

PRODUCTION OF PURE ALUMINIUM SULPHATE FROM COMMERCIAL ALUM

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Aluminium sulphate is produced within the country from imported hydrated alumina. The commercial grade alum, however, contains certain impurities due to which it cannot be used in paper and textile industries. Iron is one of the major objectionable impurities which imparts undesirable stain on fibre and fabric even if present in traces. Efforts were made towards removal of traces of iron by oxidizing ferrous iron into ferric state, which is subsequently precipitated in acidic media. Parameters for quantitative oxidation and subsequent removal established.

Key words: Iron, Aluminium sulphate, Commercial alum.

INTRODUCTION

Aluminium sulphate has great importance due to its industrial use [1]. It is suitable as a precipitating agent in sizing of paper. It is used as a coagulant and precipitating agent in sewage treatment plants [2]. It is known as filter alum, besides other common names e.g., pickle alum, cake alum and palent alum. [3]. It is also used for setting dyes [4], the white variety of alumina is used for dyeing bright colours and dark variety for dark colours.

The process used for aluminium sulphate production is well established and fairly standard among producers because of simplicity. In 1946 eight municipal plants produced 12,000 tons of alum for direct use in water purification in the USA. In 1953 seven plants produced 14,000 tons which is less than 7% of total aluminium sulphate used in water treatment [5].

Extensive investigations [6] are on record on the nature and properties of aluminium sulphate and hydroxide from alumina salts. Various hydrates, condensation or polymerization products, and a number of crystallization forms and transformations have been proposed from time to time [7]. One reason for such diverse views on the subject is due to the widely varying properties of the precipitate with regard to the nature of associated impurities, degree of hydration, adsorbability and stability [8].

Aluminium sulphate comes to the market in two grades commercial grade (0.5% iron) and iron free (0.005% iron). Commercial alum produced in the USA is made from bauxite [9] and then made iron free.

The main objective of the present investigations is to prepare aluminium sulphate free from iron by some easy and inexpensive methods for its use in medicine, drinking water and sizing of paper. Pakistan is importing commercial

grade hydrated alumina from China and aluminium sulphate is produced with the interaction of sulphuric acid is not free from iron and hence the necessity of developing a process for its purification. Oxidation procedure involving the conversion of ferrous iron into ferric state by suitable oxidants like air, nitric acid, hydrogen peroxide and persulphate has been tried.

EXPERIMENTAL

A. Analytical instruments and reagents used

1. Shimadzu Double Beam Spectrophotometer UV 200 S.
2. Thermogravimetric Balance HT-SM.

Reagents

1. Hydroxylamine hydrochlorine. (A.R. 25% w/v).
2. Sodium acetate 0.5N (17g salt/250 ml. H₂O).
3. 2'-2' Dipridyl solution. (0.2g in 100 ml. of 0.2N HCl).
4. 0.1N Potassium dichromate. It was prepared from analar grade potassium dichromate and standardised against pure iron [10, 11] wire.
5. Diphenylamine indicator. 1% in sulphur acid.
6. Stannous chloride. Dissolved 2g SnCl₂. 2H₂O crystals in hot conc. hydrochloric acid and made up to one litre.
7. Mercuric chloride, saturated solution.

1% stock solution of commercial grade alum was prepared and Al₂O₃, Fe₂O₃, FeO, SO₃ and SiO₂ were determined both by conventional as well as spectrophotometric methods. The alkali metals were determined by flame photometer, calcium and magnesium by complexometric method and water of crystallisation was found after heating at 200°. The results are shown in Table 1.

Table 1. Analysis of commercial alum.

Al ₂ O ₃	13.8%	Na ₂ O	Traces
SO ₃	38.8%	K ₂ O	"
H ₂ O	45.6%	MgO	"
Fe ₂ O ₃	1.598%	SiO ₂	"
(Fe ⁺⁺ = 1.427%)		CaO	Nil
Fe ⁺ = 0.1715%)			

B. Oxidation procedure

Oxidation with air. Commercial grade alum was dissolved in water and acidified with sulphuric acid to remove turbidity. The solution was neutralized with slaked lime and the pH was adjusted to 4.3–4.4 followed by air oxidation of iron in cold as well as in hot. The iron was subsequently precipitated and removed. The results are given in Table 2 and Fig. 1,2.

Oxidation with nitric acid. 1.2N nitric acid was used for oxidation. The volume of nitric acid varied from 0.2ml

Table 2. Effect of air on the oxidation of iron.

Time (min.)	In Cold		In Boiling	
	Time (min.)	Iron oxidized %	Time (min.)	Iron oxidized %
15	3.40	9.8		
30	6.70	12.1		
45	37.99	99.7		
60	60.34			
70	93.00			

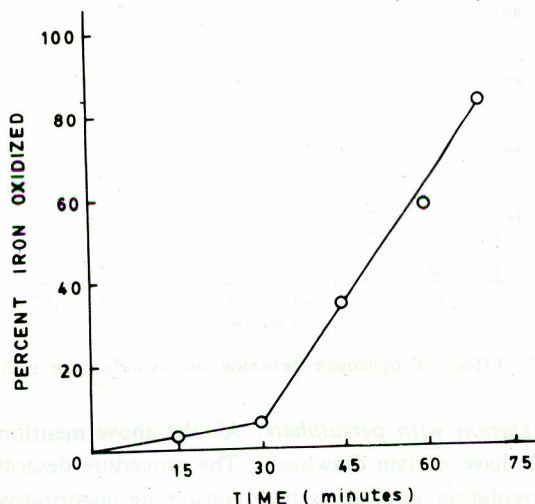


Fig. 1. Effects of air on oxidation of iron at room temperature.

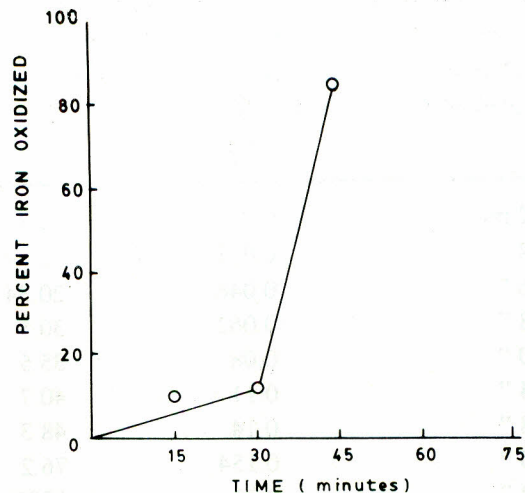


Fig. 2. Effect of air + heat on oxidation of Iron.

– 2.2ml. both in cold and after boiling for 2 min. 2.2ml. of 1.2N nitric acid are required for complete oxidation at room temperature while 1.5ml. are required when the alum solution is boiled. The results are shown in Fig. 3,4 and also in Table 3 and 4.

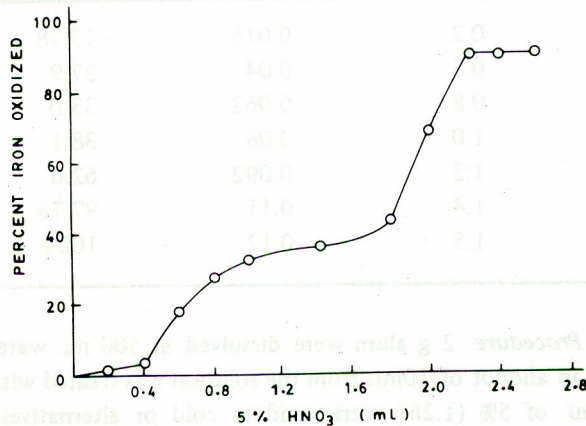


Fig. 3. Effect of nitric acid (room temperature) on oxidation of iron.

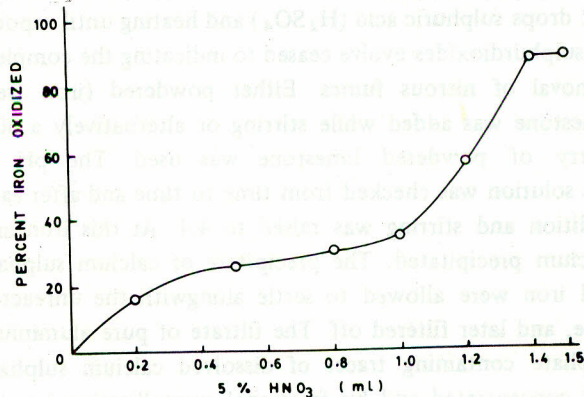


Fig. 4. Effect of nitric acid + heat (2 min.) on oxidation of iron.

Table 3. Effect of HNO₃ (cold) on oxidation of iron.

No.	1.2N HNO ₃ (added ml.)	Equivalence conc. HNO ₃ (16N)	Iron oxidized %
1.	0.2 ml.	0.015	1.3
2.	0.4 "	0.031	2.54
3.	0.6 "	0.046	20.34
4.	0.8 "	0.062	30.5
5.	1.0 "	0.08	35.5
6.	1.4 "	0.11	40.7
7.	1.8 "	0.14	48.3
8.	2.0 "	0.154	76.2
9.	2.2 "	0.17	100%

Table 4. Effect of nitric acid + heating on oxidation of iron.

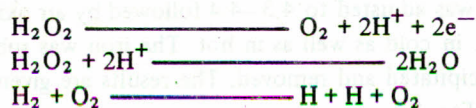
No.	1.2N HNO ₃ (added ml.)	Conc. HNO ₃ (16N)	Iron oxidized %
1.	0.2	0.015	17.78
2.	0.5	0.04	27.9
3.	0.8	0.062	33.0
4.	1.0	0.08	38.1
5.	1.2	0.092	62.6
6.	1.4	0.11	97.76
7.	1.5	0.12	100%

Procedure. 2 g alum were dissolved in 500 ml. water and an aliquot of 10ml. from the solution was treated with 2.2ml. of 5% (1.2N) nitric acid in cold or alternatively the solution was boiled for two min. with 1.5ml. dilute nitric acid for complete oxidation of iron. After adding 1-2 drops sulphuric acid (H₂SO₄) and heating until vapours of sulphurdioxides evolve ceased to indicating the complete removal of nitrous fumes. Either powdered (iron free) limestone was added while stirring or alternatively a 50% slurry of powdered limestone was used. The pH of the solution was checked from time to time and after each addition and stirring was raised to 4.4. At this iron and calcium precipitated. The precipitate of calcium sulphate and iron were allowed to settle alongwith the unreacted lime, and later filtered off. The filtrate of pure aluminium sulphate containing traces of dissolved calcium sulphate was concentrated and by fractional crystallisation i.e., by cooling the mass the precipitate of calcium sulphate separated out.

The precipitated calcium sulphate was removed from solution of aluminium sulphate. On cooling the supernatant liquid clear white crystals of Al₂(SO₄)₃. 18H₂O crystallised out. The crystals were separated from mother liquor and the later was mixed with fresh solution. (Table 3 and 4 and in Fig. 3 and 4).

Oxidation with hydrogen peroxide. Peroxide is a powerful oxidizing agent in both acid and alkaline media, the oxygen being reduced from an oxidation state of -1 to -2. However it is generally a slow oxidizing agent except with fairly powerful reducing agents [12].

According to Evan and Hush [13] the decomposition of hydrogen peroxide occurs at 80°.



As the decomposition of hydrogen peroxide occurs, oxygen evolves which reacts with ferrous ion to form ferric ion [14].

Procedure. 10ml. stock solution was added with 0.6ml. (5%) H₂O₂, and boiled for 2 min. for complete oxidation. Iron-free limestone powder or lime water was added to raise the pH to 4.3 by continuous stirring while adding. The precipitates of iron hydroxide and calcium sulphate were allowed to settle.

The precipitate was filtered off and the pure aluminium sulphate containing traces of calcium sulphate was concentrated. Calcium sulphate was separated by fractional crystallization and aluminium sulphate was crystallized. The results obtained are shown in Fig. 5 and Table 5.

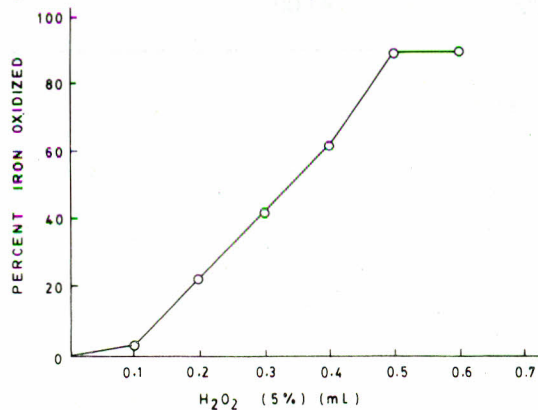


Fig. 5. Effect of hydrogen peroxide on oxidation of iron.

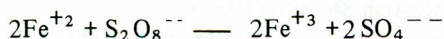
Oxidation with persulphate. All the above mentioned methods have certain drawbacks. The procedure described under oxidation with air is time consuming quantitatively though iron is oxidized. In the nitric acid oxidation

Table 5. Effect of hydrogen peroxide on oxidation of iron.

Volume of H ₂ O ₂ (ml.) Taken .5% % iron oxidized.	0.1ml.	0.2ml.	0.3	0.4	0.5	0.6
	2.34	24.2	46.1	67.97	99.7	100%

method, the presence of nitrates is highly objectionable and it is difficult to remove it.

The hydrogen peroxide method is expensive. Persulphate is considered a very strong and powerful oxidizing agent. It was therefore selected for this purpose because it ionizes into sulphate ions after oxidizing ferrous salts into ferric salts.



It has the added advantage that ordinary limestone containing iron as impurity can be used. The iron as impurity along with the iron in the alum is removed after addition of a small amount of potassium persulphate.

Procedure. 10 g. alum dissolved by adding 2ml. sulphuric acid in water to remove turbidity. The solution was then treated with calcium carbonate by slow and gradual addition of dry powder or its slurry with stirring until the pH was raised to 4.3-4.4. The precipitate was filtered and washed with hot water. The wash water was combined with the filtrate and boiled and 0.16g of potassium persulphate added. After boiling for (1.6% of the total Al₂(SO₄)₃) 2 min. the iron was allowed to settle down (Table 6 and Fig. 6), filtered and the filtrate was concentrated by heating. The fine calcium sulphate along with precipitated iron was removed by filtration. The pure aluminium sulphate was crystallized from the concentrated solution.

Table 6. Effect of persulphate on the oxidation of iron.

Persulphate ml. added (5%)	2ml.	5	10	15	20
%iron oxidization	11.1	39.26	56.97	86.53	100%

The alum solution was filtered to remove Fe⁺³ in precipitated form. The clear solution could be stored as such or concentrated to desired strength.

The solution was evaporated in a suitable evaporator to obtain basic Al₂(SO₄)₃. 18H₂O [15].

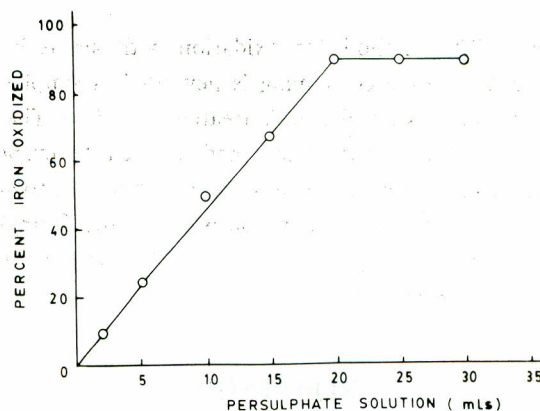


Fig. 6. Effect of persulphate + heat (2 min.) on oxidation of iron.

Crystals of aluminium sulphate were obtained and analysed according to the method given in the literature.

According to Wandell and Joel [13], Al₂(SO₄)₃ may be crystallized with difficulty from solution at ordinary temperature.

Thermogravimetric analysis. The aluminium sulphate obtained was analysed hermogravimetrically. The results are shown in graph 7. The data indicates that the resultant sample conforms to the formula Al₂(SO₄)₃. 18H₂O.

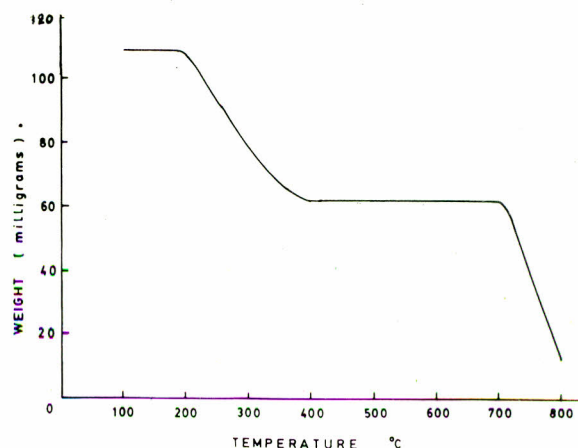


Fig. 7. Thermogram of purified aluminium sulphate.

DISCUSSION

Iron both in ferrous and ferric state is present in commercial grade alum. The ratio of ferrous to ferric is 1: 8.6 and thus it was considered imperative to oxidize the ferrous iron into ferric state.

The oxidation of Fe⁺² into Fe⁺³ was tried by different oxidants following standard methods.

All these different methods have certain limitations in one form or the other except for oxidation with per-

sulphate. The method for oxidation with air at boiling point though time consuming is nevertheless simpler and effective. The oxidized iron is treated with lime. The iron free solution is concentrated, and allowed to evaporate and crystallize. The purity of alum is comparable to analar grade alum and on analysis conforms to the formula of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ which was further confirmed by thermogravimetric analysis.

REFERENCES

1. J.W. Mellor, *Comprehensive Treatise on Inorganic Chemistry*. (1964), vol. V, p. 332.
2. M Mellor, German Pat., D.R.P. 353289 (1917).
3. Thorpe's Dictionary, I, 288.
4. Pliny, "Historia Naturalis", 34. 128, c. (77 ed. AD).
5. H.C. Faith, *Industrial Chemicals* (1957), 2nd ed. p. 75.
6. J.W. Mellor *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 5, 273 (1946).
7. R. Willstaller and H. Kraut, *Ber. Otsch. Chem. Ges.*, 56, B 149, 1117, (1925).
8. H.B. Weiser and W.O. Milligon, *J. Phys. Chem.*, 36, 3010, (1952).
9. *Encyclopedia of Chemical Technology*, vol. I, 654.
10. Arthur J. Vogel, *Quantitative Inorganic Analysis Theory and Practice* (1959), 2nd ed. p. 294.
11. W.W. Scott and N.H. Furman, *Standard Methods of Chemical Analysis* vol. 6, p. 1336.
12. Wandell M. Lotimer and J. Hildebrand, *Reference Book of Inorganic Chemistry*, 3rd ed. p. 30.
13. M.G. Evan, N.S. Hus and O. N. Uri, *Rev. Chem, Soc.*, 6, 186, (1952).
14. E. Abel, *Monatsh* 86, 326 (1955).
15. J. Counc. Sci. Ind. Res. India, 47, 597 (1974).