



Developments in Sulphuric Acid Catalysts

IICChE-FAI Seminar
On
Recent Developments in Catalysts
In
Process Industry
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The Contact Process

1. In 1901 Eugen de Haen (German Scientist) patented the basic process involving combining sulphur dioxide and oxygen in the presence of vanadium oxides producing sulphur trioxide which was easily absorbed into water, producing Sulphuric Acid
2. This process was improved remarkably by shrinking the particle size of the catalyst (e.g. 5000 microns), a process discovered by two chemists of BASF in 1914.
3. Further there was development of two types of processes : (a) Single contact single absorption **SCSA** (b) Double contact double absorption **DCDA**

Comparison between SCSA and DCDA Process

SCSA:

1. The single contact single absorption process is the older (of the two) process in the chemical industry
2. The single contact single absorption process hold more heat of the gas than the double contact double absorption process. The reason for this phenomenon is that the heat losses are less due to the absence of intermediate absorption process prior to the main absorption unit.
3. The SCSA process exists in modern plants to process Sulphur Dioxide gases with low content (3%-10% SO₂) or where the content of Sulphur Dioxide varies widely regardless of the range.
4. The disadvantage of the SCSA process lies in the fact that the maximum SO₂ conversion is about 98%. By adding a second SO₃ absorber and one or two catalysts beds, 99.5% - 99.9% conversion efficiency can be achieved.

DCDA:

1. if the product stream with gases (SO₂) and (SO₃) are passed through absorption towers twice to achieve further absorption and conversion of SO₂ to SO₃ and thereby production of higher grade Sulphuric acid.
2. Under a DCDA system, the SO₂-rich gases enter the catalytic converter, and are converted to SO₃, achieving the first stage of conversion.
3. The exit gases from this stage contain both SO₂ and SO₃ which are passed through intermediate absorption towers where Sulphuric acid is trickled down packed columns and SO₃ reacts with water increasing the Sulphuric acid concentration. Though SO₂ too passes through the tower it is unreactive and comes out of the absorption tower.

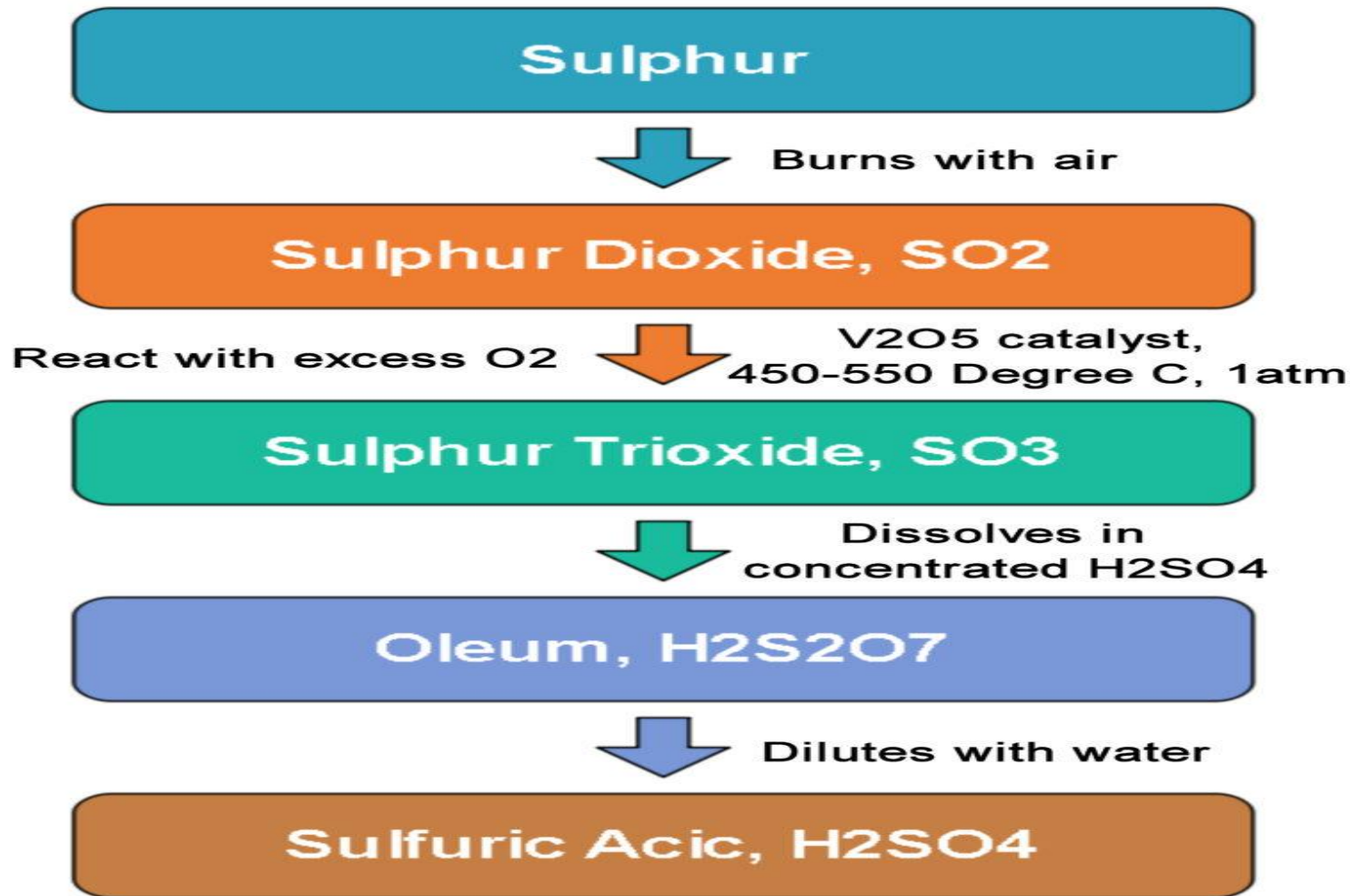
The process can be divided into five stages

- 1. Combining of sulphur and oxygen (O₂) to form sulphur dioxide, then purify the sulphur dioxide in a purification unit. Purification of the air and sulphur dioxide (SO₂) is necessary to avoid catalyst poisoning (reducing catalytic activities). To conserve energy, the mixture is heated by exhaust gases from the catalytic converter by heat exchangers.**
- 2. Adding an excess of oxygen to sulphur dioxide in the presence of the catalyst vanadium pentoxide at 450 °C and 1-2 atm absolute.**
- 3. The sulphur trioxide formed is added to sulphuric acid which gives rise to oleum (disulphuric acid).**
- 4. Hot sulphur trioxide passes through the heat exchanger and is dissolved in concentrated H₂SO₄ in the absorption tower to form oleum.**

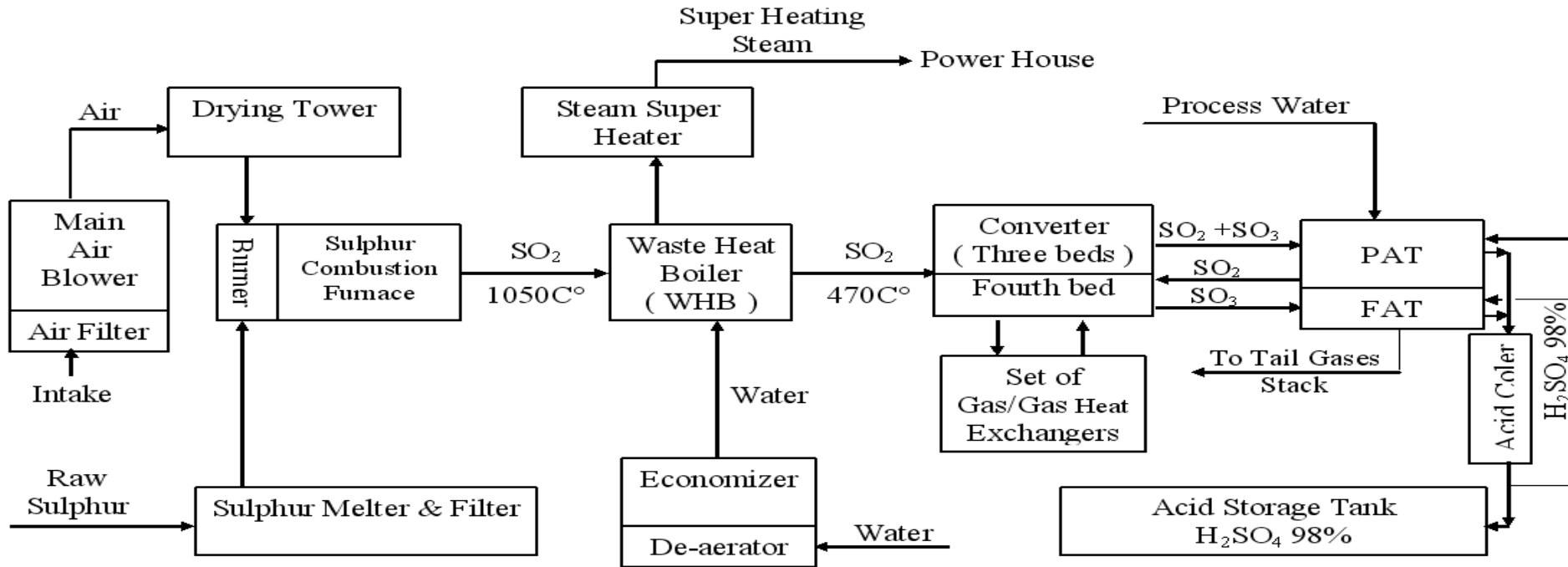


- 5. The oleum is then diluted by adding required water to form sulphuric acid which is very concentrated. Since this process is an exothermic reaction, the reaction temperature should be as low as possible**





Production Process flow sheet of Sulphuric Acid



1. Range of Application

Vanadium pentoxide series of sulfuric acid catalysts could be used in the process of sulfuric acid production, to be more specific, is the process of $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$. With the help of Vanadium Catalyst, the rate of conversion can be improved greatly. It can guarantee the air speed of operation to add 10-20% more when using type star ring catalysts or ring catalysts.

Vanadium catalyst can be applied in many fields, such as, sulfur-based acid production, pyrite-based acid production, nonferrous smelting gas-based acid production, gypsum-based acid production etc.

2. Loading and Distribution of Catalyst

For the fourth and fifth stage conversion, the common use amount of catalyst is 220-260L (t/d 100% H_2SO_4), while in the process of smelting gas-based acid production, the amount can be 1.6-1.8 m^3 (km^3 gas/h), but under the condition of using star ring shaped or ring-shaped catalyst, the amount can increase 10-20%, so as to make sure operating gas velocity much steadier.

Distribution Proportion of Catalyst

Percent Segment Bed No.	Double Conversion Double Absorption	Double Conversion Double Absorption	One Conversion One Absorption
1	20-23	19-21	20-22
2	23-25	20-22	24-26
3	23-25	20-22	24-26
4	27-30	18-20	30-32
5		19-21	

The Contact process produces Sulphuric acid

The key step is

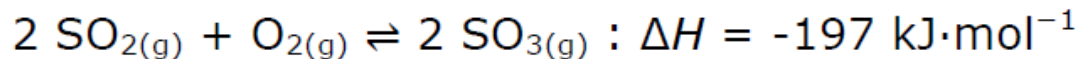


The catalyst is **Vanadium(V) oxide V_2O_5**



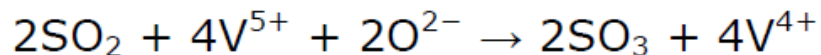
This shows why variable oxidation states make transition metals good catalysts

Sulphur dioxide and dioxygen then react as follows:

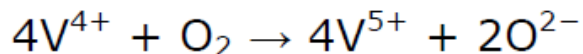


According to the Le Chatelier's principle, a lower temperature should be used to shift the chemical equilibrium towards the right, hence increasing the percentage yield. However too low of a temperature will lower the formation rate to an uneconomical level. Hence to increase the reaction rate, high temperatures (450 °C), medium pressures (1-2 atm), and vanadium(V) oxide (V_2O_5) are used to ensure an adequate (>95%) conversion. The catalyst only serves to increase the rate of reaction as it does not change the position of the thermodynamic equilibrium. The mechanism for the action of the catalyst comprises two steps:

1. Oxidation of SO_2 into SO_3 by V^{5+} :

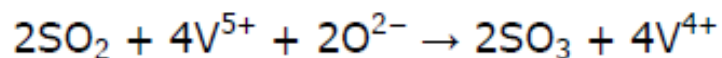


2. Oxidation of V^{4+} back into V^{5+} by dioxygen (catalyst regeneration):

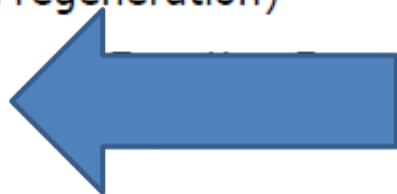
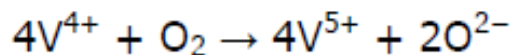


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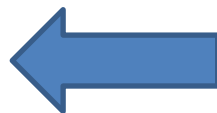
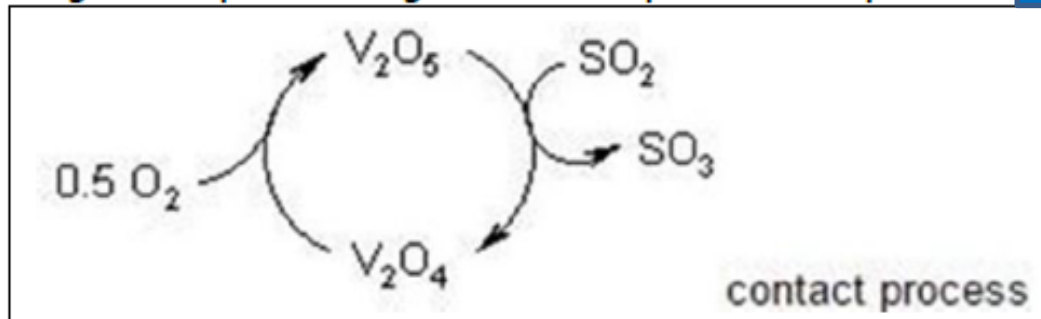
Step 1: Oxidation of SO_2 into SO_3 by V^{5+}

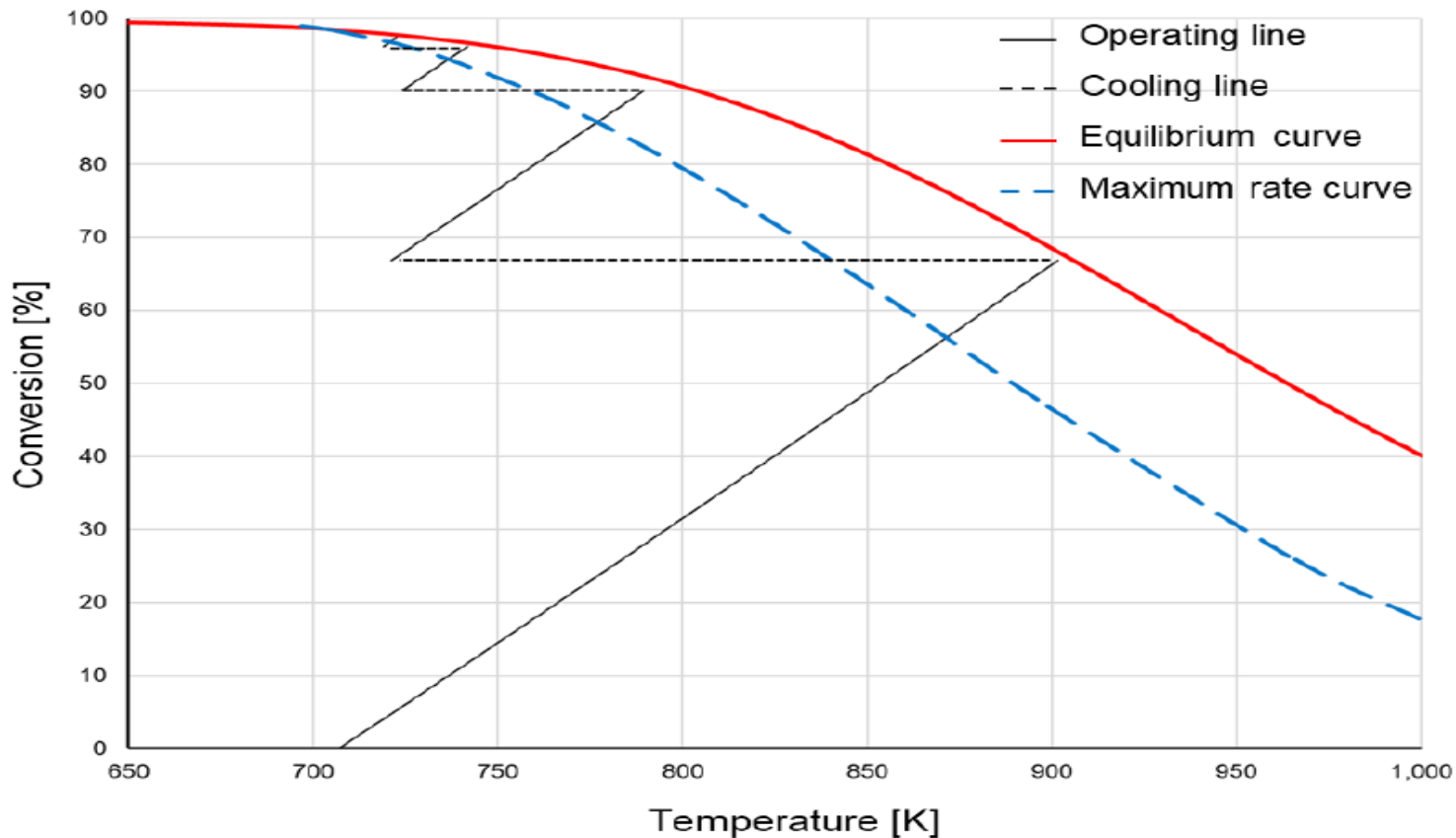


Step 2: Oxidation of V^{4+} back into V^{5+} by oxygen (catalyst regeneration)



The diagram representing the above process steps is as





Typical conversion versus temperature diagram for the case where four catalytic beds are used to conduct the SO_2 to SO_3 reaction with gas cooling between beds. The equilibrium and maximum rate curves are also drawn.

Catalyst functioning in conversion of SO_2 to SO_3

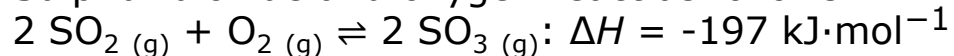
The catalyst only serves to increase the rate of reaction as it does not change the position of the [thermodynamic equilibrium](#). The action of the catalyst is not to yield more product but to make the reaction faster by forcing the reaction to reach equilibrium quickly. Nonetheless, the plant is designed in a manner to not let the reaction stay in equilibrium.

Because of vanadium being present in solid state in a reaction involving gases, so we observe a heterogeneous catalysis. Now using theory of heterogeneous catalysis the steps involved are:

1. Diffusion of reactant molecules from the bulk to the surface of Solid catalyst.
2. Adsorption of reactant molecules on the surface of catalyst.
3. Conversion of reactant into products on the surface of catalyst.
4. Desorption of products molecules.
5. Diffusion of Product molecules away from the surface of catalyst.

Temperature and Pressure Conditions

Sulphur dioxide and oxygen react as follows:



1. According to the Le Chatelier's principle, a lower temperature should be used to shift the chemical equilibrium towards the right, hence increasing the percentage yield. A low temperature would favour the forward reaction and produce more sulphur trioxide. At very low temperature the rate of combination of sulphur-dioxide and oxygen is very slow. Too low of a temperature will lower the formation rate to an uneconomical level. **The reaction brings balance at a temperature of about 450°C where the rate of combination of sulphur-dioxide and oxygen is high and rate of dissociation of sulphur-trioxide is low. Hence, the forward reaction is favoured.**
2. Further because of decrease in Volume of gases from input to output side, increase in pressure favours the forward reaction (using Le-Chatelier Principle) because **practically it has been observed that increase in pressure does not yield appreciable increase in rate of formation of sulphur-trioxide and further, because of increase in pressure the rate of corrosion of iron used in the plants increases and hence the economics of the process are disturbed.** The reaction step also involves presence of Vanadium (V) oxide as a catalyst. As stated above, the temperature for Catalyst bed ranges from 400 to 550°C depending on the requirement in form of either higher conversion or higher rate. **The suitable pressure ranges from 1.5 to 1.7 atm absolute.**

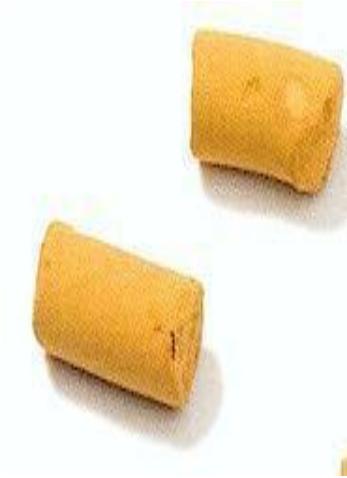
High-Vanadium Pentoxide Catalysts

1. Standard vanadium pentoxide catalyst contains approximately 6 to 8 wt% of vanadium pentoxide.
2. High vanadium pentoxide catalyst contains 7 to 9 wt% vanadium pentoxide combined with a modification to the chemical composition of the active phase.
3. The higher vanadium pentoxide content imparts a higher activity to the catalyst making it suitable for use in the lower catalysts passes where a substantial amount of the SO_2 has been converted to SO_3 .
4. Increases in activity of 10 to 20% have been achieved with this modified catalyst. Zhejiang diatomite, adds auxiliary agent in traditional vanadium-potassium (sodium)-silicon system, makes it have higher activity and thermostability.

Catalyst Shapes

1. The research into different catalyst shapes is a result of the desired to reduce catalyst bed pressure drops which translates directly into energy savings as a result of reduced blower power consumption. Reduced pressure drops also allow more dust to accumulate before pressure drops increase to the point where the plant must be shut down for catalyst screening. The catalyst shape must achieve all of the above without compromising on catalyst activity or mechanical strength.
2. Catalysts were first manufactured as **cylindrical pellets**, typically 6 to 8 mm in diameter. **Ring shaped catalyst provide a pressure drop reduction of up to 50% over pellet shaped catalyst.** A typical ring will be 10 mm diameter with a 4 mm diameter hole and 13 mm long. Larger rings provide an even bigger reduction in pressure drop and are used in special cases where rapid dust build up in the bed can occur. **The larger rings are applied in a thin layer (100 mm) on top of the regular catalyst and allow dust to penetrate further into the bed rather than in the top layer where a high pressure drop can develop in a short time.**
3. **Ribbed or daisy-shaped** rings are a further improvement on the standard rings. Ribbed catalyst is a bit larger in diameter (12 mm) than the standard ring. **The ribs on the outside of the ring increases surface area by 10% which provides more contact area for gas to migrate into the catalyst pores. Pressure drop is further reduced over the standard ring resulting in pressure drops of 80 to 85% of the pressure drop across rings.**
4. **The latest catalyst shape Quattro** has 4 internal holes, making more of the catalyst internals available for reaction. **A 30% increase in surface area is achieved with this shape over standard catalyst shapes.** The result is an increase in SO₂ conversion and a reduction in emissions.

Catalyst Shapes



Pellet Type



Ring Type



Ribbed Type



Quattro(4 hole)

Cesium-Promoted Catalysts

1. Conventional vanadium pentoxide catalyst has a strike temperature of about 400°C to initiate a self-sustaining reaction. Cesium-promoted catalyst has a much higher activity in the low temperature range resulting in a strike temperature 20 to 40°C lower than standard catalyst.
2. For applications in the first catalyst pass, cesium-promoted catalyst can allow the bed to operate at lower inlet temperatures. This is advantageous when high strength gas (14% SO₂/15% O₂) is being treated. At normal inlet temperatures of 410°C, the resulting outlet temperature would be in excess of 650°C which would exceed the typical design temperature of a stainless steel converter. Lowering the inlet temperature to 380°C results in an outlet temperature of 635°C.
3. In typical first bed installations, the cesium-promoted catalyst would make up the top 25 to 50% of the bed.

Catalyst Colour

1. Fully sulphated sulphuric acid catalyst will be characterized by a yellow, gold, orange or yellow/green colour. This colour is indicative of vanadium in its +5 oxidation state (V^{5+}).
2. If vanadium is in its +4 oxidation state (V^{4+}), the catalyst will have a green, pale green or pale blue colour.
3. Catalyst containing V^{4+} can easily and readily be oxidized back to the V^{5+} state. Catalyst that contains vanadium in the +3 oxidation state V^{3+} will appear dark blue or black in colour and cannot be converted back to the +5 oxidation state. This catalyst must be replaced since it is no longer active.

Mechanical Strength

1. The mechanical strength of the catalyst is important to minimize catalyst losses due to attrition, breakage, etc. Mechanical strength must be achieved while maintaining a porous structure. Modern catalyst can be continually operated at 630°C with short excursion up to 650°C without experiencing any mechanical damage.
2. When a catalyst bed is screened, catalysts losses are inevitable regardless of how carefully the screening operation is performed. A catalyst with sufficient strength will limit catalyst losses to 6 to 7% of the bed.
3. Losses of over 10% of the catalyst indicates that the strength of the catalyst has decreased or that the methods used to remove, screen and install the catalyst need to be revised.

Vanadium Pentoxide MSDS

Chemical Product

Name: VANADIUM PENTOXIDE

AR CAS#: 1314-62-1

Synonym: Divanandium pentoxide; Vanadic anhydride; Vanadium Pentaoxide

Chemical Name: Vanadium Pentoxide

Chemical Formula: V₂O₅

Potential Acute Health Effects:

Very hazardous in case of ingestion, of inhalation.

Hazardous in case of skin contact (irritant), of eye contact (irritant).

Slightly hazardous in case of skin contact (permeator).

Severe over-exposure can result in death.

Potential Chronic Health Effects:

First Aid Measures :

Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention.

Skin Contact: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately. Serious Skin Contact: Wash with a disinfectant soap and cover the contaminated skin with an antibacterial cream. Seek immediate medical attention.

Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation.

WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Physical state and appearance:

Solid. (Powdered solid.)

Odour: Odourless.

Taste: Not available.

Molecular Weight: 181.9 g/mole

Colour: Yellow-Orange.

Boiling Point: 1750°C (3182°F)

Melting Point: 690°C (1274°F)

Specific Gravity: 3.357 (Water = 1)

Gas Impurities (affecting catalyst performance)

1. The overall concentration of V_2O_5 generally ranges from 5 to 7 wt. % for the standard V_2O_5 catalysts and from 7 to 9% for high- V_2O_5 catalysts. The catalyst activity was shown to be improved by 10% with the one having the highest concentration.
2. The catalyst activity can also be reduced by feed gas impurities, which in turn affects the SO_2 oxidation conversion.
3. Chloride causes vanadium loss and reduction in catalyst activity.
4. Fluoride attacks the catalyst carrier whereas iron oxide and dust will progressively plug the catalyst bed causing an increase in pressure drop.
5. One plant in the past had faced arsenic poisoning due to storage of arsenic promoted spent catalyst at site. But now arsenic based catalyst usage in Fertilizer plants in India has been eliminated.
6. There is still possibility of affecting the catalyst activity in case air borne arsenic containing chemicals are present/spilled in sulphuric acid plant area.

Contaminants in gas and their effect on catalyst activity

Contaminant	Maximum Limit in the Gas	Effects
Chlorides	1.0 ppm (gas)	Chlorides cause vanadium loss and a reduction in catalyst activity.
Fluorides	0.3 ppm (gas)	Attacks the catalyst carrier.
Arsenic (as As_2O_3)	10 ppm (gas) 0.01 g/litre of catalyst	Arsenic causes vanadium loss and a reduction in catalyst activity. Effect of catalyst poisoning reaches a maximum at a temperature of $550^{\circ}C$. Above $550^{\circ}C$, a volatile compound of As_2O_3 and V_2O_5 is formed which condenses in subsequent catalyst layers.
Carbon Monoxide		Carbon monoxide reduces the conversion of SO_2 to SO_3 .
Iron Oxide		Iron oxide will plug the catalyst bed causing an increase in pressure drop.
Dust		Dust will plug the catalyst bed causing an increase in pressure drop. Dust concentrations of 0.5 mg/Nm^3 at a gas velocity of $1600 \text{ Nm}^3/\text{h m}^2$ will result in a dust build-up of 7 kg/m^3 of catalyst volume each year.

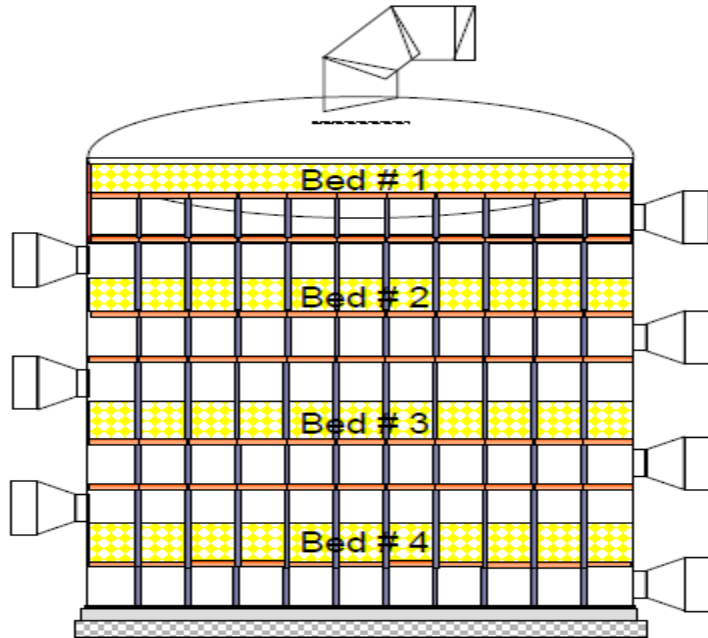
Catalyst Useful life

1. Over the course of normal plant operation, the pressure drop across the catalyst beds will increase due to the accumulation of dust in the beds and the normal breakdown of the catalyst itself.
2. Operation and maintenance of a sulphuric acid plant requires that the catalyst in the converter be periodically removed, screened and reinstalled into the converter to return the pressure drop to normal.
3. The screening operation separates the dust and catalyst fines that have accumulated in the beds. As well, the mechanical handling of the catalyst also breaks down the catalyst to a certain degree creating additional fines.
4. In some cases entire beds must be replaced due to deactivation of the catalyst, contamination, changes in suppliers, etc. All these activities lead to the creation of a waste stream that must be properly handled and disposed of to prevent damage to the environment.

Advanced Converter replacement

Technology Change

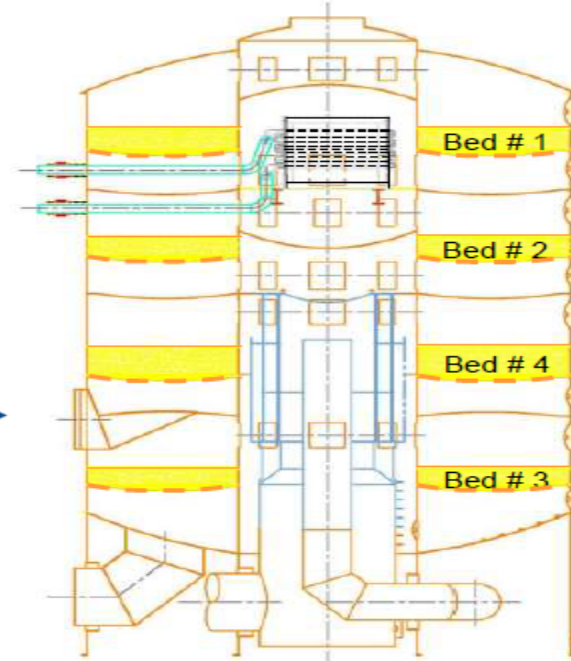
Carbon Steel
bricklined
Converter



Stainless Steel
Converter

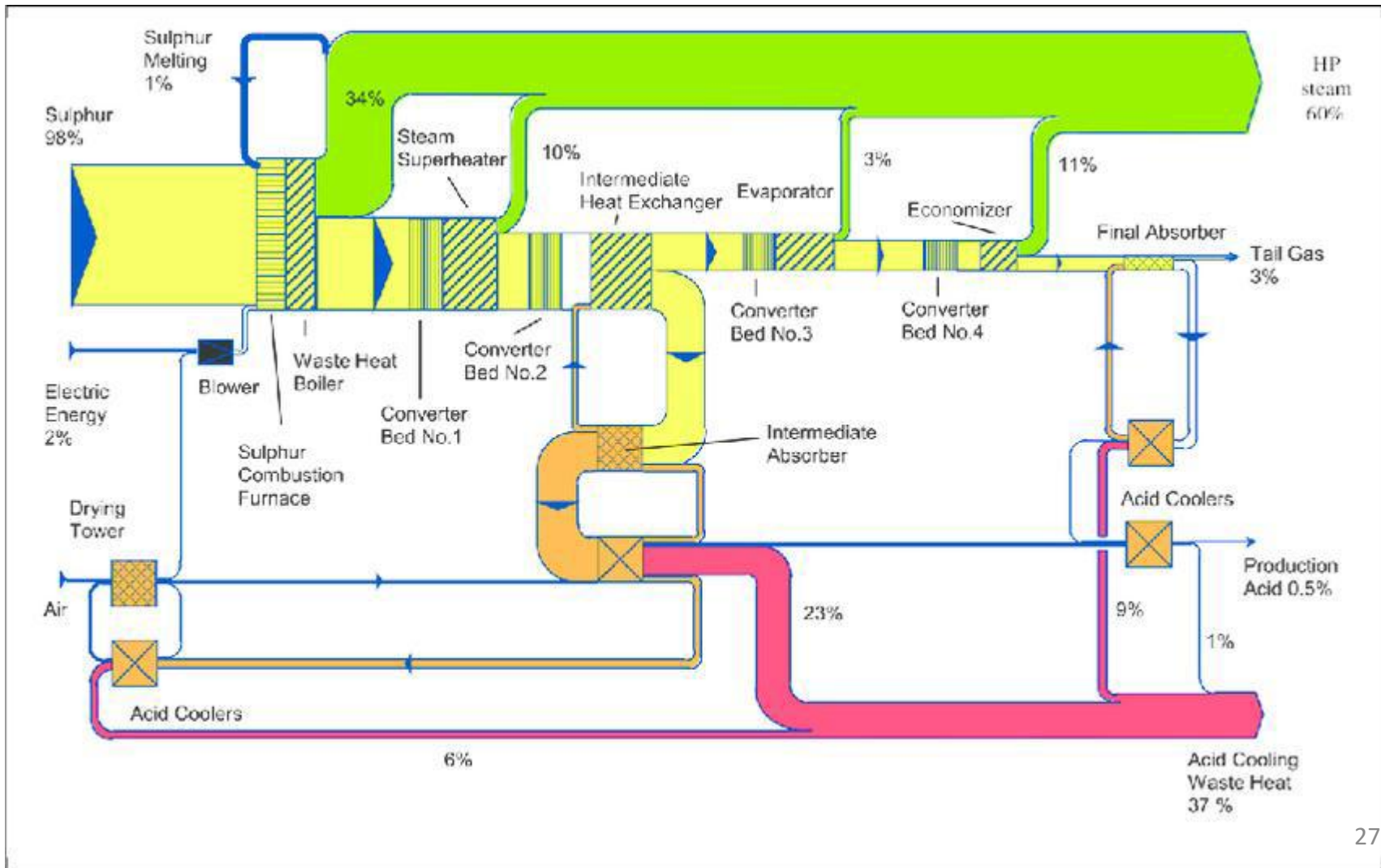


Stainless Steel
Converter with
Internal Exchangers



Advantages of a Catenary Converter in a Sulphuric Acid Plant

1. Absence of internal columns.
2. Efficient load carrying. The load path in the catenary converter design is through the inner core structure and the inner wall of the external shell all but eliminating the possibility of misalignment of division plates and the associated flexure stresses.
3. Fewer fabricated parts. This leads to a savings in material costs as well as fabrication, handling and shipping costs.
4. Fewer welded joints. The number of potential failure points and opportunities for leakage between division plates is greatly reduced.
5. Less material. Cost savings are realized in materials, handling, freight, installation labour and welding as well as time related project costs.
6. Consistent dimensions for division plates and catalyst bed gratings. The use of repetitive sizing of individual pieces is economical to fabricate.
7. Reduced construction hours. One of the key cost savings made in employing the catenary converter is a reduced number of site construction man hours. This is due to fewer fabricated parts, fewer welded joints, less materials to handle and repetitive sizing of materials.
8. Additional savings by employing internal heat exchangers. The internal core structure acts as the body for the internal heat exchangers. The results in an overall reduced footprint for the acid plant leading to savings in ducting, foundations, etc.
9. Access for catalyst screening is simplified. The absence of internal columns improves the process of screening catalyst.



Techno-advanced options for Efficient operation

1. Sulphuric acid plant as steam generation entity

- Challenges such as energy efficiency, cost constraints and environmental concerns.
- Proven to withstand the harsh conditions of acid plants, broad portfolio of corrosion-resistant heat exchangers provides outstanding heat transfer required for process efficiency.

2. High performance materials

- involves highly aggressive operating environment need wide selection of corrosion-resistant plate materials and durable, highly resilient gaskets
- tailored to fit the most demanding sulphuric acid duties. With vast industry expertise, we have to select the right material to match the sulphuric acid process thereby ensuring reliable operation, heat recovery and uptime.

3. Profit from waste heat recovery

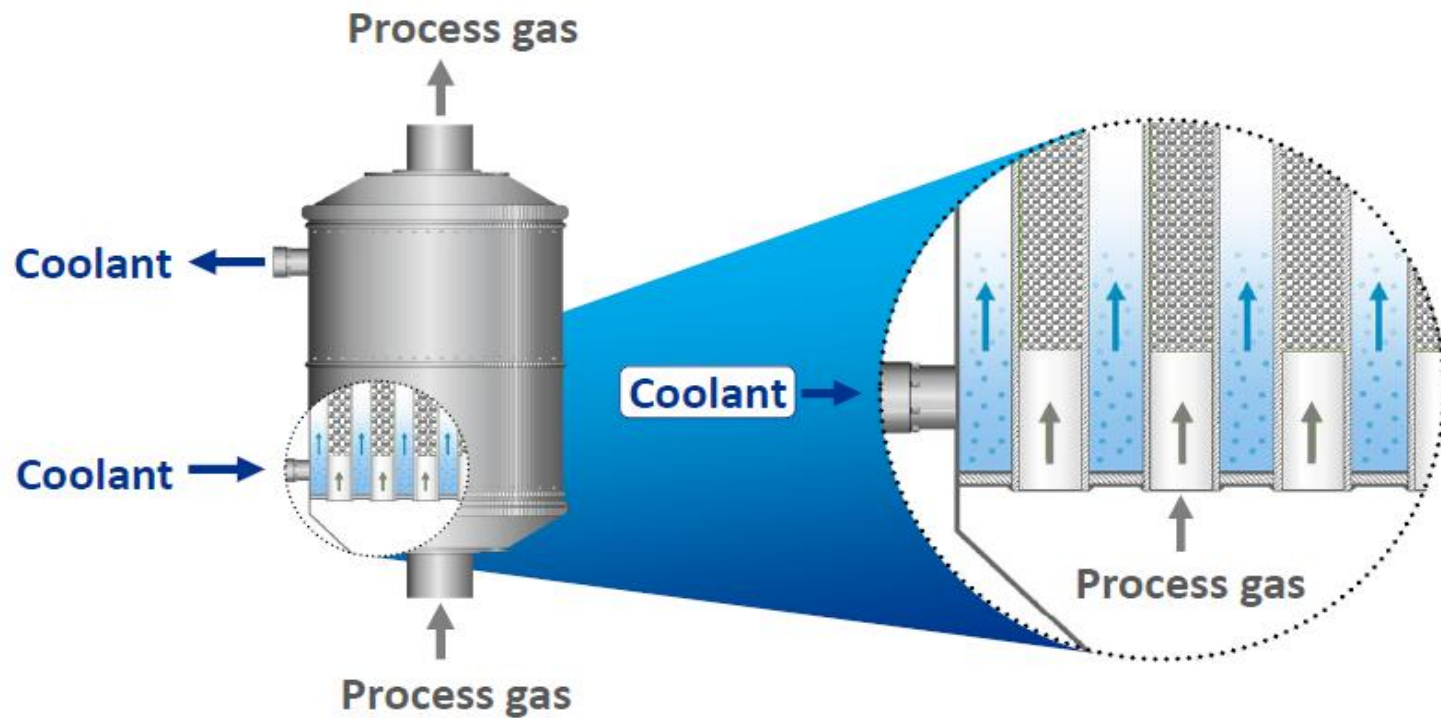
- Development of low temperature economizers in the 1980s caused sulphuric acid plant energy efficiency to peak. With approximately 70% of available heat converted into high pressure steam, and with the remaining 30% lost to the atmosphere or to cooling water in the strong acid system, the industry seemed to have reached maximum energy efficiency.

CORE-SO₂TM Process

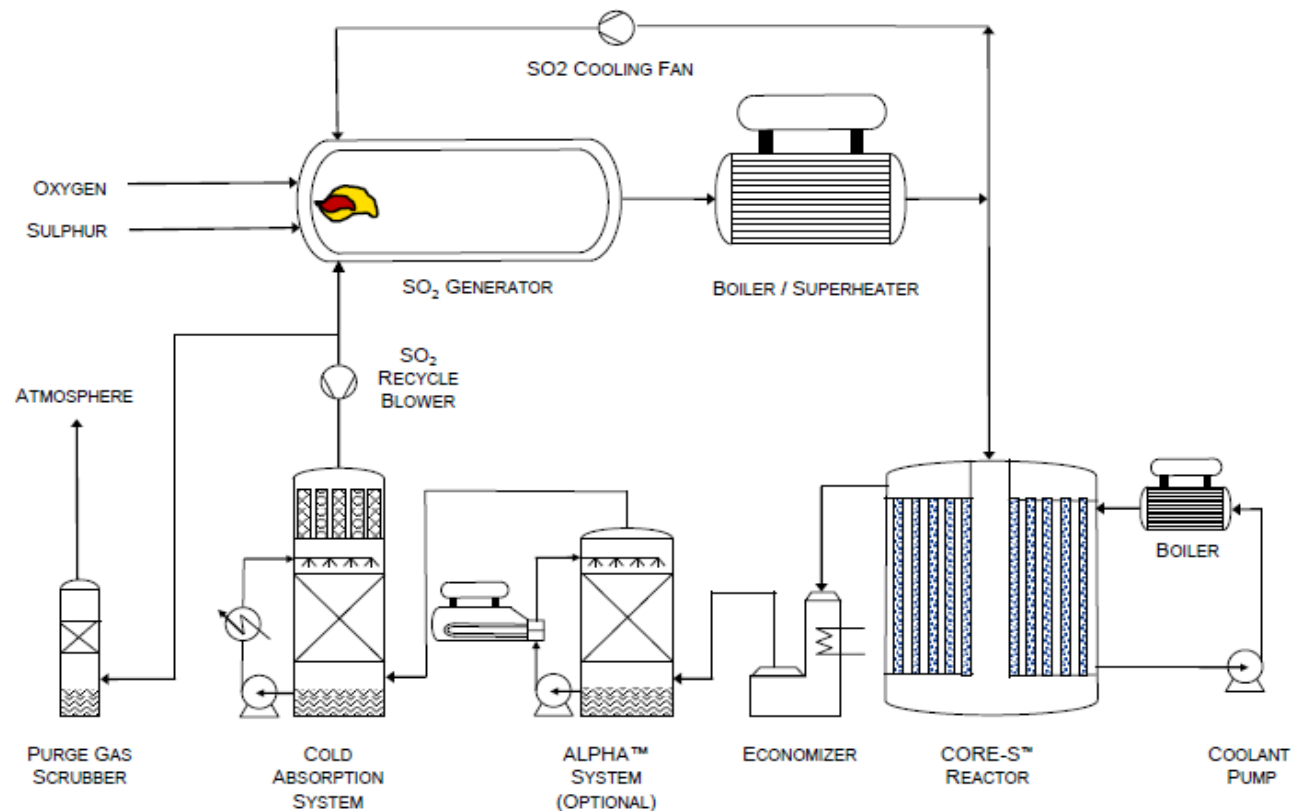
- Sulphur burning sulphuric acid production using high purity O₂
- Based on the CORE isothermal tubular reactor
- Easy to integrate within the fertilizer complex
- Drastically reduces plant size



CORE-S™ Basic features



CORE-SO₂™ Process flowsheet



CORE-S Pilot Plant Features

- Single, full-size, reactor tube (producing up to 0.5 MTPD)
- Molten salt cooling system
- Temperature measurement at 10 locations inside catalyst
- Gas mixing system capable of controlling SO₂, O₂ and N₂ concentration
- SO₂ analysis at inlet and outlet of reactor to measure conversion

- Operational since Jan 2020

- Experimental results used to validate Reactor Model
- Main test program completed December 2021
- **Currently used to support first full scale plant - Startup 2024**

CORE-SO₂TM Process Highlights

High purity
Oxygen

Stoichiometric
O₂:SO₂ ratio

Small
Equipment

Proprietary
Catalyst
Mixture

Patented
CORETM
Reactor

Molten Salt
Cooling

Controlled
Heat Release

Unconverted
Gas Recycled

Low Emissions

CORE-S Pilot Plant Features

- Single, full-size, reactor tube (producing up to 0.5 MTPD)
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Oxygen enrichment option for increased SA production

Oxygen enrichment may be considered for sulphuric acid plants, on either a short-term or long-term basis.

- Cost reduction through displacement of merchant acid consumption. Where acid requirements exceed on-site acid production and merchant acid prices are high, oxygen enrichment can be used to reduce overall operating costs.
- Cost reduction through shutting down production capacity. Where multiple sulphuric acid plant trains are in operation, it may prove to be economical to shutdown one train and boost remaining production through oxygen enrichment.

The amount of oxygen to be added is dependent on several factors including:

- desired maximum production capacity;
- furnace temperature limitations; waste heat boiler limitations;
- overall plant cooling limitations;
- pressure drop limitations;
- **materials compatibility with elevated oxygen concentrations (the limit for conventional materials is 28% oxygen).**

Areas of Development of Vanadium Catalyst

Packing density, kg/m^3

Relative geometric surface area, %

Relative pressure drop, %

Cutting hardness, N

Attrition, %

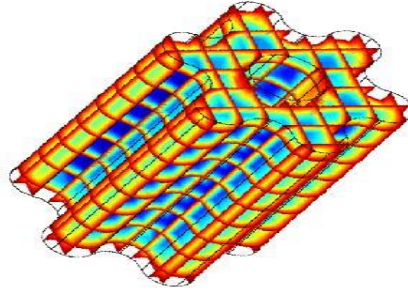
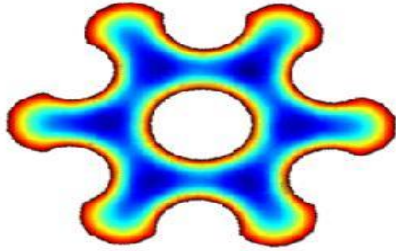
Relative activity, %

Active range, $^{\circ}\text{C}$

Ignition temperature, $^{\circ}\text{C}$

How Quattro shape catalyst can serve performance requirements

Typical issues	Can Quattro help?	How?
High emission levels	Yes	Higher geometric surface area resulting in better SO ₂ conversion.
Production capacity bottleneck	Yes	Higher geometric surface area allows for increased production rates at historically high conversion levels.
Limited bed height	Yes	Higher geometric surface area allows for higher space-time-yield.
Low ignition temperature	Yes	Higher geometric surface area resulting in better SO ₂ conversion at low temperature.
Wider operational range	Yes	The low activity of the Quattro catalyst allows for a much wider operational range.



G = **G**eometrically Optimized

E = **E**nhanced Surface Area

A = **A**ctivity Improvement

R = **R**educed Pressure Drop

1. **When gas strength remains constant, GEAR catalyst meets emissions equal to normal catalyst but with 5-10% less volume.**
2. **Less volume = smaller converter = reduced capital cost**
3. **When catalyst volume is the same as normal catalyst, improved activity in GEAR catalyst means:**
 - **Up to 25% lower emissions, or**
 - **Up to 15% increase in plant capacity**

Thank you

for

LISTENING

Questions ?

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