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Abstract: A practically important class of aluminum salts, the alums, is structural prototype (original examples) and gives their name to a large number of analogous salts formed by other elements. Aluminum alums are mostly recommended for use in drinking water treatment process, example is $AlK(SO_4)_2 \cdot 12H_2O$. The dose of alum varies from 5mg / litre for relatively clear water to about 80mg / litre for very turbid water, the average dose is about 20mg / litre.

Coagulation is a process of removing finely suspended and colloidal impurities by the addition of requisite amount of chemicals (coagulants) to water, before sedimentation.

Key words: Alums, coagulations, drinking water treatment, fine suspended particles, colloidal impurities

INTRODUCTION

Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through succession of treatment steps (Octave, 2006). Fig. 1 shows a typical situation.

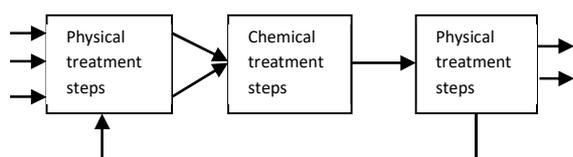


Fig. 1: Recycle

The raw materials undergo a number of physical treatment steps to put them in the form which they can be reacted chemically, then they pass through the reactor. The product(s) of the reaction then undergo further physical treatment (separations, purifications, etc.) so as to obtain the final desired product (Octave, 2006; Coulson, 2006).

In this paper, we are concerned with the chemical treatment step of the process. Economically this may be an inconsequential

unit, perhaps a simple mixing tank. Frequently, however, the chemical treatment step is the heart of the process, the thing that makes or breaks the process economically (Robert, 1981; Octave, 2006).

Definition of Alum: A white mineral salts, used medically, in dyeing etc, this definitions could be seen to be a lay-man's definition of alum.

A practically important Products of aluminum salts, the alums is structural prototypes (original examples) and gives their names to a large number of analogous salts formed by other elements (Cotton *et al.*, 1972; Greenwood, *et al.*, 1997). They conform generally to the formula: $M^+X^{3+}(SO_4)_2 \cdot 12H_2O$

Where 'M' is practically any univalent cation (Na, K, NH₄ etc), except for Li, which is too small to be accommodated without loss of stability of the structure. While 'X' is any trivalent cation (Al, Fe, V, Cr, Mn, Co, Ga, In, Rh and Ir).



When a solution containing potassium aluminum and sulphate ions is allowed to crystallize, transparent crystals of potash alum, $K^+ Al^{3+} (SO_4^{2-})_2 \cdot 12H_2O$, are obtained. The solid contains $\{K(H_2O)_6\}^+$ $\{Al(H_2O)_6\}^{3+}$ and SO_4^{2-} ions in solution (Greenwood, *et al.*, 1997). It is possible to prepare a series replaced by ammonium ion NH_4^+ , it is also possible to replace the 3-valent aluminum cation by 2-valent transition metal cations of about the same ionic size, e.g. Ti^{3+} , Cr^{3+} , Mn^{3+} , etc. The alums are isomorphous, readily forming overgrowths and solid solutions. Thus, having known these facts, one may say an alum is a transparent octahedral crystal of a univalent cations, trivalent cation and sulphate anions that conforms to the formula $M^+X^{3+} (SO_4^{2-})_2 \cdot 12H_2O$ (Cotton, *et al.*, 1972; Heys, 1975).

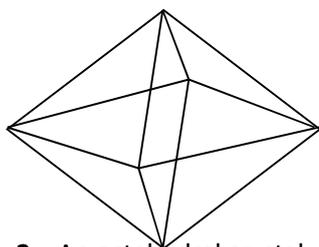


Fig. 2: An octahedral crystal

The term 'alums' is used so generally, that those alums containing aluminum are designated as aluminum alums.

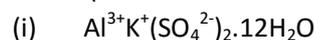
Alums are highly important in the treatment of drinking water in our modern day life (NWQMS, 2000). This is because, the addition of a calculated amount of this transparent octahedral crystalline substance (alum) bring about the coagulation and flocculation of finely suspended and colloidal impurities present in the sample of water undergoing treatment (APHA, 1985). Following these facts, alums are thus, referred to as coagulants.

This simple process referred to as coagulation process is the agglomeration of colloidal particles, which then settles at the bottom of the container (APHA, 1985; Health Canada, 1993; Liptrot, 1983). Fine particles (diameter <1micro meter) present in water as impurity may have been as a result of combustion or the chemical conversion of gaseous precursors into liquid or solid products (gas to particle conversion) (Oyem *et al.*, 2010).

Chemical Composition of Alums: Like every other chemical compounds, alums are generally made up of certain elements which includes;

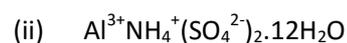
- i. Univalent cations (Na, K, NH_4 , etc)
- ii. Trivalent cations (Al, Fe, Cr, Ga, etc)
- iii. Sulphate ion
- iv. Water of crystallization

Types of Alums: Below are some examples of alums (Chemical formula and nomenclatures).



Aluminum (iii) potassium (i) sulphate (vi) – 12 – water (alum).

Potassium alum is also known as potash alum or tawas. It is aluminum potassium sulphate. This is the type of alum that you find in the grocery store used as a flocculant in drinking water purification, for pickling and in baking powder. It is also used in leather tanning, as an ingredient in aftershave and as a treatment to fireproof textiles.



Aluminum (iii) ammonium sulphate (vi) – 12 – water.

Ammonium alum is used for many of the



same purposes as potassium alum and soda alum. Ammonium alum finds applications in water purification, in tanning, dyeing textiles, making textiles flame retardant, in the manufacture of porcelain cements and vegetable glues, and in some deodorants.

- (iii) $\text{Cr}^{3+}\text{K}^+(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$
Chromium (iii) potassium (i) sulphate (vi) – 12 – water.
Chrome alum or chromium alum is a deep violet compound used in tanning and can be added to other alum to grow lavender or purple crystals. Other examples are;
- (iv) $\text{Ga}^{3+}(\text{NH}_4^+)(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$
Galinium (iii) ammonium sulphate (vi) – 12 – water.
- (v) $\text{Cr}^{3+}(\text{NH}_4^+)(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$
Chromium (iii) ammonium sulphate (vi) – 12 – water.
- (vi) $\text{Fe}^{3+}\text{K}^+(\text{SO}_4^{2-})_2 \cdot 12\text{H}_2\text{O}$
Iron (iii) potassium (i) sulphate (vi) – 12 – water (Iron alum).

We can still have some more alum prepared from other monovalent and trivalent cations.

Aluminum alums are mostly used in drinking water treatment and $\{\text{K}_2(\text{SO}_4)\text{Al}_2(\text{SO}_4) \cdot 24\text{H}_2\text{O}\}$ is the most widely used aluminum alum in this case. The dose of alum varies from 5mg/litres for relatively clear water to about 80mg/litres for very turbid water, the average dose is about 20mg/litres (NWQMS, 2000). Alum of potash (potash alum), like aluminum sulfate, is used as a mordant in dyeing, since it

form aluminum hydroxide by hydrolysis (Heys, 1975).

Properties of Alums: For any substance (chemical) to be regarded as alum, it must have the following properties;

- (i) Must be able to remove quickly and completely, fine suspended and colloidal particles from water (coagulation / flocculation).
- (ii) Must also have the advantages of removing from water, colour, odour and taste.
- (iii) Must be able to increase the acidity

of the water (Health Canada, 1993), by forming precipitated metallic hydroxide (e.g. aluminum hydroxide) and a mineral acid (H_2SO_4) which remains in solution, until it is treated with lime for pH correction (Heys, 1975; Skoog, *et al.*, 1975; Atkins, 1998).

MECHANISM OF COAGULATION

Coagulation (Colloidal Precipitates): Individual colloidal particles are so small that they are not retained on ordinary filtering median; furthermore, Brownian motion prevents their settling out of solution under the influence of gravity. However, the individual particles of most colloids can be caused to coagulate or agglomerate to give a filterable non-crystalline mass that rapidly settles out from solution (Health Canada, 1993).

Coagulation is a process of removing finely suspended and colloidal impurities by the addition of requisite amount of chemicals,



(called coagulants) to water, before sedimentation (Liptrot, 1983).

A very effective method of coagulation is increasing the electrolyte concentration of the solution by addition of a suitable ionic compound (Liptrot, 1983). Under this circumstance, the volume of the solution that contains enough ions of opposite charges to neutralize the charge on the particles is reduced. Thus, the introduction of an electroplate has the effect of shrinking the counter ion layer, with the result that the surface charge on the particles is more completely neutralized. With their effective charge decreased, the particles can approach one another more closely (Liptrot, 1983; Jain, *et al.*, 1992).

In drinking water treatment, when alum is added to water, it forms an insoluble gelatinous, flocculent precipitate. Which during its formation and decent through the water, adsorbs and entangles the fine suspended particles forming bigger flocs, which settle down easily (Greenwood, *et al.*; 1997; Health Canada, 1993; Liptrot, 1983; APHA, 1985). Coagulants like alum produce a cation e.g. Al^{3+} which neutralizes the negative charge on the colloidal clay particles. After being rubbed of their charges, the clay particles moves nearer to one another and combines to form bigger particles, which settle down due to gravity. The gelatinous precipitate formed from the addition of coagulants, has the property of removing fine suspended and colloidal particles quickly and completely (Greenwood, *et al.*; 1997; Health Canada, 1993). The coagulants also possess the advantages of removing colour, odour and

taste from water. (Skoog, *et al.*, 1975; Liptrot, 1983).

A coagulated colloid consists of irregularly arranged particle which form a loosely packed, porous mass. Within this mass, a large internal surface area remains in contact with the solvent phase (Fig. 3). Adhering to these surface will be most of the primary adsorbed ions which on the un-coagulated particles. Even though the counter – ion layer surrounding the original colloidal particles is properly considered to be part of the solution, it must accompany the particle (in the film of liquid surrounding the particle) through the processes of coagulation and filtration (Cotton *et al.*, 1972; Liptrot, 1983).

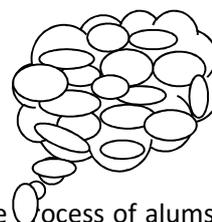
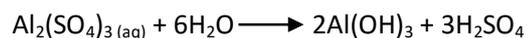


Fig 3:

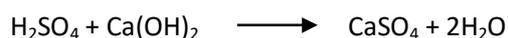
In addition, the process of alums in coagulation could be seen as a neutralization process, since the alum furnishes cations that neutralize the anions of the colloidal particles and hence, rendering them inactive. The chemical equations bellow shows the mechanism of coagulation;



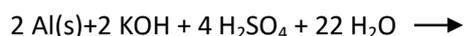
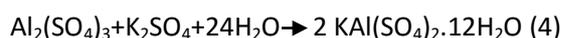
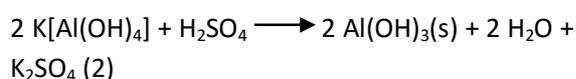
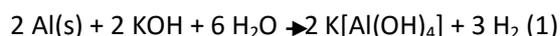
The above equations show that when an aqueous solution of alum $[Al_2(SO_4)_3]$, is added in excess into the water sample, the pH value of the solution decreased, that is, the solution turned acidic (with the precipitation of the



hydroxides of aluminum). The effluents obtained from the coagulation and flocculation processes are treated with lime for pH correction (to neutral) (Heys, 1975; Liptrot, 1983; Jain et al., 1992; Atkins, 1998).



Stoichiometry of the Preparation of Alum: To better appreciate the hydration of metal ions, it is important to know the stoichiometry of alum preparation. The stoichiometry involved in the sequence of reactions leading to the preparation of alum provides the mole relationship between aluminum and alum that is required to calculate the percentage yield.



The overall reaction for the synthesis of alum, equation (5), is obtained by adding reactions (1-4) and canceling like-species. The overall reaction stoichiometry (5) informs us that 2 moles of aluminum will produce 2 moles of alum.

Species of Hydration of Metal Ions: In a fundamental sense, metal ions simply dissolved in water are already complex, they form aquo ions (Sienko, *et al.*, 1971; Heys, 1975; Atkins, 1998).



Where M = Metal ion

X = Co-ordination

n+ = Charge of metal

$[\text{M}(\text{H}_2\text{O})_x]^{n+}$ = Aquo ion

Thus, the logical place to begin a discussion of the formation and stability of complex ions in aqueous solution is with the aquo ions themselves. From thermodynamics cycles the enthalpies of forming aqueous metal ions in water can be estimated and the results, $2.10^2 - 4.10^3 \text{ KJ mol}^{-1}$ (Table 1), shows that these interactions are very strong indeed. It is of importance in understanding the behavior of metal ions in aqueous solution, so as to know how many water molecules each of these ions binds with by direct metal-oxygen bonds (Sienko, *et al.*, 1971; Heys, 1975; Jain, *et al.*, 1992; Atkins, 1998).

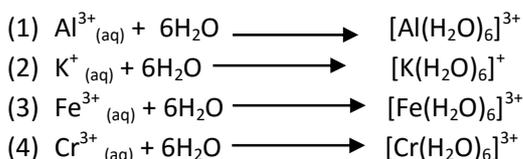
Table 1:

Enthalpies of Hydration of some ions, KJ mol^{-1}

H ⁺	1091	Ca ²⁺	1577	Cd ²⁺	1807
L ⁺	519	Sr ²⁺	1443	Hg ²⁺	1824
Na ⁺	406	Ba ²⁺	1305	Sn ²⁺	1552
K ⁺	322	Cr ²⁺	1904	Pb ²⁺	1481
Rb ⁺	293	Mg ²⁺	1841	Al ³⁺	4665
Cs ⁺	264	Fe ²⁺	1946	Fe ³⁺	4430
Ag ⁺	473	Co ²⁺	1996		
Ti ⁺	326	Ni ²⁺	2105		
Be ²⁺	2494	Cu ²⁺	2100		
Mg ²⁺	1921	Zn ²⁺	2046		



The hydration products of the following metal ions Al^{3+} , K^+ , Fe^{3+} , Cr^{3+} are shown below;



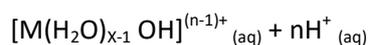
The above equations show that when metals are dissolved in water, complexes are formed, these complexes also known as aquo ions have octahedral symmetry (Sienko, *et al.*, 1971; Heys, 1975; APHA, 1985; Jain *et al.*, 1992; Atkins, 1998).

Table 2 below gives the colours of the aquo ions shown above;

Table 2:

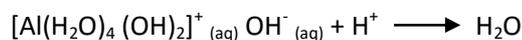
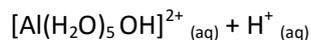
S/N	Aquo ions	Colour
1	$[Al(H_2O)_6]^{3+}$	Colourless
2	$[K(H_2O)_6]^+$	Colourless
3	$[Fe(H_2O)_6]^{3+}$	Brown form
4	$[Cr(H_2O)_6]^{3+}$	Violet form

These complexes have the ability of reducing the pH value, that is increasing the acidity of water, by the liberation of hydrogen ion, below is a formula that shows the mechanism of hydrogen ion liberation; (Sienko, *et al.*, 1971; Heys, 1975; APHA, 1985; Atkins, 1998,).



Where n = number of moles of protons donated.

Example;



Functions of Alums (Flocculation or pH

Reduction): Samples high in suspended solids may consume appreciable quantities of iodine in acid solution. The interference due to solids may be removed by alum flocculation. When 10g alum solution was dissolved in water, diluted to 100ml and concentrated ammonium hydroxide (NH_4OH) was added, sample was collected in a glass – stopper bottle of 500 to 1000ml capacity. Then added was 10ml alum solution and 1 to 2ml conc. NH_4OH . Stopper and invert gently for about 1 minute, let sample settle for about 10 minutes and siphon clear supernatant into a 250 – 300ml DO bottle until it over flows. Avoid sample aeration and keep siphon submerged at all times. Following this procedure as described above with the precipitation of the aluminum hydroxides (APHA, 1985; Liptrot, 1983; Jain *et al.*, 1992; Atkins, 1998).

The supernatant solution is preponderantly acidic, that is to say, there is a reduction in the pH value of the sample (Health Canada, 1993). The equation for the reaction is same as that under the section ‘Coagulation (Colloidal Precipitates)’, except for concentrated NH_4OH , which was used for the pH correction instead of lime $[Ca(OH)_2]$ that was used in that section (APHA, 1985; Liptrot, 1983; Jain *et al.*, 1992; Atkins, 1998).

The equation for the reaction is given as;



Solubility of Alums: For coagulation to be effective, alums must be soluble in water. The



solubility of the various alums in water varies greatly, sodium alum being readily soluble in water, while cesium and rubidium alums are only sparingly soluble (Greenwood, et al; 1997). The various solubilities at temperatures T (°C) of some alum are shown in table 3.

Table 3:

At temperature T, 100 parts water dissolve:

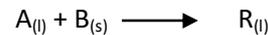
T (°C)	Ammonium alum	Potassium alum	Rubidium alum	Cesium alum
0	2.62	3.90	0.71	0.19
10	4.50	9.52	1.09	0.29
50	15.9	44.11	4.98	1.235
80	35.20	134.47	21.60	5.29
100	70.83	357.48		

From table 3, it is seen that the solubility of alum is directly proportion to the operating temperature of the process.

Rate Equation: Considering heterogeneous reactions, since more than one phase is present, the movement of material from phase to phase must be considered in the rate equation. Thus the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics terms, this mass transfer terms are different in type and numbers in the different kinds of heterogeneous systems; hence, no single rate expression has a general application (Octave, 2006).

Assume, when dilute 'A' diffuses through a stagnant water film onto a plane surface consisting of 'B', reacts there to produce 'R' which diffuses back into the mainstream. The

overall rate expression and result for the liquid/solid reaction is given as;



By diffusion, the flux of A to the surface is

$$r''_{A1} = (1/S) (dN_A/dt) = - \mathcal{D}/x^* (C_{Al} - C_{As}) = k_l(C_{Al} - C_{As}) \quad (i)$$

the reaction is first order with respect to 'A', so based on unit surface

$$r''_{A2} = (1/S) (dN_A/dt) = k'' C_A \quad (ii)$$

At steady state the flow rate to the surface is equal to the reaction rate at the surface (steps in series). So

$$r''_{A1} = r''_{A2}$$

From Eqs. (i) and (ii)

$$k_l(C_{Al} - C_{As}) = k'' C_{As}$$

From which

$$C_{As} = [(k_l)/(k_l + k'')] C_{Al} \quad (iii)$$

By substituting Eq. (iii) into either Eq. (i) or (ii) then eliminating C_{As} which cannot be measured, gives

$$r''_{A1} = r''_{A2} = r''_A = - (1)/[(1/k_l) + (1/k'')] C_{Al} = - k_{overall} C_{Al}, \quad [\text{mol}/\text{m}^2.\text{s}] \quad (iv)$$

This result, Eq. (iv) shows that 1/k_l and 1/k'' are additive resistances.

where;

'A' = Alum in water

'B' = Fine suspended solid particle in water



$r''_{A1} = r''_{A2} = r''_A$ = rates of reactions with respect 'A'.

C_{Al} = Concentration of 'A' in liquid phase (mol/m³)

C_{As} = Concentration of 'A' on surface of solid (mol/m³)

K_i, k_1, k'' = reaction rate constants

N_A = amount of 'A' used

t = time of reaction

\mathcal{D} = molecular diffusion coefficient (m²/s)

$X^* = (C_{Al} - C_{As})$

ensure that any residual amount of this chemical, byproducts of their reactivity or minor contaminants in their formulations do not pose an unacceptable health risk.

Alums are added to drinking water mainly to reduce or eliminate the incidence of waterborne disease, for other public health measures, and to improve the aesthetic quality of the water. Any chemical used in, on, or near drinking water sources, or used during the treatment of drinking water should:

- be effective for the desired outcome
- not present a public health concern
- not result in the chemical, its byproducts or any contaminants exceeding drinking water guideline values.

CONCLUSION

The production of safe drinking water economically, is vital for society. In recent decades, there have been numerous examples throughout the world of poor water quality impacting adversely on human health. Such episodes are common in most parts of Nigeria, especially in the rural areas, but the terrible consequences of compromised disinfection and blooms of cyanobacteria serve to remind us of the need for drinking water treatment.

Addition of alums to make water safe for consumption is economically viable, this is widely practiced by the water industry and has generally been accepted by the community. However, safeguards must be sufficient to

RECOMMENDATIONS

Only calculated amount of alum should be added in a sample of drinking water under treatment and must be administered only by a competent person.

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