

# **Original Research Article**

## **Risk of residual aluminum in treated water with aluminum sulphate**

### **Abstract**

Water treatment by aluminum sulphate is the most used process in water purification water to remove unwanted microorganisms. The inorganic coagulants are partially hydrolyzed salts. Their dissolution in water depends mainly on the pH thereof. However, there are still residues after dissolving aluminum. The determination of residual aluminum in the treated water is determined by the metered addition method. The treated water from the treatment plant contained 210 g / L residual aluminum for an average dose of 40mg / L of aluminum sulphate. The residual aluminum in treated water exceeds WHO standards (200µg / L), and far from the recommended standards of 100 g / L in all searches.

We made trials with laboratory flocculators under the same conditions that station. The residual aluminum obtained by the same metered addition method, is 182 mg / L, 13.33% less than the WHO standards.

one another trial is carried out with a dose of 40 mg / L alum, as adjuvant we used a bentonite from M'Zila (Algeria) with a dose of 3mg / L. This test has helped reduce the amount of residual aluminum in raw water 20.48%, lower than the recommended standards


In order to investigate the causes of this excess, we made trials with laboratory flocculators under the same conditions that station. The residual aluminum obtained by the same metered addition method, is 182 mg / L, 13.33% less than the WHO standards.


The dry residues were characterized by analysis by scanning electron microscope and EDX (MEB-EDX) for show the different spectra of the aluminum in the dry residue. The crude bentonite is characterized by the elemental chemical method using X-ray fluorescence.

Keywords. Aluminum sulphate, bentonite, residual aluminum, MEB-EDX, fluorescence X.


### **INTRODUCTION**


The residual aluminum present in water that has been treated clarification with aluminum sulphate may be the result of an overdose or no conditions favourable to its hydrolysis (pH and temperature). The Flocculants bind to in suspension particles and cause them to precipitate as sludge at the bottom of flocculators and decanters. If the conditions are not met some of the aluminum remains in solution. Epidemiological studies have mounted the dangers of aluminum and some countries have taken precautionary there's no long ago. Canada, for example,

35 tolerates only than 100µg / L in the treated water. in France, epidemiology  
 36 research team of Professor Jean François Dartigues University of Bordeaux has  
 37 published several articles in the American Journal of epidemiology (Rondeau et  
 38  2000; RONDEAU and COMMENGES, 2001; RONDEAU et al, 2006.)  
 39 treating the aluminum relationship and Alzheimer's disease. Much work  
 40 advocating a tolerable threshold limited to 100µg / L in water used for drinking,  
 41 while remaining vigilant about monitoring in water treatment plants. The  
 42 inorganic monomeric aluminum represents their main fraction of aluminum after  
 43 treatment of the water (62% of total).

44 A study performed in Europe estimated that the intake of aluminum from drinking  
 45 water is less than 5% of daily intake from other sources  food, utensils, medicines  
 46 etc.), (SOLLARS et al., 1989).

47 An estimated total daily average intake of 8.26 mg or the share contributed by the  
 48 water is less than 0.4 mg of aluminum.

49 Higher concentrations are found in drinking water in relation to the quality of raw  
 50 water over loaded if the pH is not controlled properly during the steps of and  
 51 optimizing the dose in steps of coagulation , decantation and filtration  
 52 (MEGHZILI et al, 2012; American Water Works Association Research  
 53 Foundation, 1993). In distribution networks disinfection the process can be  
 54 limited if we find high levels of residual aluminum that retains and protects   
 55 microorganisms (American Water Works Association Research Foundation, 1993.  
 56 COSTELLO., 1984). The best results are obtained with pH 6 and 7, minimum  
 57 solubility range of aluminum hydroxide during coagulation (LETTERMAN and  
 58 DRISCOLL., 1988).

59 The chemistry of aluminum in water can be described by several forms (BAES  
 60 and Mesmer  1976; and MOTEKAITIS MARTELL, 1988; JEAN PIERRE  
 61 MARC HENRY JOLIVET and 1998...):

62 → five monomers:  $Al^{3+}$ ,  $Al(OH)^{2+}$ ,  $Al(OH)_2^+$ ,  $Al(OH)_3^0$ ,  $Al(OH)_4^-$

63 → three polymers:  $[Al_2(OH)_2]^{4+}$ ,  $[Al_3(OH)_4]^{5+}$ ,  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

65 → a precipitate:  $Al(OH)_3$

66 Of aluminum mononuclear hydrolytic products combine to form polynuclear  
67 species in solution (Rondeau et al., 2000). Aluminum begins to polymerize when  
68 the pH of an acidic solution substantially increases beyond 4.5: (BERTSCH and  
69 PARKER., 1996)



71 Polymerization produces larger structures gradually and eventually lead to the  
72 formation of the Al<sub>13</sub> polycation (Parker and BERTSCH., 1992a, 1992b).

73 According to Jones and BENOIT (1986) the aluminum in the treated water is  
74 largely located in dissolved forms. The dissolved aluminum is defined as  
75 aluminum that passes through a 0.22µm filter (MEGHZILI et al., 2012).

76 In highly charged water, it is important to control the total aluminum content by  
77 optimizing coagulation and filtration processes. We must control the dosage of the  
78 coagulant and coagulation pH, because it must be accompanied by good stirring  
79 allowing good flocculation of suspended solids will facilitate their decantation  
80 before the step of filtration.


81 Neglect of these steps may cause an increase of residual aluminum. The pH is  
82 one factor that determines the form of aluminum present in water and her  
83 solubility increases in lower pH (MARTELL and MOTEKAITIS., 1989).


84

## 85 1. MATERIALS AND METHODS

### 86 1.1. Operating procedure

87 Analytical results of the raw water the treated water station are shown in  
88 Table 1

89 Tab . Physic-chemical analysis of water supply (Central Laboratory of  
90 the company's petrochemical industries, ENIP).

Parameters	Units	Raw water	Treated water station
Aspect	-	Disorder	Limpid 
pH	-	8.10	7.78
Conductivité	µs/ cm	418	425

TDS	mg/L	360	340
MES	mg/L	42	Traces
Chlorures	mg/L	78.55	72.73
Carbonates	mg/L	Traces	Traces
Bicarbonates	mg/L	132.41	127.32
Ca	mg/L	50.79	50.79
Mg	mg/L	14.40	14.40
TH	°F	18.6	18.6
Sulfates	mg/L	46.23	44.20
Phosphates	mg/L	Trace	Traces
Potassium	mg/L	4.9	4.9
Sodium	mg/L	9.3	8.3
COD	mg/L	38.02	1.68
Ammonium	mg/L	0.42	Traces
Nitrites	mg/L	Trace	Traces
Nitrates	mg/L	Traces	Traces
Total iron	mg/L	1.91	1.88
Cuivre	mg/L	0.37	0.36
Mercure	µg/L	3.80	0.76
Aluminium	µg/L	-	210.00
Turbidité	NTU	8.87	2.96
Organic matter content	Mg O <sub>2</sub> /L	8.70	5.55

## 1.2. Determination of the content of aluminum in the treated water

### 1.2.1. Principle

The aluminum with cyanine R Erichrome forms a red complex at pH 6. After 5 minutes, the analysis is performed at the wavelength of 535 nanometers. The method used is that of uploading

#### - Equipment


UV / visible type Shimadzu UV-1605.

98 - **reagents**

99 - Solution Erichrome cyanine R

100 - Acetic acid buffer solution pH 6

101 - Ascorbic Acid

102 - Solution 0.1 M EDTA 

103 - Sulphuric acid 0.05 M


104 - Al Solution 0.1 g / L

105 1.2.2. Procedure

106 Adjust the water sample at a pH of 3-3.5

107 Put 10ml of sample in 5 100mL flasks. In the first flask was added all reagents  
108 except for the aluminum standard solution (to adjust zero the spectrophotometer).

109 In other vials we put all reagents except EDTA and adding an increasing dose of  
110 standard aluminum. The absorbance of the solution of each flask was then  
111 measured is curve plotted  $A = f(C)$ , the absorbance versus concentration  
112 aluminum and from this curve the amount was determined of aluminum in the  
113 sample.

114 1.2.3. Description of tests jar-test 

115 The tests were conducted in a laboratory flocculator comprising six agitators and  
116 six 500mL beakers. The water to be treated is placed in each beaker. The rapid  
117 stirring is carried out at 200 rev / min; at time zero, are added increasing doses of  
118 alum in each of the beakers. the phase stirring rapid lasts three minutes. The  
119 rapid stirring followed by 17 minutes of slow stirring at 45 t / min. After  
120 decanting for 30 minutes, is taken a quantity of supernatant for analyze residual  
121 aluminum. The optimum dose of aluminum sulphate is 40 mg / L (determined by  
122 jar-test). In Table 2 we present the results of quality parameters analysis.

123 **Table II. Results of analyzes of quality parameters**

Parameters	Results of analyzes (jar-test)			
	Raw water	(jar-test) Aluminum sulphate	Treated water station (sulfate Al)	Aluminum sulphate +Bentonite
Doses (mg/L)	-	40	40	40 +3

Temperature (°C)	28	29,5	28	29
Conductivity (µs/cm)	545	538	559	576
pH	8,10	7,32	7,61	7,79
Salinity	0,3	00	00	-
Turbidity(NTU)	4,47	1,04	2,10	3,37
Organic matter (mg O <sub>2</sub> /L)	11,2	4,12	4,34	1,97
TH °F	21,00	20,40	26,20	-
TAC °F	11,50	9,70	8,10	-
%elimination turbidity	0	76,73	53,00	24,25
% élimination organic matter	0	63,21	61,25	42,41
Residual Aluminum (µg/L)	No detected	0,182	0,210	0,167

124

125 In Table 7, we have considered only the monitoring of the residual aluminum in  
 126 the jar-tests and water the treated in station, then to the same dose was added a  
 127 dose of 3 mg / L of bentonite as an adjuvant .to the end, the results will be  
 128 compared between them .

129

### 130 1.3. Analysis of solid materials

#### 131 1.3.1. Characterization bentonite

132 Bentonite is characterized by the entreprise National Products Non Ferrous  
 133 Mining and Useful Products (ENOF) in 2007.

134 **Table.3. Physico-chemical characteristics of the bentonite**

Surface spécifique m <sup>2</sup> /g	pH	Masse spécifique g/cm <sup>3</sup>	Capacité d'échange (Meq/100g)	Cations échangeables (meq/100g)			Na/ca
				Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>2+</sup>	
65,00	9,00	2,71	75,8	43,60	25,20	4,80	0,58

135

136 **Table 4. Mineralogical characteristics of bentonite**

Montmorillonite	Quartz	Carbonates	Feldspaths	Biotites
45 à 60%	15 à 20%	8 à 10%	3 à 5%	8 à 10%

137

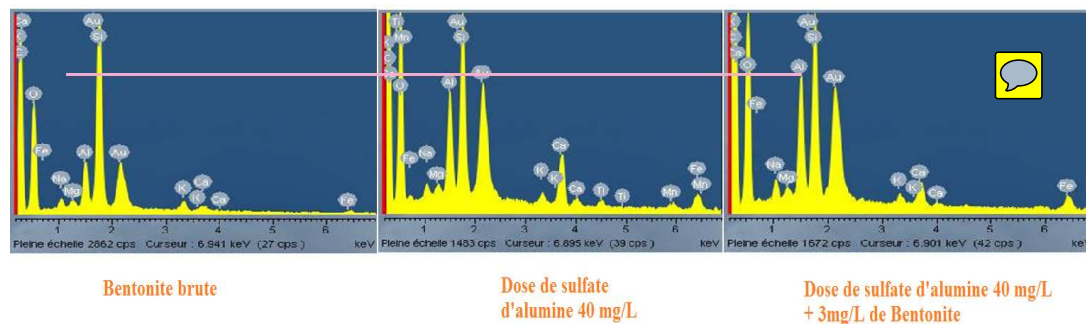
### 138 1.3.2. Electronic scanning microscopy

139 This operation allows to directly visualize the morphology (shape, size ) particles  
 140 and possible surface roughness .She is consists to scanned, line by line , the  
 141 surface of the particles by an incident beam of high energy electrons, thereby  
 142 causing the emission of secondary electrons of low energy. These are sent to a  
 143 detector which transmits the signal to a screen of which the scanning is  
 144 synchronized with the scanning of the sample. The contrast of the image reflects  
 145 the relief of the sample. These secondary electrons allow reconstruction of picture  
 146 magnified of the surface.

147 The laboratory clichés scanning electron microscopy were performed using a  
 148 Philips XL 30 microscope equipped with a field effect gun . The sample is  
 149 prepared by depositing the powder on the aluminum support coated with a thin  
 150 layer of graphite whose surface is adhesive. It is then metalized by vacuum, by  
 151 sputtering a layer of gold having a thickness between 10 and 20 nm.

### 152 1.3.3. MEB-EDX dry residues

153 Figure 1 shows the various spectra of the minerals present in different samples.  
 154 The peaks of aluminum varies from one sample to another. The higher amounts of  
 155 aluminum are located on the sample 3 and the second and lowest peak on the  
 156 sample 1. Figure 1 shows a larger concentration of aluminum on the cliché 3.



157

158 **Figure 1. The different spectra of dry residues of the three samples**

159 1.3.4. Fluorescence X

160 Fluorescence spectrometry is an elemental analysis method using the physical  
 161 property of the material for determine the concentrations of the pure in elements  
 162 .The X-ray spectrum emitted by the material is characteristic of the sample  
 163 composition. The spectrum analysis allows deducing the elemental composition of  
 164 the mass concentrations. The powder to be analyzed is put into a cup, and then  
 165 pressed onto a pellet of boric acid. The apparatus used is a fluorescence  
 166 spectrophotometer X MagiX Panalytical.

167 **Table 5. Quantification of raw bentonite sample**

Analyte	Compound of formula	Concentration %	Méthod of calculating
Na	Na <sub>2</sub> O	2.796	Calculated
Mg	MgO	2.913	Calculated
Al	Al <sub>2</sub> O <sub>3</sub>	14.031	Calculated
Si	SiO <sub>2</sub>	69.665	Calculated
P	P <sub>2</sub> O <sub>5</sub>	0.082	Calculated
S	SO <sub>3</sub>	0.491	Calculated
K	K <sub>2</sub> O	2.407	Calculated
Ca	CaO	4.098	Calculated
Ti	TiO <sub>2</sub>	0.350	Calculated
Mn	MnO <sub>2</sub>	0.168	Calculated
Fe	Fe <sub>2</sub> O <sub>3</sub>	2.879	Calculated
Rb	Rb <sub>2</sub> O	0.009	Calculated
Sr	SrO	0.041	Calculated
Cl	Cl	0.069	Calculated

168

169 **Table 6. Percentage of mass concentrations**

Element	Concentration %	Element	Concentration %
O	48.60	K	2.00
Na	2.07	Ca	2.93
Mg	1.76	Ti	0.210
Al	7.43	Mn	0.106



Si	32.6	Fe	2.01
P	0.0359	Rb	0.00844
S	0.197	Sr	0.0347
Cl	0.0690		

## 170 2. DISCUSSION OF RESULTS

171 We considered only the followed of residual aluminium.

172 **Table 7. Monitoring the residual aluminum in the different samples**

	Réactifs	Dose (mg/L)	Al résiduel	% Al résiduel/total Al
Water treatment station	Alumina sulphate	40	0,210	5,77%
Jar-test	Alumina sulphate	40	0,182	5,00%
Jar-test	Alumina sulphate	40	0,167	4,58%
	Bentonite	+ 3		

173

174 The 40 mg dose of aluminum sulphate / L gives 3.64 mg / L of aluminum. water  
 175 treated of station contains 5.77% of the total aluminum and thus constitutes the  
 176 residual aluminum. The pH water arriving at the station has a value of 8.10, less  
 177 favorable for the polymerization leading to the formation of the Al<sub>13</sub> polycation.  
 178 After treatment the pH does not exceed 7.61 and the minimum solubility range of  
 179 aluminum hydroxide during coagulation is at a pH of between 6-7 for best yields  
 180 (LETTERMAN and DRISCOLL., 1988) .

181 Aluminum sulfate, in addition to its action on the reduction of suspended solids  
 182 intervenes on lowering the pH. A pH of 7.61 obtained after treatment with  
 183 aluminum sulfate confirmed that there was no optimization of the various steps of  
 184 clarification (dose, pH, residence time, stirring etc.).

185 For the jar-test performed with SA of 40 mg / L, 5% of the total aluminum  
 186 remains in solution, limit advised in all work on the residual aluminum in drinking  
 187 water treatment.

188 The jar-test performed with 40 mg / L SA and 3mg / L bentonite, residual  
 189 aluminum is 4.58% of the total aluminum, well below the 5% recommended.

190 According Sollars et al (1989), in a study of aluminum in drinking water in  
191 Europe have also shown that the aluminum contribution of drinking water is less  
192 than 5%.

193 The optimum dose determined by jar-test has eliminated 95% of the total  
194 aluminum after filtration.

195 Incidentally, during the process of agglomeration or coagulation, much of  
196 aluminum contained in the aluminum salts added is hydrolyzed to give the  
197 aluminum hydroxide which precipitates and becomes part of the floc . This  
198 aluminum is therefore part of the sludge generated by the treatment process. It is  
199 possible that a small amount of added aluminum remains in the treated water, or  
200 in colloidal particle form ( $\text{Al}(\text{OH})_3$ ) or in soluble form ( $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_4^-$ ),  
201 according the conditions of processing. A fault in the spillway of the sludge,  
202 incorrect scraping, the flow of the unsettled slurry pumps, which can cause release  
203 of the aluminum contained in the sludge and thus constitute a further addition to  
204 aluminum residual.

205 By studying the electronic scanning microscopy images and spectra in the jar-tests  
206 1, 2 we find that the aluminum peaks are important in the second test. For a dose  
207 of 40mg / L of SA, 5% of the total aluminum is residual, the remainder is with the  
208 settled particles. In station, and under the same conditions, the residual aluminum  
209 is 5.77% of the total aluminum. In the resort this is explained by the non  
210 homogeneity of treatment (agitation, dosage, residence time) because it must meet  
211 the urgent need of drinking water because its capabilities are no longer sufficient  
212 to satisfy a growing of population.

213 In addition a portion of the aluminum present in sludge may be salted out when  
214 the sludge removal if it is not done automatically or when the sludge discharge  
215 pumps are stopped. Bentonite, as adjuvant reduced the residual aluminum to a  
216 lower level due to its cation exchange capacity (75.8 meq / 100 g of bentonite)  
217 and the possibilities of retention in their foliar spaces. The bentonite used contains  
218 14.031%  $\text{Al}_2\text{O}_3$  compound, or 7.43% of aluminum, which may in turn be  
219 hydrolyzed to form other polymers, polycations  $\text{Al}_{13}$ , which promote good  
220 decantation and reduce the residual aluminum.

## 221 CONCLUSION

222 The aluminum sulfate is used as a coagulant in the treatment of surface water;  
 223 generally their pH is close or greater than 8, to facilitate the removal of turbidity.  
 224 The turbidity removal also results in reduction of pathogenic microorganisms and  
 225 also reduces the formation of by-products (organic matter) before disinfection, to  
 226 prevent the formation of compounds organochlorine responsible for certain  
 227 cancers. Disinfection can be hindered by high levels of residual aluminum.. It is  
 228 imperative, in the surface water treatment process, to work in optimum conditions  
 229 can lead to a minimum aluminum concentration in drinking water. In water  
 230 loaded, an adjuvant of the coagulation-flocculation can help to reduce the residual  
 231 aluminum, as is the case with natural bentonite. The conditions for hydrolysis of  
 232 aluminum (pH,  $t^{\circ}$ , agitation and water time stay) allow the formation of the  $Al_{13}$   
 233 polycation responsible for a good flocculation and reduced residual aluminum  
 234 including its harmfulness described in several studies.

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