

The present invention relates to a basic aluminium chlorosulphate, the process for producing it and its use as a flocculating agent. The treatment of effluents, sewage, spring waters or river waters almost always comprises a stage in which suspended materials are removed. Products are known which have a coagulating effect on these suspended or dissolved materials in the aqueous system to be treated, these being materials which cannot be separated in a reasonable time by natural separation. Moreover, these products convert these materials into coagulated flakes which are easy to filter and separate from the liquid phase.

The patents FR 2,036,685, FR 2,226,361, and FR 2,534,897 describe products of this type and their applications. European Patent Application EP 218,487 describes a product intended to reduce the quantity of aluminium remaining in the water after treatment.

A chlorosulphate has now been found which is very effective and very simple to use.

The chlorosulphate according to the invention is a basic aluminium chlorosulphate which is in the form of an aqueous solution, characterized in that it comprises a product having a certain degree of polymerization and of composition represented by the expression:



in which:

- x denotes an alkaline-earth substance, preferably calcium

- n, m, p and k denote the molar concentrations (mol/l) of the components in solution

- less than 20 % of the SO_4^{2-} ions can be precipitated by reacting with barium chloride at ambient temperature,

the basicity : $\frac{3n+2k-m-2p}{3n}$ of which is between 45

and 70 %.

Advantageously, products according to the empirical formula above are chosen, in which the ratio of aluminium equivalent to chlorine, i.e. 3 n/m is lower than 2.8 and preferably lower than 2.75.

Although it is possible to have a wide range of basicity, normally products are used which have a basicity in the range 50 to 70 %. Different basicity values may be preferred, according to the product applications. In particular, when preparing potable water, it has been observed that, the higher the basicity, the lower the values of residual aluminium.

The nonprecipitation of most of the SO_4^{2-} ions in the product by barium salts indicates that this sulphate is complexed. Determination of the total content A of sulphate contained in the product is carried out in a customary manner by precipitating barium sulphate using a solution of barium chloride and hydrochloric acid which is added to the sample at its boiling point. When barium chloride is introduced at ambient temperature (i.e. 15 to 25°C) into a nonacidified sample, in a stoichiometric quantity in relation to the SO_4^{2-} ions present in the product, the dry weight of the precipitate formed after 1 hour is related to the content B of so-called "non-complexed" SO_4^{2-} ions.

The difference A-B is called "content of complexed SO_4^{2-} ions".

The product of the invention, which is in the form of an aqueous solution containing from 5 to 15 % by weight expressed as Al_2O_3 , is mixed with an aqueous solution of barium chloride (for example from 5 to 20 g/l). The mixture is homogenized and the precipitate allowed to form in the course of about 1 hour, then filtration is carried out through a sintered glass crucible of porosity grade No. 4. All these operations, from mixing the chlorosulphate with the BaCl_2 up to the filtration take place at ambient temperature, i.e. between 15 and 25°C. The filtrate still contains the SO_4^{2-} ions of the product of the invention which were not precipitated in the form

of BaSO_4 and which are thus complexed. To find out this quantity of complexed SO_4^{2-} , the product is destroyed by adding hydrochloric acid to the filtrate and bringing to the boil. Then the SO_4^{2-} ions are precipitated with a 5 to 15 % by weight aqueous solution of BaCl_2 . Measuring the weight of BaSO_4 precipitated gives the percentage of SO_4^{2-} ions which can be precipitated by reacting with barium chloride at ambient temperature in comparison with the total amount of SO_4^{2-} in the product.

Advantageously, the products have less than 10 % of SO_4^{2-} ions which can be precipitated under normal conditions, and preferably less than 5 %, i.e. more than 95 % of the SO_4^{2-} ions are complexed.

The present invention also relates to a process for preparing these products. The process is characterized in that:

a) an aqueous solution of aluminium oxide, HCl and H_2SO_4 in the proportions indicated below is prepared,

b) this solution is brought into contact with an alkaline-earth metal compound, using the molar ratios, with respect to the aluminium, indicated below.

c) the alkaline-earth metal sulphate is removed.

Step a) is carried out by bringing aluminium oxide into contact with hydrochloric acid and sulphuric acid in an aqueous medium. Aluminium oxide is understood to mean all products of the alumina or aluminium hydroxide type. It is preferred to use the alumina produced by the Bayer process or the aluminium hydroxides which are byproducts of the surface treatments of aluminium.

Advantageously, aluminium oxide is attacked by a mixture of concentrated hydrochloric acid and concentrated sulphuric acid at a temperature in the range 70 to 115°C. This temperature range is not essential, but merely corresponds to a reaction period of one or two hours which is compatible with the industrial application of the process. It is possible to add aluminium oxide to a mixture of acids or to react aluminium oxide with one acid followed by the other, or to add the acids in several portions. It is preferred to use a mixture of

hydrochloric acid and sulphuric acid to attack the aluminium oxide, then add a further amount of concentrated sulphuric acid once part of the aluminium oxide has been dissolved.

5 Advantageously, a solution of hydrochloric acid more concentrated than 20 % by weight is used and preferably a 33 % by weight solution. It is also advantageous to use sulphuric acid having a concentration of at least 60 % by weight. The quantity of hydrochloric acid,
10 expressed in moles, is between 1.89 and 2.44 times the quantity of aluminium oxide expressed in moles of Al_2O_3 , and preferably in the range 1.95 to 2.40.

 Likewise, the quantity of sulphuric acid, expressed in moles, (used in one or more portions) is
15 between 1.37 and 1.73 times the quantity of aluminium oxide expressed in moles of Al_2O_3 , and preferably between 1.42 and 1.68.

 The chlorosulphuric solution of aluminium from step a) is subsequently brought into contact with the
20 alkaline-earth metal compound. This alkaline-earth metal compound may be selected, for example, from calcium carbonate, hydroxide, oxide or bicarbonate. It is possible to use a mixture of these products, for example calcium carbonate and calcium hydroxide, calcium car-
25 bonate being preferred. Advantageously, the alkaline-earth metal compound is in divided form, such as a powder. Although the procedure may be performed at any temperature, it is preferred to bring the chlorosulphuric aluminium solution to between 60 and 100°C for bringing
30 it into contact with the alkaline-metal compound.

 Generally 10 or 30 minutes are taken for this contacting procedure, which corresponds to customary technological conditions, but it is not beyond the scope of the invention to operate over a few minutes or over
35 several hours.

 The quantity of the alkaline-earth metal compound, expressed in moles, is between 1.63 and 1.70 times the quantity of aluminium oxide introduced in step a), expressed in moles of Al_2O_3 , and preferably between 1.65

and 1.68. The mixture may be left stirred when all of the alkaline-earth metal compound has been mixed with the chlorosulphuric solution of aluminium. The temperature used is not specified, but generally settles at between
5 30 and 60°C.

Advantageously, this conclusion of step b) lasts for from 15 minutes to 2 hours. Subsequently, it only remains to separate the alkaline-earth metal sulphate. Customary methods may be used, such as filtration or
10 centrifuging. This separation is preferably carried out above ambient temperature, for example between 30 and 60°C.

The filtrate contains the basic chlorosulphate of the invention dissolved in water. The concentration may
15 be modified by adding water. The product of the invention takes the form of this solution containing between 5 % and 15 % by weight of aluminium, expressed as Al_2O_3 . This form has the advantage of being stable (no appearance of the solid phase) for several months at ambient temper-
20 ature.

The present invention also relates to the application of these products as coagulating and flocculating agents for water treatment, particularly water purification to produce potable water.

25 Among the basic aluminium chlorosulphates of the invention, those which simultaneously
- have a basicity higher than 60 %
- and the weight ratio $\text{Cl}/(\text{total } \text{SO}_4^{2-})$ of which is between 4.5 and 8, exhibit, when employed within the
30 context of processes for treating aqueous media, a rate of treatment, at the optimum flocculation, which is lower for closely allied properties relating to the aluminium remaining in solution (residual Al).

The following examples illustrate the invention
35 without limiting it.

EXAMPLE 1 : PREPARATION OF A PRODUCT ACCORDING TO THE INVENTION

Step a): 3.09 moles of a powder containing 99 % of $\text{Al}(\text{OH})_3$ are poured into a glass reaction vessel

containing 3 moles of HCl in the form of 331.9 g of a 33% solution and 1.45 moles of H_2SO_4 as a 78% solution. The mixture is heated to 70°C and then the temperature stabilizes at 102°C . After dilution with 374 g of water, 1 mole of 78% sulphuric acid is added. The temperature increases to 112°C in the course of 20 minutes. The duration of this step was about 2 hours.

Step b): After cooling to 93°C , 2.60 moles of CaCO_3 , i.e. 481.5 g of a 54% slurry of CaCO_3 are introduced in the course of 30 minutes. The reaction vessel is left stirred for 1 hour 30 minutes, the temperature having dropped to 61°C .

Step c): After cooling to 40°C , the mixture is filtered in a filtration apparatus under vacuum. The cake is washed with 100 g of water. The dry cake weighs 362 g and contains by weight 7.73 % of aluminium expressed as Al_2O_3 , 53.4 % of SO_4^{2-} , 1.35 % of Cl^- , the remainder being calcium. 1111 g of filtrate having a relative density of 1.224 were collected and were diluted with 109 g of water. The product obtained is in the form of a solution.

The solution weighs 1220 g, has a relative density of 1.201 and contains by weight 10.09 % of Al expressed as Al_2O_3 , 8.11 % of Cl^- , 1.83 % of SO_4^{2-} , 1.78 % of complexed SO_4^{2-} and 1.08 % of Ca^{2+} i.e. the ratio (Al equivalent)/Cl is 2.6, 97.3 % of the SO_4^{2-} ions being complexed.

The basicity is 64.18 % and the weight ratio $\text{Cl}/(\text{total } \text{SO}_4^{2-})$ is 4.43.

EXAMPLE 2 : PREPARATION OF ANOTHER PRODUCT ACCORDING TO THE INVENTION

The operation was carried out as in Example 1, but using different proportions of reactants. Starting again from 3.09 moles of $\text{Al}(\text{OH})_3$, the duration of step a) is 2 hours. Step b) lasts 2 hours and begins at 90°C .

Step a):

Final temperature : 113.4°C

HCl : 3 moles

H_2SO_4 : 2.6 moles

Step b):

Final temperature : 63°C

CaCO₃ : 2.6 moles in the form of a 54% slurry

After separation of the calcium sulphate (step c)
5 and dilution with water, the following product is obtained, the percentages being by weight of the solution.

Percentages in the solution

	AL ₂ O ₃	10.59 %
	Cl	8.35 %
10	Total SO ₄ ²⁻	2.13 %
	Complexed SO ₄ ²⁻	2.13 %
	Residual Ca	0.77 %
	Al equivalent /Cl	2.65
	Basicity	61.29
15	Complexed SO ₄ ²⁻ ions	100 %
	Cl/(total SO ₄ ²⁻)	3.92

EXAMPLE 3 : PREPARATION OF ANOTHER PRODUCT
ACCORDING TO THE INVENTION

The operation was carried out as in Example 1,
20 but using different proportions of reactants. Starting from 3.09 moles of Al(OH)₃, the duration of step a) is 2 hours. Step b) lasts 2 hours and begins at 90°C.

Step a):

Final temperature : 112°C

25 HCl : 2.81 moles

H₂SO₄ : 2.25 moles

Step b):

Final temperature : 62°C

CaCO₃ : 2.38 moles in the form of a 54% slurry

30 After separation of the calcium sulphate (step c) and dilution with water, the following product is obtained, the percentages being by weight of the solution.

Percentages in the solution

35	AL ₂ O ₃	9.96 %
	Cl	7.72 %
	Total SO ₄ ²⁻	1.50 %
	Complexed SO ₄ ²⁻	1.50 %
	Residual Ca	0.66 %

Al equivalent /Cl	2.69
Basicity	63.2 %
Complexed SO_4^{2-} ions	100 %
Cl/(total SO_4^{2-})	5.15

5 EXAMPLE 4 : PRODUCTS NOT ACCORDING TO THE
INVENTION

 Their empirical formula is expressed in the same form as those of the products of the invention.

10 4a) A basic aluminium chlorosulphate is produced according to the prior art, which is in the form of a solution containing, in % by weight:

Al	10.3 (expressed as Al_2O_3)
Cl	9.09
Total SO_4^{2-}	2.49
15 Basicity	51.32 %, the basicity being defined as for the product of the invention.

 The concentration of complexed SO_4^{2-} ions is 1.64, i.e. $1.64/2.49$, i.e. 65.9 % of the sulphate, is complexed. The ratio (Al equiv.)/Cl is 2.37 and Cl/(total SO_4^{2-}) is 3.65. The product is produced by reacting alumina with HCl and H_2SO_4 as in the patent FR 2,036,685.

20 4b) Another basic aluminium chlorosulphate is produced occurring in the form of a solution containing in % by weight:

25 Al	8.3 (expressed as Al_2O_3)
Cl	5.21
Total SO_4^{2-}	5.02
The basicity is	49.8 %

 The concentration of complexed SO_4^{2-} ions is 1.5, i.e. $1.5/5.02$ i.e. 29.9 % of the sulphate is complexed. The ratio (Al equiv.)/Cl is 3.32 and Cl/(total SO_4^{2-}) is 1.04.

35 This product is produced by a process which comprises a step in which a slurry of calcium chloride and calcium carbonate (chlorocarbonate slurry) is prepared, a step in which the chlorocarbonate slurry is brought into contact with aluminium sulphate, then a step in which the reaction mixture thus obtained is separated, this being done by separating a cake of calcium sulphate

and a filtrate containing the basic aluminium chloro-sulphate. This process is described in European Patent Application EP 218,487.

5 Using quasi-elastic light scattering, an apparent hydrodynamic diameter ΦZ was measured on this product, giving 700 Å.

4c) A product of the same type as in 4b) is produced. The concentrations are:

	Al	8.55 (as Al_2O_3)
10	Cl	6.82
	Total SO_4^{2-}	2.74
	Complexed SO_4^{2-}	1.93
	The basicity is	57 %

The percentage of complexed SO_4^{2-} is thus
15 $1.93/2.74 = 70.4 \%$ and the ratios (Al equivalent)/Cl: 2.62 and Cl/(total SO_4^{2-}):2.49.

EXAMPLE 5

This example illustrates the application of the product according to the invention.

20 The product of the invention is compared with the products of Example 4.

Trials are carried out in test jars according to the following operating method:

- one-litre beaker
- 25 - temperature $15^\circ C$
- river water
- Hydrocure type SLH6 test jar
- rapid stirring for 1 min 30' after addition of the flocculant then slow stirring, i.e. sufficient to
30 produce coalescence, but avoiding separation of the flocs.

Separation is subsequently allowed to occur for 3, 10 or 20 min according to Tables 1 to 7.

- measurement of the aluminium remaining in the
35 water using a colorimetric method using chromazurol, after filtration of the separated water for 20 min, on a $0.45 \mu m$ filter.

The following tables show the type of water to be treated, its PH, the turbidity expressed in NTU and the

organic matter in mg of oxygen per litre of water.

The product used is referenced by the number of the example. The turbidity of the water at the surface after x minutes of separation, the final PH, the organic matter and the aluminium remaining in the water (residual Al) in ppb ($\mu\text{g/litre}$) are shown.

Tables 1 to 7 show the results.

TABLE 1

Water type : Seine water

PH 7.97

Turbidity 42 NTU

Organic matter (O.M.) 6.96 mg O_2/l

PRODUCT (Example No.)	QUANTITY IN g/m^3 (of Al_2O_3)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
4a	4	2.1	1.45	1.3	7.7	2.76	148
1	4	1.8	1.35	1.2	7.84	2.72	97

TABLE 2

Water type : Marne water

PH 8.02

Turbidity 60 NTU

Organic matter (O.M.) 6.68 mg O_2/l

PRODUCT (Example No.)	QUANTITY IN g/m^3 (of Al_2O_3)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
4a	3	1.7	1.6	1.5	7.78	2.94	152
4c	3	1.7	1.55	1.45	7.80	2.78	152
1	3	1.8	1.6	1.45	7.80	2.66	118

TABLE 3

Water type : Marne water

PH 8.26 (was modified by adding sodium hydroxide)

5 Turbidity 55 NTU

Organic matter (O.M.) 5.94 mg O₂/l

10

PRODUCT (Example No.)	QUANTITY IN g/m ³ (of Al ₂ O ₃)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
4a	3	1.55	1.55	1.35	7.90	2.12	216
4c	3	1.6	1.55	1.3	7.92	2.14	212
1	3	1.7	1.55	1.45	7.97	2.08	165

TABLE 4

Water type : Oise water

15 PH 7.99

Turbidity 9.9 NTU

Organic matter (O.M.) 5.64 mg O₂/l

20

PRODUCT (Example No.)	QUANTITY IN g/m ³ (of Al ₂ O ₃)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
1	3	1	0.88	0.80	7.88	2.94	89
4a	3	0.98	0.93	0.91	7.84	3.10	123
4b	3	1.2	1.02	0.91	7.82	3.08	120

TABLE 5

25

Water type : Oise water

PH 8.24 (after adding sodium hydroxide)

Turbidity 21 NTU

Organic matter (O.M.) 6.92 mg O₂/l

PRODUCT (Example No.)	QUANTITY IN g/m ³ (of Al ₂ O ₃)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
1	3	0.94	0.83	0.72	8.08	2.86	163
4a	3	1.05	1	0.99	8.03	2.86	242
4b	3	1.25	0.99	0.93	8.02	2.88	238

It can be seen that even with a very basic water the product of the invention enables a concentration to be achieved which is below the maximum permissible figure of 200 µg/l given in the European Council Directive of 15 July 1980.

TABLE 6

Water type : Seine water

PH 7.97

Turbidity 42 NTU

Organic matter (O.M.) 6.96 mg O₂/l

PRODUCT (Example No.)	QUANTITY IN g/m ³ (of Al ₂ O ₃)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
4a	4	2.1	1.45	1.3	7.7	2.76	148
2	4	2.2	1.2	1.3	7.77	2.72	117
1	4	3	1.4	1.3	7.81	2.72	104

TABLE 7

Water type : Marne water

PH 8.02

Turbidity 60 NTU

Organic matter (O.M.) 6.68 mg O₂/l

5

10

PRODUCT (Example No.)	QUANTITY IN g/m ³ (of Al ₂ O ₃)	TURBIDITY OF THE SUPERNATANT			Final PH	O.M.	Residual Al
		3'	10'	20'			
4a	3	1.7	1.6	1.5	7.78	2.94	152
4c	3	1.7	1.55	1.45	7.80	2.78	152
2	3	1.8	1.6	1.5	7.82	2.72	128
1	3	1.8	1.6	1.4	7.80	2.66	118

Example 6

This example consists in comparing the results for turbidity and for residual aluminium of the products according to the invention in Examples 1 and 3 when they are employed at low rates of treatment: 1, 1.5, 2 and 3 g/m³ as Al₂O₃.

Trials are performed in a test jar according to the procedure described in Example 5 in a water of the Seine water type.

Table 8 shows the values of pH, turbidity and of the quantity of organic matter of the Seine water, which were measured before treatment with the aid of the products of Example 1 and 3 (tests A to P).

Table 8

Test No.	WATER pH	TURBIDITY (NTV)	OM (mgO ₂ /l
A			5.88
B-C			6.08
D-E	8.02	8.2	
F-G	8.05	7.4	
H-I		10	5.88
J-K		10	5.48
L	8.1	12	4.68
M-N	8	8.3	
O-P	7.91	12	

The mean values of the results obtained are repeated in Table 9, the product of Example 3 being taken as reference. The percentages shown are obtained as follows:

$$\text{difference in the parameter } x (\%) = \frac{\text{value of } x \text{ in Example } i}{\text{value of } x \text{ in Example 3}} \times 100 - 100$$

with $i = 1 \text{ or } 3$

N.B. The differences are really significant only when their absolute value is higher than or equal to 5 %.

TABLE 9

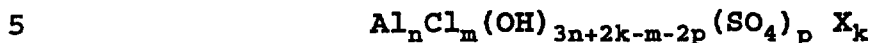
PRODUCT (EXAMPLE No.)	QUANTITY IN g/m3 (Al ₂ O ₃)	DIFFERENCE IN				
		TURBIDITY OF THE SUPERNATANT (%)			O.M (%)	residual Al (%)
		3'	10'	20'		
1 3	1	14 0	9.3 0	8.9 0	-0.7 0	- 0
1 3	1.5	18 0	9.2 0	6 0	1.8 0	- 10 0
1 3	2	20 0	9.9 0	3.3 0	0	0
1 3	3	5.25 0	0.34 0	-2.4 0	- 0	- 0



CLAIMS

1. Basic aluminium chlorosulphate in the form of an aqueous solution, characterized in that it comprises:

- a product of formula:



in which:

- n, m, p and k denote the molar concentrations (mol/l) of the components in solution

10 - x denotes an alkaline-earth substance, preferably calcium

- less than 20 % of the SO_4^{2-} ions can be precipitated by reacting with barium chloride at ambient

temperature the basicity : $\frac{3n+2k-m-2p}{3n}$ of which is

between 45 and 70 %.

15 2. Product according to Claim 1, characterized in that the ratio (Al equivalent)/Cl, $3n/m$, is lower than 2.8.

3. Product according to Claim 1 or 2, characterized in that the basicity is between 50 and 65 %.

20 4. Product according to one of Claims 1 to 3, characterized in that the ratio Al equivalent/Cl is lower than 2.75.

5. Product according to one of Claims 1 to 4, characterized in that less than 5 % of the SO_4^{2-} ions can be precipitated by reaction with barium chloride at ambient temperature.

25 6. Process according to one of Claims 1 to 5, characterized in that

- its basicity is higher than or equal to 60 %

30 - the weight ratio Cl/ SO_4 is between 4.5 and 8.

7. Process for the manufacture of basic aluminium chlorosulphate according to Claim 1, characterized in that:

35 a) aluminium oxide, hydrochloric acid and sulphuric acid are brought into contact in aqueous solution in the following proportions:



$$1.89 < \frac{\text{HCl}}{\text{aluminium}} < 2.44$$

$$1.37 < \frac{\text{H}_2\text{SO}_4}{\text{aluminium}} < 1.73$$

5 the aluminium being expressed as Al₂O₃, the ratios being molar,

b) this solution is brought into contact with an alkaline-earth metal compound, the molar ratio of the alkaline-earth metal compound to the aluminium expressed
10 as Al₂O₃ being between 1.63 and 1.70,

c) the alkaline-earth metal sulphate is removed.

8. Process according to Claim 7, characterized in that the alkaline-earth metal compound is selected from calcium carbonate, hydroxide, oxide and bicarbonate.

15 9. Process for treatment of an aqueous medium, characterized in that a product according to one of Claims 1 to 6 is used.