Original Research Article

Risk of residual aluminum in treated water with aluminum sulphate

Abstract

The Water treatment by aluminum sulphate is the most used in water treatment to remove unwanted microorganisms. 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 method ajouts dose. Water treated the from 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. The residual aluminium obtained by the same metered ajouts 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 (Bottero and al., 1980).

Epidemiological studies have mounted the dangers of aluminum and some countries have already taken their precautionary. The Canada, for example, tolerates only than 100µg / L in the treated water (Hill., 1989). In France, epidemiology research team of Professor Jean François Dartigues University of Bordeaux has published several articles in the American Journal of epidemiology (Rondeau and al., 2000; RONDEAU and COMMENGES, 2001; RONDEAU and al, 2006.) treating the aluminum relationship and Alzheimer's disease. Much work advocating a tolerable threshold limited to 100µg / L in water used for drinking, while remaining vigilant about monitoring in water treatment plants. The inorganic monomeric aluminum represents their main fraction of aluminum after treatment of the water (62% of total).

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

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

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

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

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

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

→ a precipitate: $Al(OH)_3$

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

$$2Al\,(OH)(H_20)_5^{2+} \rightleftharpoons Al_2(OH)_2(H_20)_8^{4+} + 2H_20$$

Polymerization produces larger structures gradually and eventually lead to the formation of the Al13 polycation (Parker and BERTSCH., 1992a, 1992b).

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

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

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

1. MATERIALS AND METHODS

1.1. Operating procedure

Analytical results of the raw water the treated water station are shown in Table I

Table I. Physic-chemical analysis of water supply (Central Laboratory of 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_2/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.

- **reagents**

- Solution Erichrome cyanine R
- Acetic acid buffer solution pH 6

- Ascorbic Acid
- Solution 0.1 Mole EDTA (Éthylène Diamine Tétra-Acétique)
- Sulphuric acid 0.05 Mole
- Al Solution 0.1 g / L

1.2.2. Procedure

Adjust the water sample at a pH of 3-3.5

Put 10ml of sample in 5 100mL flasks. In the first flask was added all reagents except for the aluminum standard solution (to adjust zero the spectrophotometer). In other vials we put all reagents except EDTA and adding an increasing dose of standard aluminum. The absorbance of the solution of each flask was then measured is curve plotted A = f (C), the absorbance versus concentration aluminum and from this curve the amount was determined of aluminum in the sample.

1.2.3. Description of tests jar-test

Jar test is carried out as per the procedures outlined in paragraph 1.2.

The tests were conducted in a laboratory flocculator comprising six agitators and six 500mL beakers. The water to be treated is placed in each beaker

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

Table II. Results of analyzes of quality parameters

Parameters	**Raw water**	**(jar-test) Aliminum sulphate**	***Treated water station (sulfate Al)***	**Aliminum 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_2/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

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

1.3. Analysis of solid materials

1.3.1. Characterization bentonite

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

Table.III. Physico-chemical characteristics of the bentonite

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

Table IV. Mineralogical characteristics of bentonite

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

1.3.2. Electronic scanning microscopy

This operation allows to directly visualize the morphology (shape, size) particles and possible surface roughness (image 1, 2 and 3). She is consists to scanned, line by line , the surface of the particles by an incident beam of high energy electrons, thereby causing the emission of secondary electrons of low energy. These are sent to a detector which transmits the signal to a screen of which the scanning is synchronized with the scanning of the sample. The contrast of the image reflects the relief of the sample. These secondary electrons allow reconstruction of picture magnified of the surface.

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

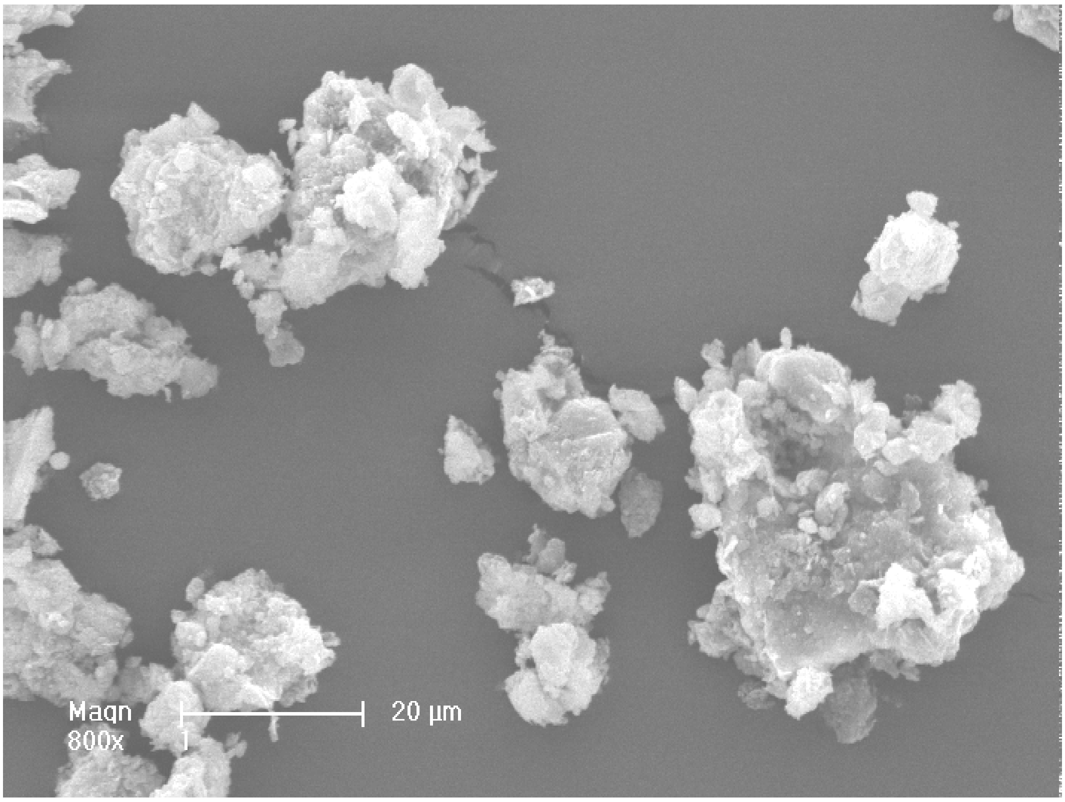

Figure 1. Image the morphology raw bentonite particles

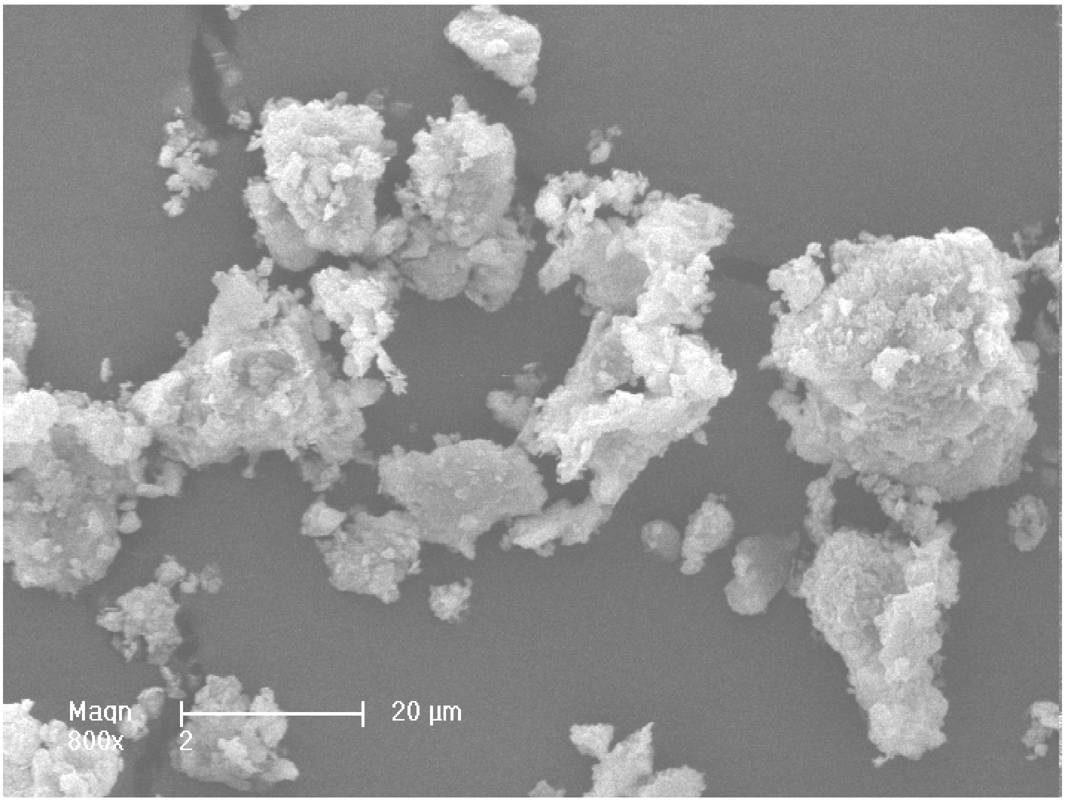

Figure 2. Sample image with a dose of aluminum sulfate 40 mg / L

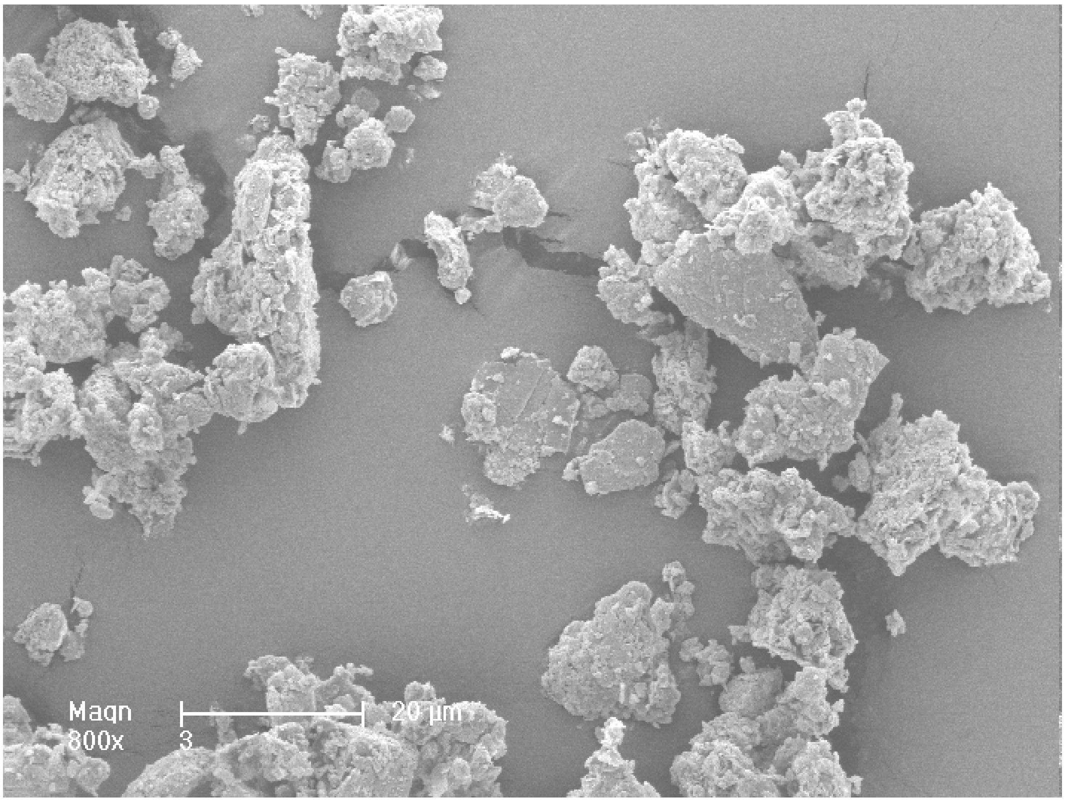

Figure 3. Sample image with a dose of aluminum sulfate 40 mg / L + 3 mg of bentonite

1.3.3. MEB-EDX dry residues

Figure 4, 5, 6 shows the various spectra of the minerals present in different samples. The peaks of aluminum vary from one sample to another. The higher amounts of aluminum are located on the sample 3 and the second and lowest peak on the sample 1. Figure 3 shows a larger concentration of aluminum on the cliche 3

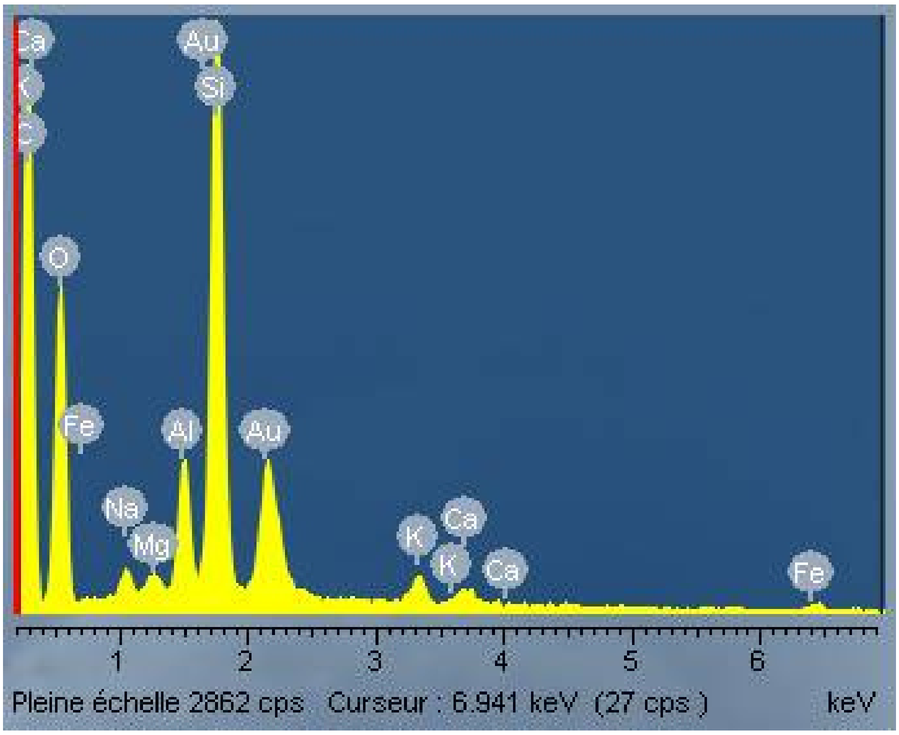

Figure 4. Raw bentonite

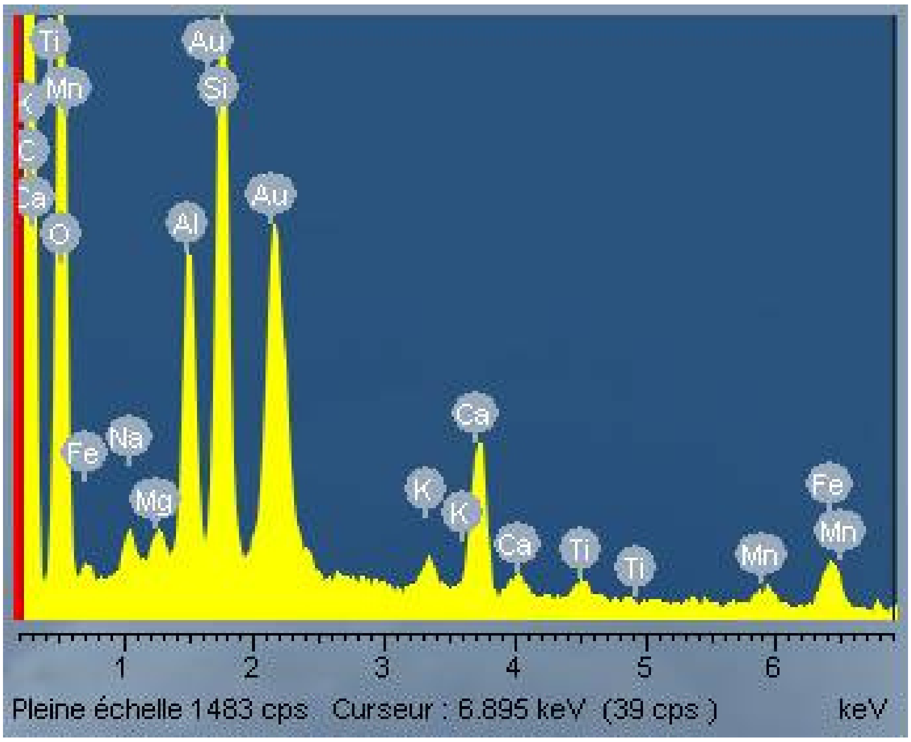

Figure 5. Dose of aluminum sulphate 40 mg / L

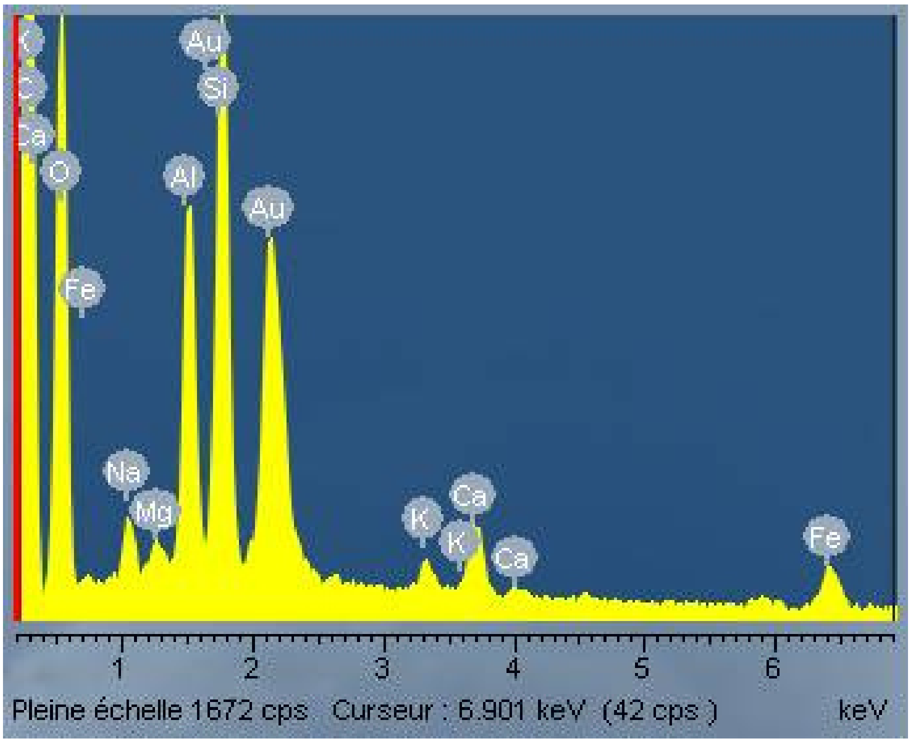

Figure 6. Dose of aluminum sulphate 40 mg + 3 mg bentonite

1.3.4. Fluorescence X

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

Table V. Quantification of raw bentonite sample

Analyte	Compound of formula	Concentration %	Méthod of calculating
Na	Na_2O	2.796	Calculated
Mg	MgO	2.913	Calculated
Al	Al_2O_3	14.031	Calculated
Si	SiO_2	69.665	Calculated
P	$P2O_5$	0.082	Calculated

S	SO_3	0.491	Calculated
K	K2O	2.407	Calculated
Ca	CaO	4.098	Calculated
Ti	TiO_2	0.350	Calculated
Mn	MnO_2	0.168	Calculated
Fe	Fe_2O_3	2.879	Calculated
Rb	Rb_2O	0.009	Calculated
Sr	SrO	0.041	Calculated
Cl	Cl	0.069	Calculated

Table VI. 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		

2. DISCUSSION OF RESULTS

We considered only the followed of residual aluminium.

Table VII. Monitoring the residual aluminum in the different samples

	Réactifs	Dose (mg/L)	Al résidual	%Al résidual/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		

The 40 mg dose of aluminum sulphate / L gives 3.64 mg / L of aluminum. water treated of station contains 5.77% of the total aluminum and thus constitutes the residual aluminum. The pH water arriving at the station has a value of 8.10, less favorable for the polymerization leading to the formation of the Al13 polycation. After treatment the pH does not exceed 7.61 and the minimum solubility range of aluminum hydroxide during coagulation is at a pH of between 6-7 for best yields (LETTERMAN and DRISCOLL., 1988) .

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

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

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

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

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

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

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

In addition a portion of the aluminum present in sludge may be salted out when the sludge removal if it is not done automatically or when the sludge discharge pumps are stopped. Bentonite, as adjuvant reduced the residual aluminum to a lower level due to its cation exchange capacity (75.8 meq / 100 g of bentonite) and the possibilities of retention in their foliar spaces. The bentonite used contains 14.031% Al_2O_3 compound, or 7.43% of aluminum, which may in turn be hydrolyzed to form other polymers, polycations Al_{13}, which promote good decantation and reduce the residual aluminum.

CONCLUSION

The aluminum sulfate is used as a coagulant in the treatment of surface water; generally their pH is close or greater than 8 for surface water, what which does not facilitate turbidity removal, because their removal also results in reduction of pathogenic microorganisms and also reduces the formation of by-products (organic matter) before disinfection, to prevent the formation of compounds organochlorine responsible for certain cancers. Disinfection can be hindered by high levels of residual aluminum It is imperative, in the surface water treatment process, to work in optimum conditions can lead to a minimum aluminum concentration in drinking water. In water loaded, an adjuvant of the coagulation-flocculation can help to reduce the residual of aluminum, as is the case with natural bentonite. The conditions for hydrolysis of aluminum (pH, t °, agitation and water time stay) allow the formation of the Al13 polycation responsible for a good flocculation and reduced residual aluminum including its harmfulness described in several studies. The tests have shown that if one respects the conditions of hydrolysis of aluminum (Table II), we arrive at an acceptable level of residual aluminum.

BIBLIOGRAPHIC REFERENCES

AMERICAN WATER WORKS ASSOCIATION RESEARCH FOUNDATION (1993). Aluminum in drinking water and Alzheimer's disease: a resource guide. AWWA Research Foundation and the American Water Works Association. 115 pp.

BAES C. F.et MESMER R. E. (1976). The hydrolysis of cations, *Wiley*, New York, 496 p.

BERTSCH, P.M. ET D.R. PARKER (1996). Aqueous polynuclear aluminum species. In : G. Esposito (éd.),The environmental chemistry of aluminum, 2e éd., CRC Press, Boca Raton (Fla.), p. 117-168.

BOTTERO J.Y., CASES J.M., FIESSINGER F. AND POIRIER J.E. (1980). Studies of hydrolyse aluminium chloride solutions. 1. Nature of aluminium species and composition of aqueous solutions. Journal of physical chemistry 84, 2933-2939.

COSTELLO, J.J (1984). Postprecipitation in distribution systems. J. Am. Water Works Assoc., 76: 46-49

JEAN PIERRE JOLIVET and MARC HENRY (1994). De la solution à l'oxyde. Condensation des cations en solution aqueuse. Savoirs Actuels. interEdition/CNRSEdition.

Hill, R.J. and Hill, M (1989). An exposure assessment of the health hazards associated with the intake of aluminium. Part II of a report on the effects of aluminium on human health. Préparé pour le Ministère de la Santé et du Bien-être, Ottawa (1989).

JONES, K.C. and BENOTT BG(1986). Exposure of man to environmental aluminum- exposure commitment sassements. Total environ., 52., 65-82.

LETTERMAN, R.D. and DRISCOLL, C.T (1988). Survey of residual aluminium in filtered water. J. Am. Water Works Assoc., 80: 154-158.

MARTELL, A.E. et MOTEKAITIS, R.J(1989). Coordination chemistry and speciation of Al (III) in aqueous solution. Dans: Environmental chemistry and toxicology of aluminum. T.E. Lewis (dir. de publ.). Lewis Publishers, Chelsea, MI. pp. 3-17.

MEGHZILI B, BOUSSAA M, MEDJRAM MS (2012). Aluminium résiduel et optimisation des étapes de la clarification dans les stations de traitement des eaux. *ScienceLib Editions Mersenne* : Volume 4 , N ° 120118.

PARKER, D.R. and P.M. BERTSCH (1992a). Identification and quantification of the «Al13» tridecamericpolycation using ferron, Environ. Sci. Technol., 26: 908-914.

PARKER, D.R. and P.M. BERTSCH (1992b). Formation of the «Al13» tridecameric polycation under diverse synthesis conditions, Environ. Sci. Technol., 26: 914-921.

RONDEAU V, COMMENGES D, JACQMIN-GADDA H and DARTIGUES JF (2000). Relationship between aluminum and silica concentrations in drinking water and Alzheimer's disease: an 8-year follow-up study. Am J Epidemiol, 152, 59-66.

RONDEAU V, COMMENGES D (2001) The Epidemiology of Aluminium and Alzheimer's Disease, In Aluminum and Alzheimer's Disease, the Science that Describes the Link, C. Exley, (Editor), Elsevier Science B. V.

RONDEAU V, IRON A, LETENNEURL, COMMENGES D, DUCHENE F, ARVEILER B and DARTIGESJ-F (2006). Analysis of the effect of aluminum in drinking water and transferring C2 allele on Alzheimer's disease. Eur J Neurology 13, 1022-1025.

SOLLARS, C.J., BRAGG, S., SIMPSON, A.M. et PERRY, R (1989). Aluminium in European drinking water. Environ. Technol. Lett., 10: 131-150.