

MANUFACTURING METHODS:-

As described above, sulfuric acid is an important raw material for phosphate fertilizer production and to a much lesser extent for nitrogen and potassium fertilizers. World production of sulfuric acid was about 121 million tons in 1977 and about half of this production was used in the fertilizer production.

About 58% of the world's production was based on elemental Sulfur, 25% on Pyrite and 17% on other sources. Of the other sources, the principal one was the by-product sulfuric acid recovered from smelting operations.

In general terms, the sulfuric acid is produced by catalytic oxidation of sulfur dioxide to sulfur trioxide, which is subsequently absorbed in water to form sulfuric acid. In practice the sulfur trioxide is absorbed in sulfuric acid which is kept at a controlled concentration (usually 98%) by the addition of water.

There are no major variations of commercial interests on this mentioned chemistry. There are alternatives as to source of Sulfur dioxide and method of conversion to sulfur trioxide. The two most common methods for the conversion of sulfur dioxide to sulfuric acid are

1. Lead Chamber Process:
2. Contact Process

Lead Chamber Process:

This is an old process and was introduced in Europe in near the middle of 18th century. This method uses nitrogen oxides as oxygen carrying catalysts for the conversion of sulfur dioxide to sulfur trioxide. The reactions which produce the sulfur trioxide and sulfuric acid take place within the huge lead chambers or in packed towers which may be substituted for the chambers. Chambers process produced acid of concentration less than 80 %. The major disadvantage includes the limitations in throughput, quality and concentration of the acid produced. All known new plants use the Contact process although some older Chamber process plants may still be in use.

Contact Process:

In the contact processes, the sulfur dioxide is converted to sulfur trioxide by the use of metal oxide catalyst. Platinum was once widely used as catalyst but because of its excessive first cost and susceptibility to poisoning, it has been largely replaced by vanadium oxide. The vanadium pentoxide is dispersed on a porous carrier in a pellet form. The characteristics of the catalyst which can be used are mentioned as follows:

1. Porous carrier having large surface area, controlled pore size and resistance to process gases at high temperature; in pellet form if used in fixed bed and powdered form if used for fluidized bed. Ex- Alumina, silica gel, zeolites.

2. Active catalytic agent:
Vanadium pentoxide in this case. Preparations are generally kept secret for the competitive reasons but they usually consist of adding water soluble compounds to gels or porous substrates and firing at temperature below the sintering point.
3. Promoter:
Alkali and/or metallic compounds added in trace amounts to enhance the activity of the catalytic agent.

Advantages of the V_2O_5 catalyst

1. Relatively immune to poisons.
2. Low initial investment and only 5% replacement per year.

Disadvantages of V_2O_5 catalyst

1. Must use dilute SO_2 input (7-10%).
2. As a catalyst it is less active and requires high oxygen or sulfur dioxide to give economic conversions
3. Requires larger converters and thus higher initial investment.

Now the SO_3 gas is passed to an absorption tower where it is absorbed in recirculating concentrated acid. There are many variations in the contact process depending upon the types of raw materials available and other considerations; also a number of engineering variations are in use by many different design/construction firms offering services in this field.

Main disadvantages of the contact process are that concentrated acid (98%) of high purity can be produced directly and that compact plants of quite high capacity have now become rather common place.

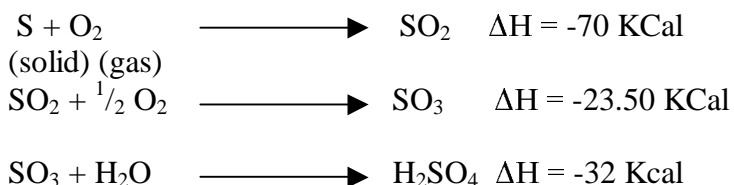
THE PRODUCTION OF SULFURIC ACID BY CONTACT PROCESS:

RAW MATERIALS:

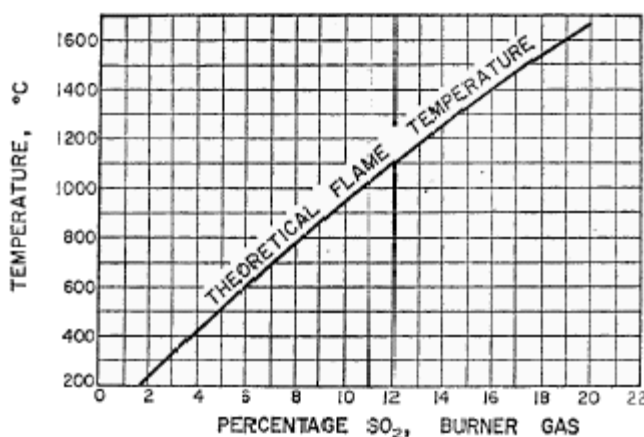
One of the early raw materials for the sulfuric acid was sulfate of iron or vitriol. By heating the solid sulfate and condensing the fume an oil of vitriol resulted. The rectified oil of vitriol (ROV) is concentrated acid and the brown oil (BOV) is about 77% Sulfuric Acid. The raw materials for sulfuric acid manufacture are chiefly Sulfur, Pyrites, Spent oxide, anhydrite and gases from the smelting of metalliferous ores, from the purification of natural gas and from refining operations.

CHEMISTRY OF SULFURIC ACID PRODUCTION:

The equations governing the production of sulfuric acid are:



The first reaction expressing the combustion of sulfur is strongly exothermic; sulfur on burning gives about one third of the heat of combustion of coal, and this heat raises the temperature of combustion gases roughly in accordance with the graph as shown



This heat is high in temperature and there is plenty of it, consequently it is worth utilizing and the hot gases are led across pipes through which the water passes. The water is heated, steam is raised and the gases are cooled. This is the arrangement in the water tube boiler. In the fire tube boiler the hot gases pass through the tubes which are surrounded with water.

The second equation is also exothermic and it's apparent that the equation gives a decrease in volume, three volumes become two volumes and this reaction would be aided by pressure. High conversions are however, obtainable with catalysts at 400 to 500°C with a small excess of oxygen and the use of pressure.

The third equation represents the absorption of sulfur trioxide to form sulfuric acid. It is exothermic and the absorbing sulfuric acid has to be cooled continuously; the heat is available at a relatively low temperature and is not worth recovering. Sulfuric acid is used for the absorption of sulfur trioxide as it has been found in practice that sulfur trioxide and water form a mist, which is difficult to separate from the gas and that under these conditions the absorption, is not complete. The strength of the acid is best about 98%.

SULFUR HANDLING AND STORAGE:

Sulfur used for the production of sulfuric acid is practiced to handle as solid in bulk, from ship to wagon and from wagon to cool off and solidify; it can then be broken up and shovelled into wagons for disposal. It consists of carbonaceous matter and inorganic ash.

Although commercial sulfur is over 99% sulfur, the impurities present as dust in the plant gases tend to be filtered out by the catalyst and a blanket or layer of hardened dust on the catalyst detracts from the efficiency of conversion. In consequence some manufacturers filter the molten sulfur through leaf filters to remove some of the impurities and so obtain a longer period before the plant has to be shut down for cleaning away the dust and sieving the top layers of the catalyst from it. However, the filter leaves have to be removed for the replacement of the filtering medium and for the removal of the accumulated sludge, and these unpleasant operations, together with the installation cost of the equipment, have to be weighed against the benefits of having slightly less dusty gases.

SULFUR BURNING:

There are several types of burners for sulfur. One is revolving cylinder containing pool of molten sulfur which is combusted by the passage of air over its surface. Another type is a brick lined vertical cylindrical vessel in which is erected a pile of fire brick in the form of a pyramid, and on to this structure molten sulfur is pumped to be met by a stream of co-current dry air for its combustion. A third variety is in the form of a burner similar to an oil burner.

The quantity of air is regulated to give between 8 to 10% SO_2 .

In the starting up the plant with a vertical burner the fire-brick is first heated by the burning of a fuel gas. The gas, when a sufficiently high temperature has been reached is cut off and the liquid sulfur is pumped over the brick-work. A measured amount of air is passed down the burner and the sulfur burns to sulfur dioxide providing sufficient heat in normal operation to raise the temperature of the gases to some 810-900 °C. If the air contains 21% oxygen and sulfur is burned to give 10% sulfur dioxide gas, then 11% oxygen and 79% nitrogen will form the residual gases. Some excess oxygen is necessary over and above that required to combine with the sulfur and the sulfur dioxide. Out of the 11% oxygen, 5% will be required to combine with the dioxide to form the trioxide leaving an excess of 6%. This is adequate but if attempts were made to have a 14% sulfur dioxide gas then 14% from the 21% oxygen would be taken up in forming sulfur dioxide and another 7% would be required to convert the dioxide to trioxide. This would leave no excess oxygen and an excess has shown to be essential for a good conversion of the dioxide.

When sulfur burns, the gases rise to a temperature depending on the dioxide concentration; with 8% sulfur dioxide the temperature is about 750 °C. In the diagram, the gas temperatures are plotted against the dioxide concentrations. To withstand these

temperatures the burner is brick lined and the area of the brickwork radiates heat and helps to burn the sulfur completely in the time given by the volume of the burner for the passage of the gases.

The composition of the gas can be varied by altering either the air or the sulfur to the burner. The very hot gases containing the ash from the sulfur are led straight into the waste heat boiler.

THE WASTE HEAT BOILER:

The object of the waste heat boiler is to utilize the heat in the gases to generate steam. A water tube boiler consists of tubes among which gases pass, the tubes being full of water. The gases heat the tubes which in turn raise the temperature of the water. The boiler is in the form of cylinders connected by hairpin shaped tubes arranged across the path of gases. The tubes are kept filled with water (to prevent burning) and are connected at the top to a steam drum, a cylindrical vessel in which water is kept at a constant level by an automatic feeding device. The steam drum, where the water boils, is above the tubes and serves to supply water to the boiler and for the release of steam. The surface area of the water inside the drum must be sufficient to minimize the carryover of the spray with steam which is led off from the top of the drum and then through super heater tubes by which the steam is heated several degrees above its condensation temperature to give it superheat and make it free from droplets, dry and suitable for use in turbines or other steam engines. The water circulates from the steam drum to the sludge drum, another cylindrical shaped vessel at the bottom of the boiler, from which the solids, deposited from the evaporating water, are sludged out and the solid content of the boiler water controlled. The water circulates through the hairpin tubes upwards to another cylindrical drum and then passes from this intermediate drum upwards again through another set of hairpin tubes to the steam drum. The pressure under which steam is generated depends upon the purpose for which it is to be employed.

There are the usual auxiliaries which are associated with a boiler, the feed pumps for pumping the feed water into the drum against the boiler pressure, the feed water preparation tank where phosphates and alkali are added to the water to prevent boiler corrosion, and the economizer which heats the boiler feed water near to the temperature of the water in the boiler drum. The feed water is sometimes preheated by exhaust steam from the boiler feed pumps before being heated in the economizer. Preheat may be to 100°C and the final temperature of the feed water say 215°C. The economizer and the super heater obtain their heat from the sulfurous gases at convenient points in the process usually from the converter after the second and third stages. Cold water in the economizer tubes could cause local condensation from the sulfurous gases and result in corrosion. After the first stage of conversion there is another waste heat boiler similar in construction to the first boiler but smaller and the two boilers use the same steam drum. The inlet gas temperature to the converters should be 380-400°C and the waste heat boiler is designed to take away the heat from the gases until their temperature is in this range. This reduction in temperature is about 400°C and corresponds to several tons of steam an hour from the moderate size sulfur burning plant.

The temperature of the exit gases is controlled by a by-pass on the waste heat boiler. The amount of heat evolved is dependent upon the quantity of sulfur and the temperature on the proportion of sulfur dioxide in the gases. The higher the temperature, the higher is the proportion of heat which is to be removed. It is best to gauge this so that the waste heat boiler by-pass in normal operation is almost shut.

The waste heat boiler design takes into consideration the following factors. The area of the tubes must be adequate to take the requisite amount of heat from the gases. This is dependent upon the amount of heat transferred per unit of tube area, which itself is dependent upon the velocity of gases over the tubes and the temperature difference between the gases and the boiler water

GAS DRYING:

It has been found in practice that if moisture is present in the gases before conversion, a sulfur trioxide mist will form after the converters, which is extremely difficult to absorb in the acid absorbers. There are several theories to account for this. It may be that the sulfur trioxide particles are surrounded by a film of acid and the aggregates are sufficiently small to pass through the absorbers and out into the atmosphere, giving rise to inefficient absorption and causing a local nuisance. These mists can be destructive to vegetation, damaging to buildings and extremely unpleasant to life in the vicinity. It is therefore essential to use dry air for sulfur burning or install special plant for absorbing the mist, which is a difficult proposition.

Air is dried in a drying tower which uses strong sulfuric acid for this purpose. The tower consists of a mild steel vertical cylinder lined with acid-resisting brick and packed with ceramic rings. The acid is distributed down the tower and air is blown upwards counter-current to the acid by a blower which also serves to give the air sufficient force to pass through the whole of the sulfuric acid plant to atmosphere after the absorbers.

The vapor pressure of water above acids of high concentrations at ordinary temperatures can be extremely low and consequently under the right conditions (95-98% H_2SO_4 at 35°C or less) the acid removes nearly all the water vapor in the air that is down to $30\text{mg}/\text{m}^3$.

The tower has to be of a sufficient diameter not to require a significant pressure drop for the gases to pass through it and to have an adequate surface area of packing for the absorption of water from the air to take place in the time which the gases take to pass through the tower volume. Consequently the gas velocity up the tower must be small, and this will determine the minimum diameter of the tower. The amount of acid used in the tower has to be significant to wet the surface of the packing without flooding and not to become so dilute that its vapor pressure becomes appreciable. The amount of water in air at a given temperature and relative humidity is known and hence the minimum quantity of 98% acid on the drying tower can be calculated.

It is common practice to use acid from the absorption section on the drying tower; the heat of dilution is then removed on the absorption coolers but coolers are sometimes provided on the drying section with a bleed-off to the absorption circulation system.

GAS FILTRATION:

The gas from the burners after passage through the waste heat boiler contains ash from the sulfur and some scale from the waste heat boiler and gas lines. These solid impurities are best removed before the gases enter the converter; otherwise the dust accumulates on the layers of catalyst and causes channeling through the catalyst layers, irregular contact and pressure drop.

The filter consists simply of the wide diameter vessel filled with the filtering medium which is commonly the lumps of quartz. The vessel is of squat cylindrical shape in mild steel. The gases pass downwards to assist in the removal of the solids at a velocity which is slow because of the wide diameter of the vessel. When the filter is first put into service, the pressure drop is several m atmospheres, but when it is ready for opening and cleaning, this pressure drop rises to some 100m atmosphere. The interval between removals of dust depends on the ash content of the sulfur; a filter usually lasts three to six months and this period would be extended if the molten sulfur were also filtered before burning.

In many cases the gas filtration unit may not be present and thus this step may be treated as the auxiliary unit, depending upon the requirement. In the flow sheet given, the gas filtration unit is not shown.

CONVERSION:

The converter is a reactor and its objective is to combine the sulfur dioxide with the residual oxygen in the gases to form sulfur trioxide. The conversion is aided by a catalyst and the more sensitive the catalyst the lower the temperature at which the conversion takes place and more favorable the equilibrium but in general sensitive catalyst are more readily poisoned. In practice it is necessary to have a catalyst which is sufficiently robust to resist poisoning but is active enough to give good conversion at about 400 C. The converter consists of a tall cylindrical vessel of sufficient diameter (generally 3.5 to 5.5m) to give a low gas velocity, inside which there are three or four trays for quantities of catalyst. Between the catalyst sections there are devices for cooling the gases to keep the temperature entering the later catalyst sections in the region of 405 to 440 C. The first catalyst pass contain relatively little catalyst because the reaction is rapid and the temperature rises sharply; the second a little more, and the last stages most of the catalyst, where both the sulfur dioxide and oxygen are less concentrated.

After the passage through the first catalyst tray when the gas temperature has risen from about 410 C to over 600 C, the gases pass into an external waste heat boiler to raise steam and bring the gas temperature down to 430 C and at this temperature the gases enter the

second catalyst tray. On passing through the catalyst the temperature again rises but this time not so much, and after the second tray sufficient heat can be removed by superheating the steam raised in the waste heat boilers. The super heater tubes are led from the boiler into a space underneath the catalyst bed in the path of the gases. The temperature is again brought down to about 430°C and after the third pass the gases are similarly cooled. In the final section, which contains most of the catalyst, the temperature rise is small as the reaction has been brought near the equilibrium value in the previous passes and only relatively small amounts of sulfur dioxide and oxygen remain to react. After leaving the catalyst the gases are at 400 to 450°C; they are passed through the economizer where the temperature is reduced to a lower value. The gases then pass through an air cooler to the absorbers.

The catalyst consists of vanadium in the form of small pellets or cylinders. The total volume is arranged to give the time of contact necessary for the reaction to take place. The speed of the reaction depends on the activity of the catalyst. A conversion of sulfur dioxide to trioxide of between 98 and 99 % is achieved.

The equilibrium is given by

$$K_p = \frac{(P_{SO_3})}{(P_{SO_2}) (P_{O_2})^{1/2}}$$

$(P_{SO_2}) (P_{O_2})^{1/2}$ should be as high as practicable to give a good value for (P_{SO_3}) . If there is excess of oxygen $(P_{O_2})^{1/2}$ will increase in value but too great an excess will diminish (P_{SO_2}) initially. On some converters, air is introduced between the converter stages which acts as a cooling medium and provides the additional excess of oxygen.

A graph showing K_p plotted against temperature is given in the figure below:

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Below 400°C the reaction is very slow but above 630°C the reaction is fast but the equilibrium is becoming unfavorable, the reaction goes more quickly the higher the temperature, but the equilibrium becomes unfavorable. The aim in running the converter

is to maintain a pattern of temperature which experience has shown will give the optimum conversion. These temperatures depend on the catalyst activity, gas strengths and other factors. Figures for four stage converter for temperatures and conversion are given as follows:

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The running of the converter consists in close observance of temperatures, the pressure drops and the sulfur dioxide conversion. The temperature rise across the catalyst is the measure of the amount of reaction taking place. Pressure drops across the bed of catalyst, if they are abnormally high, indicate a partial blockage and channeling through the catalyst, which would be accompanied by a small temperature rise. A high pressure drop across the first pass may necessitate shutting down the plant and screening the top layer of the catalyst which has possibly become choked with dust.

ABSORPTION:

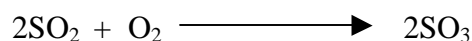
The gas leaving the reactor is cooled further in a heat exchanger as mentioned above and before entering the absorption tower where the Sulfur trioxide is absorbed in a recirculated stream of concentrated sulfuric acid. The sulfuric acid is maintained at desired concentration (usually 98% H₂SO₄) by the addition of water and its temperature is controlled in the desired range of 70 to 90 C measured at the tower inlet by cooling the recirculated acid.

Some of the acid goes to the air drying tower mentioned previously where the moisture from the incoming air supplies some of the water needed in the reaction. Since, the heat released in this step is at a low temperature level, little use can be made of it.

In the above mentioned Single Absorption process, the recovery of the sulfur as sulfuric acid is 97-98% and the remainder is lost to the atmosphere as Sulfur dioxide. In many countries, the discharge of this amount of Sulfur dioxide to the atmosphere is environmentally unacceptable. Therefore most of the plants use a Double Contact Double Absorption Process (DCDA)

The gas after passing through three catalyst bed goes to the first absorption tower where the Sulfur trioxide is removed. The gas is then reheated to about 420 C, passed through the fourth catalyst bed, then cooled and sent to a second absorption tower.

In the reaction



removal of the reaction product sulfur trioxide facilitates more efficient conversion in the last catalyst bed. The DCDA process reduces the sulfur dioxide loss to less than 2Kg of sulfur dioxide/ ton of the sulfuric acid. High efficiency mist eliminators are also required to limit the loss of sulfuric acid mist to less than 0.05Kg/ton of sulfuric acid.

Thus the recovery in a DCDA plant should atleast be 99.8%.

THE TAIL GAS:

The gas from the absorption section contains about 0.15 % sulfur dioxide which oxidizes in part to sulfur trioxide and forms mist. At this concentration, corresponding to a conversion efficiency of over 98%, the effluent is tolerable and no further treatment of gas is required. In exceptional cases where the oxygen content is low or for other reasons where the conversion is down, the gases can be scrubbed with ammonia liquor and then treated by electrostatic precipitator.

STORAGE:

The last part of the sulfuric acid plant is the storage and the pumping system. The tanks are large flat cylinders which are sometimes of more than 1000 tons capacity. The pumping of acid is commonly done by the centrifugal pumps, the submerged glandless type on smaller tanks where the shaft can be less than about 10ft in length. The absence of gland leaks makes for a neat and clean pumping section. The storage installation should be calculated to maintain continuity of supply, if this is required, during the shutdowns of the acid plant and to cater for peak demands.

DEVELOPMENTS:

The use of the DCDA system adds 10 to 15% to the cost of the plant in comparison with the older Single Absorption Process. It also uses more energy and produces less steam or other recoverable energy. An alternative which is less expensive is to recover the sulfur dioxide from the single absorption plant by ammonia scrubbing. Scrubbing the gas with the ammonia solution produces an ammonium sulfite solution which is then acidulated with sulfuric acid. The liberated sulfur dioxide is returned to sulfuric acid plant and a concentrated ammonium sulfate solution remains which may find use in a fertilizer industry.

Operation of the sulfuric acid plant has some advantages,

1. The equipment is smaller and less expensive
2. Less Catalyst is required.
3. Equilibrium condition and reaction rates are more favorable in the conversion and absorption steps.

The solubility of sulfur dioxide in sulfuric acid increases with the increase in pressure and with the decrease in temperature. In a conventional plant operating at 1 atm and with an acid temperature 110°C, the solubility of sulfur dioxide in sulfuric acid is only 8ppm. However, increasing the pressure to 8 atm and lowering the temperature to 49°C, the sulfur dioxide solubility is increased to 190ppm. Under these conditions a substantial amount of sulfur dioxide can be transferred in the acid stream to the air drying tower and then to the incoming air stream. Many authors have pointed out that there is no theoretical limit to the amount of sulfur dioxide that can be recycled or recovered; it depends on the rate of recirculation of the acid between the absorber and the air drying towers.