ℓ in filtered water, compared to raw water at all raw water Al concentrations (Licsko and Szakal, 1988). It is known that, for every 1 mg/ℓ of $Al_2(SO_4)_3$ that precipitates as $Al(OH)_3$, 0.5 mg/ℓ of alkalinity (expressed as $CaCO_3$) is consumed. Experiments of Licsko and Szakal (1988) demonstrated that low initial alkalinity (alkalinity prior to the addition of $Al_2(SO_4)_3$) and high feed rates of $Al_2(SO_4)_3$ (say Condition 1) as well as high initial alkalinity and low feed rates of $Al_2(SO_4)_3$ (say Condition 2), would result in either low pH (< 6 for Condition 1) or high pH (> 8 for Condition 2). These two conditions (1 and 2) increased soluble Al in treated water. This showed the effect of initial alkalinity (alkalinity prior to the addition of aluminium sulfate) on the dissolved Al concentration.

There existed a slight difference between the model systems and surface waters as far as the range of pH was concerned in which dissolved Al concentrations of less than 0.2 mg/ℓ were measured. Thus in model systems the pH range in which the dissolved Al concentration was lower than 0.2 mg/ℓ was 5.25 to 7.25 but for surface waters the range of pH was 5.7 to 7.5. Licsko and Szakal (1988) attributed this pH variation to the difference in ion contents between the waters tested. In these pH ranges more than 95% of the Al ions introduced were transformed to a solid form (aluminium hydroxide precipitate).

Jasim et al. (1997) investigated the reduction of Al in drinking water in a pilot-scale water treatment plant located at H A Weeks Water Treatment Plant, Windsor Utilities Commission, Windsor, Ontario. The authors reported that pH depression (when alum was used with sulphuric acid (Case 1) down to as low as 6.5 yielded a significant reduction in soluble Al concentration, compared to use of $Al_2(SO_4)_3$ without the addition of sulphuric acid (Case 2). Soluble Al levels for Case 1 were 30, 40 and 75 µg/ℓ at pHs of 6.5, 6.7 and 6.9 respectively. For Case 2, soluble Al levels were 120, 140, and 150 µg/ℓ at pHs of 7.3, 7.5 and 7.6 respectively. These experiments show that soluble Al is dependent on the pH value.

Patterson (1985) reported that the treatment technology for Al removal was limited to chemical precipitation by pH adjustment. This practice is well established in potable water treatment, where Al compounds are commonly employed as treatment chemicals. Jekel (1991) also reported that the primary physico-chemical process involved in removing Al species is the precipitation of $Al(OH)_3$ in the pH range of 6.5 to 8.0. Sulphate has the effect of broadening the pH range of coagulation to the acid side (pH = 6.0) and it also acts as a catalyst in the formation of solid $Al(OH)_3$ particles.

Conventional solid-liquid separation steps (settling, flotation and rapid filtration) are applied after pH correction or coagulation. The residual Al concentration is generally controlled by the pH value and the quality (ability to produce low turbidity) of the rapid filtration step (Jekel, 1991). Jekel (1991) measured the residual Al content of filtered water and turbidity of four water treatment facilities in Germany. The data showed that residual turbidities of less than 0.15 NTU resulted in an Al residual of 0.1 mg/ℓ. Jekel (1991) recommended that the necessary technology for turbidity control down to 0.15 NTU could be double-layer filtration, optimised filter operation or the secondary addition of a coagulant aid (polymer or ferric ion).

Reijnen et al. (1992) reported that a double-layer filter bed consisting of a 1 m sand layer (0.8 to 1.2 mm fraction) and a 1 m hydro anthracite layer (1.4 to 2.5 mm) at a filtration rate of 7.5 m/h was able to remove 30 to 60% of Al introduced in a softening plant by the addition of lime. The wide range (30 to 60%) for Al removal could be attributed to the fact that:

- the lime softening plant used different limes containing a wide range of (0.1 to 0.55%) Al_2O_3 and
- the source water was groundwater, containing varied levels of divalent cations such as calcium and manganese.

Reijnen et al. (1992) further reported that secondary filtration through a 0.9 m sand bed (0.8 to 1.25 mm fraction) at a filtration rate of 2.3 to 4.6 m/h was able to remove about 80% of the Al added for the purpose of coagulating 0.2 mg/ℓ of Fe that escaped the first filtration in a treatment plant. Reijnen et al. (1992) also found that the Al concentration in groundwater (Netherlands) was reduced from about 0.1 to about 0.025 mg/ℓ when the water was filtered through a 2 m deep bed of limestone. The pH value rose from 6.2 to 7.6.

Nilson (1992) indicated that high [Al] can be reduced by chemical treatment. The experiments conducted by Nilson (1992) showed that [Al] in raw water was reduced from 150 µg/ℓ to less than 5 µg/ℓ when the water passed through a bed of apatite (calcium phosphate minerals).

In this experiment the raw water which had an Al content of 0.15 mg/ℓ was reduced to 0.005 mg/ℓ, but the pH rose from 5.8 to 6.5 because the apatite had an alkalising effect. A disadvantage was that some phosphate was dissolved from the apatite. Phosphate is not good in the treated water as it provides a conducive milieu for growth of algae/bacteria in the distribution system.

Monteagudo (1989) recommended the use of deionisation and reverse osmosis for removing Al from water to be used in dialysis units.

The general effectiveness of water treatment processes available for Al removal is shown in Table 2. From the table, it can be seen that treatment by cation exchange resin, reverse osmosis and electrodialysis would remove 90 to 100% of Al present in water. Treatment methods namely aeration/stripping, chemical oxidation/disinfection and ion exchange (anion) are ineffective for Al removal. Processes such as coagulation, sedimentation and filtration (combined) as well as lime softening are moderately effective in Al removal. Table 2 shows that not many data are available to predict the removal efficiency of activated carbon. But preliminary analysis at Buffalo Pound Water Treatment Plant

TABLE 2
TREATMENT PROCESSES FOR THE REMOVAL OF ALUMINIUM FROM WATER[a]

Sl No	Process	Efficiency %	Remarks
1	Aeration and stripping	0 - 20	Poor
2	Coagulation process, sedimentation, filtration	0 – 60	Fair
3	Lime softening	40 - 70	Fair to good
4	Ion exchange-anion resin	0 – 20	Poor
5	Ion exchange-cation resin	90 – 100	Good to excellent
6	Reverse osmosis	90 – 100	Excellent
7	Ultrafiltration	------	Not available/Insufficient data
8	Electrodialysis	90 – 100	Excellent
9	Chemical oxidation/ Disinfection	0 – 20	Poor
10	GAC-adsorption	-----	Not available/Insufficient data
11	PAC-adsorption	-----	Not available/Insufficient data
12	Activated alumina	-----	Not available/Insufficient data

[a] Reproduced from Water Quality and Treatment (1990) *A Handbook of Community Water Supplies*. Pontius FW (ed.) AWWA Publication (4th edn.) Copyright© 1990, McGraw-Hill Inc., New York. Reproduced with permission of the McGraw-Hill Companies.

(BPWTP), Saskatchewan, Canada, showed that Al in sand filtered effluent of (37 µg/ℓ) was reduced to (13 µg/ℓ) when passed through granular activated carbon contactors and the corresponding removal efficiency was 65%. This indicates that soluble Al is adsorbed in activated carbon. Detailed studies are underway at the plant, in order to evaluate the removal efficiency of activated carbon for Al.

Regulation of aluminium in drinking water

The United States Environmental Protection Agency (USEPA) promulgated a secondary maximum contaminant level range of 0.05 to 0.2 mg/ℓ in its Phase II rule published in 1991(Federal Register, 1991). The purpose of this standard is to ensure removal of coagulated material ahead of the distribution system. The USEPA preferred to specify a range rather than adopt a specific number since raw water quality and operating conditions of each water treatment plant differs considerably and this kind of range would provide flexibility for water treatment plants. The Swedish level of 0.10 mg/ℓ was also fixed exclusively to avoid problems in the distribution systems. In Canada, the Ontario Ministry of Environment has an operational (not a regulatory) guideline of 0.1 mg/ℓ for residual Al. But at present there is no Canadian guideline value on the maximum acceptable concentration of Al in drinking water (Gammie, 1996). Table 3 shows the limit adopted by some countries for Al in drinking water. The maximum allowable concentration of Al in drinking water is 0.2 mg/ℓ in the European Economic Community (now European Union). The World Health Organisation (WHO) has proposed a guideline value of 0.2 mg/ℓ. These values are not based on any assessment of risks to health but they provide a compromise between the use of Al salts in water treatment and discoloration (due to $Al(OH)_3$ floc) of distributed water. Except for the maximum permissible concentrations established by the former European Economic Community, all the other values are guidelines.

Conclusions

Speciation of Al in drinking water varies from plant to plant depending on pH, temperature of water during treatment, and type of organic and inorganic ligands present in a raw water source. Treatment conditions such as the amount of $Al_2(SO_4)_3$ added and filtration efficiency can also influence the speciation results. Separation of particulate and dissolved forms of Al and use of cation exchange resin to separate inorganic and organic fraction of Al are important facets of Al speciation studies in water supplies. A review of literature indicates that pore size and type of filter material could significantly affect dissolved and particulate Al measurements. A drawback of the cation exchange method is that it could probably overestimate inorganic Al due to high resin affinity for Al and further it is questionable whether organically complexed Al in the original solution remains complexed during its passage through the column of exchange resin.

At present there is no regulatory requirement for Al based on health effects since health effects of Al are still under investigation. Processes contributing to concentration levels, speciation, and fate of residual Al must be better understood before drinking

TABLE 3
INTERNATIONAL WATER QUALITY STANDARDS FOR ALUMINUM IN DRINKING WATER

Organisation/ Government	Guideline levels (mg/ℓ)	Maximum acceptable concentration (mg/ℓ)	Reference
WHO	0.2	----	Letterman and Driscoll (1994)
EEC	0.05	0.2	Letterman and Driscoll (1994)
Belgium	0.05	0.1	Nilsson (1990)
FRG	0.05	0.2	Nilsson (1990)
Sweden	----	0.1	Nilsson (1990)
Switzerland	0.05	0.5	Nilsson (1990)
USEPA	0.05	0.2	Letterman and Driscoll (1994)
AWWA Recommended Operating Level	----	0.2	Letterman and Driscoll (1994)
1986 Proposed Illinois Regulation	0.1	-----	Driscoll and Letterman (1988)
New York State guidelines on Al in filtered water for pilot-plant studies. Minimum percent of recorded values 95 75 50	 < 0.15 < 0.09 < 0.05	 ---- ---- ----	Letterman and Driscoll (1994)
Finland	----	0.2	Nilsson (1990)
Denmark	0.05	0.2	Nilsson (1990)
Austria	----	0.2	Nilsson (1990)
California Code of Regulations(maximum contaminant level)		1.0	Letterman and Driscoll (1994)

water standards for Al can be proposed and applied. Development of an Al guideline value should take into consideration both particulate and dissolved phases. The technical and economic feasibility of designing operational procedures that minimise either dissolved Al or particulate Al should be evaluated on a case-by-case basis.

As an operational tool to minimise Al residuals in finished water, utilities should consider determining the relationship between residual Al and turbidity in their water. Water utilities treating surface water using $Al_2(SO_4)_3$/PACl (polyaluminium chloride) and ferric salts should be surveyed to assess how the various coagulants affect residual Al speciation and its concentration in drinking water.

Available medical and scientific evidence does not support any definite link between Al in drinking water and neurological disorders (AWWA, 1997). Prudence, however, dictates that water utilities using $Al_2(SO_4)_3$ should routinely monitor and voluntarily limit the Al residual in the finished water. An operational value of 100 to 200 mg/ℓ, which is generally recommended on an aesthetic basis, should be acceptable. In this context, guideline values on arsenic and disinfection by-products requiring elevated doses of coagulants and higher pH (above the pH for minimum solubility for Al) required to minimise Pb and Cu levels in distribution systems, should be kept in mind. Until medical evidence on health effects is conclusive or the bioavailability of Al in drinking water is significant in comparison with the other modes of entry into the body, any strict regulation limiting the level of Al in drinking water may not be required.

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