ALUMINUM SULFATE AND ALUMS

1. Introduction

Aluminum sulfate octadecahydrate [7784-31-8], $Al_2(SO_4)_3 \cdot 18H_2O$, and its aqueous solutions are used primarily in the paper (qv) industry for sizing and as a flocculating agent in water (qv) and wastewater treatment. This material is often called papermakers' alum or alum. Because this salt is precipitated from aqueous solution, aluminum sulfate hydrate [17927-65-0], $Al_2(SO_4)_3 \cdot nH_2O$, can have variable composition and is sometimes referred to as cake alum or patent alum. The solid commercial hydrate, generally written as the 18-hydrate, is typically dehydrated to correspond to from 17.0–17.5% Al_2O_3 where $n = 13-14$ (1,2). This dehydrated form is called dry alum, ground or lump. Aluminum sulfate solutions are typically 7.5–8.5% Al_2O_3 and are known as liquid alum.

Confusion arises in the nomenclature of alum because double salt compounds, $M(I)Al(SO_4)_2$, where M is in the +1 oxidation state, have also traditionally been called alums. In particular, potassium aluminum sulfate [15007-61-1] $KAl(SO_4)_2 \cdot nH_2O$, is referred to as ordinary alum or potash alum.

Anhydrous aluminum sulfate [10043-01-3], $Al_2(SO_4)_3$, is a specialty item used in food applications.

2. Properties

Over 50 acidic, basic, and neutral aluminum sulfate hydrates have been reported. Only a few of these are well characterized because the exact compositions depend on conditions of precipitation from solution. Variables such as supersaturation, nucleation and crystal growth rates, occlusion, nonequilibrium conditions, and hydrolysis can each play a role in the final composition. Commercial dry alum is likely not a single crystalline hydrate, but rather it contains significant amounts of amorphous material.

2.1. Hydrates. Aluminum sulfate hydrates, $Al_2(SO_4)_3 \cdot nH_2O$, where n ranges from 0 to 27 have been reported (3–6). Relative decreasing vapor pressure studies indicate the presence of an octadecahydrate, hexadecahydrate, dodecahydrate, dihydrate, and the anhydrous salt, assuming that basic aluminum sulfates are not formed during the dehydration (3).

Thermal analysis of the dehydration of $Al_2(SO_4)_3 \cdot 18H_2O$ shows loss of 15 moles of water between 40°C and 250°C and 3 moles between 250°C and 420°C (7). Heating rate can affect the product. Although rapid heating can fuse hydrated aluminum sulfate containing >35% water and puff material containing 25–35% water, these problems do not occur during slow heating in an agitated bed. An aluminum sulfate hydrate can dissolve in its water of crystallization during heating.

2.2. Solubility. The aqueous solubility of a typical commercial aluminum sulfate, $Al_2(SO_4)_3 \cdot nH_2O$, where $n = 14-18$, is shown compared to the solubility of the octadecahydrate in Table 1 (2,8). Differences in solubilities probably

Table 1. **Aqueous Solubility of Aluminum Sulfate Hydrates, $Al_2(SO_4)_3{\cdot}nH_2O$**

Temperature, °C	Solubility, $\frac{\text{g anhydrous salt}}{\text{100 g satd soln}}$	
	$n = 18^a$	$n = 14-18^b$
0	27.5	23.9
10	27.6	25.1
20		26.6
25	27.8	
30	28.0	28.8
35	28.4	
40	28.8	31.4
50	29.9	34.2
60	31.0	37.2
70	32.8	39.8
80		42.2
82	36.6	
90		44.7
95	41.9	
100		47.1
103	46.9	

[a] Ref. 8.
[b] Commercial hydrate data from ref. 2.

result from small amounts of impurities such as iron, and the slight excess of Al_2O_3 base present in technical grade commercial aluminum sulfate hydrate.

Aqueous solutions of aluminum sulfate can hydrolyze at temperatures of about 150°C (9) resulting in products having a formula such as $3Al_2O_3{\cdot}4SO_3{\cdot}9H_2O$, which is structurally related to alunite [12588-67-9], $K_2Al_6(SO_4)_4(OH)_{12}$ (10).

2.3. Crystallization. Acidified aluminum sulfate solutions can be supercooled 10°C or more below the saturation point. However, once nucleation begins, the crystallization rate is rapid and the supersaturated solution sets up. The onset of nucleation in a gently stirred supersaturated solution is marked by the appearance of silky, curling streamers of microscopic nuclei resulting from orientation effects of hydraulic currents on the thin, platelike crystals. Without agitation, nucleation in an acidified solution, in glass tubes, can yield extended crystalline membranes of such thinness to exhibit colors resulting from optical interference.

2.4. Other Properties. The formula weight for the octadecahydrate is 666.45 and its specific gravity is 1.69 at 17°C (11). Other physical properties such as percentage of Al_2O_3 in alum liquor vs specific gravity at 15.6°C, pH as a function of alum concentration, heat evolved on mixing $Al_2(SO_4)_3{\cdot}18H_2O$ and water, viscosity of aqueous alum solutions as a function of temperature, crystallization temperature of $Al_2(SO_4)_3{\cdot}18H_2O$ as a function of the alum concentration, and the boiling point of alum solutions as a function of the alum concentration have been reported (2,11). Representative data are given in Tables 2 and 3.

Table 2. **Aluminum Sulfate Solution Properties**

Composition, % Al_2O_3	pH[a]	Specific gravity at 15.6°C[b]	Crystallization temperature, °C[c]
2.0	2.9		
4.0	2.4	—	−4
5.0		1.182	−6
5.5		1.204	
6.0	2.1	1.222	−8
6.5		1.246	
7.0		1.269	−11
7.5		1.291	
8.0	1.9	1.314	−15
8.2			−16
8.4			−14
8.5		1.337	
8.6			8
8.8			29

[a] Values are for neutral alum solutions; commercial alum liquor contains excess H_2SO_4, and values run about 0.5 pH units lower; slightly basic alum solutions, some excess Al_2O_3, have values of about 0.5 pH units higher.
[b] Values depend on alum producing point; for example, at 8.0% Al_2O_3, range can be 1.311 to 1.334.
[c] Values are for the 18-hydrate, $Al_2(SO_4)_3{\cdot}18H_2O$.

3. Manufacture

In the United States, aluminum sulfate is usually produced by the reaction of bauxite or clay (qv) with sulfuric acid (see SULFURIC ACID AND SULFUR TRIOXIDE). Bauxite is imported and more expensive than local clay, generally kaolin, which is more often used. Clay is first roasted to remove organics and break down the crystalline structure in order to make it more reactive. This is an energy intensive process. The purity of the starting clay or bauxite ore, especially the iron and potassium contents, are reflected in the assay of the final product. Thus the selection of the raw material is governed by the overall economics of producing a satisfying product.

The optimum conditions for roasting the clay and the optimum strength (30–60%) of the sulfuric acid used depend on the particular raw material. Finely ground bauxite or roasted clay is digested with sulfuric acid near the boiling

Table 3. **Dissolution Time of Dry Alum, $Al_2(SO_4)_3{\cdot}14.3H_2O$, and Heat Evolved on Mixing**

Dry alum added to 378.5 L H_2O, kg	Dissolving time, min at			Heat evolved on mixing at 18°C, kJ[a]
	4°C	16°C	38°C	
91	9	6	2	8
181	15	9	3	18
272	25	15	5	26

[a] To convert J to cal, divide by 4.184.

point of the solution (100−120°C). The clay or bauxite-to-acid ratio is adjusted to produce either acidic or basic alum as desired and solids are removed by sedimentation. If necessary, the solution can be treated to remove iron. However, few, if any, of the many methods claimed to be useful for iron removal have been used industrially (12). Instead, most alum producers prefer to use raw materials that are naturally low in iron and potassium.

The clear supernatant solution is decanted and sold in liquid form or concentrated to approximately 61.5° Bé and then allowed to solidify to form blocks that are crushed, ground, and graded. A typical analysis for the dry product is: total Al_2O_3, 17.0−17.5%; Fe_2O_3 <0.5%; water of composition 42−43%; insoluble <1.0%. Liquid alum contains 7.5−8.5% Al_2O_3. At concentrations >8.5% Al_2O_3, crystallization of the solution may occur.

The iron-free grade of aluminum sulfate hydrate contains less than 0.005% iron as Fe_2O_3. It is manufactured from pure alumina trihydrate [12252-70-9] $Al_2O_3{\cdot}3H_2O$, rather than from bauxite or clay. Although a technical or commercial grade alum can be treated to remove iron, such processes are not sufficiently economical to meet the requirements for the iron-free grade (12). The presence of iron can cause discoloration or staining of the product employing the aluminum sulfate.

A process to produce aluminum sulfate from coal ash has been reported (13).

4. Economic Aspects

In the United States 79 companies produced aluminum sulfate in 1997 (14). The total U.S. production was 1161×10^3/t on a 17% Al_2O_3 basis.

The United States exported 7690 t of aluminum sulfate and imported 23,500 t in 2000 (15).

Aluminum sulfate hydrate is marketed as material commercial or technical grade containing a maximum of 0.5% Fe_2O_3. The commercial grade is available as a dry ground product containing from 17.0 to 17.5% Al_2O_3, 57−59% $Al_2(SO_4)_3$, and as an aqueous solution containing from 7.5 to 8.5% Al_2O_3. The price of aluminum sulfate from $152 to 292 /t in October 2002 (16).

5. Health and Safety Factors

Aluminum sulfate is orderless. When it is heated or burned, irrirant sulfur oxide fumes are produced.

The ACGIH threshold limit (TWA) is 2.0 mg/m^3 OSHA PEL is 2.0 mg/m^3 (17).

6. Uses

The pulp and paper industry and potable and wastewater treatment industry are the principal markets for aluminum sulfate. Over half of the U.S. aluminum sulfate produced is employed by the pulp and paper industry. About 37% is used to precipitate and fix rosin size on paper fibers, set dyes, and control slurry pH. Another 16% is utilized to clarify process waters. The alum sold for these purposes is usually liquid alum. It is frequently acidic as a result of a slight excess of H_2SO_4. Aluminum sulfate consumption by the pulp and paper industry is projected to remain constant or decline slightly in the near term because of more efficient use of the alum and an increased use of alkaline sizing processes (18).

Aluminum sulfate is used as a flocculating agent or coagulant in water and wastewater treatment (see FLOCCULATING AGENTS). This use, excluding the 16% employed in process water treatment by the pulp and paper industry, accounts for 44% of U.S. consumption. Alum sold to municipalities in the United States is required by the American Water Works Association (AWWA) to be basic as a result of a slight excess of Al_2O_3. When alum is added to water, positively charged hydrated or hydroxylated aluminum ions neutralize and adsorb negatively charged colloidal and suspended matter in the water causing the material to floc and settle out (19). Increased use of organic polymeric coagulants and combinations of organic and inorganic coagulants has decreased somewhat the aluminum sulfate market. Polyaluminum chloride, basic aluminum sulfate (20–22), and a more recent basic aluminum chlorosulfate (23,24) are all effective coagulants. The near term market for aluminum sulfate in water treatment is projected to remain flat.

Other uses for aluminum sulfate include tanning (see LEATHER), and as a pH stabilizer, cement (qv) hardening accelerator, mordant in dyeing (see DYES AND DYE INTERMEDIATES), anticaking agent, fire extinguisher, and as a flame retardant additive, a use which dates to the early Egyptians (see FLAME RETARDANTS). Wood (qv) and cellulose (qv) treatment, catalysis (qv), and pharmaceutical and cosmetic applications are known (see COSMETICS AND PHARMACEUTICALS). Japanese literature suggests uses as an absorbent for odor and gases (25). Alum is effective in reducing the phosphate content of sewage and wastewater and in combating the eutrophication of lakes (26,27). Russian literature cites uses in drilling muds (28).

Aluminum sulfate is a starting material in the manufacture of many other aluminum compounds. Aluminum sulfate from clay could potentially provide local sourcing of raw materials for aluminum production. Processes have been studied (29) and the relative economics of using clay versus bauxite have been reviewed (30). It is, however, difficult to remove impurities economically by precipitation, and purification of aluminum sulfate by crystallization is not practiced commercially because the resulting crystals are soft, microscopic, and difficult to wash effectively on a production scale (31–33).

Patents have been issued for the production of animal litter from ammonium sulfate (34,35).

7. Other Alums

The word alum is derived from the Latin *alumen,* which was applied to several astringent substances, most of which contained aluminum sulfate (25). Unfortunately, the term alum is now used for several different materials. Papermakers' alum or simply alum refers to commercial aluminum sulfate. Common alum or ordinary alum usually refers to potash alum which can be written in the form $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$, or it can refer to ammonium alum, ammonium aluminum sulfate. The term is also applied to a whole series of crystallized double sulfates $[M(I)M'(III)(SO_4)_2{\cdot}12H_2O]$ having the same crystal structure as the common alums, in which sodium and other univalent metals may replace the potassium or ammonium, and other metals may replace the aluminum. Even the sulfate radical may be replaced, by selenate, for example. Some examples of alums are cesium alum [7784-17-0], $CsAl(SO_4)_2{\cdot}12H_2O$; iron alum [13463-29-1], $KFe(SO_4)_2{\cdot}12H_2O$; chrome alum [7788-99-0], $KCr(SO_4)_2{\cdot}12H_2O$; and chromoselenic alum [17855-06-0], $KCr(SeO_4)_2{\cdot}12H_2O$.

Pseudoalums are a series of double sulfates, such as iron(II) aluminum sulfate [22429-82-9], $FeSO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$, containing a bivalent metal ion in place of the univalent element of ordinary alums. These pseudoalums have different crystal structures from those of the ordinary alums.

In industrial practice it is generally the aluminum content of alums that is important. Because aluminum sulfate is widely available, other alums are more specialty items and are no longer produced in quantities comparable to those of aluminum sulfate (19).

7.1. Ammonium Aluminum Sulfate. Ammonium aluminum sulfate [7784-26-1], $NH_4Al(SO_4)_2{\cdot}12H_2O$, is also known as ammonium alum or ammonia alum. It is a colorless crystal having a strong, astringent taste; formula weight 453.33; mp, 94.5°C; sp gr 1.64; and solubility of 12.0 g per 100 mL H_2O at 20°C (8). It is soluble in dilute acid and insoluble in alcohol. The material dehydrates at about 250°C (36) to porous, dry ammonium alum [7784-25-0], $NH_4Al(SO_4)_2$, formula weight 237.14, which is also called dried or burnt alum. Decomposition of the anhydrous material begins at 280°C and γ-Al_2O_3 is formed between 1000 and 1250°C.

Ammonium alum is manufactured by crystallization from a mixture of ammonium sulfate and aluminum sulfate or by the treatment of aluminum sulfate and sulfuric acid with ammonia gas. Ammonium alum is used in medicine, as a mordant in dyeing, dressing furs in tanning, paper sizing, and water purification. It can be used in baking powders (see BAKERY PROCESSES AND LEAVENING AGENTS). It has also been used as the starting material to produce finely powdered aluminum oxide for the manufacture of synthetic corundum gems (see GEMS, SYNTHETIC) (19).

7.2. Potassium Aluminum Sulfate. Potassium aluminum sulfate [7784-24-9]. $KAl(SO_4)_2{\cdot}12H_2O$, is a white, astringent crystal known as potassium alum, ordinary alum, or potash alum. Its formula weight is 474.39; mp 92.5°C; sp gr 1.75; and solubility 11.4 g per 100 mL H_2O at 20°C (8). It is soluble in dilute acid and insoluble in alcohol. It dehydrates at about 200°C to porous desiccated potassium alum [10043-67-1], $KAl(SO_4)_2$, a dried or burnt alum, which has a formula weight of 258.20.

Potassium alum is manufactured by treating bauxite with sulfuric acid and then potassium sulfate. Alternatively, aluminum sulfate is reacted with potassium sulfate, or the mineral alum stone, alunite, can be calcined and leached with sulfuric acid. Alunite is a basic potassium aluminum sulfate [1302-91-6], $K_2Al_6(SO_4)_4(OH)_{12}$, sp gr 2.58–2.75.

Potassium alum, which also occurs naturally as the mineral kalinite [7784-24-9], $KAl(SO_4)_2{\cdot}12H_2O$, sp gr 1.75, is used in tanning skins, as a mordant in dyeing, and in the pharmaceutical and cosmetic industries (see PHARMACEUTICALS; COSMETICS). It is used as a styptic pencil and as a hardening agent and set accelerator for cement and plaster. The ACGIH threshold limit value TWA is 2 mgAl/m^3 (12).

7.3. Sodium Aluminum Sulfate. Sodium aluminum sulfate [7784-28-3], $NaAl(SO_4)_2{\cdot}12H_2O$, known as sodium alum, is a colorless crystal having an astringent taste; mp 61°C; and sp gr 1.675. It is the most water soluble alum: 75 g per 100 mL H_2O at 20°C (8). It is soluble in dilute acid and insoluble in alcohol.

Sodium alum occurs naturally as the mineral mendozite. Commercially, it is produced by the addition of a sodium sulfate solution to aluminum sulfate. Small amounts of potassium sulfate, sodium silicate, and soda ash can be added to improve product handling and performance. After adjustment of the ratio of aluminum sulfate to sodium sulfate, water is evaporated to give a hard cake in the cooling pans. This cake is further heated in roasters and ground to a fineness of 99% through a 100-mesh (~150 μm) sieve.

In the United States, sodium aluminum sulfate is used as a leavening agent in baking applications.

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