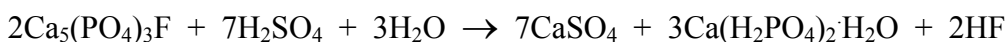


THE MANUFACTURE OF SULFURIC ACID AND SUPERPHOSPHATE

Superphosphate is the fertiliser most commonly used in New Zealand to ensure that soil has a sufficiently high phosphorous content. It is manufactured from the reaction between sulfuric acid and 'phosphate rock' (rock rich in the mineral fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$):



The sulfuric acid is manufactured on site in a three step process:

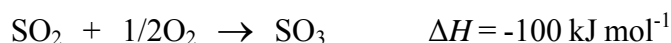
Step 1 - Production of sulfur dioxide

Sulfur (a byproduct from the refining of oil) is melted, impurities filtered off, and then burnt in oxygen to give SO_2 in accordance with the following equation:



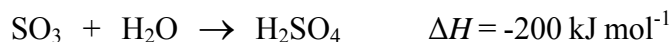
Step 2 - Conversion to sulfur trioxide

The SO_2 is then reacted with oxygen, in the presence of a V_2O_5 catalyst, to give SO_3 :



Step 3 - Absorption of SO_3 to form sulfuric acid

Finally the SO_3 is absorbed into a counter-current flow of H_2SO_4 , to give more H_2SO_4 :



This sulfuric acid is then used to produce superphosphate, with the excess being used in the production of aluminium salts or sold directly as sulphuric acid. The superphosphate is also produced in a three step process.

Step 1 - Phosphate rock blending and grinding

The phosphate rock is ground until at least 75% is less than 75 μm (microns) in diameter, and then analysed for composition. The proportions of various minerals present are altered to give the desired composition.

Step 2 - Superphosphate manufacture

Phosphate rock, sulfuric acid and water are mixed and then allowed to dry and react to give the superphosphate - a mixture of CaSO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O}$.

Step 3 - Granulation

The cake of superphosphate is then ground to give particles no more than 6 mm in diameter.

INTRODUCTION

To maintain a high level of animal and crop production, land usually requires the application of phosphate to supplement that occurring naturally. In New Zealand and Australia this is supplied mainly as superphosphate fertiliser.

Superphosphate is manufactured by reacting insoluble phosphate rock with sulfuric acid to form a mixture of soluble mono-calcium phosphate and calcium sulphate (approximately 9% phosphorous) which is able to be used by plants.

In many other parts of the world it is more cost effective to use triple superphosphate fertiliser. In this process phosphate rock is reacted with phosphoric acid to produce a product with 21% phosphorous. Triple superphosphate plants are more capital-intensive but with a more concentrated product these plants can service a greater area.

However, this product does not contain sulfur whereas superphosphate contains 13% sulphur. In many parts of the world areas of sulfur deficiency are showing up, and there is a trend back to single superphosphate. Other “high analysis” fertilisers are also available, such as di-ammonium phosphate (DAP) which contains 20% phosphorous and 18% nitrogen.

THE MANUFACTURE OF SULFURIC ACID

More sulfuric acid (by mass) is produced world-wide than any other chemical. The superphosphate industry relies on the production of sulfuric acid as one of the primary raw materials. All New Zealand fertiliser plants use the “contact process”. This article is based on the Farmers Fertiliser Limited plant at New Plymouth. Farmers Fertiliser Limited is a subsidiary of Fernz Corporation Ltd.

The process of manufacturing sulfuric acid can be described as three basic reaction steps.

Step 1 - Production of sulfur dioxide

This reaction is described by the equation:



Elemental sulfur is purchased on the international market having been recovered as a by-product of the oil refining process. This sulfur is melted by steam coils at 140°C in brick lined tanks. The molten sulfur is filtered to remove any impurities (usually iron or organic compounds). Lime is added to reduce the acidity of the molten sulfur therefore reducing its corrosivity.

The molten sulfur is pumped to the burner where it is burnt in an excess of dry air. The gas exiting the burner is maintained at 8 - 9%v/v sulfur dioxide and approximately 830°C due to the heat produced by the exothermic reaction. The sulfur dioxide/air gas mixture is then passed through the hot gas filter, where any ash contamination is removed.

Step 2 - Conversion to sulfur trioxide

The sulfur dioxide is converted to sulfur trioxide by reacting with oxygen over a catalyst. This reaction is described by the equation:



This reaction occurs in the converter, a four-stage reaction vessel with each stage

consisting of a solid catalyst bed through which the gas is passed. The catalyst used is vanadium pentoxide (V_2O_5) and potassium sulphate dispersed on a silica base which forms a porous support, giving a large surface area for reaction. It is believed that the V_2O_5 increases the rate of the overall chemical reaction by oxidising the SO_2 to SO_3 and being re-oxidised itself by the oxygen in the gas stream.

This reaction is exothermic and its equilibrium constant decreases with increasing temperature (Le Chatelier's Principle). **Figure 1** shows the percentage conversion of SO_2 to SO_3 that would be reached at an SO_2 concentration of 8% v/v and a range of gas temperatures. However, the reaction rate is also temperature dependent, so that if the temperature becomes too low the equilibrium point will not be reached. In practice, the gas temperature must be maintained between 400 - 500°C to maintain a high reaction rate and also a high conversion equilibrium.

As the reaction is exothermic, heat is generated across each of the catalyst beds. This heat must be removed between each stage to maintain the optimum reaction temperature into the following stage. The temperature rise through each catalyst bed and the inter-stage cooling is shown in **Figure 1**.

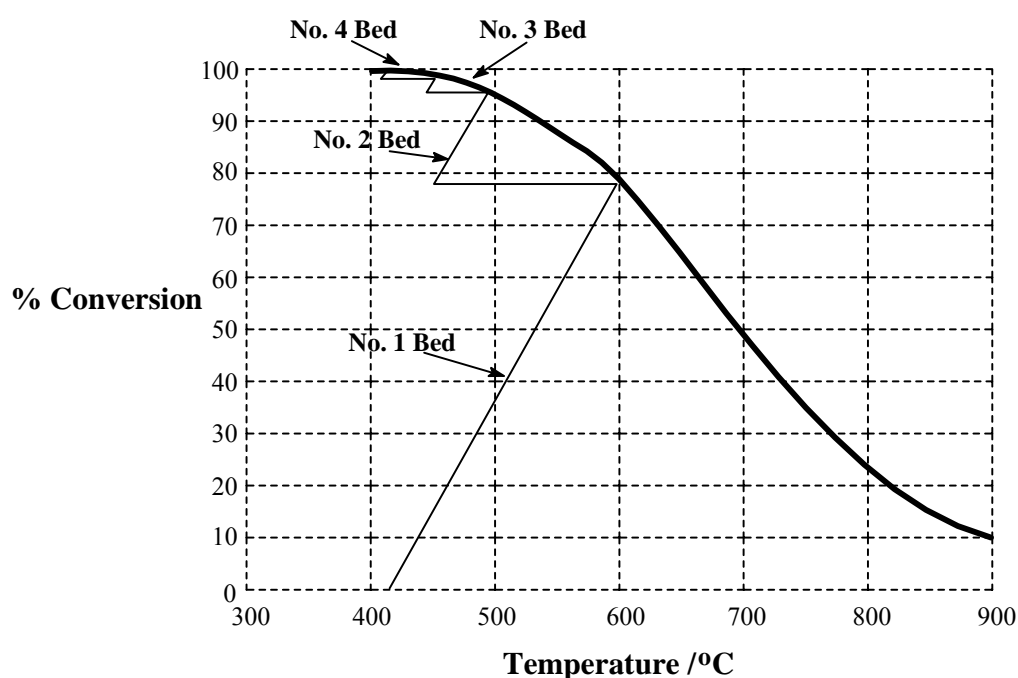


Figure 1 – The effect of temperature on the conversion of SO_2 into SO_3

The greatest degree of cooling is required between the first and second stages. Cooling after the second and third stages is by injection of dried air. The gas exiting the converter is used to pre-heat the boiler feed water. A simplified process flow diagram is shown in **Figure 2**.

Step 3 - Absorption of SO_3 to form sulfuric acid

The gas is passed to the absorption tower, a packed tower where SO_3 is absorbed into a counter-current flow of 98 - 99% sulfuric acid. The overall reaction can be

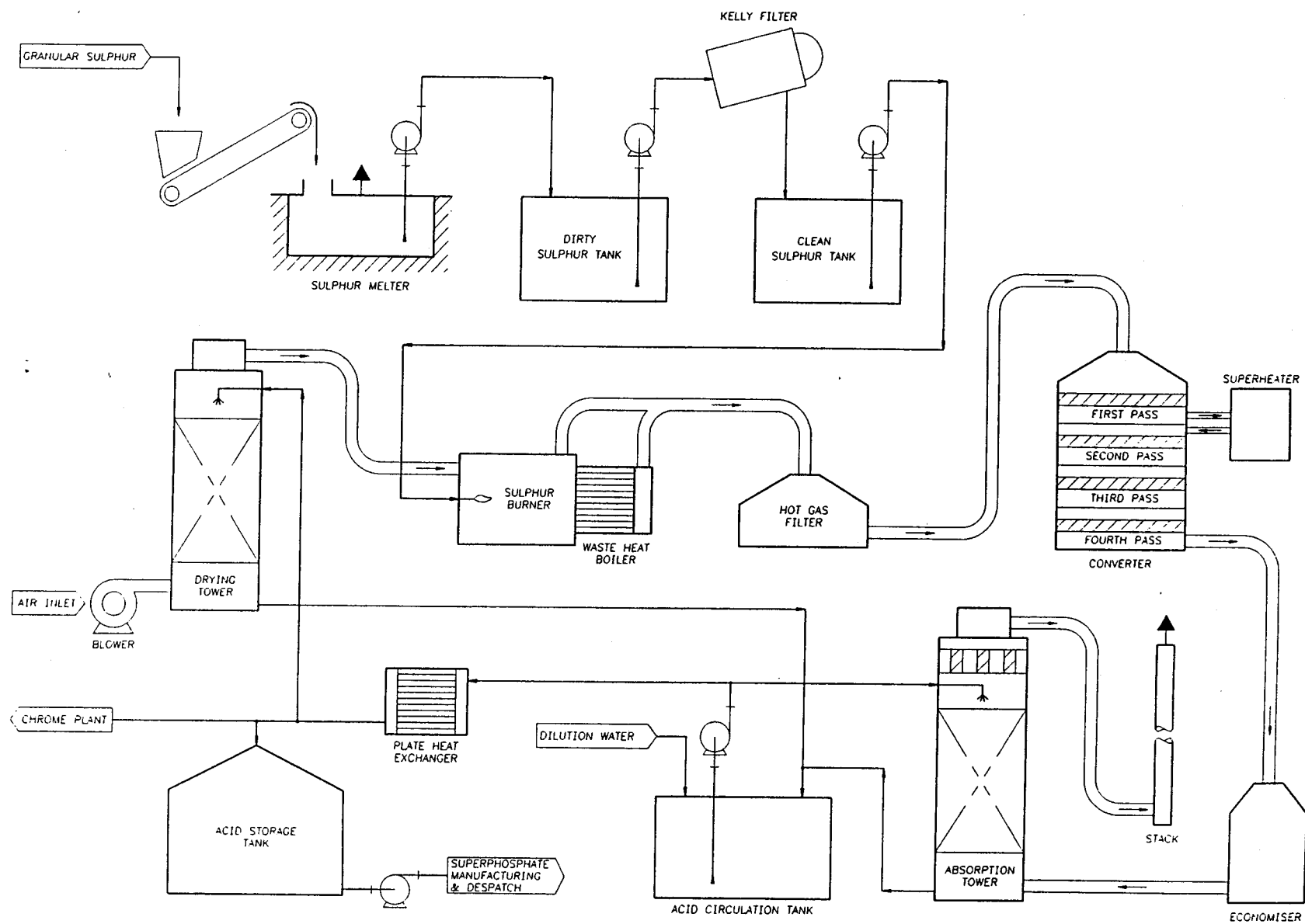


Figure 2 - Process flow diagram of the sulfuric acid plant

described by the following equation, where sulfur trioxide reacts with the free water to produce sulfuric acid:



The circulating sulfuric acid must be maintained at about 98% concentration and 70°C to maximise the absorption efficiency. The acid strength is important because the vapour pressure of sulfur trioxide above sulfuric acid is at a minimum at an acid strength of 98% (see **Figure 3**). At higher concentrations the increased vapour pressure is caused by SO₃ and at lower concentrations the water vapour pressure increases sharply and the resultant acid mist is not readily re-absorbed and escapes to the atmosphere.

The sulfuric acid is circulated at such a rate that there is only a very small increase in concentration through the absorber tower. Dilution water is added to the circulating acid tank and also as atmospheric water absorbed in the drying tower. A stream of sulfuric acid is continuously bled off and cooled through a plate heat exchanger before being passed into the storage tanks.

The overall conversion from sulfur to sulfuric acid is greater than 98.5%. The plant operates under an air discharge permit which controls emissions of sulfur dioxide and total acidity.

Traditionally mild steel has been used as the primary material of construction for process equipment containing 98% sulfuric acid. The corrosion rate is reasonably low, except at the air/liquid interface where atmospheric moisture encourages corrosion. The trend is now towards more sophisticated materials including teflon-lined steel pipework to reduce iron contamination of the sulfuric acid.

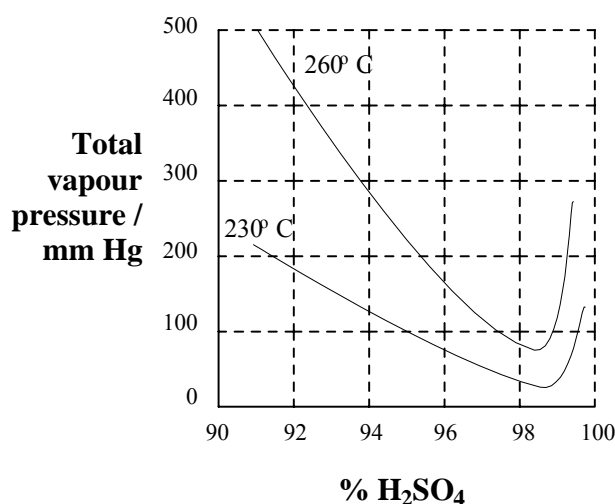
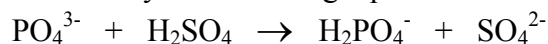


Figure 3 – Vapour pressure above sulfuric acid

As well as being used in the manufacture of superphosphate, sulfuric acid is transported by road tanker to IChem Ltd, Morrinsville, where it is used in the manufacture of aluminium salts (see article). Sulfuric acid is also sold commercially at either 98% concentration or diluted by IChem Ltd to 74%.

THE MANUFACTURE OF SUPERPHOSPHATE

The basic reaction in the manufacture of superphosphate is the reaction of insoluble phosphate rock with sulfuric acid to form the soluble calcium di-hydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$. This is described by the following equation:

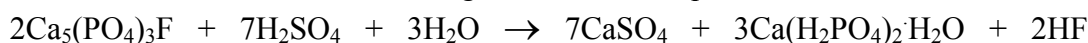


The phosphate rock, imported from Nauru, Jordan, Morocco, Israel and the USA, is mainly fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and is equivalent to 70 - 85% $\text{Ca}_3(\text{PO}_4)_2$ by weight. The actual composition of the phosphate rock varies with the source. The sulfuric acid is produced on the site as described in the previous section.

The reactions occurring during the production of superphosphate are complex and are usually summarised as follows:

1. $\text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{H}_2\text{SO}_4 \rightarrow 5\text{CaSO}_4 + 3\text{H}_3\text{PO}_4 + \text{HF}$
2. $\text{Ca}_5(\text{PO}_4)_3\text{F} + 7\text{H}_3\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow 5\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{HF}$

These reactions can be combined to give the overall equation:



There are other reactions occurring at the same time. For example, virtually all the HF reacts with other silica minerals associated with the fluorapatite (silicates, quartz) to form silicon tetrafluoride. These gaseous emissions are recovered as hydrofluosilicic acid (H_2SiF_6) in the scrubbing system. Carbonates in the rock also react with sulfuric acid.

The production of superphosphate consists of three distinct steps. See the process flow diagram (**Figure 4**).

Step 1 - Phosphate rock blending and grinding

Phosphate rock from different sources have different phosphate, fluoride and silica contents. These rocks are mixed in the blending plant to produce a product with a total phosphate concentration of 15%. The phosphate rock mixture is passed through a hammer mill which reduces the particle size to 0.5cm or less. The coarsely ground rock is then passed through an air swept roller mill (Bradley Mill) to attain a rock grit of approximately 75% less than 75 microns. The powdered rock is stored in a large hopper. The powder handling system is fitted with a dust collection system.

Step 2 - Superphosphate manufacture

The ground rock and sulfuric acid are reacted in a horizontal mixer. The feed rates are approximately:

- Phosphate rock - 25 tonnes/hour
- 98% Sulfuric acid - 14.5 tonnes/hour
- Water - 6 tonnes/hour

A continuous flow of the sloppy mix drops out of the mixer into the Broadfield Den. The den consists of a slowly moving floor (approx. 300 mm/min) to enable setting of the 'cake' and reciprocating sides, which prevent the superphosphate adhering to the walls. The partially matured superphosphate cake is cut out of the den with a rotating

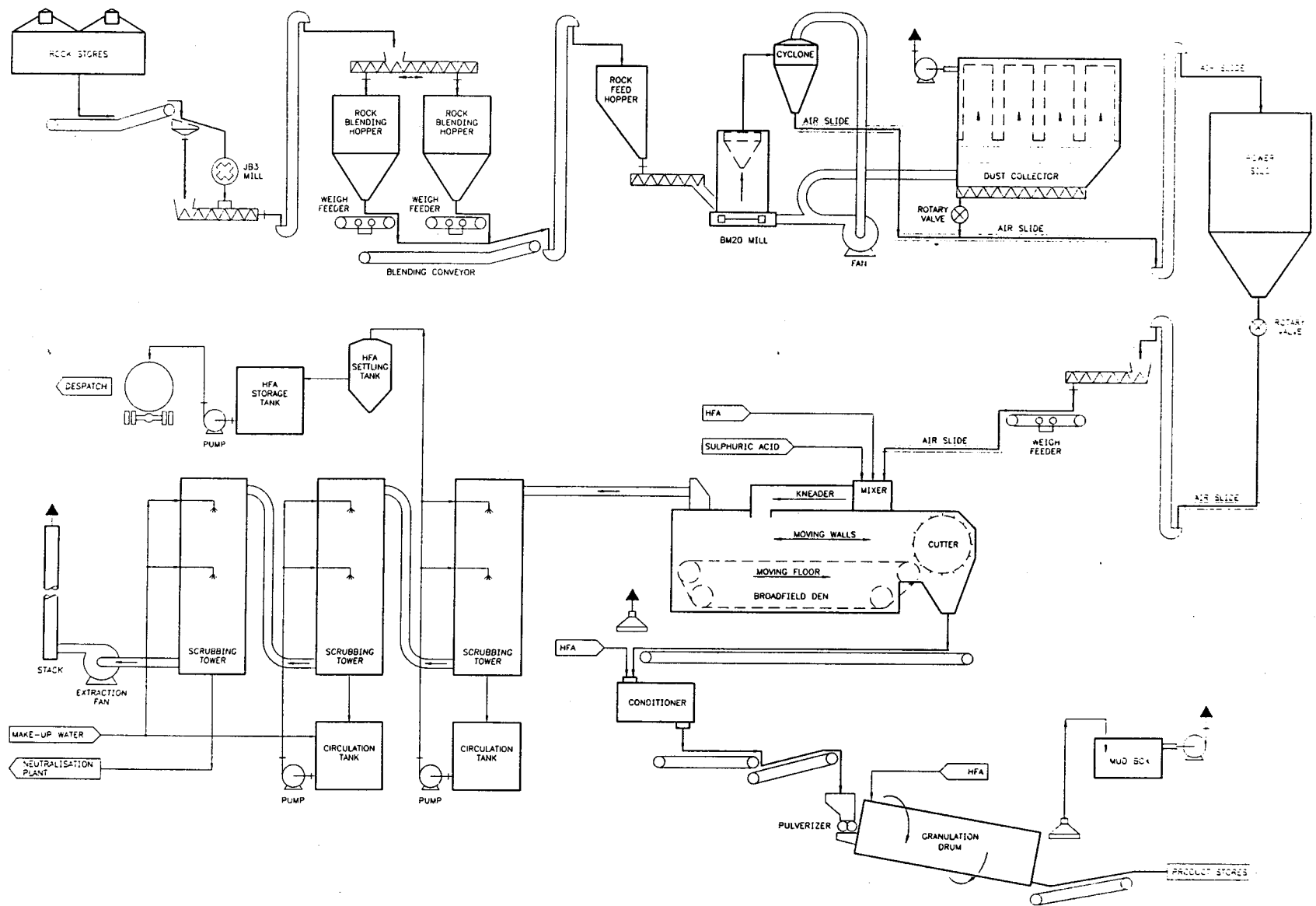


Figure 4 - Process flow diagram of the superphosphate plant

cutter wheel after a retention time of approximately 30 minutes.

Additives such as limestone, potassium chloride (potash) and ammonium sulphate may be added to the superphosphate before it is worked further in the conditioner. The conditioner consists of a set of rotating paddles which break-up and knead the product. Water is usually added to improve the product consistency for granulation.

Step 3 - Granulation

The granulation process is important in producing superphosphate of the required physical properties. The granulation circuit consists of a pulveriser, granulation drum and classifier. The pulveriser breaks up any lumps in the product before it is fed to the granulation drum. The granulation drum rolls and agglomerates the superphosphate to form granules. The incline of the drum and the feed rate determine the retention time and bed depth. The granules are passed out of the end of the drum and through a classifier (wire screen). Oversize granules (>6 mm) are recycled through the drum via the pulveriser while the finished product is conveyed to the product stores.

The superphosphate continues to cure in the store for about two weeks and the product is “dressed” (oversize is passed through a hammer mill after screening) before dispatch.

Trace elements and other nitrogen or potassium-containing compounds can be dry-blended with superphosphate to give complete fertilisers to meet different requirements.

UTILITIES

A drying tower is used to to dry the air in which the molten sulfur is burned. This is a packed tower in which air is blown counter-current against a stream of concentrated sulfuric acid, which absorbs any moisture.

The heat generated by the exothermic reaction between molten sulfur and oxygen is recovered in a waste heat boiler to produce steam which is then used for process heating and also to drive a steam turbine which produces electricity. The electricity is used on site and any excess is exported to the local power supplier.

In addition a gas scrubber is used to prevent any hydrofluosilicic acid from being released into the atmosphere.

THE ROLE OF THE LABORATORY

The laboratory is responsible both for quality control and for research. Firstly, the laboratory monitors the exact composition of the phosphate rock blend (which varies significantly depending on the source of the rock). This is important as the physical properties of the finished product (particle size, dryness, friability, etc.) which are critical if the fertilizer is to be easily spread and interact with the soil in a satisfactory way depend on these parameters.

Secondly, research is conducted both on site and through scientists at the Fernz

Corporation Ltd. Development Laboratory. Research and development work is currently focused on improving environmental performance particularly with regard to minimising gaseous emissions.

ENVIRONMENTAL IMPLICATIONS

The most significant potential environmental hazards are dust (from the grinding of phosphate rock) and gaseous hydrofluosilicic acid (from the reaction between hydrofluoric acid and silica or quartz) emissions. These are both carefully monitored, and a dust catcher and gas scrubber are used.

Article revised by Jenny Simpson and Jonathon Petherick (Farmers Fertiliser Ltd) and Lisa Donaldson (IChem Ltd) from the previous edition of Chemical Processes in New Zealand. Editing and summary by Heather Wansbrough.