The Lurgi Energy Recovery System in Sulphuric Acid Plants

by

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Abstract:

A system has been developed for recovery of energy from circulating sulphuric acid, with particular emphasis on security of operation and ease of installation into existing sulphuric acid plants. The key elements of the system is a venturi absorber with a dedicated acid circulation system that is installed upstream of the primary absorption tower. Energy is recovered in sulphuric acid circulating at approximately 190 °C and generates low pressure (up to 517 kPa) steam in a boiler. Materials of construction are chosen for their inherent resistance to corrosion and do not rely on extremely close control of operating parameters for security of operation. The design permits the existing absorption system to remain intact for "stand-by" service should the energy recovery system be taken out of service. This presentation will describe the design of the system, materials of construction, amount of energy recovered, and operating experience of units in production over several years.

Introduction

Energy recovery in the form of high-pressure steam was optimized in Europe already in the late sixties. Keywords in this context are:

- Main blower after the drying tower
- Boiler elements for heat dissipation instead of air injection
- Hot absorption Venturi tower
- Co-generation

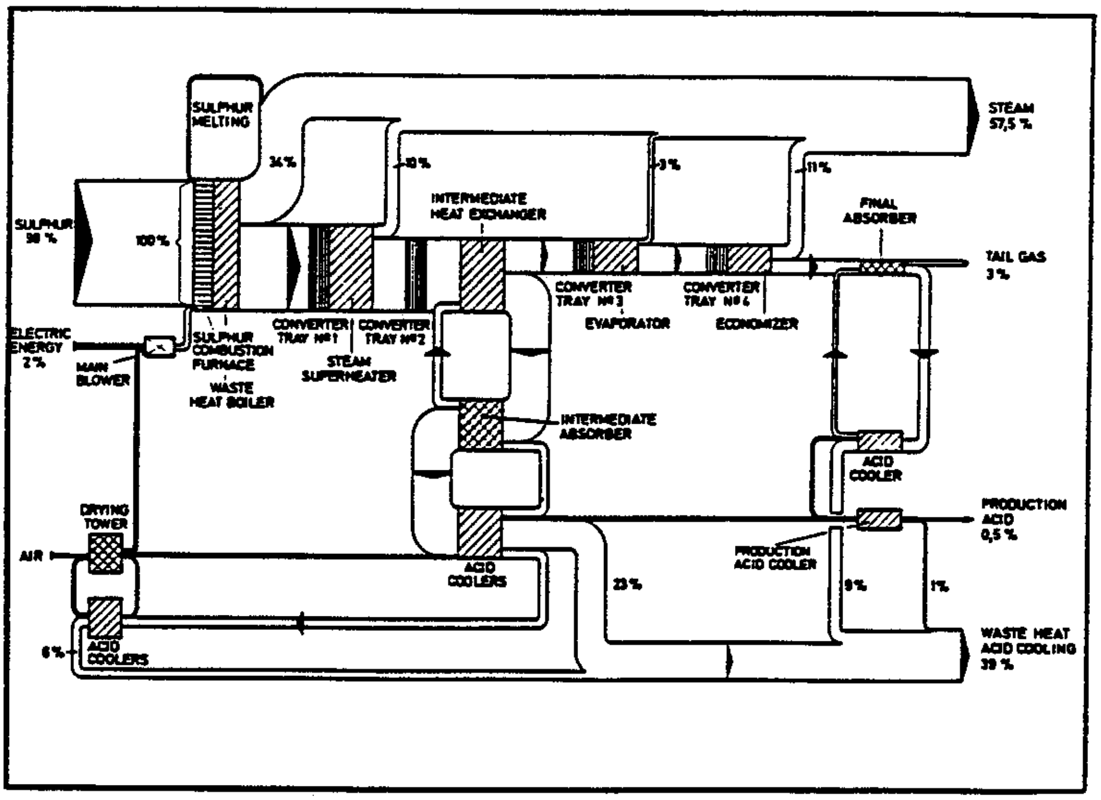

Fig. 1 Energy flow diagram of a double catalysis sulphuric acid plant based on sulphur combustion (with 10 Vol.% SO_2 gases)

Fig. 1 shows a typical energy flow diagram featuring a sulphuric acid plant based on sulphur burning. The reaction heat released by burning the raw material, sulphur, and by catalytic oxidation of SO_2 to SO_3 along with the reaction with water to form sulphuric acid constitute 98 % of the energy input. Approximately 2 % of the energy is introduced into the system as heat of compression from the main blower drive.

In the classic process cycle, 57.5 % of the total energy is recovered as high-pressure steam, approx. 3 % is dissipated with the tailgas via the stack, 0.5 % is lost as sensible heat in the product acid and 39 % is lost as waste heat in the acid cooling system. This distribution may vary according to the SO_2 content of the gases at the outlet of the sulphur furnace, but in principle these proportions remain constant. We as plant designers have, for more than 25 years now, been undertaking efforts to find an adequate use for the 39 % energy that accrues as waste heat, to the benefit of our customers. As this energy comes essentially from the acid circuits, this problem is after all merely limited to the properties and characteristics of the materials used for the respective heat exchangers in the acid circuits.

A number of heat recovery systems has been built by Lurgi since 1976 and three main areas of application have emerged:

- 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.).

The examples below [1] illustrate that virtually the complete reaction heat of a sulphuric acid plant has been utilized to the full.

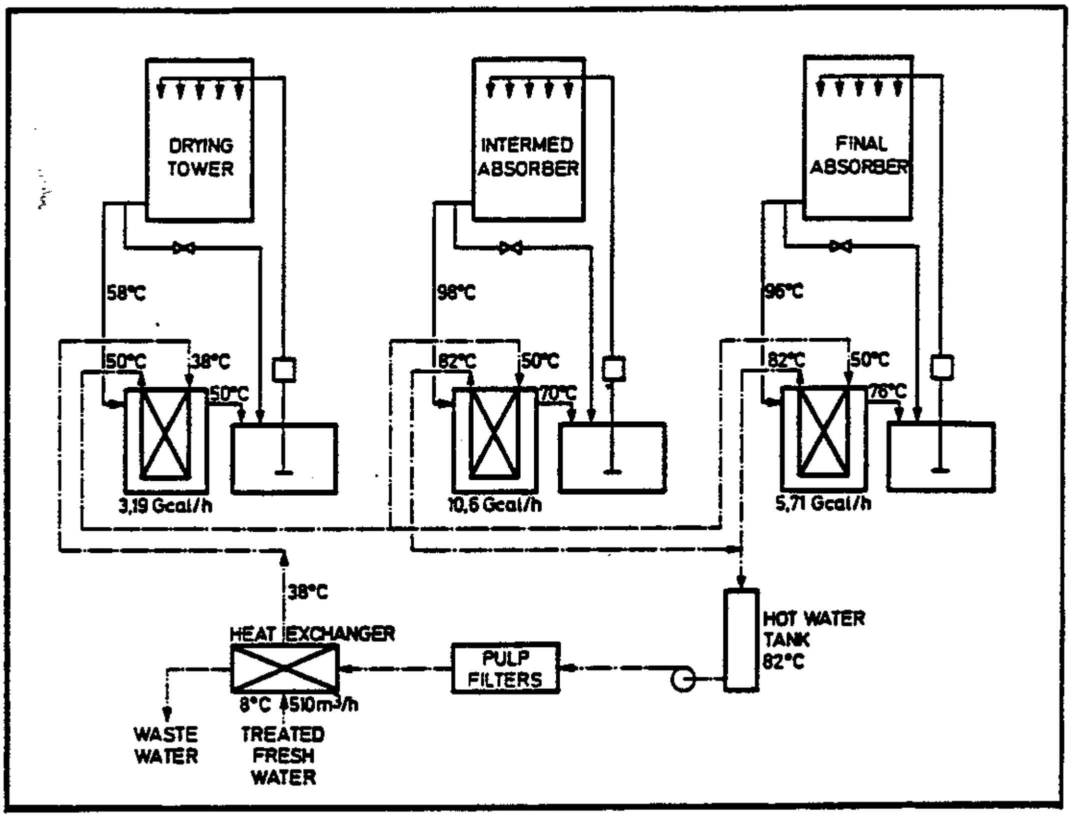

Fig. 2 Production of hot water by acid waste heat recovery from a 940 stpd double catalysis plant

The plant whose diagram is shown in Fig. 2, went on stream in 1976. In this plant, the total acid heat is used for the production of hot water for direct industrial consumption. The 940 stpd double catalysis plant based on pyrite roasting is heating 510 m3/h of treated fresh water, passed through a series of acid heat exchangers of the dryer, the intermediate and the final absorber up to a temperature of 85 °C, corresponding to a heat value of about 80 million kJ/h. The hot water is used directly for filter washing in a pulp mill located a few hundred meters away.

Another acid heat recovery system supplying hot water of 90 °C for town district heating was installed in Denmark in 1978. The system recovers about 45 million kJ/h from the intermediate absorption system of a 825 stpd sulphuric acid plant. These systems have been equipped with Teflon tank coil heat exchangers. Also, in an integrated acid heat recovery system for four sulphuric acid production units in Germany which has been commissioned in 1980, Teflon tank coil heat exchangers were used. The heat is being sold by long-term contract to a power plant and is partly used for boiler feed water preheating and partly supplied to an urban district heating system during cold season.

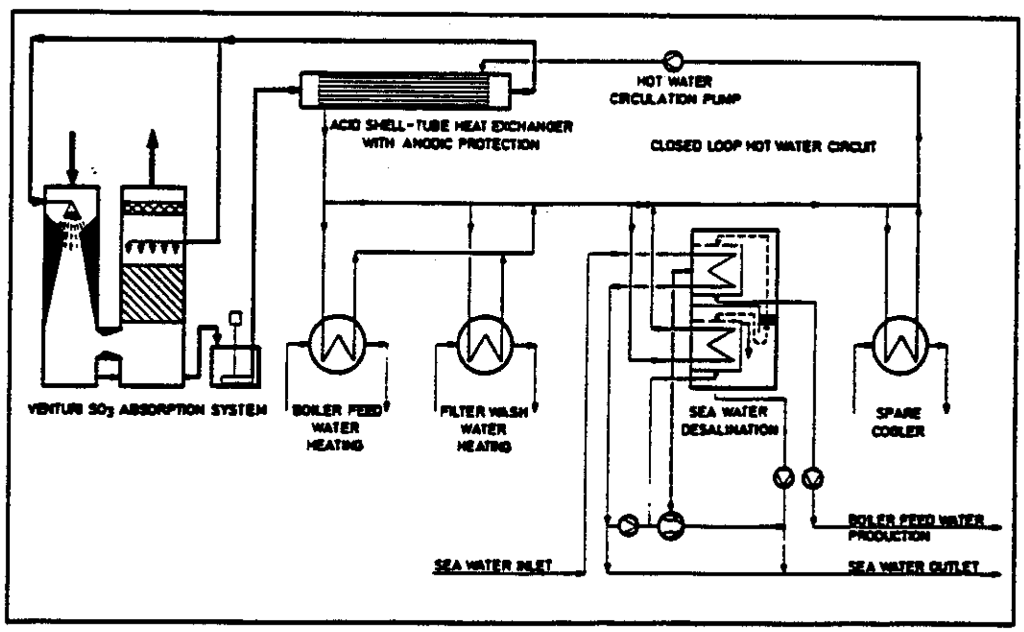

Fig. 3 Absorber acid waste heat recovery and utilization with a closed-loop hot water circuit

Fig. 3 shows another example of a closed loop hot water circuit for acid waste heat recovery which has been designed and engineered by Lurgi for a 700 tpd sulphuric acid plant in Southern France. The system is equipped with an anodically protected shell-and-tube acid heat exchanger of stainless steel. Demineralized water, circulating through the closed loop system, is heated to a temperature of 90 °C. The acid heat recovered in the closed loop system is used for preheating boiler feed water of the steam system, for heating filter wash water of an adjacent phosphoric acid plant and for producing boiler feed water from sea water by distillation in a thermally integrated vacuum evaporation unit.

There are many more examples of Lurgi-built plants in which practically the total chemical energy available was exploited.

All of these examples proved to be great commercial success for the plant operators, since a tailored solution was offered in each individual case. Most of the heat recovery systems were installed in existing plants. The point was, therefore, to make maximum use of units, equipment and special absorption towers.

Sulphuric acid coolers

With reference to the heat exchangers employed, developments on materials of construction can be described as follows:

- Teflon coils
- Glass heat exchangers
- Stainless steel with anodic protection
- Stainless steel without anodic protection

It is of course our objective as plant designers to offer a universal solution for all sulphuric acid plants irrespective of their location, to produce steam, for instance, 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 sulphuric acid of a temperature of 160 to 190 °C (320 to 380 °F) at a strength of 94 to 99 % on the acid side, and boiler water at a pressure of 5 to 10 bar on the water side.

Absorption towers

As temperature levels were raised, conventional absorption towers reached their operation limits. In order to permit a high temperature level to be reached, i.e. high acid temperatures on the one hand and the usual, high absorption efficiency on the other, cooling/absorption had to be effected in two steps (stages). The Venturi absorber (Fig. 4) developed by Lurgi meets these criteria [2].

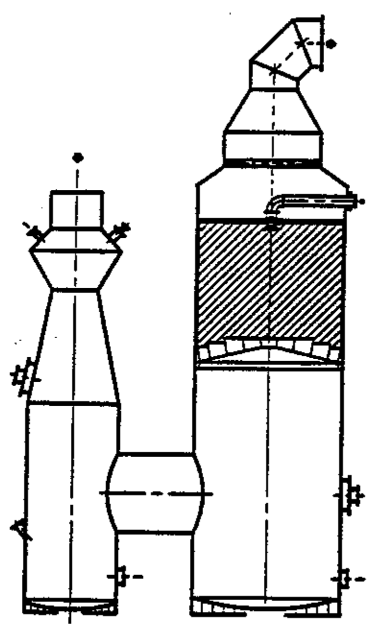

Fig. 4 Venturi-tower absorption unit

Because the gas and absorber acid are flowing in cocurrent in a Venturi system, the gas temperature at the Venturi absorber outlet is higher than in the conventional countercurrent absorber working with acid of the same inlet temperature. Thus, less heat is transferred from the gas to the absorber acid and dissipated through the acid cooling system. Running the absorber at a higher acid temperature reduces gas heat losses still further. The Venturi absorption system consists of vertical and horizontal Venturi scrubbers arranged in series. In each case, the acid is injected through a nozzle into the gas inlet of the Venturi unit. After the Venturi units, the gas passes through a packed tower.

The intensive mixing of the injected acid with the turbulent gas stream in the Venturi unit provides a large liquid/gas interface and, consequently, favourable mass and heat transfer conditions. As early as 1974, a Venturi unit was used as intermediate condensation/adsorption unit in the first wet-dry catalysis plant. This Venturi unit based on a Südchemie/Lurgi-patented process condenses moisture-laden, preconverted gases of 300 °C.

This type of Venturi system has rendered satisfactory service in a large number of sulphuric acid plants, even in the very large units that are standard today.

Metallic material for acid heat exchanger

The task was to find a metallic material which would exhibit at least the following properties:

- Acceptable corrosion rate in a temperature range of 150 to 200 °C (300 to 390 °F) and within a concentration range of 94 to 99 % sulphuric acid, and preferably without anodic protection.
- Adequate mechanical strength under the mentioned operating conditions.
- Reasonable price.

In cooperation with Metallgesellschaft and with the support of many companies and institutions [3] we tested a great many commercial construction materials, at lab-scale to begin with, and then using a material test unit, installed in the sulphuric acid plant at Ruhr Zink, Datteln, Germany (see Fig. 5).

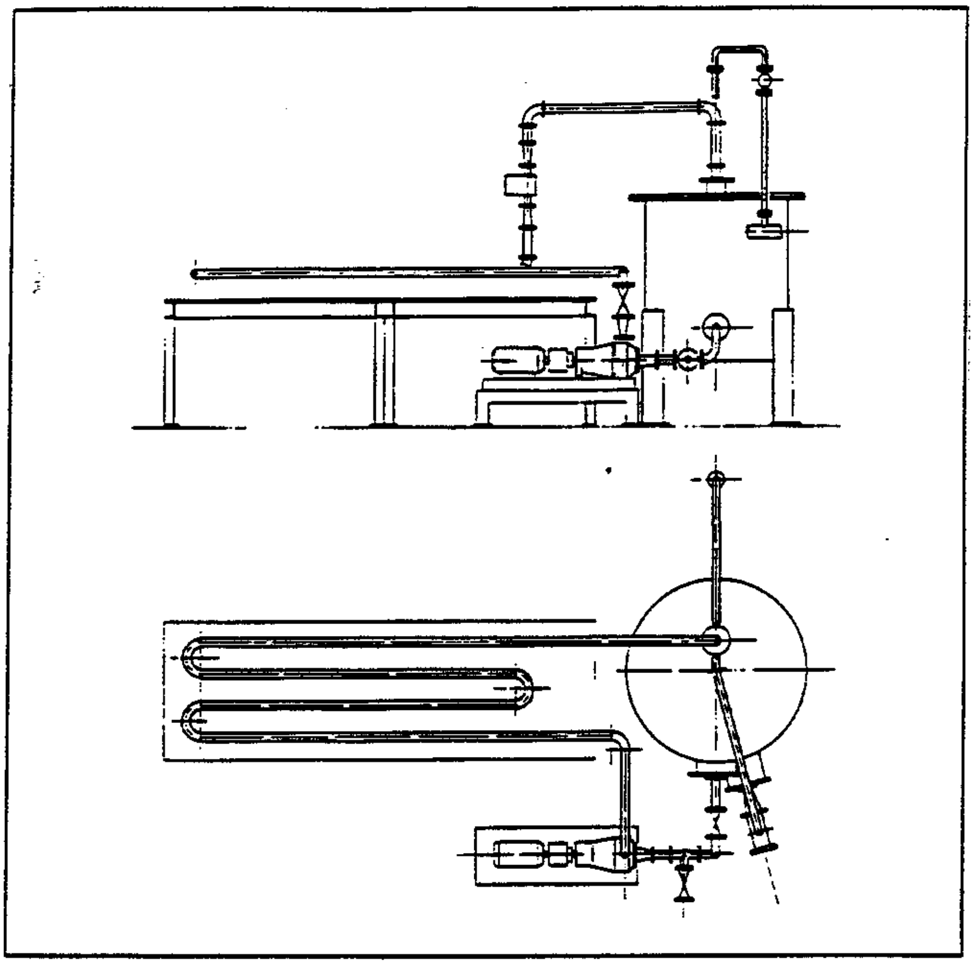

Fig. 5 Material test unit at Ruhr Zink Datteln, Germany

Sulphuric acid of 98.5 to 98.7 % strength was continuously withdrawn from the intermediate absorption circuit in order to avoid test acid from becoming concentrated with corrosion products as this may alter the results. The acid was heated to test temperature in a brick-lined tank with quartz glass candles and then pumped through the test section by means of a cast silicon iron pump.

The following parameters were adjusted for the test operation:

a)	Flow velocity	0.6 to 2.5 m/s
b)	Exchange of the total acid volume every	0.5 to 2 h
c)	Temperatures	100, 125, 150, 175 °C
d)	Test period	500 to 900 h

Laboratory tests already proved the material to be particularly corrosion-resistant under the required conditions. The product in question is the material 1.4575 which used to be marketed by Thyssen under the name of "Superferrit" and is now sold by VDM as "Cronifer 2803".

The results of the laboratory and field tests are illustrated in the corrosion diagram for material 1.4575 for sulphuric acid concentration and temperature (see Fig. 6).

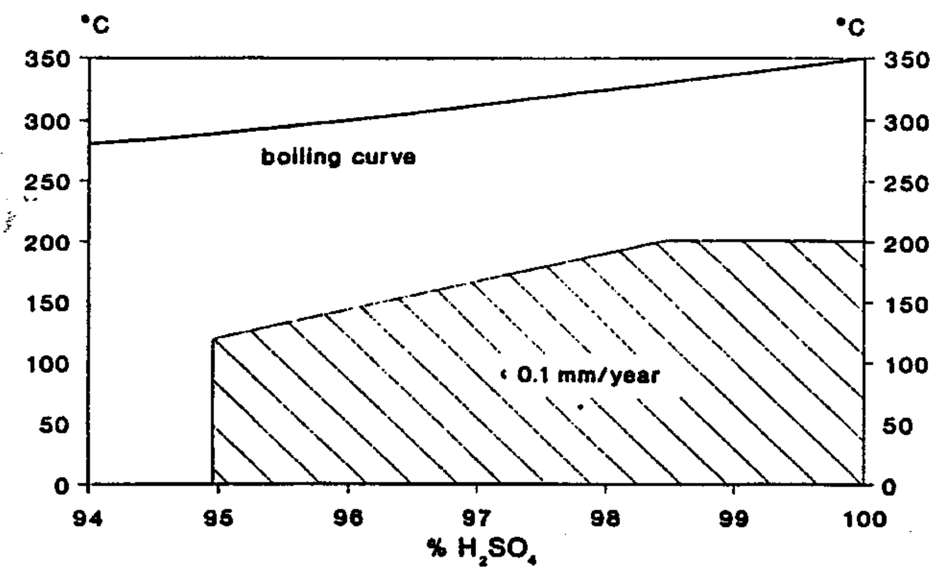

Fig. 6 Range of operation for Superferrit 1.4575 in concentrated sulphuric acid

As mentioned, for the attainment of corrosion rates under 0.1 mm/year, anodic protection is not needed for the conditions described. A striking feature is the wide range of acid strengths (95 to 100 % H2SO4) within which the material is resistant to corrosion.

In 1988, we installed a Venturi scrubber in a sulphuric acid plant in Austria which was made of this material. This Venturi served as a pre-absorber upstream of an existing conventional intermediate absorber. It is made completely of material 1.4575, without brick lining and without packing. Sulphuric acid and gas are fed in cocurrent via three nozzles situated at the top of the tower. The aim was to test the material in actual operation at acid temperatures of 120 to 160 °C. Apart from that, two heat exchangers equally made of material 1.4575 were installed in the circuit.

Over the years, regular inspections were carried out and corrosion rates inside the Venturi scrubber and the acid coolers were practically not measurable.

Approximately at the same time, in 1988, we sold an energy recovery system which was commissioned in 1989 (see Fig. 7).

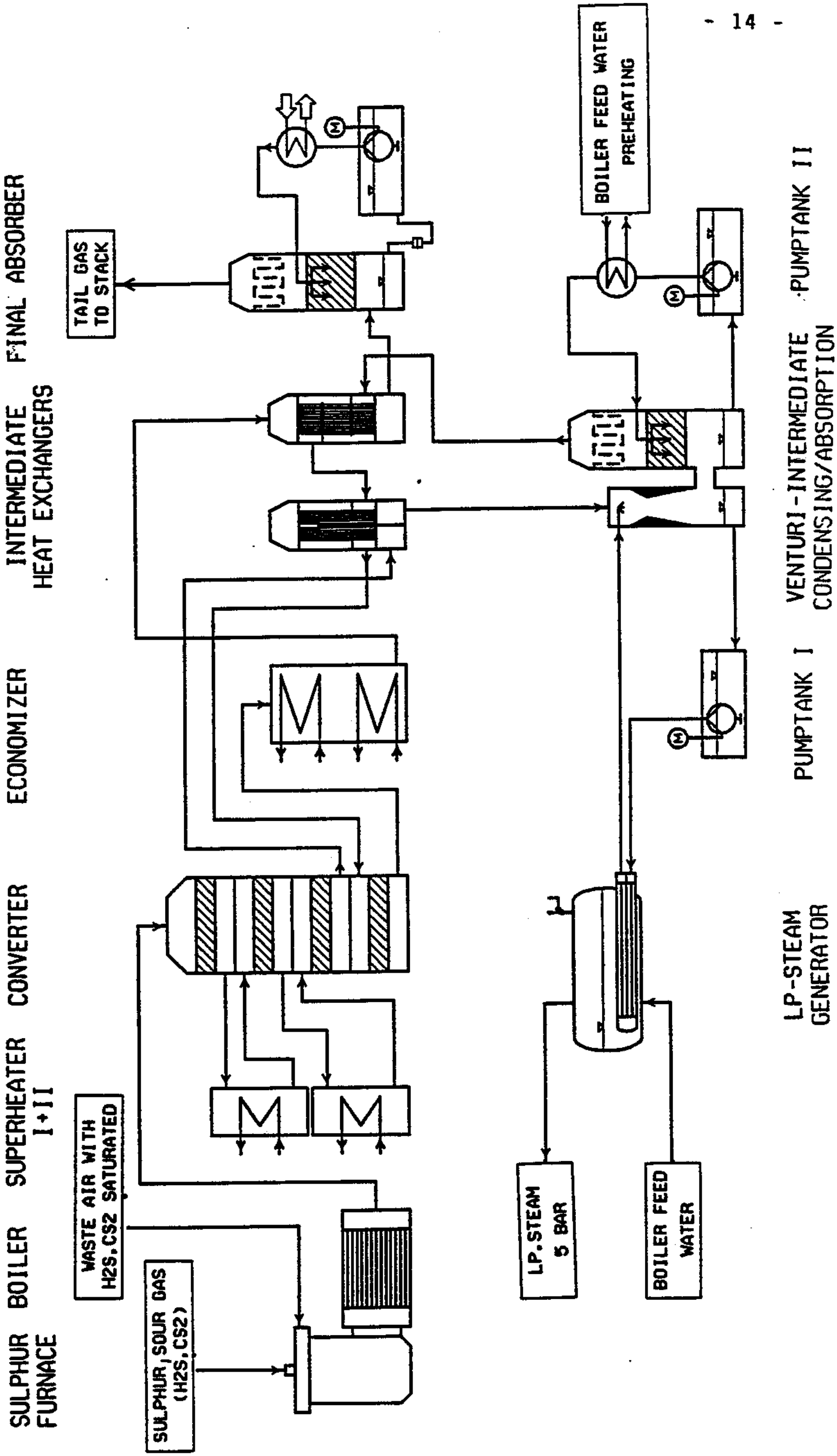

Fig. 7: Wet-dry catalysis plant with energy recovery system

This energy recovery system was installed in the afore-mentioned wet dry catalysis unit. The existing intermediate absorption tower was already equipped with two circuits - one for the Venturi scrubber and a second one for the downstream packed tower. Therefore, only the steam generator had to be tied into the Venturi circuit. The acid circulation pump and the acid piping were replaced to adapt them to withstand the higher temperatures.

The SO3 containing gases enter the Venturi at a temperature of approx. 300 °C (570 °F). Acid temperature at the Venturi scrubber inlet is 172 °C (340 °F). Due to SO3 absorption, the reaction with the water contained in the gas, i.e. by adding water into the Venturi, the acid temperature rises to 195 °C (380 °F). 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. This steam generator produces 4.5 t/h of saturated steam at 5 bar (73 lb/in2) which are directly put to use in the plant.

About 90 % of the SO3 contained in the gas are absorbed in the Venturi section, which means that sulphuric acid concentration has to be monitored and controlled in the Venturi circuit. For a start, we injected low-pressure steam into the Venturi top, primarily because in this specific case gas is already wet, containing up to 30 g H2O/Nm3. By doing so we expected to obtain a favourable mixture of SO3 and water. The disadvantage of this injection of steam is, of course, that even more energy is introduced into the system and the steam generator has to be dimensioned for an about 20 % higher capacity. At some point during operation, the steam injection system was failing. To continue production, diluting water was added to the Venturi direct. It turned out that monitoring and control are just as simple and immediate as when adding steam. For this reason, the plant now operates with direct injection of water.

The gas leaves the Venturi section at a temperature of approx. 190 °C to enter the downstream packed tower, the acid circulation system of which operates at a temperature of 70/90 °C. Practically, there is only sensible heat that has to be dissipated as the SO3 is largely absorbed in the Venturi scrubber. However, the dimensions of the acid-cooling system are such that the sulphuric acid plant is also operative without Venturi and energy recovery system. In this mode, the steam generator is bypassed. The heat is transferred via cross flows from the Venturi circuit to the tower circuit. While the downstream packed tower is a conventional absorption tower in most respects, it does require a high-efficiency (Brownian diffusion) mist eliminator to remove the fine mist resulting from condensation of H_2SO_4 vapors.

The customer would only accept the energy recovery system subject to the following provisions:

- Operation of the sulphuric acid plant must not become more complicated.

- The sulphuric acid plant must be able to continue operation even if the energy recovery system does not work properly.

And these requirements are complied with:
Only three parameters are monitored and controlled. The acid concentration of the Venturi circuit, steam pressure of the low-pressure steam system and the pump tank level. All the other temperatures follow automatically, the rate of circulating sulphuric acid remains constant and the steam rate produced is only dependent on the capacity of the plant. The amount of steam produced can, however, be influenced by allowing a smaller or

larger quantity of hot acid to pass from the Venturi section into the tower section. Acid piping and the heat exchanger of the low-pressure steam generator are constructed of material 1.4575 or enamelled. Any other plant items contacted with acid are made of brick-lined mild steel. For reasons of absorption efficiency, acid concentration should be kept at 98.5 %.

Safety Devices

Apart from the acid concentration control already mentioned, a second measuring device for concentration incorporating an alarm is installed.

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.

Two failures occurred since the first start-up of the plant. The first was clearly identified as a faulty weld seam. The second failure occurred a few days after a pipe rupture in one of the superheaters upstream of the intermediate absorption tower.

As a consequence of the superheater damage, large quantities of steam together with preconverted gas flowed into the intermediate absorption unit generating an extremely large amount of heat, at the same time diluting the circulating acid. We assume that at that time the sulphuric acid had a strength of less than 93 % at boiling point.

Although subsequent to this event, no leakages were noted at the steam generator, we presume that the unit was "predamaged" as it were. We would assume that the damage proper occurred due to mechanical strain after recommissioning.

Now, what does a new plant, specifically designed for this system look like (Fig. 8)?

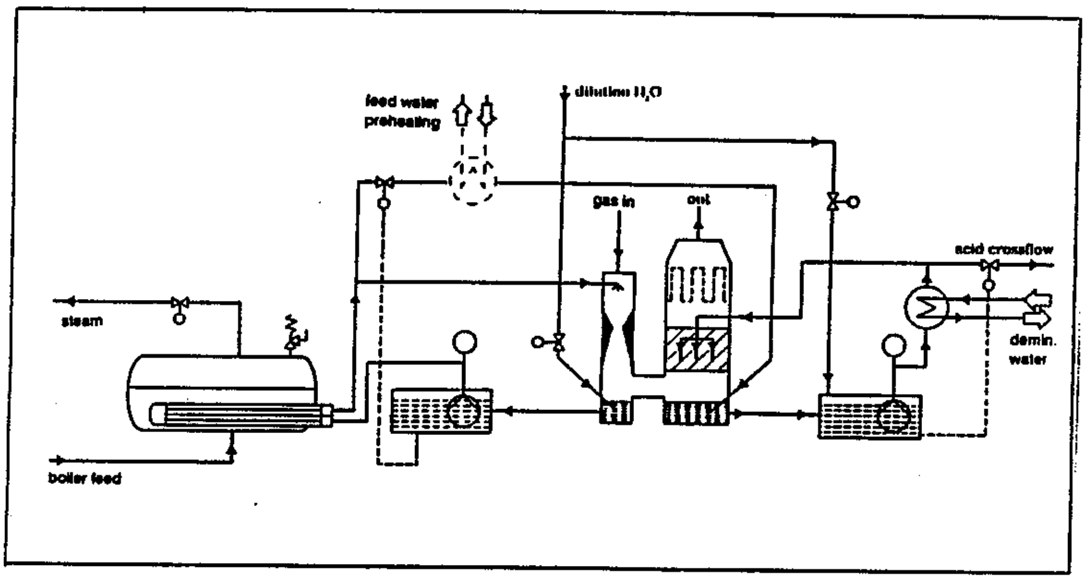

Fig. 8 Energy recovery system in sulphuric acid plants

The energy recovery system tower system consists of a venturi and the close-coupled conventional absorption tower. Both vessels are made of brick-lined carbon steel. The conventional tower has a packed section and candle-type high-efficiency mist eliminators. Each vessel has an independent pump tank and acid circulating system with one or more vertical acid pumps. The conventional tower acid circuit has a standard acid cooler.

The acid cooling system is sized to remove all of the primary absorption heat in the event the energy recovery system is not in service, to ensure that the energy recovery system can not cause the acid plant to lose production.

The steam generation section consists of a typical kettle-type evaporator to which a tube bundle heat exchanger is flange-mounted. Hot sulphuric acid is pumped through the tubes which are surrounded by boiler water. In this heat exchanger, the sulphuric acid is cooled down and then injected into the Venturi top via a number of nozzles. The strength of the sulphuric acid is controlled by adding water through the Venturi top. In the conventional section, the water is added via the tower. The hot acid produced in the Venturi circuit passes into the pump tank of the tower circuit where it is cooled and used to preheat boiler feed water for instance.

What quantities of energy can be recovered using this circuit? Starting from boiler feed water at 105 °C, a standard double catalysis system using a 2 + 2 or 3 + 1 circuit, up to 0.5 t/t of acid can additionally be recovered as low-pressure steam. In addition boiler feed water can be heated as required in any place of the plant, in economizers or in acid coolers of the final absorbers.

Therefore, the high-pressure boiler system and the low-pressure system generate 1.4 + 0.5 ton of steam per ton of sulphuric acid.

This system is particularly suited for retrofitting existing plants, without losing its flexibility and its reliability of operation. The only prerequisite is sufficient space to locate the Venturi section as close as possible to the absorber. Of course, allowance has to be made for the space required for the pump tank and the boiler section. Retrofitting will have virtually no effect on plant operation when the Energy Recovery System is out of service.

The energy recovery system of a plant currently under construction and scheduled to go on stream in autumn 1992 is shown in Fig. 9.

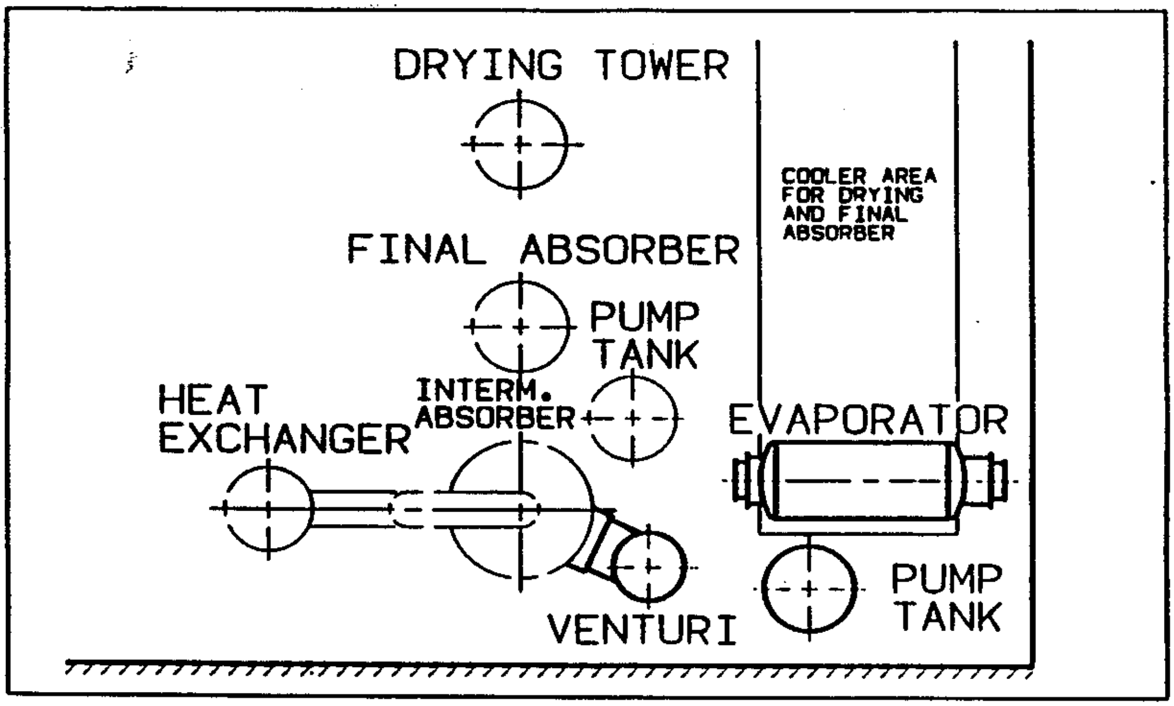

Fig. 9 Arrangement of Energy Recovery System

The plant incorporates both an entirely new construction and a retrofit. The sulphuric acid plant downstream of a pyrite roasting plant will be adapted to sulphur burning, the plant capacity will be increased by 60 % and the energy recovery system will be installed.

The existing acid coolers will be adapted. For reasons of space available, the new steam system will be located to the side, the former gas dryer will be used as an air dryer. The rest of the acid system remains unchanged.

A retrofit for a 2000 tpd sulphuric acid plant will occasion the following cost:

a) TIC of equipment including Venturi section, pump tank and acid pump, boiler system including heat exchanger, acid piping, instrumentation

approx. US$ 4,000,000

b) connection of gas ducts and dilution water to the Venturi section, depending on the actual location,

The Lurgi energy recovery system boasts many advantages, the most important of which may be summarized as follows:

- Saturated steam is produced up to 75 PSIG:

- For acid piping and the heat exchanger, a ferritic alloy will be used as construction material which features corrosion rates of less 0.1 mm/a when used in a temperature range of up to 200 °C and in a concentration range of 98 to 99.5 %, 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 sulphuric 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.

<u>Literature</u>:

[1] Dr U. Sander, H.J. König:
Energy savings and waste heat utilization in sulphuric acid and phosphoric acid plants
Presented at the Joint Meeting of AICHE-IMIQ
October 15 to 17, 1980, Acapulco, Mexico

[2] A.I. More:
Sulphur, Sulphur Dioxide and Sulphuric Acid
The British Sulphur Corporation Ltd. 1984

[3] M. Renner:
Hochlegierte Austenite für die Anwendung in ruhender und bewegter, hochkonzentrierter Schwefelsäure (> 95 %)