BASIC ALUMINIUM SULPHATE: COAGULANT AND SYNTHESIS INTERMEDIATE

The Azanza Berrueta - Acideka Foundation was set up on 28/04/2003 to ensure that the innovation, development and application of technologies benefit industry and society in general. The publication of this article pursues the fulfilment of the Foundation's founding objective.

SUMMARY

Aluminium sulphate is a reagent used in coagulation processes that has been displaced by pre-polymerised aluminium salts (aluminium polychlorides). However, despite this, it is still an inexpensive reagent that can be used successfully.

The preparation of basic aluminium sulphate improves the efficiency of conventional aluminium sulphate with regard to optimum coagulation interval, reduction of turbidity, reaction speed in cold water etc... and can also be used as a reagent when synthesising aluminium polychloride in general.

INTRODUCTION

Drinking water is a scarce commodity. It is estimated that only 0.4% of the world's water is fit for human consumption, therefore it is essential to invest in water purification to ensure that everyone has access to this vital resource. Water purification is the process by which water is treated so that it can be consumed by humans without posing a health risk (1).

The physico-chemical treatment consists of a coagulation phase, a flocculation phase, followed by decanting and filtration. The process consists of adding compounds to neutralise the charge of the colloid and break its stability. In the first step of coagulation, the colloids are destabilised by neutralisation of their charges, resulting in the formation of larger particles. Subsequently, in flocculation, the clots are bound together to increase their volume (2,3), favouring their subsequent decanting and filtration.

In general, coagulants can be organic or inorganic. Organics are generally polyamines with cationic charge of varying molecular weight. Inorganic coagulants are based on iron and aluminium salts. In drinking water treatment, aluminium salts are more commonly used and in wastewater treatment, iron salts (ferric chloride, ferrous chloride, ferric sulphate, etc.) are more commonly used. The following can be distinguished within the aluminium salts:

1.- Simple salts (aluminium sulphate, aluminium chloride, etc.).

2.- Pre-polymerised salts (aluminium polychloride, aluminium polychlorosulphate, etc.).

1.-Simple salts: aluminium sulphate

It is a simple salt resulting from the reaction of sulphuric acid with aluminium hydroxide. Its effectiveness in coagulation depends on how, and to what degree, the hydrolysis reaction of the aluminium cation occurs when it is added to the water to be treated. This means that the type of water, reaction time and temperature, etc. will play an important role in determining the effectiveness of the product.

Such reactions can be described in a simple way by the following equations (4-6):

$$Al^{3+} + H_2O \longleftrightarrow |Al(OH_2)_6|^{3+}$$

$$|Al(OH_2)_6|^{3+} + H_2O \longleftrightarrow |Al(OH_2)_5OH|^{3+} + H_3O^+$$

$$2|Al(OH_2)_5OH|^{3+} + H_3O^+ \longleftrightarrow |Al_2(OH)_2|^{4+} + H_3O^+$$

$$3|Al(OH_2)_5OH|^{3+} + H_2O \longleftrightarrow |Al_3(OH)_4|^{5+} + H_3O^+ ...$$

The process would ideally continue until the compounds of the type below are obtained in the most favourable hydrolytic process (which never occurs in its entirety):

$$|Al_{13}O_4(OH)_{24}(H_2O)_{20}|^{7+}$$

which are the most effective species in the coagulation-flocculation process.

Therefore, at the end of the process, and depending on the degree of progress of the hydrolysis reaction (which will depend on the temperature, ionic strength of the medium, reaction time, etc.), a balance is obtained between different species, some of which have the best properties for the coagulation process, given their polymeric character. However, these species are not normally present in the concentration conditions suitable for effective coagulation. That is to say, the content of polymeric species is very low, and those formed as a result of hydrolysis are not chemically the most efficient as they are deficient in both molecular weight and concentration.

All these processes are well described in the references (7-12):

2.-Pre-polymerised salts

1)- Aluminium polychlorides: $Al_n(OH)_mCl_{3n-m}$

2)-Aluminium polychlorides: $Al_n(OH)_m(SO_4)_xCl_{3n-m-2x}$

Compared to simple salts, they have the advantage that the active species are already pre-formed before the reagent comes into contact with water.

In this type of reagents the active fractions are of the type:

$$|Al_{13}O_4(OH)_{24}(H_2O)_{20}|^{7+} \qquad |Al_{12}(OH)_{24}(H_2O)_{12}(SO_4)|^{10+}$$

The type and amount of active species depends on the mode of synthesis: starting reagents, polymerisation temperature etc.

The advantages of using pre-polymerised salts can be summarised as follows:

1)- Increased reaction speed: Accelerates the long process of mantle generation in decanters.

2)- Good behaviour at low temperatures: Booster doses are not necessary and there is no post-coagulation effect under extreme low temperature conditions.

3)- Increase of the optimal pH range for coagulation: In many cases, the use of reagents to adjust the coagulation pH is not necessary or, if necessary, the dose of reagents can be reduced.

4)- Increase in the speed and quality of decanting: The formation of larger and heavier flocs allows a greater compaction of the mantle formed in the settling tanks, and an increase in the settling velocity, even at high ascending velocities. This makes it possible to increase the treatment capacity of the sewage treatment plant without modifying its facilities. In many cases even the use of flocculants is eliminated.

5)- Increase in filter runs: This is a consequence of the previous effect, as the quality of the decanted water improves and filter saturation occurs later.

6)- More efficient use of the amount of aluminium dosed with a consequent reduction of residual aluminium in the treated water.

ENSAYO JAR TEST

In order to have a clear idea of the optimal operating conditions of the products used in the treatment of drinking water, a series of small-scale tests are carried out, where the concentrations of coagulant and flocculant are varied, as well as the agitation speeds and the expected times at each stage, in order to simulate what will occur during the process that takes place in the plant. For this purpose, there is specialised equipment for this type of testing which is jar test equipment.

These devices are usually equipped with six jugs, into which one litre of water of the sample to be tested is poured. Subsequently, different concentrations of coagulant are added to each of the beakers, subjected to a controlled stirring process and finally allowed to settle. The exact parameters of speed, settling time etc... are adjusted according to the conditions of the sewage treatment plant for which the test is carried out.

Typical parameters to be determined are turbidity, temperature, pH (13,14), reaction rate, settling quality, floc size etc. Some of these parameters are very subjective, so the test has a very important qualitative component.

The American Public Health Association (APHA) defines turbidity as "an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in a straight line through the sample" (15). The intensity of scattered light increases with suspended solids (16). When a beam of light passes through ultrapure water, the path of the water remains relatively unchanged.

The World Health Organization (WHO 2011) states that turbidity levels of water to be disinfected should be <1.0 NTU. (17)

The measurement of the parameter aluminium is important because it is related to the development or acceleration of Alzheimer's disease, therefore a level of 0.2 milligrams per litre of aluminium in drinking water is proposed.

METHODOLOGY

Three aluminium polysulphates, named CAL-CARB, SBA 60% and CARB-CARB, have been synthesised. The synthesis route used in these products has been the basification of aluminium sulphate by alkaline agents. There is a lot of literature that describes both synthesis and stabilisation methods, which are described in the literature (18-30) that has been used as a basis. Depending on the type of synthesis, the aluminium polysulphate obtained may or may not present stability problems.

RESULTS

Table 1: Characteristics of the synthesised aluminium polysulphates and liquid aluminium sulphate.

	Aluminium polysulphates			Aluminium sulphate
	SBA 60%	CAL-CARB	CARB-CARB	
Density at 20ºC (gr/cc)	1.3416	1.3019	1.2867	1.3223
%Al_2O_3	8.21	7.95	8.16	8.00
Basicity	55.89	53.52	62.21	5.24
% Sulphates	17.18	16.95	15.33	23.16
pH at 20 ºC	4.20	3.99	4.20	2.86

During the jar test, aluminium polysulphate has two peculiarities compared to conventional aluminium salts and aluminium sulphate itself:

1.- The product must be added undiluted, because if it is mixed with water the product hydrolyses quickly and loses efficiency.

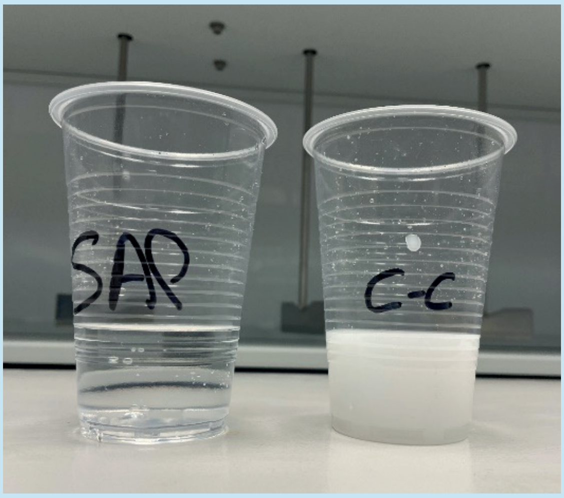

Figure 1: hydrolysis of carb-carb when preparing the sample in diluted form

2.- The blade of the jar test equipment must be in motion when dosing the product as it has been proven that if the product is added while stationary, it does not flocculate, it hydrolyses with the water in a short time and the product is not effective.

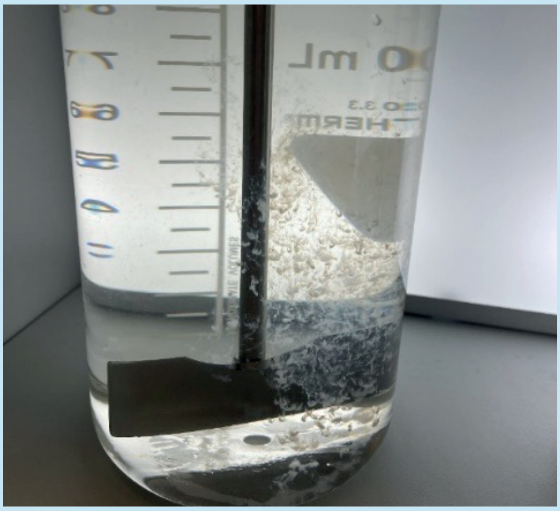

Figure 2: Loss of effectiveness of polysulphate in the absence of agitation

It is observed that, if the product is added with the equipment stopped and subsequently started, the hydrolysis products remain in suspension, the water to be purified takes on a milky appearance and no quality flocs are formed. On further agitation, the precipitated matter disintegrates.

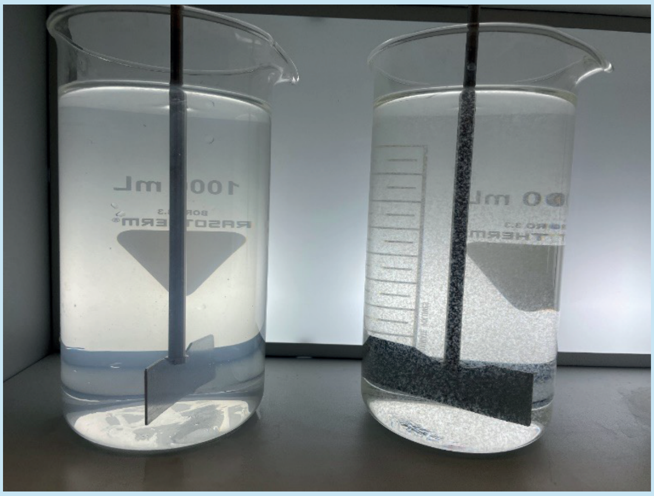

Figure 3: Comparative effect of aluminium polysulphate added without agitation (left photo) and with agitation (right photo).

Taking these precautions into account, different efficiency tests are carried out using water of different turbidity and modifying the coagulation pH:

1.- Efficiency of aluminium polysulphates versus conventional liquid aluminium sulphate as a function of inlet water turbidity.

Type of sample: Ebro water > Low turbidity

Raw water characteristics		
Variable	Unit	Value
Turbidity	NTU	9.46
pH		7.14
Temperature	°C	18

Jar-Test Conditions		
Time	Action	RPM
3 minutes	Rapid agitation	180
10 minutes	Slow agitation	20
10 minutes	Decanting	

A sweep is made at different concentrations of aluminium sulphate from 30 to 55 ppm, and the optimum dosage is 45 ppm.

	S Al	CARB-CARB-E	SBA 60% E	CAL-CARB-E
Dose (ppm)	45	45	45	45
Flocs	*	***	***	***
DT (decanted turbidity.)	2.39	0.66	0.6	0.74
FT (filtered turbidity)	0.8	0.64	0.62	0.71
Aluminium (ppb)	1250su	106	138	180

Polysulphates are found to be more efficient than aluminium sulphate in terms of turbidity, aluminium and floc size. Among the three polysulphates, CARB-CARB-E is slightly superior in terms of floc size, and has a lower level of residual aluminium.

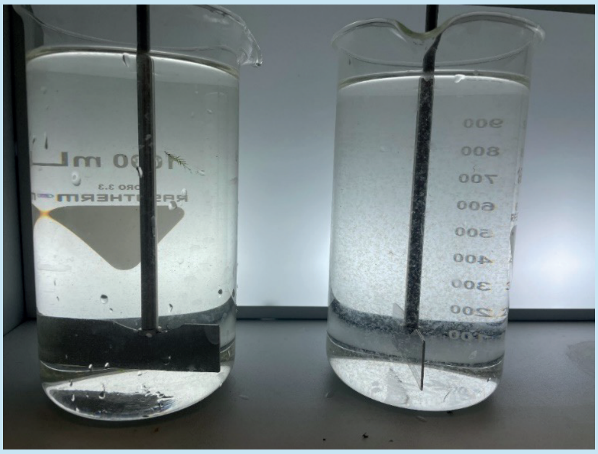

Figure 4: First minute of slow stirring comparison S AL (left) and CARB-CARB (right)

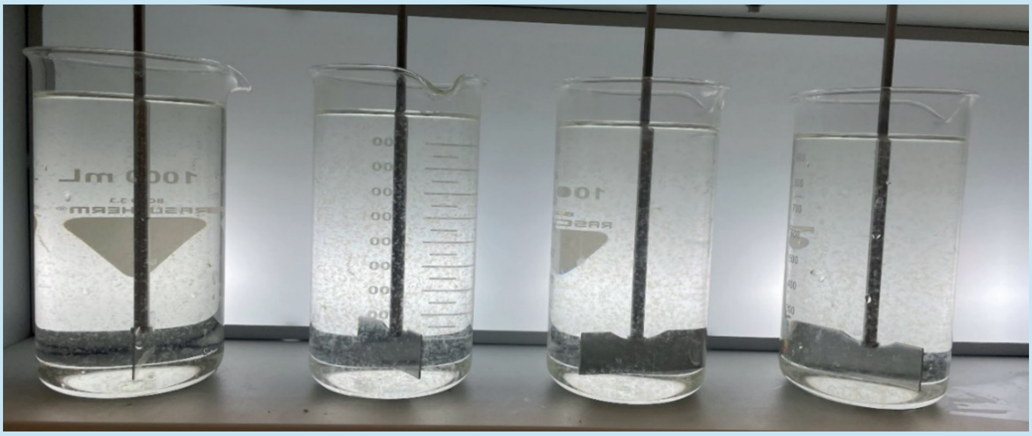

Figure 5: 20 minutes of slow agitation

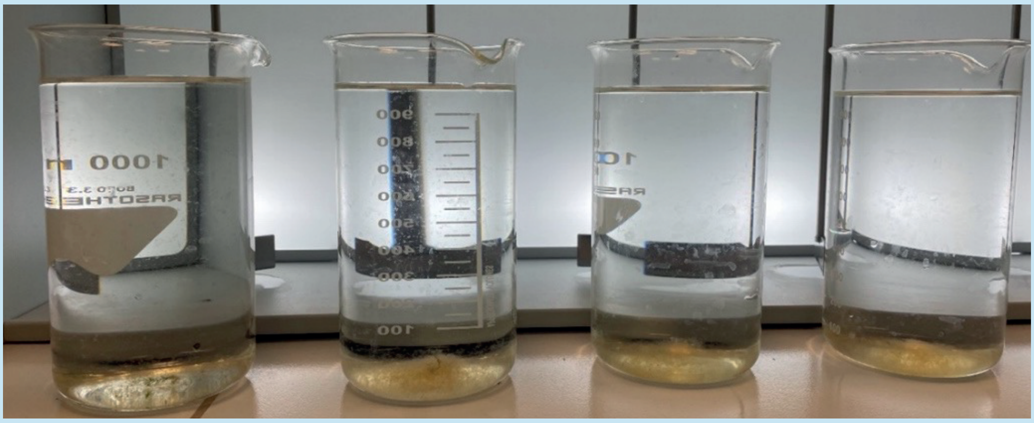

Figure 6: Decanting

Type of sample Ebro water > Average turbidity

Raw water characteristics		
Variable	Unit	Value
Turbidity	NTU	20.8
pH		8.38
Temperature	°C	9

Jar-Test Conditions		
Time	Action	RPM
3 minutes	Rapid agitation	180
10 minutes	Slow agitation	20
10 minutes	decanting	

The three polysulphates are again compared with aluminium sulphate. An optimum dose of 45 ppm of aluminium sulphate was obtained.

	S Al	CARB-CARB-E	SBA 60% E	CAL-CARB-E
Dose (ppm)	45	45	45	45
Flocs	***	*	*****	*****
DT	3.57	17.9	2.4	1.14
FT	2.38	12.8	2.45	1.2
Aluminium (ppb)	457	486	196	203
pHf	7.23	7.8	7.82	7.82

It is observed that, in this type of water, CARB-CARB is not a valid product and flocculates aluminium sulphate better. SBA 60% and CAL-CARB show good coagulation-flocculation and are much more effective than aluminium sulphate.

Figure 7: 20 minutes of slow agitation.

Type of sample Ebro water > High Turbidity

Raw water characteristics		
Variable	Unit	Value
Turbidity	NTU	60.6
pH		8.47
Temperature	°C	10

Jar-Test Conditions		
Time	Action	RPM
3 minutes	Rapid agitation	180
10 minutes	Slow agitation	20
10 minutes	Decanting	

A sweep is made at different concentrations of aluminium sulphate, resulting in the optimum dose being 50 ppm.

	S Al	SBA 60%-E	CAL-CARB-E	CARB-CARB-E
Dose (ppm)	50	50	50	50
Flocs	***	*****	*****	*
DT	6.97	1.64	1.76	40.5
FT	2.03	1.44	1.5	18.9
Aluminium (ppb)	492	182	20	554SU

In the first minute of slow agitation, SBA 60%E and CAL-CARB-E show a much higher floc quality than the rest. After 20 minutes of shaking, the size of the latter is still much larger than the rest. On the other hand, CARB-CARB does not work properly because the initial turbidity of the water is high.

Figure 8: 10 minutes of slow agitation

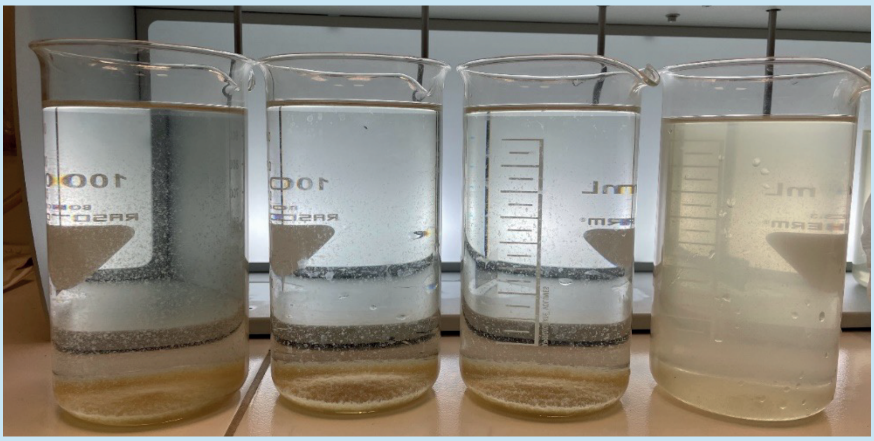

Figure 9: Decanting

2.- Efficiency of CAL-CARB aluminium polysulphate versus conventional aluminium sulphate as a function of pH.

The following test consists of comparing the range of action of each coagulant as a function of pH. Therefore, the optimum dosage of aluminium sulphate in the respective water is calculated without adjusting the pH. Once the optimum pH has been obtained, a sweep is carried out by varying the pH of the water from 10 to 3, by adding diluted sodium hydroxide and diluted nitric acid.

Type of sample: Ebro water > Low turbidity

Raw water characteristics		
Variable	Unit	Value
Turbidity	NTU	8.44
pH		8.08
Temperature	°C	21

Jar-Test Conditions		
Time	Action	RPM
3 minutes	Rapid agitation	180
10 minutes	Slow agitation	20
10 minutes	Decanting	

The optimum dosage of the product without pH adjustment is 45 ppm and the pH of the coagulation is around 6.9. This dose is taken as a reference and a pH sweep is performed.

	ALUMINIUM SULPHATE									
Dose (ppm)	15	20	25	30	35	40	45	50	55	60
Starch	1	1	1	1	1	1	1	1	1	1
DT	7.67	4.81	3.55	2.79	1.58	2.12	2.22	2.11	1.53	1.2
FT	4.74	2.21	1.84	1.39	1.43	2.03	1.43	1.73	1.96	2.06
Aluminium (ppb)	841	652	515	502	430	275	207	333	450	523
Floc	-	-	-	-	-	*	**	**	**	**

Using 45 ppm CAL-CARB polysulphate as the optimum dose, the same test as above is repeated and the result is obtained:
It is observed that aluminium sulphate is only effective in a pH range between 7 and 6, and aluminium polysulphate has a pH range between 9 and 4.

	CAL-CARB										
INITIAL PH	10.02	9.51	8.95	8.59	8.16	8.08	6.8	6.1	5.01	3.95	3.11
Dose (ppm)	45	45	45	45	45	45	45	45	45	45	45
Starch (ppm)	1	1	1	1	1	1	1	1	1	1	1
DT	11.6	3.02	2.14	2.52	2.01	2.15	1.47	1.65	2.29	2.63	10.39
FT	9.6	1.4	1.41	1.25	1.42	1.44	0.96	1.19	1.67	1.98	8.24
Aluminium (ppb)	1253	1050	145	121	127	145	56	59	100	120	670
final pHL	10.01	9.46	8.74	8.2	8	7.33	6.67	6.55	5.11	3.96	3.15
Floc	*	*	**	**	***	***	***	**	**	**	*

GENERAL CONCLUSIONS:

- It confirms the fact that there is an optimum basicity of the product which varies according to the turbidity of the initial water where it is to be used. CARB-CARB polysulphate does not work in all the waters tested and its efficiency depends on the characteristics of the raw water: for waters with low turbidity its performance is far superior to the rest, obtaining satisfactory turbidity and aluminium values. On the other hand, this product is not efficient when high turbidity raw water is used, and aluminium sulphate becomes more effective. For low turbidity (< 10 ntu), the optimum basicity is around 62%.

- SBA 60% and CAL-CARB have the same efficiency in all cases and are always superior to aluminium sulphate.

- As for the optimum pH for coagulation, in the case of aluminium sulphate it is found to be around 7, and small deviations from this value lead to an excessive increase in the residual aluminium value.

- In addition to a large difference in floc size, turbidity and residual aluminium, it is observed that the synthesised polysulphates have a wider range of optimum coagulation pH than aluminium sulphate. This range is between 9 and 4.

- Aluminium polysulphates should be added undiluted and stirred because they lose their functionality.

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