



# Outotec<sup>®</sup> Sulfuric Acid Plants

Outotec's sulfuric acid plants are designed as total concepts. They incorporate highly efficient off-gas treatment facilities and most modern contact acid plants to achieve maximum sulfur-dioxide conversion efficiency as well as the best product acid quality.

**Outotec**



## Full range of technologies and services

Outotec as the leading sulfuric acid plant designer, is able to offer vast and worldwide experience for any sulfuric acid plant project. Our activities include plants for the production of sulfur dioxide, for the roasting of sulphidic ores, and the combustion of elemental sulfur, as well as plants for special processes, in particular for the thermal decomposition of iron sulphate and spent sulfuric acid.

Our portfolio is complemented by processes for the production of liquid  $\text{SO}_2$  and  $\text{SO}_3$ , oleum of various concentrations and special high-grade sulfuric acid.

Outotec's scope of services encompasses activities commencing with feasibility studies and comprises lump sum turn-key installations with extensive technical support throughout the lifetime of the plant.



### Proven track record

The world capacity of the sulfuric acid industry had reached almost 160 million tpy by the beginning of the new millennium. Over the past nine decades, we have built more than 600 sulfuric acid plants, the total capacity of which corresponds to over 30% of world production.



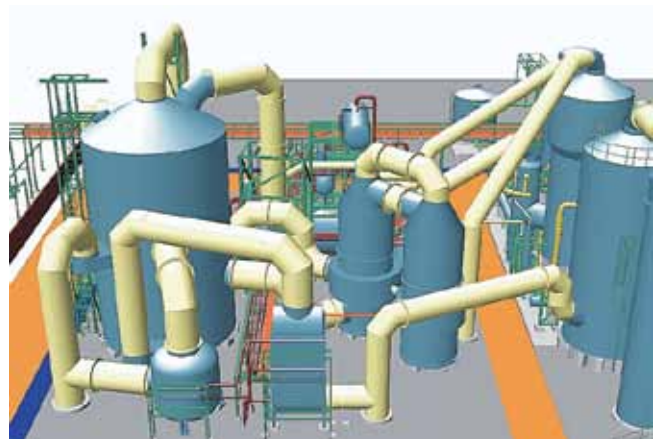
Since the introduction of the Bayer AG double absorption process in 1964, former Lurgi Metallurgie (since 2001 part of Outotec) has supplied more than 180 double absorption units with a total annual output of over 30 million tons of sulfuric acid monohydrate. These include plants with a capacity of up to 7,900 tpd. Seventeen of these units are designed to be operated in autothermal conditions, processing smelter gases containing less than 6.5% SO<sub>2</sub>. Five units are able to handle sulfur dioxide concentrations up to 18%.

Close relationship to our customers have been instrumental in making Outotec plants a synonym for quality and availability.

#### Benefit from our expertise

Outotec's broad expertise is based on comprehension of the process technologies as well as sound operating experience. This knowledge is transferred into each project, thus providing a plant of:

- High availability
- Easy operability
- Focus on performance
- Low maintenance
- Using various feedstocks
- Maximising energy recovery
- Minimising emissions





Sulfur combustion furnace and fire tube boiler.

## Sulfur combustion

### Integrated sulfur handling technologies

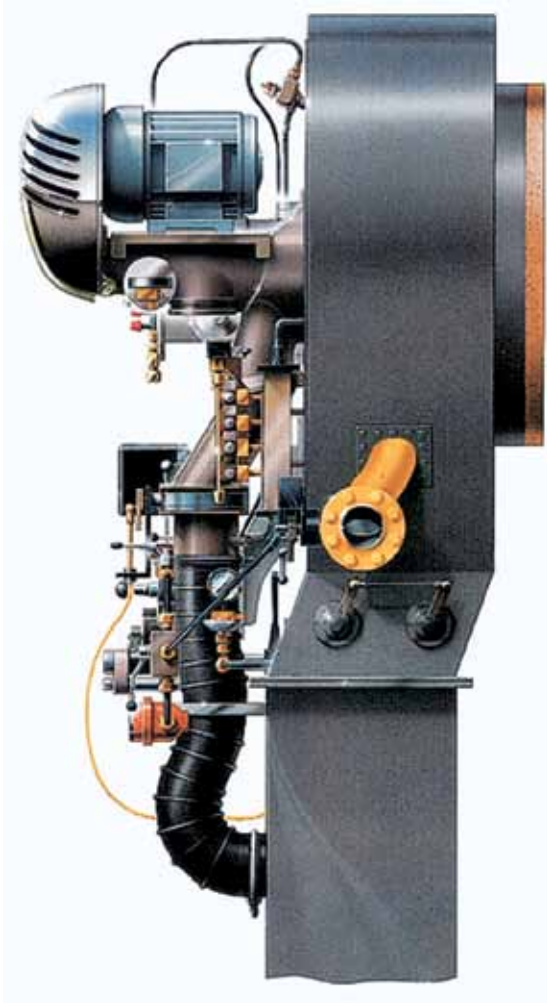
Known as a process step placing strong demands on both material and operators, our sulfur handling equipment has been designed with ease of operation in mind.

As sulfur is admitted to combustion in molten condition, most plants already receive it in liquid form. In some cases where solid sulfur is delivered, we provide facilities for melting and filtration which condition the sulfur for combustion.

Outotec designs and supplies loading and unloading stations for solid and liquid sulfur as well as sulfur filtration and sulfur storage units.

### Our expertise covers:

- Solid sulfur unloading
- Solid sulfur storage
- Sulfur melting
- Sulfur filtration
- Liquid sulfur storage
- Liquid sulfur loading
- Liquid sulfur unloading



#### Facts about the Outotec LURO® burner:

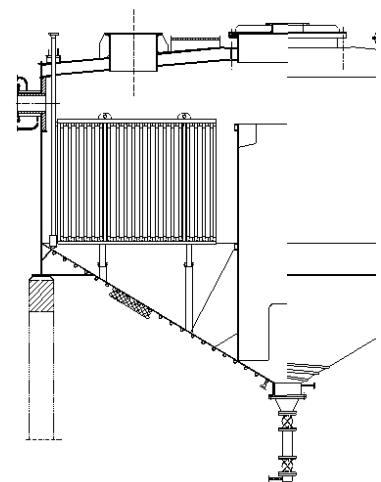
- 5 tpd up to 600 tpd of sulfur per atomizer
- Turn down ratio: 1:5 without the need to change any equipment
- SO<sub>2</sub> concentrations: over 18 vol.-% in continuous operation
- The extremely high specific furnace loads permit the design of small specific furnace volumes
- Operated on gas or fuel oil, the LURO burner is also used during start-up periods, when the sulfur furnace and converter are heated up
- Equipped with safety devices

#### Flexibility, superior atomization and reliability with Outotec LURO® burner

We apply spinning-cup atomizers instead of nozzle guns in sulfur combustion. Being the result of over 60 years experience with rotary cup burners, the Lurgi/Saacke-developed LURO burner is the best choice because of its superior atomization and operability.

Liquid sulfur is fed into the burner at virtually atmospheric pressure thereby avoiding the need for costly high-pressure pumps and piping. The spinning cup, rotating at high speed, ensures excellent atomization of sulfur. A system of adjustable guide-vanes imparts a tangential component to the combustion air. The resulting spiral path of the gases through the furnace not only effectively keeps the flame central but simultaneously prevents unvaporized sulfur droplets from impinging on the furnace wall.

Sulfur melting tank.

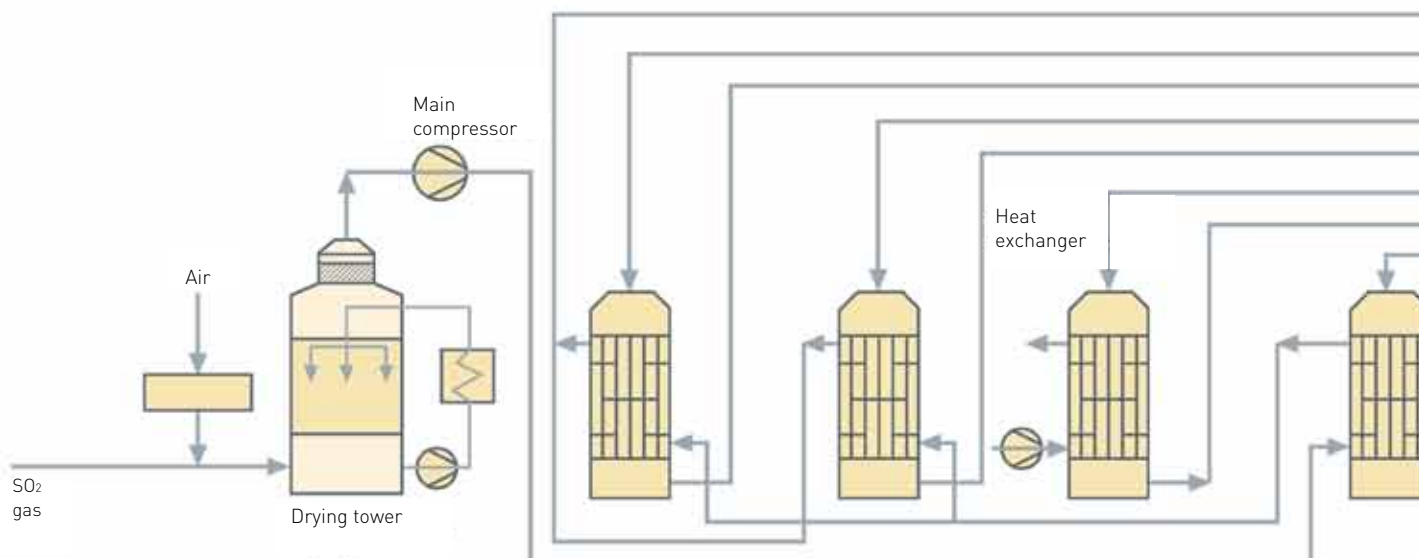




## Single absorption process for dilute off-gases

The single absorption process retains more gas heat than the double absorption process. As a result, approx. 10% more steam is produced per ton of sulfuric acid in a sulfur burning single absorption plant.

Typical process flow sheet for a single catalysis plant.



Prior to the introduction of the double absorption process, the ordinary contact or single absorption process was the standard means of sulfuric acid production. Today, single absorption plants are used only for processing off-gases of extremely low sulfur dioxide content, such as highly dilute smelter off-gases.

Before entering the drying tower, the cleaned sulfur dioxide-containing gases are generally diluted to achieve an  $O_2/SO_2$  ratio of at least 1:1. The dried gases are then compressed to the pressure required to overcome the pressure drop of the overall plant. Although this is about 10 kPa less than the pressure drop in a comparable double-absorption plant, almost the same specific blower capacity is needed on account of the substantially higher specific gas volume that results from the greater dilution of the feed gas. The feed gas is heated stepwise in a series of indirect gas-gas heat exchangers, first cooling the hot gases from the catalyst bed and then the gases between the individual beds. The cooled sulfur trioxide-rich gases from the last bed are passed into the  $SO_3$  absorber.

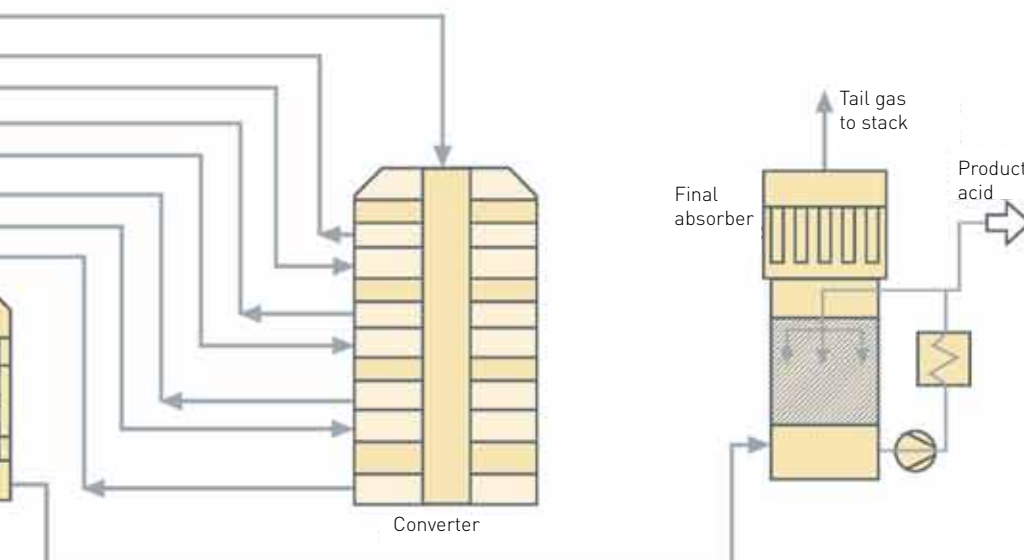
Because of the favorable energy balance, a single absorption plant can also process gases with a lower sulfur dioxide content. The lowest  $SO_2$  concentration, at which autothermal operation can be maintained in continuous operation, is 2 vol.-%.

At low feed-gas concentrations and with the help of highly active catalysts, tail gas  $SO_2$  concentrations are attained that are equivalent to the levels associated with standard double absorption plants based on high  $SO_2$  concentrations.

An existing single absorption plant can be brought into conformity with stringent environmental legislation either by retrofitting an intermediate absorption stage, or by the addition of a tail gas purification system, e.g. our PERACIDOX<sup>®</sup> system.

#### Facts about single absorption:

- **Plant capacities: 50 to 7,900 tpd Mh**
  - **Feed-gas concentrations: >2 vol.-%**
  - **Conversion efficiency: 98–99%**
  - **Specific cooling energy consumption: 15–25 kWh per t Mh**
  - **Specific power consumption: 1–1.56 GJ per t Mh**
  - **Specific catalyst quantity: 200–260 l per t Mh**
- Mh=Monohydrate=100%  $H_2SO_4$ g**





## Double absorption process for higher production yields with smaller equipment

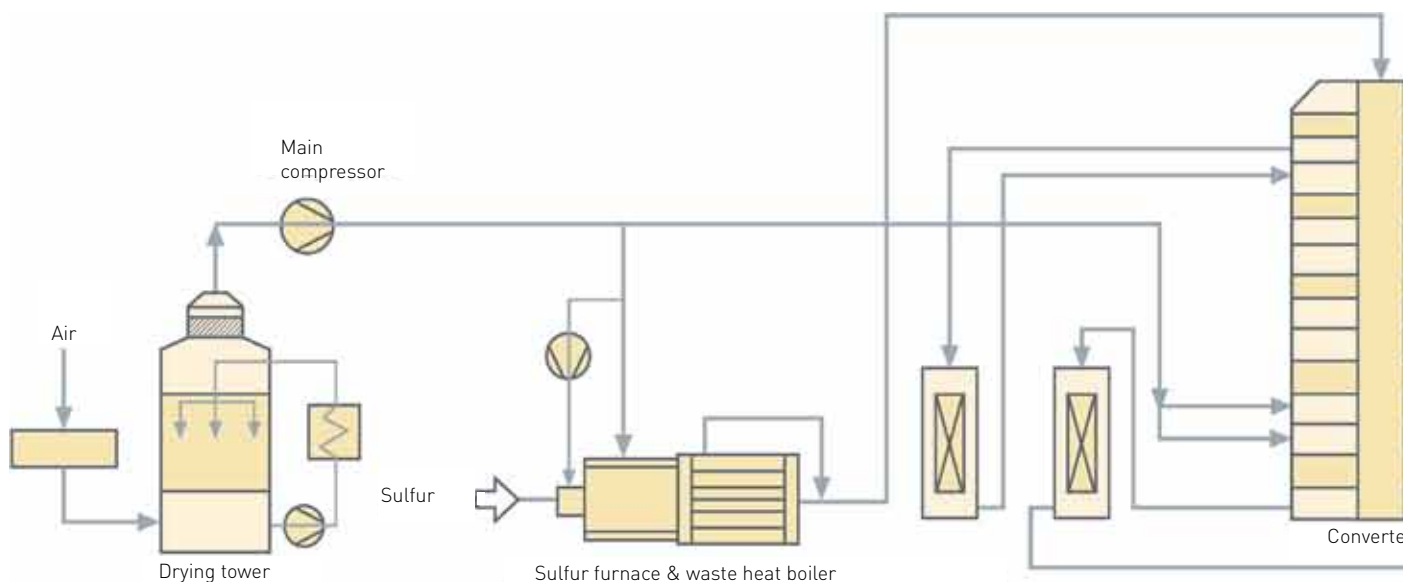
The most commonly used process for acid production in new plants is the double absorption process. Another option is an ordinary contact process without intermediate absorption.

A major advantage of the double absorption process is the ability to feed gases with higher  $\text{SO}_2$  concentrations than would be possible with the single catalysis process. This means smaller gas volumes and consequently smaller equipment with comparable production capacities.

Sulfuric acid production based on sulfur combustion is an exothermic reaction generating a considerable amount of heat which may be converted to high-pressure steam. The gas leaving the fourth or fifth pass enters the economizer where it is cooled by boiler feedwater. The gas leaving the economizer enters the final absorbing tower. Equipment of various designs can be used for drying and absorption and the same applies to the cooling of the circulating acid.

If oleum is to be produced, an additional tower has to be installed upstream of the intermediate absorber.

Typical process flow sheet for a sulfur burning double catalysis plant.





Within a given overall process concept, many variations in detailed design are possible, depending on customer needs.

#### Details tailored for customer's specific needs

The principal steps in the process consist of burning elemental sulfur in atmospheric oxygen to form sulfur dioxide, the catalytic oxidation of sulfur dioxide in the presence of a solid catalyst to form sulfur trioxide, and absorbing the sulfur trioxide in concentrated sulfuric acid.

Atmospheric air is dried with 95–96 wt.-% sulfuric acid and used for the combustion of elemental sulfur. The  $\text{SO}_2$  gas is cooled in a waste-heat boiler and converted into  $\text{SO}_3$ , in either a 4-layer or a 5-layer converter. Between the first and the second catalyst bed, the hot gas is cooled in a steam superheater.

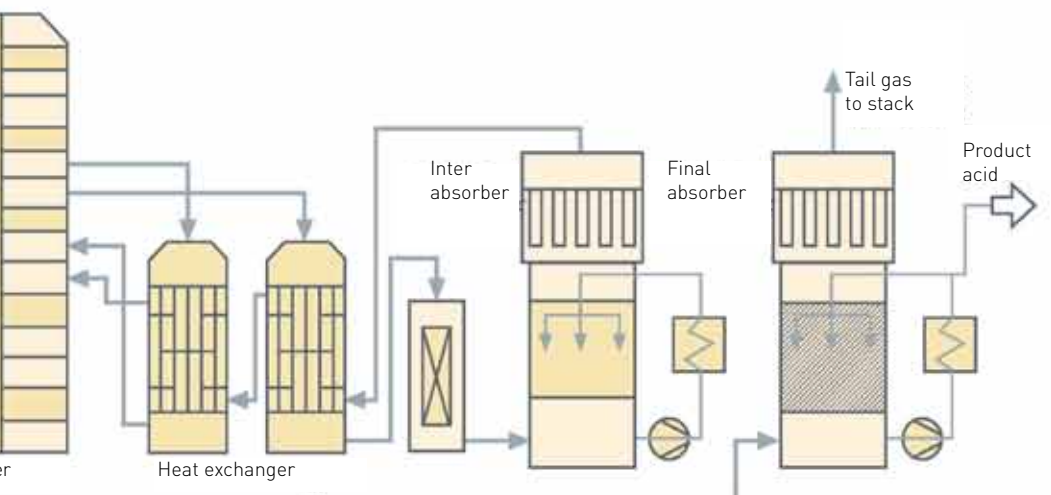
After the second layer, the gas is cooled in a second superheater or economizer and then admitted to layer three. After the third layer, the converted gas is cooled in a gas/gas heat exchanger and an economizer en route to the intermediate absorber.

Subsequent to the absorption of  $\text{SO}_3$ , the residual  $\text{SO}_2$  gas is preheated again to conversion striking temperature in the heat exchanger prior to entering the fourth layer.

In the case of a five-pass converter, the hot  $\text{SO}_3$  gases coming from the fourth layer are cooled by adding cold air before they enter the fifth and the last layer.

#### Facts about double absorption process:

- Plant capacities: 50 to 7,900 mtpd Mh
  - Specific HP-Steam production: up to 1.4 t/mt Mh
  - Conversion efficiency of  $\text{SO}_2$ : up to 99.9%
  - Specific sulfur consumption: <330 kg/mt Mh
  - Specific cooling energy: ca. 2 GJ
  - Specific power consumption: 40–60 kWh/mt Mh
  - Specific catalyst quantity: 150–200 l/mtpd Mh
- Mh=Monohydrate=100%  $\text{H}_2\text{SO}_4$





## Spent Acid Regeneration for safe decomposition of sulfuric acid

The decomposition of sulfuric acid at high temperatures, developed by former Lurgi Metallurgie in the 1930s, is still the safest and, in most cases, the only method of achieving a product of original high quality.

The regeneration of spent sulfuric acid produces acid at much higher cost than that produced from conventional raw materials, such as elemental sulfur. On the other hand, the crucial question of economics cannot be answered by comparing production costs alone.

With the increasingly stringent environmental regulations, costs for the ecologically acceptable disposal of spent acids must be added, when comparing the costs of conventional acid production.

The thermal decomposition of spent sulfuric acid is governed by the equilibrium constants:

- Efficient decomposition only takes place at a temperature of around 1,000°C
- High oxygen contents provoke reversal reactions from  $\text{SO}_2$  to  $\text{SO}_3$ , whereas very low  $\text{O}_2$  contents cause insufficient decomposition of organics and ammonia, as well as the formation of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{COS}$

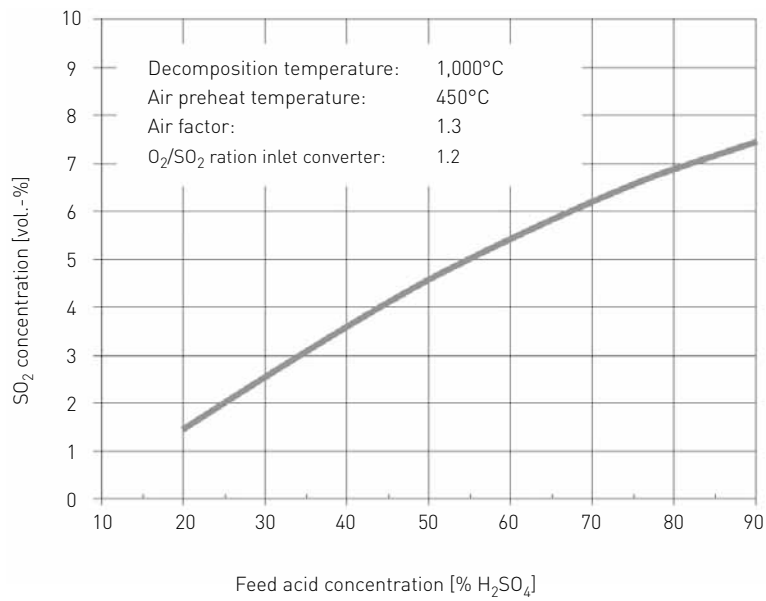
To ensure complete decomposition of the acid and combustion of the organic impurities, the temperature needs to be around 1,000°C and the conditions have to be oxidising. In practice, the temperature required for this strongly endothermic process is supplied directly by means of hot flue gases from the combustion of fossil fuels or sulfur-containing fuel. A large proportion of the additional heat can be recovered when the gases leaving the reactor are cooled from 1,000°C to about 350°C.

Depending on the intended use of the recovered energy, different waste-heat systems may be employed. One typical approach consists of a gas-gas heat exchanger, installed downstream of the furnace in which the decomposition products are cooled indirectly from 1,000°C to 350°C. Simultaneously, the furnace combustion air is heated to 450°C. Usually, only about a third of the hot air generated in this heat exchanger is required by the fuel oil burners in the decomposition furnace. The remainder can be used, for example, to generate steam in the waste heat boiler.

The associated system for processing the decomposition gases normally consists of a wet-gas cleaning section and a double absorption sulfuric acid plant. The latter system is similar in design to conventional acid production plants based on  $\text{SO}_2$  gases from metallurgical processes. Because the volume of combustion gas introduced into the decomposition furnace depends on the required process heat, the total specific gas volume and the resulting  $\text{SO}_2$  concentration of the gases at the furnace exit become a function of the spent acid concentration.

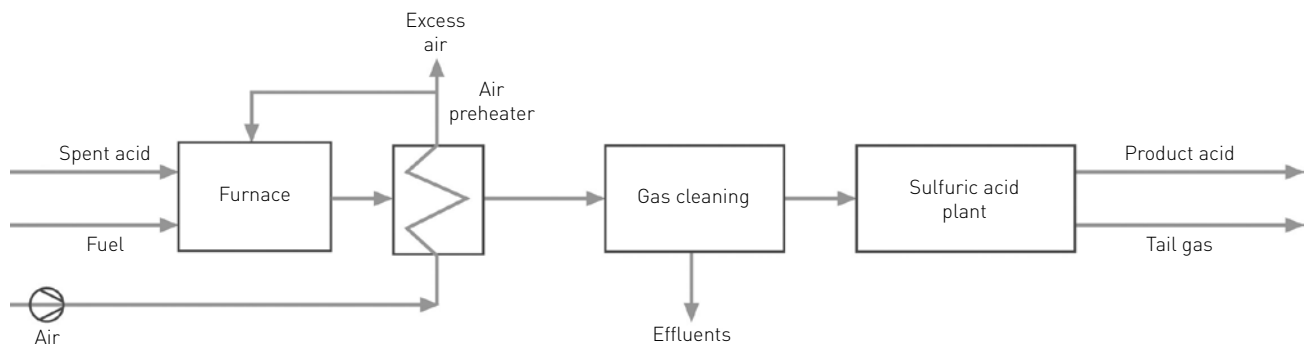
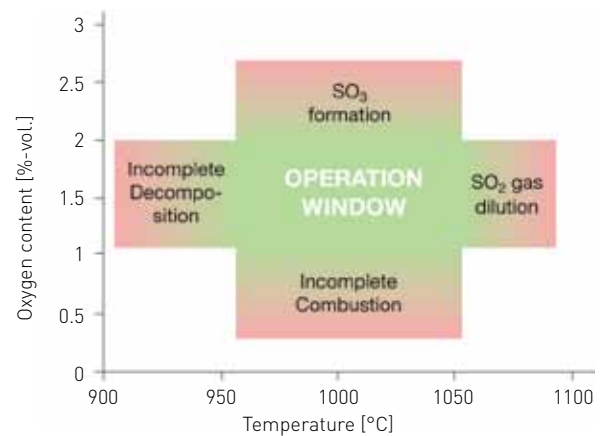
### Our expertise covers:

- Preconcentration
- Thermal decomposition
- Energy Recovery
- Gas Cleaning Systems



Since both the investment and operating costs of the sulfuric acid plant increase considerably with lower SO<sub>2</sub> concentrations, efforts should be made to provide as high a sulfur dioxide concentration as possible. The easiest way to achieve this is to burn sulfurous fuels. If H<sub>2</sub>S gas is available, it can entirely replace fuel oil or fuel gas. Elemental sulfur can also be employed.

When seeking an optimum solution for solving spent acid problems, it is evident that each case must be considered individually. Outotec offers a thorough investigation not only of technical feasibility, but also of the economics relating to the marginal conditions of each customer's specific situation.



# Efficient heat recovery improves plant economy

With rising energy prices and the increasing need to make more efficient use of thermal energy, the economic importance of waste heat recovery will grow. More stringent environmental regulations for certain types of energy production will contribute to the significance of energy savings.

In the manufacture of sulfuric acid in a sulfur-burning plant, approximately 98% of the energy input comes from the intrinsic chemical energy of the reactants. The remainder comes from the main blower drive as heat of compression. In the classic process cycle, in which 57% of the total energy is recovered as high-pressure steam, 3% is dissipated with the tail gas via the stack, 0.5% is lost as sensible heat in the product acid, and nearly 40% is available as low level heat in the acid cooling system.

In all of these examples, almost the complete reaction heat of a sulfuric acid plant has been utilized. A universal solution for all sulfuric acid plants, irrespective of their location, is to produce steam with the waste heat from acid circuits. A prerequisite for this is the availability of a heat exchanger, which in the long run withstands both sulfuric acid of a temperature of 160 to 190°C at a concentration of 94 to 99% w/w on the acid side, and boiler water at a pressure of 5 to 10 bar on the water side. As temperature levels rose, conventional absorption towers began to reach their operation limits. To permit the use of high acid temperatures without sacrificing absorption efficiency, cooling/absorption has to be effected in two stages. Our Lurgi Venturi absorber meets these criteria.

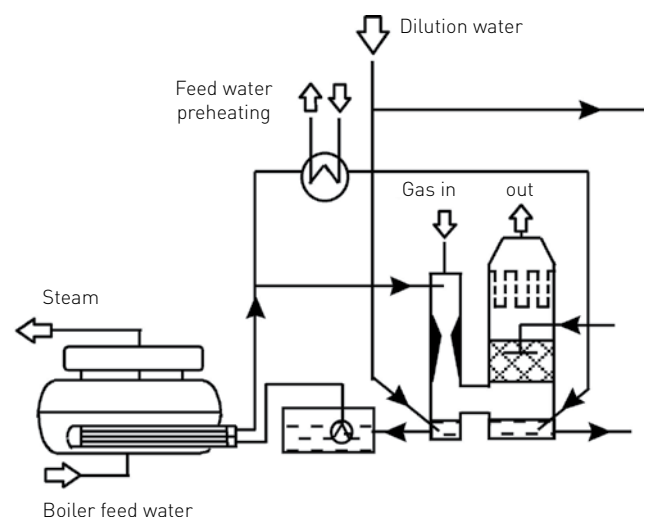
## Facts about heat recovery

- Saturated steam is produced up to 10 bar
- Acid piping and the heat exchanger are designed to be used in a temperature range of up to 200°C and in a concentration range of 95 to 100% w/w, a feature which provides the operator with additional safety in normal operation
- The other components are made of conventional construction materials (brick-lined tower) and are therefore not subject to corrosion even under the most extreme circumstances

- The acid concentration control both in the Venturi section and in the conventional section is straight forward and simple
- The sulfuric acid plant can continue operation even when the energy recovery system and in particular, the steam section, is out of operation. Then the plant is run according to the standard mode
- The system allows for retrofitting of existing plant as long as there is sufficient space available in the area of the absorption section

## We have built a number of heat recovery systems since 1976 with three main areas of application:

- Production of hot water which is fed into communal and domestic heat supply systems
- Production of hot water for phosphoric acid concentration
- Production of hot water for industrial utilization (filter washing, sea water distillation, etc.)

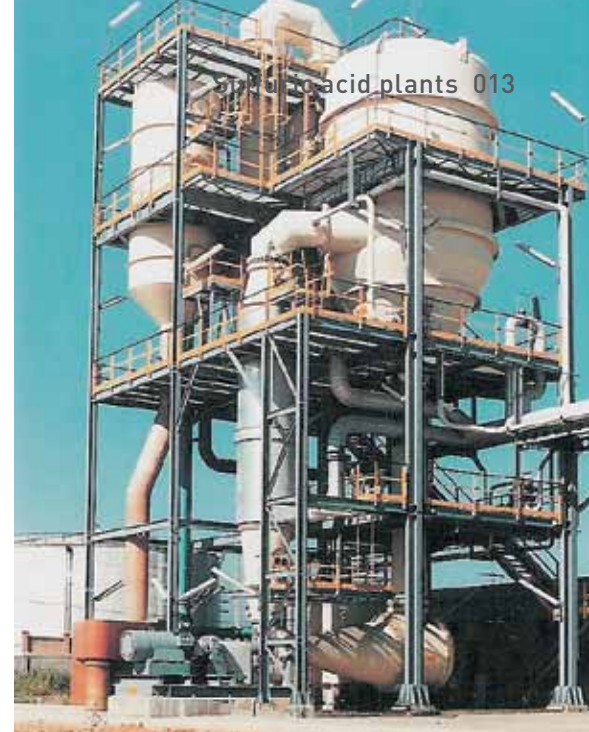


### Outotec HEROS® heat recovery system

As plant designers, we have been making strenuous efforts for over 30 years to find a satisfactory use for the energy that accrues in the form of waste heat that benefits our customers. Outotec HEROS® heat recovery system has been successfully used since 1989.

The  $\text{SO}_3$  containing gases enter the Venturi at a temperature of  $200^\circ\text{C}$ . Acid temperature at the Venturi absorber inlet is  $172^\circ\text{C}$ . On account of the absorption of  $\text{SO}_3$ , and its reaction with water introduced in the Venturi, the acid temperature rises to  $195^\circ\text{C}$ . About 95% of the  $\text{SO}_3$  contained in the gas is absorbed in the Venturi section, which means that the sulfuric acid concentration has to be monitored and controlled in the Venturi circuit. The hot acid flows by gravity into a pump tank, from which it is pumped using a vertical pump through the steam generator and then again into the Venturi.

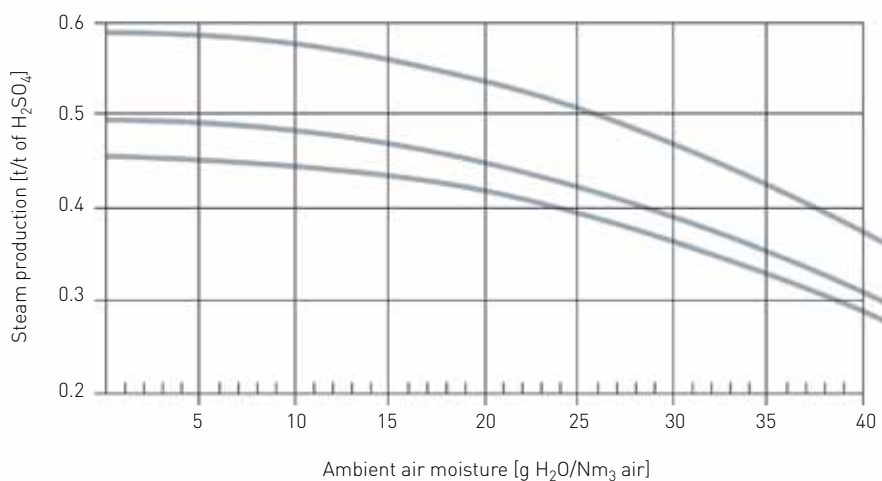
What quantities of energy can be recovered using this circuit? Starting from boiler feed water at  $105^\circ\text{C}$ , up to 0.6 t/t of acid can additionally be recovered as low-pressure steam. The precise amount depends on different factors, which are illustrated in the diagram:



Phosphoric acid pre-concentration unit.

**Apart from conventional process controls as acid temperature and concentration further measures are:**

- Continuous measurement of the corrosion rate
- Leak monitoring with acoustic alarm
- Measurement of boiler water conductivity and pH including the corresponding interlocking systems)





## Tail gas treatment improves the air and reduces effluents from single as well as double absorption plants

Outotec Peracidox® process reduces the residual SO<sub>2</sub> content of tail gases from double-catalysis plants and thus improves the air and reduces effluent emissions.

The Peracidox process is an oxidative sulfur dioxide removal process developed by former Lurgi Metallurgie and Südchemie for purifying the already very dilute tail gas from sulfuric acid plants. It does not lead to any by-products or waste, producing only sulfuric acid, which is recycled to the main sulfuric acid plant.

Hydrogen peroxide is used to oxidize sulfur dioxide to sulfuric acid:  $\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$





#### Benefits of Outotec Peracidox®

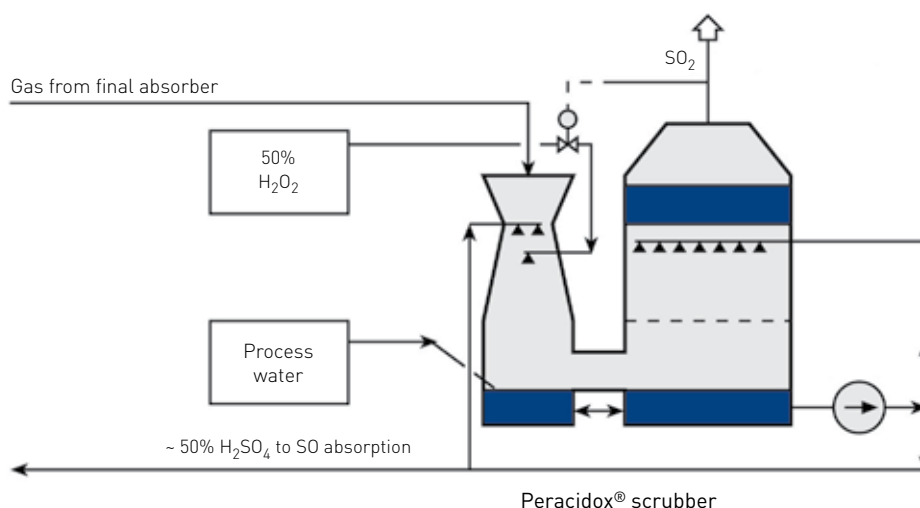
- No additional chemicals (sulfuric acid as product, no waste water, no residues)
- Low opacity
- High conversion efficiency (virtually stoichiometric)
- High reliability
- Low investment cost
- High flexibility with respect to various SO<sub>2</sub> contents of the gas

Tail gas leaving the final absorber of the sulfuric acid plant is washed in a two-stage Peracidox scrubber with dilute sulfuric acid in which the hydrogen peroxide is dissolved. The attainable sulfur dioxide content in the off gas is as low as 20 ppm SO<sub>2</sub>. Sulfuric acid vapour and residual sulfur trioxide are reduced accordingly.

The oxidant is introduced into the acid circuit of the first scrubbing stage at a stoichiometric rate proportional to the sulfur dioxide to be removed. Any residual oxidant in the solution overflowing to the first scrubbing stage finally reacts there with the entering tail gases.

The overflow withdrawn from the circuit of the first stage thus only consists of dilute sulfuric acid; the optimum concentration is 50-wt% H<sub>2</sub>SO<sub>4</sub>. It is introduced into the final or intermediate absorber of the main acid plant in place of process water.

The process is characterized by its relatively small amount of mechanical equipment required. It can also be used to improve the tail gas conditions during start-up and shut down periods, when the conversion efficiency of the catalyst is not optimized.



*Outotec develops and provides technology solutions for the sustainable use of Earth's natural resources. As the global leader in minerals and metals processing technology, Outotec has developed over decades several breakthrough technologies. The company also offers innovative solutions for the chemical industry, industrial water treatment and the utilization of alternative energy sources. Outotec shares are listed on the NASDAQ OMX Helsinki.*

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