

# THE MANUFACTURE OF ALUMINIUM SULFATE

Aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , is widely used by industry in New Zealand. Its most common applications are in the pulp and paper industry and in the purification of water. In both these instances alum is used as a source of  $\text{Al}^{3+}$ , a highly charged ionic species. Negative particles, such as those which discolour our raw water supplies, are attracted to this cation, react with it and then precipitate out of solution as ionic solids.

Alum (as aluminium sulfate is commonly called) is manufactured in a simple two-step process from aluminium trihydrate and sulfuric acid according to the following reaction:



The first step involves mixing the ingredients in a reactor, and the second is the process of crushing the material to make the various grades of solid alum that are sold.

The major potential environmental hazard posed by this process is changes to the pH of surrounding watercourses, and so all effluent and nearby water sources are pH monitored. Effluent is also monitored to control the level of suspended solids.

## INTRODUCTION

Aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), commonly called alum, is produced as white crystals which are non-combustible and soluble in water. This 'dry' hydrate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ) is 17%  $\text{Al}_2\text{O}_3$  and is also sold as a 47% w/w aluminium sulfate solution which is 8%  $\text{Al}_2\text{O}_3$ . It is also sold in solid form as kibbled, ground or dust.

### Uses of aluminium sulfate

Aluminium sulfate has been used by man since 2000 BC, when the Egyptians used a mineral alum as a mordant in dyeing. It has long been used in paper sizing to improve durability and ink receptivity and in water treatment to clarify water. Other uses for alum include wastewater treatment, as a waterproofing agent and accelerator in concrete, as a clarifier for fats and oils and as a foaming agent in fire foams.

The aluminium ion has a high charge which makes it an excellent coagulant for colloidal<sup>1</sup> matter. In aqueous solution a number of hydrolysis species form e.g.  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Al}(\text{OH})_4^-$ , dependent on pH.

This property means that alum can be used to remove particles from water. The free  $\text{Al}^{3+}$  ions hydrate to form highly charged species such as  $\text{Al}_8(\text{OH})_{20}^{4+}$ . These are attracted to negatively charged species, which include the most common colloidal species in water:

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<sup>1</sup> A colloid is a system in which one substance is finely divided up within another system, e.g. fog is a colloid of water droplets finely divided up within the continuous medium of the air, and milk is a colloid of fat globules finely divided up within an aqueous solution.

clays and CaCO<sub>3</sub>. These coagulated particles are attracted to precipitated Al(OH)<sub>3</sub>, and coagulated particles stuck to the surface of an Al(OH)<sub>3</sub> gel precipitate out of the solution. The clarified water is then typically filtered. Every raw water has its optimum pH at which alum performs best. Jar tests (mini clarifier experiments) are carried out to optimise the dose in water treatment plants. The dose rate, the dose point and whether pH adjustment is necessary are determined for each plant.

In paper making the alum reacts with rosin sizes of various types, helping to attach the newly formed rosin aluminates to fibres. Sizing makes the paper water resistant. Alum, which exhibits a cationic charge, is also used to flocculate anionic trash including paper fines and other anionically charged material by neutralisation, in a similar way to water treatment, improving drainage, retention and strength of the material.

## THE MANUFACTURING PROCESS

Fernz Corporation Ltd have manufactured aluminium sulfate in New Zealand since the 1930's first under Farmers Fertiliser NZ Ltd and now as FERNZ Chemicals NZ Ltd at Morrinsville.

Aluminium sulfate is produced according to the following exothermic reaction:



Alum is generally produced batchwise in a reactor. The reactor is a stirred vessel made of materials resistant to the acidity and heat of the reaction.

The product produced until the mid 1960s was a lower grade aluminium sulfate made from bauxite or high alumina clays. This product generated silica waste and had too high a level of iron for papermakers, the major users of alum. In 1965 Farmers Fertiliser NZ Ltd changed to using aluminium trihydrate as a raw material for alum to satisfy the paper market.

### Raw materials

Aluminium trihydrate is purified from bauxite. Commercial bauxite (30-75% Al<sub>2</sub>O<sub>3</sub>) deposits occur in Australia, Jamaica, France, Guyana, Guinea, the USA and Brazil. Bauxite ore is dissolved in strong caustic soda to form sodium aluminate. The aluminium trihydrate is then precipitated by neutralisation (usually with carbon dioxide) or by autprecipitation (the Bayer process).

The other raw material, sulfuric acid, is manufactured for superphosphate production at Farmers Fertiliser Ltd. Acid arrives by road tanker and is pumped into storage tanks.

### Step 1 - Reacting the raw ingredients.

The aluminium trihydrate is transported and stored in one tonne bags. Each bag is carried by hoist to the feed hopper, where it is opened and conveyed to the reaction tank. The reaction water, trihydrate and sulfuric acid batch is stirred for a period of time with water vapour exiting through the stack.

## **Step 2 - Making the final product**

After the reaction period either liquid or solid alum is made. If liquid, the concentrated batch is run into the dilution tank filled with the dilution water where it cools over time. The liquid alum is then filtered and pumped to storage. There are overhead load out facilities at Morrinsville where a number of liquid chemicals are available in dispatch tanks for road tankers.

If solid is made, the concentrated alum is run into the casting pans where it sets, aided by fan cooling. The pans are forklifted to storage racks and from there they are taken to the Crushing Plant and dropped into a hopper. The pieces are broken further by a large kibbler followed by a small kibbler and then screened. Oversize particles go to a bagging hopper and are sold as kibbled product. The screened alum is rotary crushed and further screened to either return to the rotary crusher or be bagged as ground product. Dust is continually collected through an extraction system and is sold as product. The Crushing Plant is flexible and the ratio of kibbled to ground aluminium sulfate is variable.

## **ENVIRONMENTAL IMPLICATIONS**

All site effluent is managed by a Distributed Control System (DCS). Site run off and any spills are collected in sumps. All collection sumps have level probes which, once a limit is reached, start the sump pumps which pump the water through a common pH pot. If the pH is outside limits then the water goes to holding tanks where it is used with reaction water. If the pH is acceptable the water is discharged to the effluent stream. The effluent stream is pH monitored and is analysed for suspended solids. A variety of compounds and elements including soluble aluminium are analysed for off-site and the results reported to Environment Waikato.

The trihydrate bags are either sold for reuse or provided to the local council as containers for recycled plastic and aluminium cans.

FERNZ Chemicals NZ Ltd, Morrinsville is ISO9002 registered.

## **THE ROLE OF THE LABORATORY**

The product is analysed for  $Al_2O_3$  content, basicity, pH and insolubles in the on-site laboratory before delivery to customers. At regular intervals a random sample is analysed for heavy metals by an independent laboratory. The product is manufactured in accordance with the NZ Standard for Supply of Aluminium Sulfate for Use in Water Treatment.

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