

# ISMA\* Technical Conference

Stockholm, Sweden  
14-18 September 1959

*\*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*



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## TECHNICAL MEETINGS - STOCKHOLM

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### CONTACT SULPHURIC ACID PLANTS - RECOVERY OF LOST SO<sub>2</sub>

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### INTRODUCTION

The normal losses of SO<sub>2</sub> from contact plants are, of course, in combination with the substances leaving the plant. If we eliminate the acid product, which contains only very small amounts of dissolved SO<sub>2</sub>, this leaves only the gaseous effluent from the absorption tower. Varying from one plant to another, the concentration of SO<sub>2</sub> ranges from 0.12 to 0.3% of the total volume, that is from 2 to 5% of the SO<sub>2</sub> leaving the washtower. This loss is in the first place due to the fact that catalytic oxidation is incomplete, although it does occur with conversion rates of 97 to 98%.

The advances made in the preparation of vanadium catalysts and in the equipment for the conversion unit - towers, exchangers and control systems - have been so tremendous that today it is possible to attain a stable conversion rate of 98% with pyrites gases, so that any further improvement could only involve an uneconomic consumption of catalyst and power.

Thus we must concentrate our efforts on the second cause of the loss which - except in sulphur-burning plants, which are not discussed in this paper - is due to the solubility of SO<sub>2</sub> in the sulphuric acid circulating in the drying towers.

It is usual when drying sulphurous gases to use as a dehydrating agent highly concentrated sulphuric acid which has a very low water vapour pressure. Hence, the acid circulating through the drying tower absorbs moisture and becomes diluted. In the adjacent absorption tower, however, the acid becomes more concentrated by the fact of absorbing SO<sub>3</sub>. By effecting an exchange of acids circulating through the two towers, the concentration in both is continuously maintained at the optimum level for the absorption of H<sub>2</sub>O and SO<sub>3</sub> respectively.

## GAS DRYING SYSTEMS

This exchange of acids is effected on the plant in several ways, the two chief ones being:

1) the combined circulation system (fig.1)

A single pump circulates the acid through both the drying and the absorption towers; the acids run down from the bottom of the towers into a single container where they mix and after a suitable addition of water reach the optimum concentration of 98.5%  $H_2SO_4$ .

2) the separate circulation system (fig.2)

Each of the two towers has its own pump and a fraction of the circulating fluid is exchanged between the two systems. For the absorption tower the acid concentration will be maintained at 98.5%, while the concentration in the drying tower will be lower, though it may reach 95 to 96%  $H_2SO_4$ . In this connection it should be stressed that the concentration of the acid circulating in the drying tower will be higher the more intensive the exchange of acids from the two cycles.

In point of fact, both these systems find practical applications in industry.

## INFLUENCE OF THE SOLUBILITY OF THE $SO_2$

At first sight, it would seem that the combined circulation system is the more attractive both because of its simplicity and because it can supply a more concentrated acid to the drying tower. But there is a secondary consideration which works in favour of the separate circulation system. We must bear in mind that:

- 1) Sulphuric acid, even at high strength, will dissolve  $SO_2$
- 2) in the drying tower the gases have a partial pressure of  $SO_2$  very much higher than those in the absorption tower (0.06 as against 0.0015  $kg/cm^2$ )

in order to understand that the exchange of acids from the two cycles will give rise to a transfer of  $SO_2$  from the drying tower to the absorption tower. In the absorption tower, the  $SO_2$ -rich acid will release it in gas form and the  $SO_2$  is lost. Obviously, this loss is proportional to the amount of acid which is exchanged between the drying tower cycle and the absorption tower cycle and is thus substantially higher where the system is combined than when the cycles are separate.

It is interesting to compare the amounts lost in the two cases.

a) Combined circulation

Taking the combined circulation first, we must first establish the circulation factor, which we will take as 45 times the production figure; thus, in a plant producing 1  $kg/hr$   $H_2SO_4$ , each of the two towers would be washed with 45  $kg/hr$  of acid. Let us also take:

temperature of the acid entering the drying tower	60°C	
solubility of SO <sub>2</sub> in sulphuric acid at concentrations between 94 & 98.5%, at a temperature of 60°C and a pressure of 1 kg/cm <sup>2</sup> SO <sub>2</sub> (*)	0.012	$\frac{\text{g SO}_2}{\text{g H}_2\text{SO}_4}$
concentration of SO <sub>2</sub> in the gases: entering the drying tower	0.06	
entering the absorption tower	0.0015	

We mention in passing that the sulphurous gas should reach the drying tower at a temperature not higher than 39.4°C, because this is the temperature at which the gas with its 6% SO<sub>2</sub> content carries exactly the right amount of water vapour to dilute the SO<sub>2</sub> to form acid with the 98.5% H<sub>2</sub>SO<sub>4</sub>, when the conversion rate is 97.5%

With reference to system (1), it can easily be seen that half the amount of acid leaving the drying tower is passed on to the absorption tower.

The SO<sub>2</sub> lost for each kg of acid produced will thus be:

$$\frac{45}{2} (0.06 - 0.0015) \times 0.012 = 0.016 \text{ kg SO}_2/\text{kg H}_2\text{SO}_4$$

Expressing this amount as H<sub>2</sub>SO<sub>4</sub> instead of SO<sub>2</sub> and relating it to 100 kg of acid product, we get a percentage loss of:

$$1.6 \frac{98}{64} = 2.4\%$$

## b) SEPARATE CIRCULATION SYSTEMS

Let us now see the state of affairs when separate circulations are used. (See fig.2)

In this case we must take into account the moisture content of the sulphurous gas when it reaches the drying tower. We will assume that the gas is saturated, at the existing temperature, with 15°Bé acid which is what is normally circulated in the washtowers.

To calculate the SO<sub>2</sub> loss in this case, we must first establish the weight "q" of 98.5% acid which for each kg of H<sub>2</sub>SO<sub>4</sub> produced will be transferred from the absorption system to the drying system as a function of the concentration "c" of the acid circulating in the drying tower. It must be borne in mind that the difference in weight between the amount of acid at concentration "c" which the drying system transfers

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(\*) Cf. Seidell - Solubilities of Inorganic & Organic Compounds 3rd edn (1940) Miles & Fenton; Suppl. to 3rd edn (1952) Miles & Carson. The solubility of SO<sub>2</sub> in sulphuric acid at concentrations between 94 and 98.5% H<sub>2</sub>SO<sub>4</sub> varies slightly (+ 5%) from the value which for ease of calculation is assumed to be constant.

to the absorption system and the amount of acid at 98.5% which the absorption tower transfers to the drying tower must equal the weight of water vapour removed from the moist sulphurous gases in the drying tower. Let "F" be the weight of water vapour contained in the volume of gas at 6% of SO<sub>2</sub> which is needed to make 1 kg H<sub>2</sub>SO<sub>4</sub>, this weight being a function of the temperature, and we can express in the following equation that the quantities of H<sub>2</sub>SO<sub>4</sub> in the two exchanges are equal:

$$q \times 0.985 = (q + F) \times c$$

and hence:

$$q = \frac{c \times F}{0.985 - c}$$

The amount "q" comprises q<sub>0</sub> = 0.985 x q kg H<sub>2</sub>SO<sub>4</sub>, hence

$$q_0 = F : \left( \frac{1}{c} - \frac{1}{0.985} \right)$$

Taking into consideration that in the range of concentration in question the product of the solubility of the SO<sub>2</sub> in the amount of acid contained in one unit by weight of H<sub>2</sub>SO<sub>4</sub> remains practically constant and equals 0.012, we can say that the amount of SO<sub>2</sub> lost per kg of H<sub>2</sub>SO<sub>4</sub> produced will be:

$$q_0 \times (0.06 - 0.0015) \times 0.012 = 0.07 \times 10^{-2} \times q_0 \frac{\text{kg SO}_2}{\text{kg H}_2\text{SO}_4}$$

Expressing this amount as H<sub>2</sub>SO<sub>4</sub> instead of SO<sub>2</sub> and relating it to 100 kg of acid product, we get a percentage loss of:

$$0.07 \times q \times \frac{98}{64} = 0.107 \times q_0 \%$$

Finally, substituting for q<sub>0</sub> its value as a function of "F" and "c", the percentage loss will be:

$$0.107 \times F / \left( \frac{1}{c} - \frac{1}{0.985} \right) \%$$

Using this equation and taking into account the values of "F" derived from the values of the water vapour pressure of the 15 Bé acid at temperatures between 15 and 39.4°C, we have worked out the attached figure 3 which covers all cases which might arise in practice.

### GAS EXTRACTION TOWER

First we would stress that the changeover from combined to separate circulation systems reduced SO<sub>2</sub> losses from 2.4% to a level which, in practice, can easily be held at about 0.5% when working with the gases at 32°C and the drying tower acid at 96% H<sub>2</sub>SO<sub>4</sub>.

Fig.3 shows how this loss can be still further reduced:

- a) by reducing the temperature of the gases coming from the washtower; as a general rule, such an arrangement is not feasible because it requires extensive and therefore costly cooling surfaces;

- b) by lowering the concentration of the acid circulating in the drying tower, but this would cause a deterioration in the drying conditions of the sulphurous gases.

With reference to this question, that is, to ensure the optimum drying conditions, care should be taken to maintain the acid circulating in the drying tower at the highest possible concentration by means of an active exchange of acids.

Following this line of thought, we had the idea of inserting in the flowline of the acid transferred from the drying to the absorption tower a device to extract the  $\text{SO}_2$  content of the acid and recycle this  $\text{SO}_2$  back to the drying tower. This was the origin of the gas extraction tower.

a) With low  $\text{SO}_2$  concentration ( $\leq 8\%$ )

Figure 4 illustrates the system followed in our plants, and not only in the new ones, it is also put into the old ones as convenient.

The gas extraction tower, which is shown schematically in figure 5, is a small tower packed with Raschig rings through which the acid is passed from top to bottom to remove the  $\text{SO}_2$ , while air is blown counter-current, and subsequently passes to the drying tower.

Naturally, this air causes a dilution of the sulphurous gases but it should be noted that dilution was also carried out previously, since the roasting gases were too rich in  $\text{SO}_2$  for a good conversion rate. The concentration of the gases leaving the battery of furnaces never falls below 7% and sometimes reaches 8%, while the gases must not be passed to the converters with a  $\text{SO}_2$  content above 6.5%.

Thus, taking the measures described, we have been able to eliminate completely the loss of  $\text{SO}_2$  due to the solubility of this gas in the acid, while at the same time the concentration of the acid in the drying tower could be raised from 97 to 97.5%.

To give an idea of size, the tower illustrated in fig. 5 is adequate for a 100 ton/day contact plant. The first gas extraction tower of this type has been in operation for about 6 years. A number of checks have been introduced to ensure the practical efficiency of the gas extraction tower. The first method, a very simple one, consists in comparing the  $\text{SO}_2$  concentration at different points - when the air which dilutes the gases is passing through the extraction tower and when it is drawn out at a different place, thus causing the gas extraction to stop.

Another method consists in measuring the volume of air leaving the gas extraction tower and determining its  $\text{SO}_2$  content by the Reich method. Finally, a third method consists in measuring the volume of acid passing through the gas extraction tower as if it were stationary and determining analytically the  $\text{SO}_2$  content on entering and leaving the tower.

All these methods gave good agreement on the fact that  $\text{SO}_2$  recovery is practically complete.

b) With high SO<sub>2</sub> concentration ( $\geq 10\%$ )

The idea of extracting the SO<sub>2</sub> content of the acid led to a further interesting development in those contact sulphuric acid plants which are equipped with fluidized bed roasters. This method of roasting, as is well known, produces sulphurous gases with a high SO<sub>2</sub> concentration (about 13%) and the necessity to dilute them to 6 - 6.5% for the converters demands that a large amount of air be blown in (almost equal to the volume of sulphurous gases to be diluted). In other words, the gas extraction potential was large. Thinking along these lines, we saw the possibility of adopting a system, slightly different from those already described, possessing all the advantages of the combined circulation system and yet losing none of the advantages of the separate circulation system with the gas extraction tower.

We would have three towers: the absorption tower, through which would pass the total volume of the gases leaving the converters; the drying tower, through which would pass the gases containing 13% SO<sub>2</sub>; the gas extraction tower, through which would pass an equal volume of air to give a final mixture containing 6.5% SO<sub>2</sub>. The gas extraction and drying towers would thus be equal in size and half the size of the absorption tower. This arrangement is shown in figure 6.

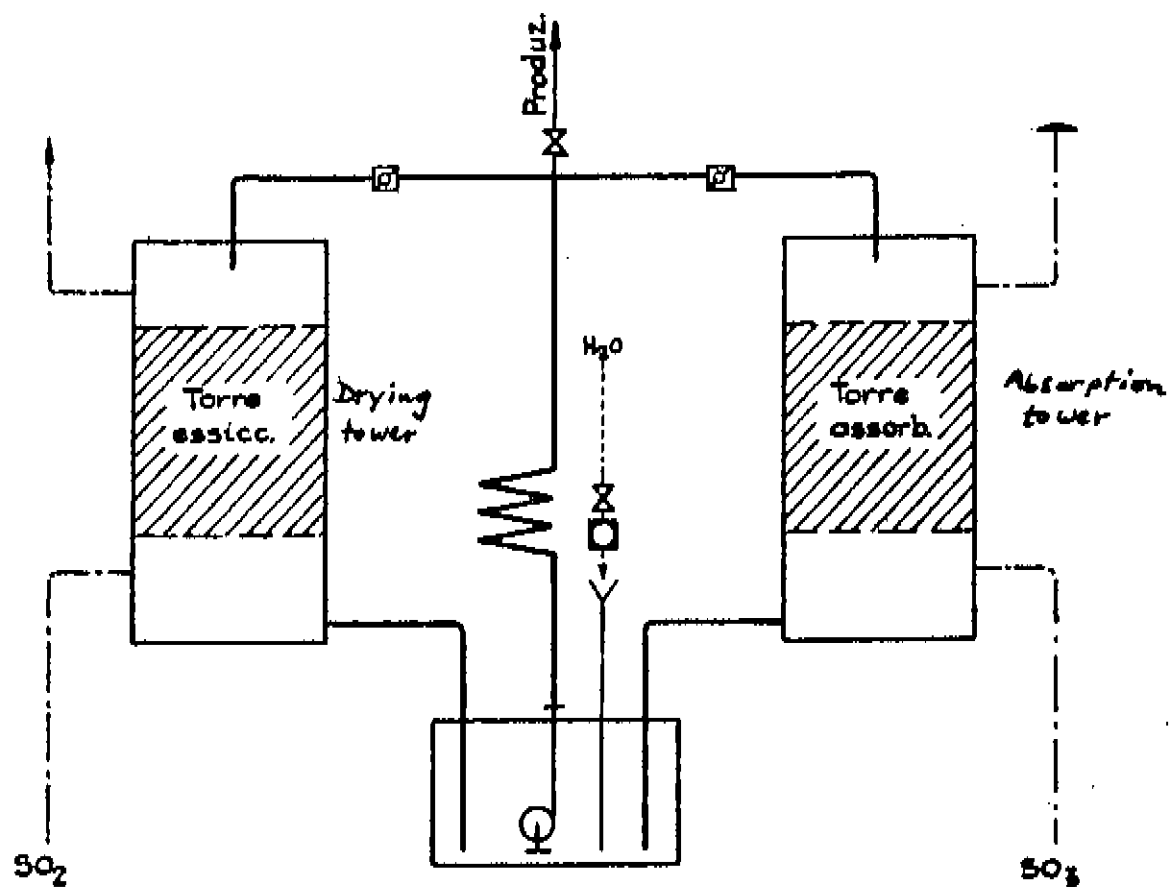
The acid leaving the absorption tower is divided into two equal parts:

the first is combined with the acid leaving the gas extraction tower and from there is sent to the top of the absorption tower;

the second is mixed with the acid leaving the drying tower and from there is passed to the top of the drying tower (50%) and the gas extraction tower (50%)

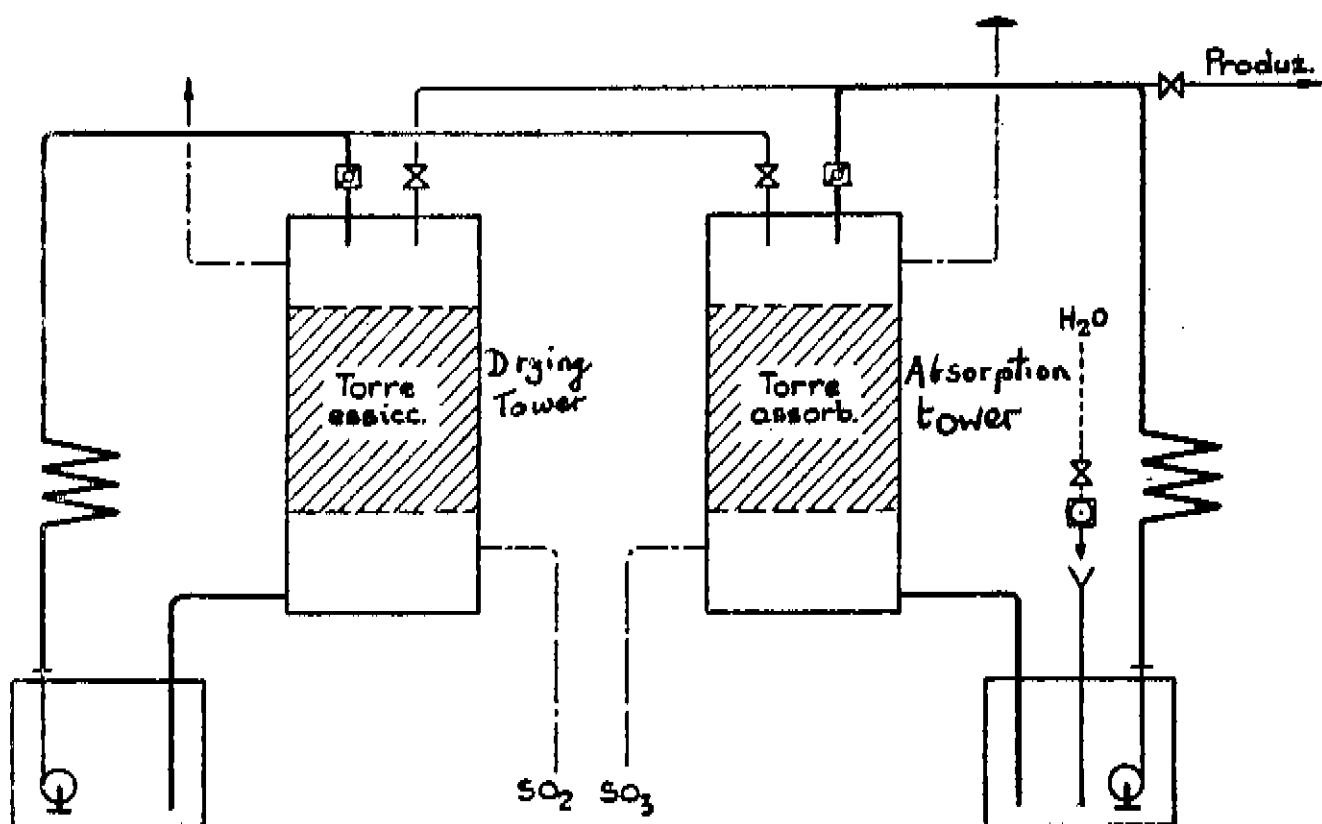
By this means we have the following advantages:

- 1) the acid circulating in the drying and gas extraction towers (which also does the job of drying agent) always has a concentration of about 98%.
- 2) the acid passed to the absorption tower had always had the SO<sub>2</sub> extracted because it comes partly from the gas extraction tower and partly from the absorption tower.
- 3) there is no need to adjust the differences between one circulation and the other because the level is the same in the two vessels which are connected with each other.



**CIRCOLAZIONI UNITE**      **COMBINED CIRCULATION**

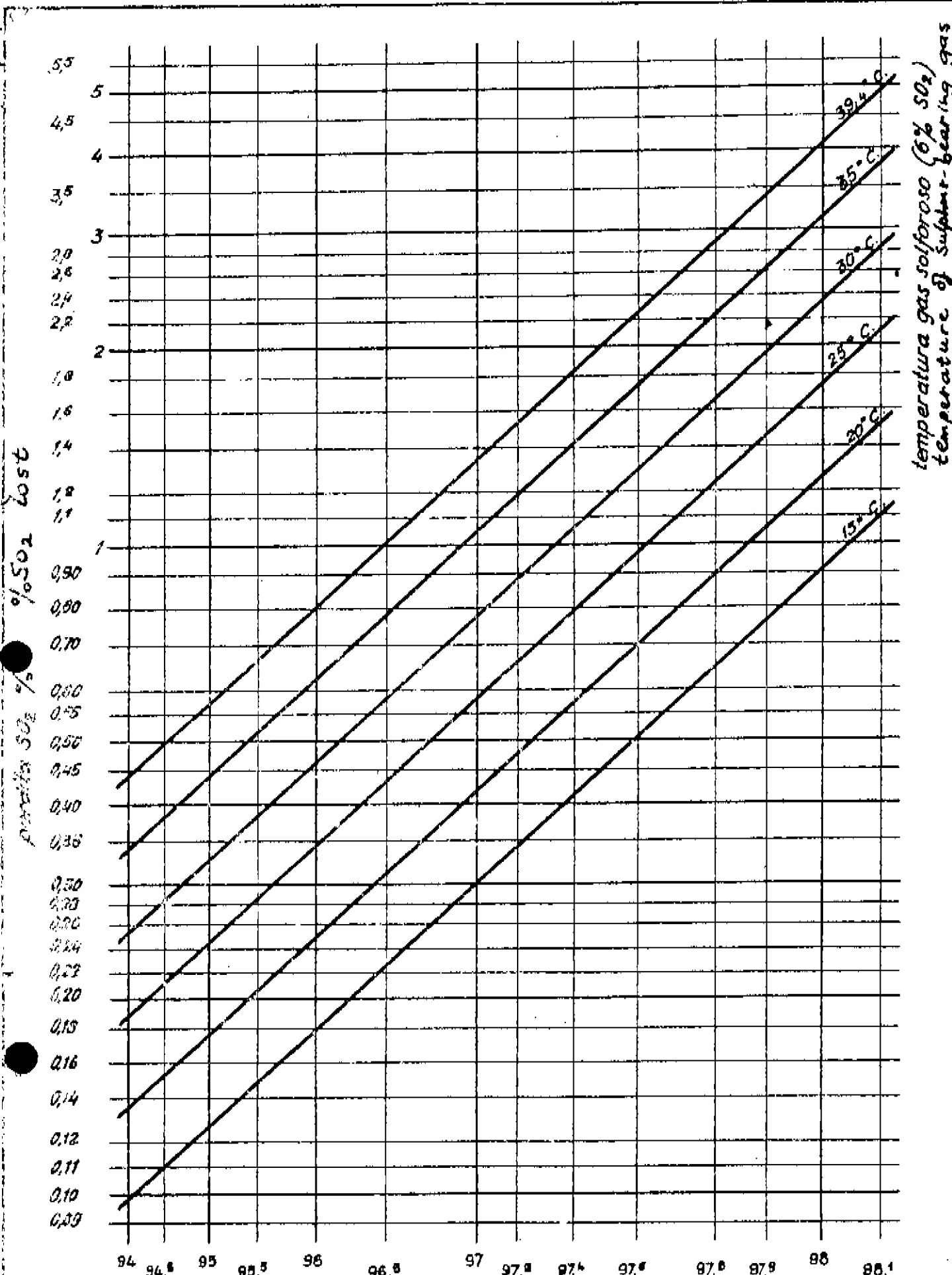
**1**



**CIRCOLAZIONI SEPARATE**      **SEPARATE CIRCULATION**

**2**

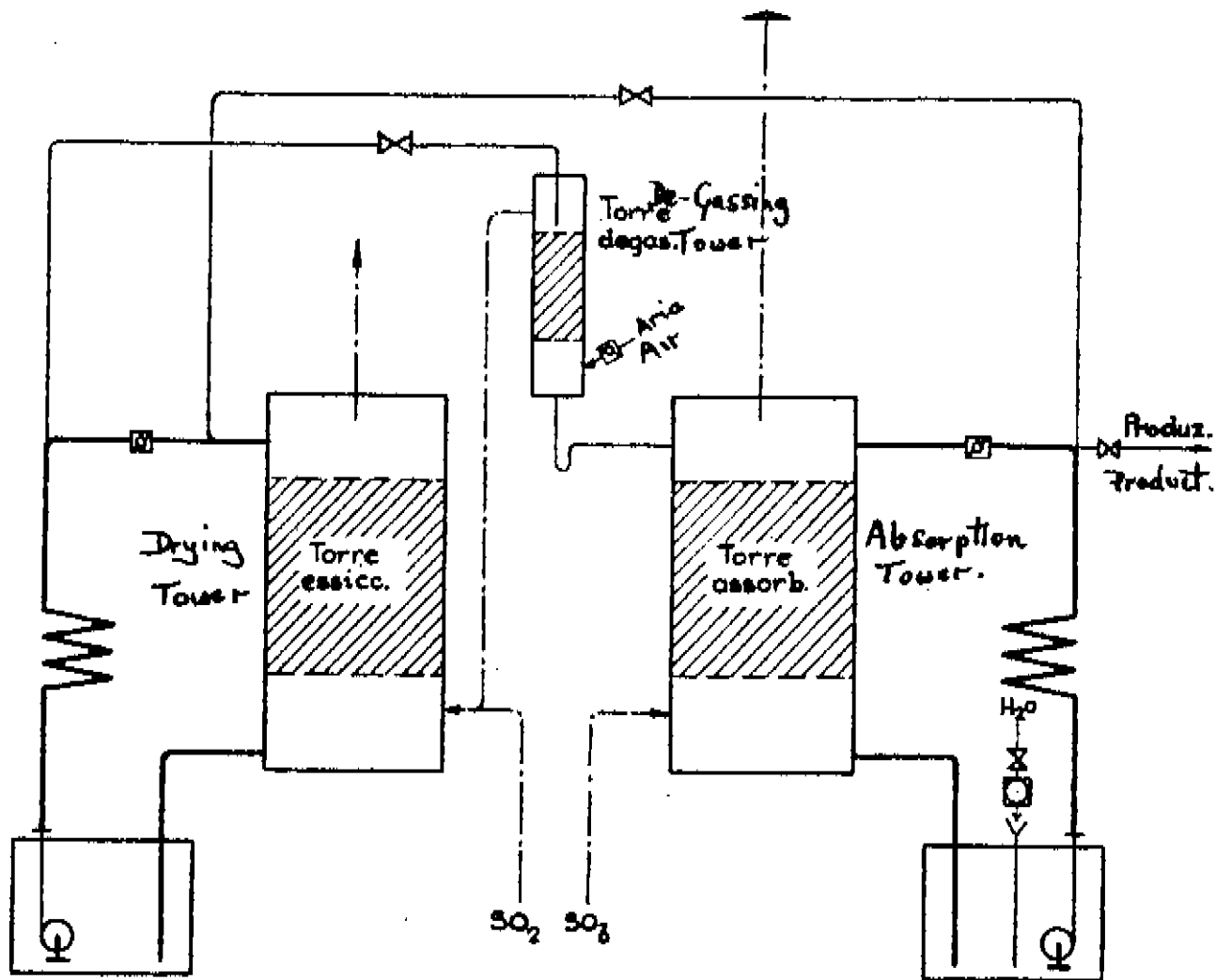




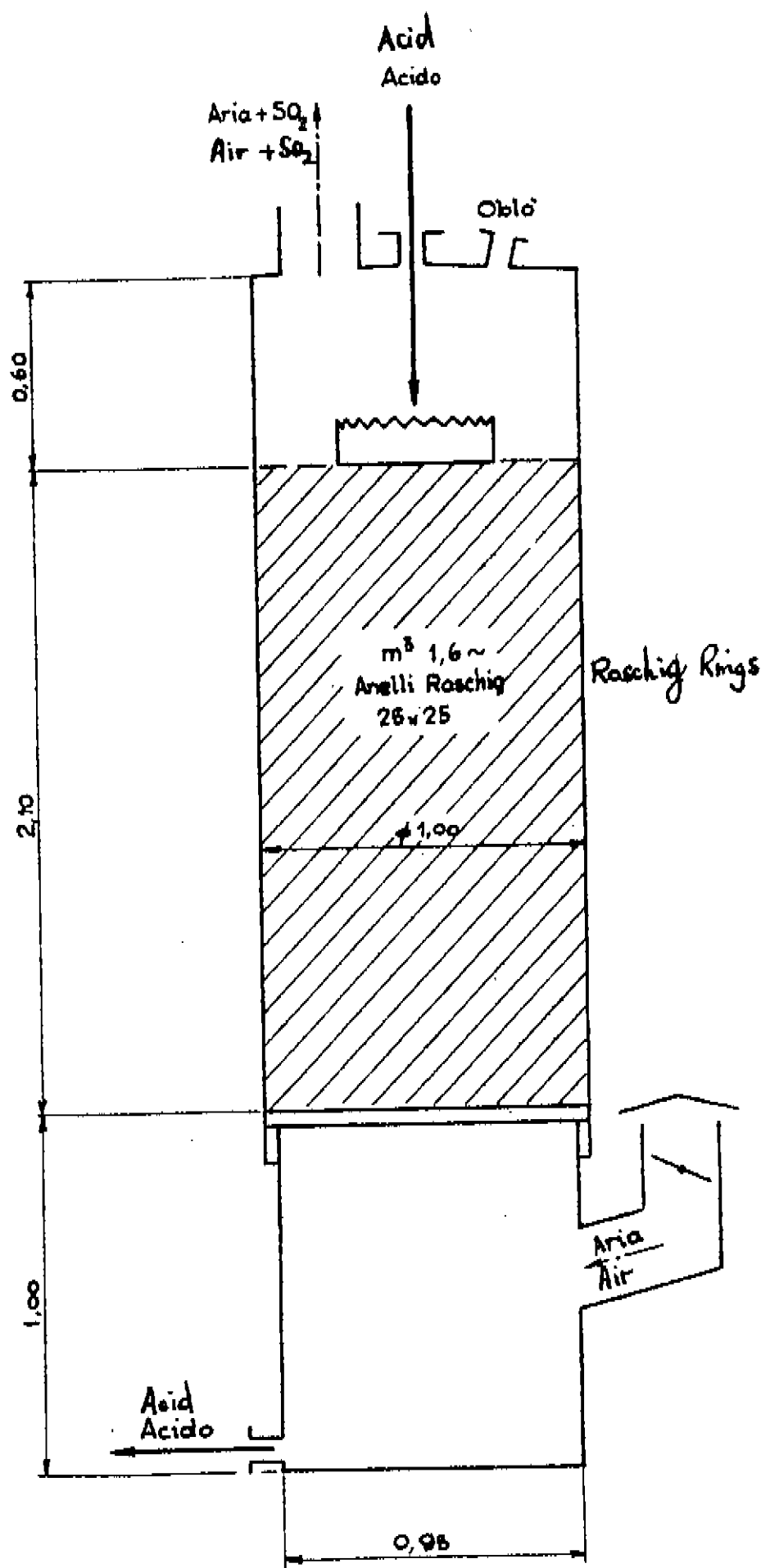
temperatura gas solforoso (6% SO<sub>2</sub>)  
 temperature of sulfur-bearing gas

% H<sub>2</sub>SO<sub>4</sub> torre essiccante  
 drying tower

**PERDITA DI SO<sub>2</sub> IN PERCENTO DELLA  
 PRODUZIONE**      LOSS OF SO<sub>2</sub> as % of OUTPUT

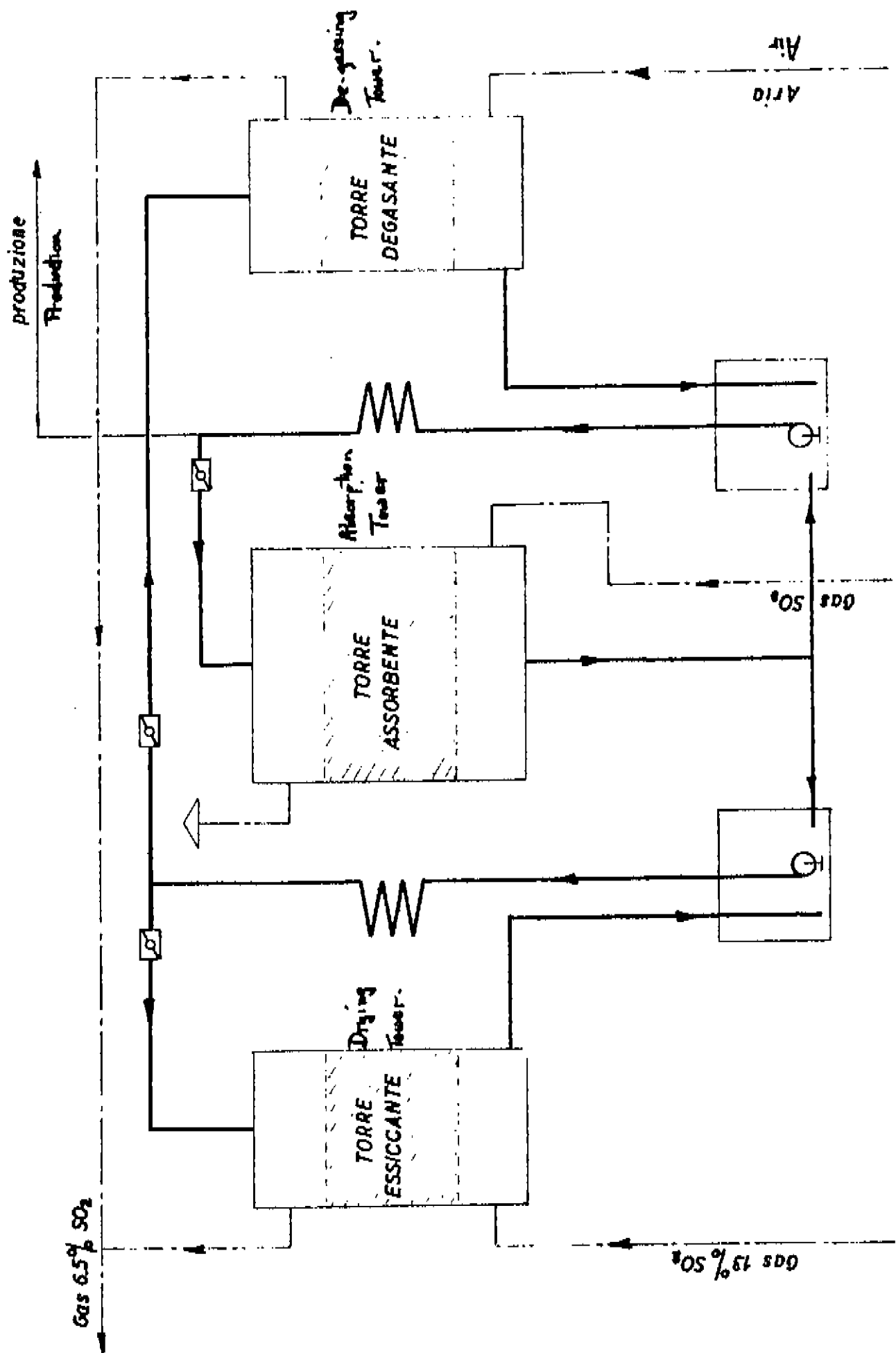


**SCHEMA CIRCOLAZIONI SEPARATE CON TORRE DEGASANTE** Separate circulation with De-gassing Tower.



**TORRE DEGASANTE PER IMPIANTI DA**  
**100 T./GIORNO H<sub>2</sub>SO<sub>4</sub>** Degassing Tower for 100t/day H<sub>2</sub>SO<sub>4</sub> plant

**5**



CIRCOLAZIONI INCROCIATE

6