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

Purification of pyrites roasting gases in a **contact**
sulphuric acid plant

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1. This paper describes the various problems encountered during modification of the gas purification system in a contact plant, and also the solutions adopted.

The diagram in Fig.1 shows the initial arrangement of the purification plant in the factory before re-designing. The chief disadvantages of the old purification plant were as follows:

- a) frequent blocking of the first tower, so that the plant had to be stopped while the packing was cleaned;
- b) excessive pressure drop;
- c) appreciable acid losses in the purification plant (4% of production) and contamination of effluent with purge acid.

The main objects of our study were :

- a) to purify the gases by passing them through concentrated acid in the first tower, in order to make them fit for super-phosphate manufacture;
- b) to use the first tower without packing;
- c) to reduce the number of towers;
- d) to remove the HF from the gases.

2. A purification system depends essentially on the pyrites used, the type of furnaces and the local conditions created by the factory drainage.

We used pyrites with the following composition :

S.....	44.5%
Zn.....	2.0 to 4.0%
Pb.....	0.7 to 1.4%
As.....	0.3 to 0.6%
NaCl....	0.03 to 0.05%
Se.....	0.002 to 0.003%
F.....	0.007 to 0.015%

Our furnaces were of the Herreshof multi-stage type and there was heavy distillation of lead from the pyrites.

Finally, we were not permitted to discharge acid effluents into the sewage system.

To obtain a complete purification of the gases, the following stages occur:-

1. dust removal
2. cooling and scrubbing
3. acid-mist removal

in order to ensure that all impurities are completely eliminated.

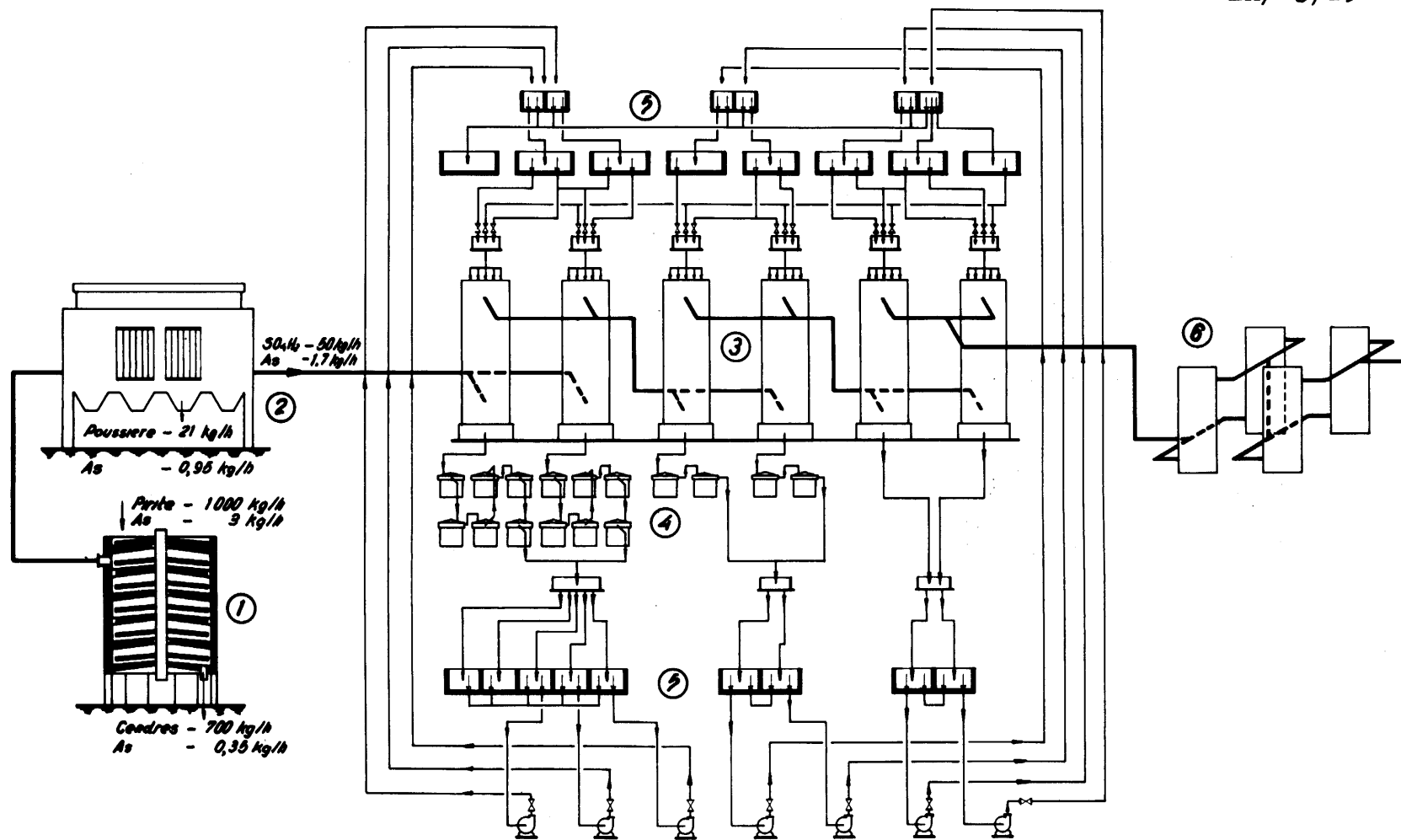
We describe below the various stages in the system we adopted.

3. Dust removal The gases leaving the furnaces carry off a considerable quantity of dust consisting mainly of oxides of iron and lead (resulting from the oxidation of the lead volatilized in the furnaces) and various sulphates. The composition of the dusts, expressing their main elements in terms of oxides and anhydrides, is as follows:

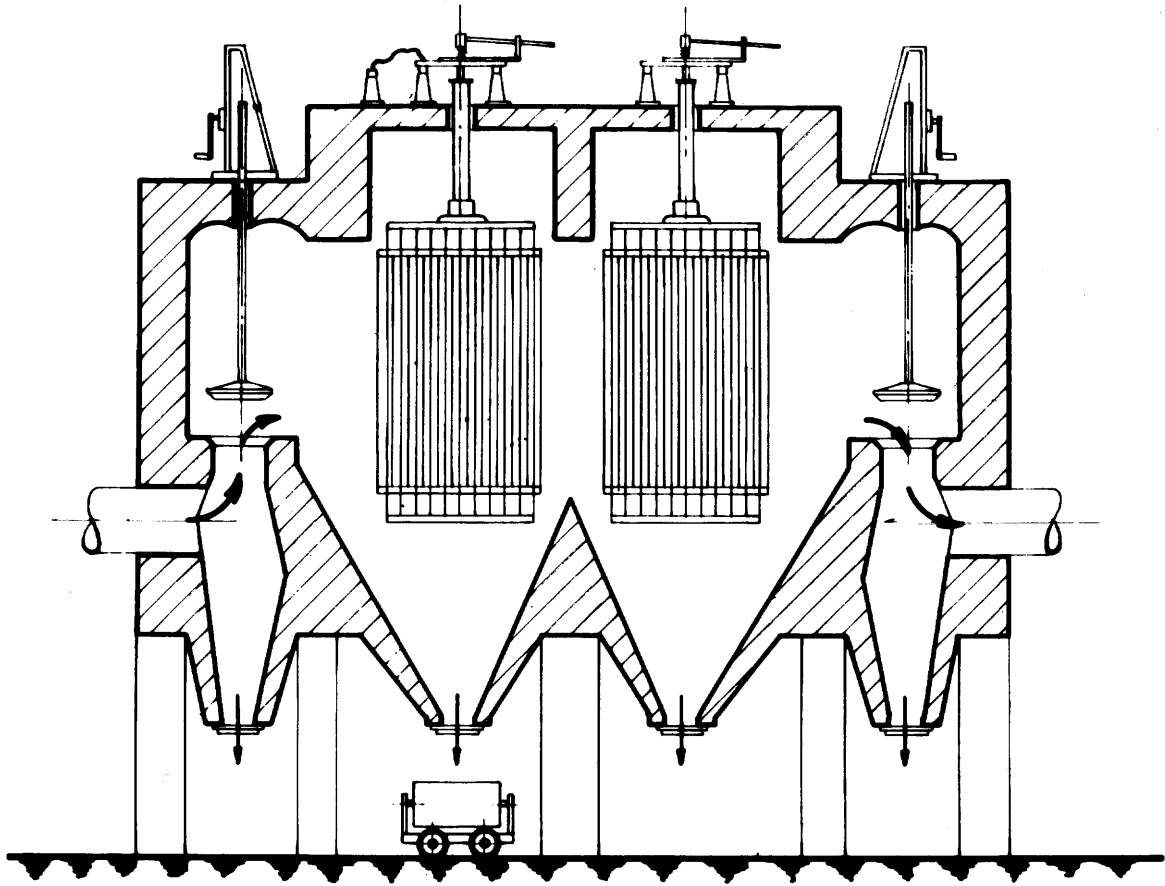
Fe ₂ O ₃	20%
PbO.....	49%
As ₂ O ₃	5%
SO ₃	19%
SiO ₂	3%
Various.....	<u>4%</u>
	100%

the dust content of the gases being 2 g/m³.

The high percentage of lead oxide dusts of particle size < 5μ required a high efficiency in the dust removal system. Electrostatic precipitators are recognized as one of the most efficient means of removing dusts of very fine particle size. We have therefore always used them in our factories, in spite of the expense. The electrostatic precipitator used was of the plate type with the gases passing through horizontally and having a single electrical field. Fig. 2 is a diagram of the precipitator. The operating data for the precipitator are:



- 1 - FOUR DE GRILLAGE
 2 - FILTRE A GAZ CHAUD
 3 - TOUR DE LAVAGE
 4 - REFRIGERISSEURS
 5 - RESERVOIR DE CIRCULATION
 6 - EPURATION ELECTROSTATIQUE DES GAZ HUMIDES



ÉLECTROFILTRE À GAZ CHAUD

Fig. 2

gas throughput	$\approx 3 \text{ m}^3/\text{s}$
mean gas temperature	450°C
operating voltage	38 000 V
power per m of discharge electrode .	$55 \mu\text{A}/\text{m}^2$
power per m^2 of collecting electrode	$165 \mu\text{A}/\text{m}^2$
mean intensity of field.....	$3,500 \text{ V}/\text{cm}$
specific surface area	$148 \text{ m}^2/\text{m}^3/\text{s}$
free vertical surface	8.9 m^2
gas speed	$0.31 \text{ m}/\text{s}$
retention time	15.8 s
Reynolds number	2100
power consumption per flow unit	$0.91 \text{ kW}/\text{M}^3/\text{s}$
efficiency	97%
rappet system	hammers

4. Cooling and scrubbing

For our modification we studied a purification system comprising only two towers, one without packing and the other packed, cooling and scrubbing being done with sulphuric acid. The functions of these two towers are as follows:

Tower No. 1 (no packing) - to do most of the cooling of the gases and to remove any dust not removed in the precipitator. Part of the arsenic is removed here. There is no packing in this tower to eliminate blockages caused by the dusts.

Tower No. 2 (packed) - the gases are completely cooled here and have their remaining impurities removed, i.e., arsenious anhydride, hydrochloric acid and selenious anhydride. The concentration of the recirculation acid in this tower is about 5%. This tower is packed so as to give the maximum area of contact between the gases and the acid, thus providing optimum scrubbing. Fig. 3 shows the gas purification plant after modification.

The main requirements of the cooling and scrubbing are:

a) to ensure efficient gas cooling, not only to reduce the entrainment of acid-mist, but also to provide optimum conditions for the scrubbing;

b) to ensure complete removal of arsenic and other

impurities.

The question of hydrofluoric acid removal will be considered separately.

We shall first report on our study of arsenic removal.

4.1 Arsenic removal As can be seen from the diagram, all impurities are removed by the recirculation acid in tower No.1, with the exception, of course, of the sludges which are retained in the sedimentation tanks and condensers.

Therefore the purge acid in tower No.1 should remove all the arsenic in solution. Should this not be the case, there would be As_2O_3 incrustation, particularly on the condensers, which would cause a great deal of trouble in the purification plant; including failure of the cooling process or blockage of the pipes and spray nozzles.

We first determined the solubility curves of As_2O_3 in sulphuric acid at different concentrations and temperatures. We used for this work the arsenical dusts picked up in a collector at the intake end of the purification system.

Fig. 4 shows the curves obtained, the solubility being expressed as a percentage by weight of As. We chose As rather than As_2O_3 to simplify the calculation.

To make it easier to refer to this graph, we converted it into another which shows the quantity of sulphuric acid needed to remove 1 kg of As at different concentrations and temperatures.

Using this graph, it is possible to determine either the acid concentration in tower No.1, if As removal is effected with acid produced in the purification system, or the quantity of acid to be fed into the purification plant to give a certain operating concentration.

4.1.1. Closed circuit purification plant

In Fig.1 we show that the quantity of As to be removed is 1.7 kg/h, and since production of sulphuric acid in the purification plant is 50 kg/h (100%), we have:

$$\frac{50 \text{ kg } 100\% \text{ H}_2\text{SO}_4}{24}$$

kg As

*Expédition
et réception
d'acide*

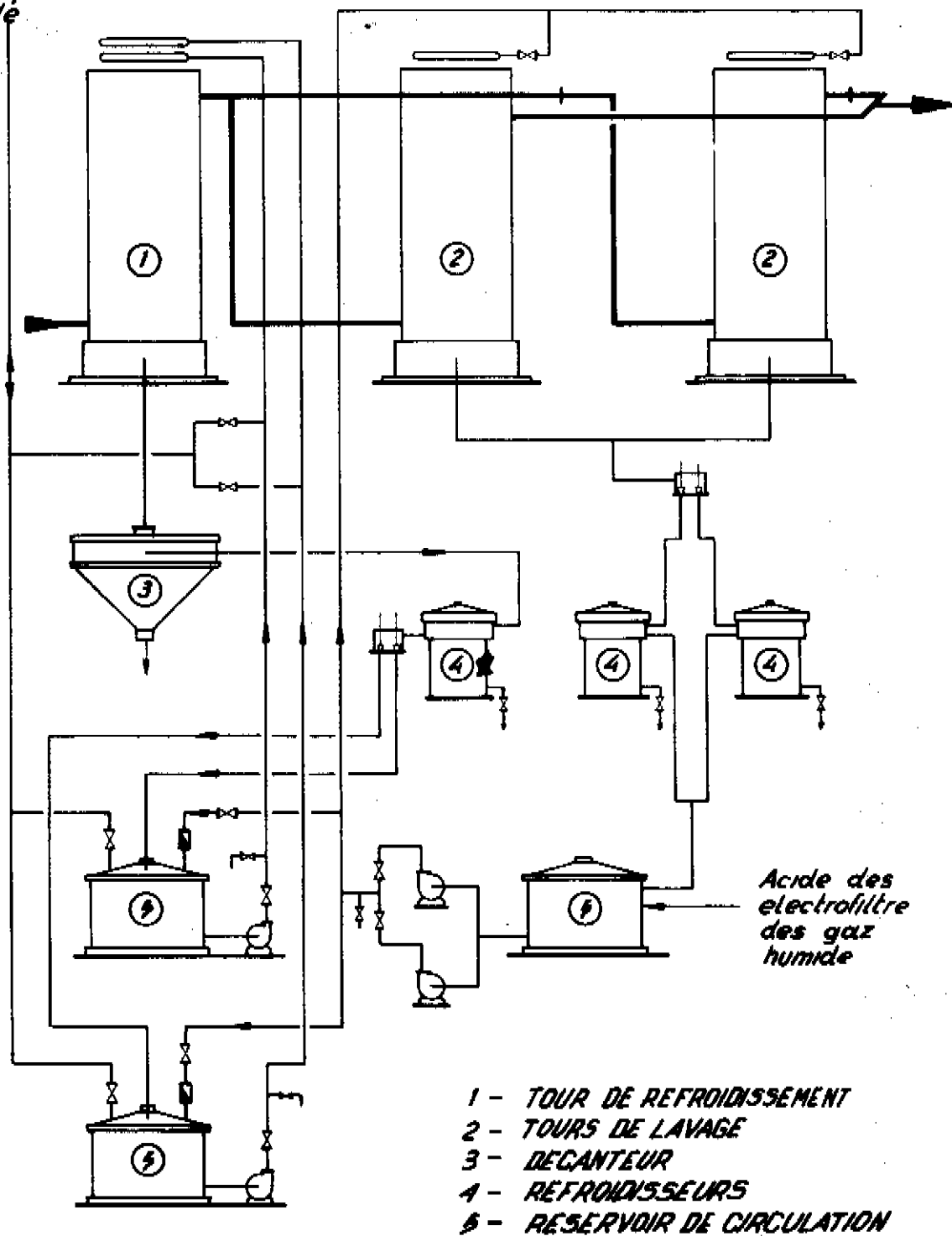


Fig. 3

SOLUBILITÉ DE L'ARSENIC DANS L'ACIDE SULFURIQUE

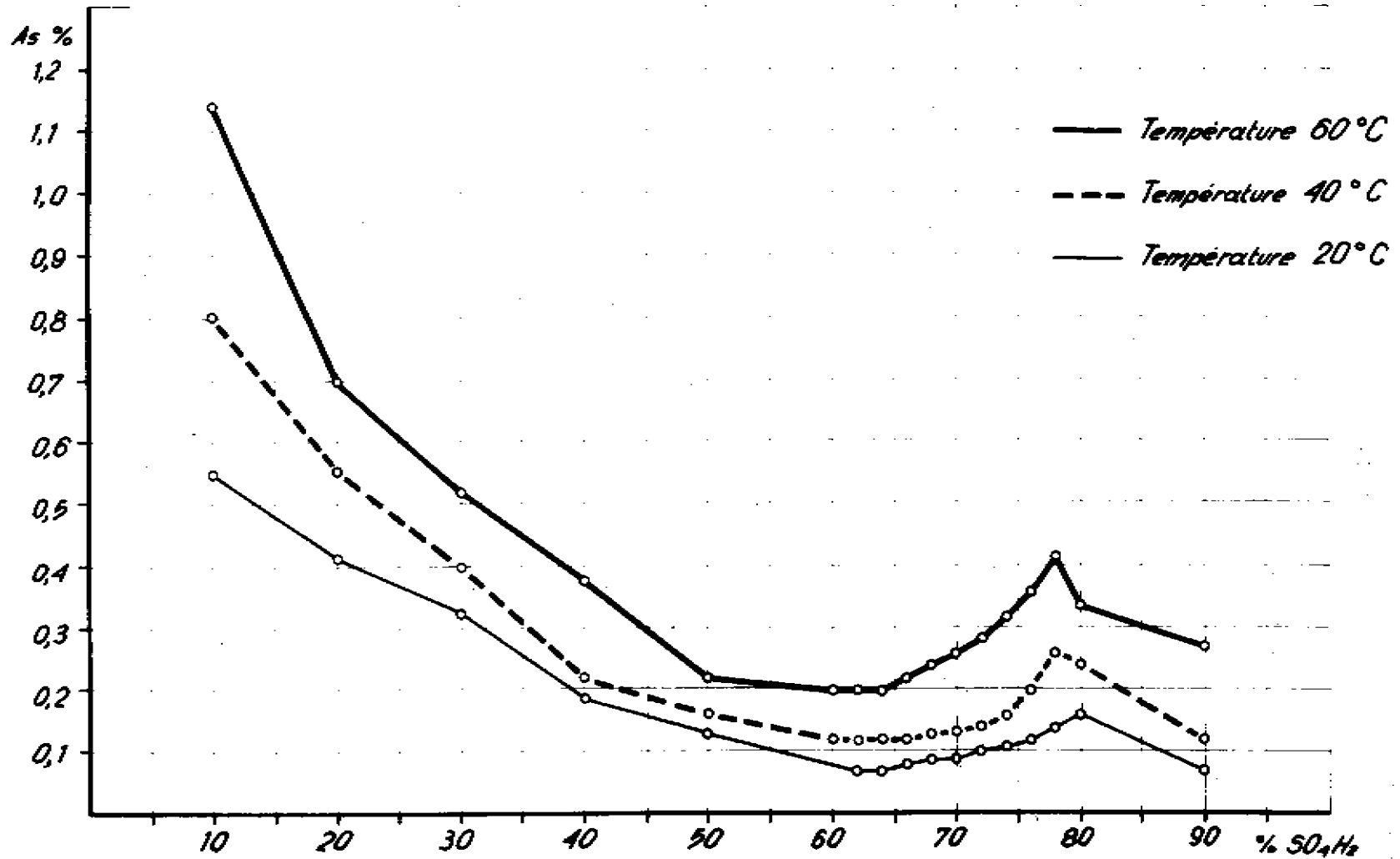


Fig. 4

so that the highest acid concentration we can work with will be 18% if the purge gas is at 40°C, which is its normal temperature. We are, however, working with slightly lower concentrations to be on the safe side, in view of the variations in the composition of the pyrites. We use a concentration of 10-12%. Lower concentrations should not be used, or otherwise large quantities of lead sulphate may crystallize out, causing dangerous deposits in pipes, spray nozzles, pumps, etc.

This acid cannot be used for anything, which means that it has to be passed out in the effluent which creates the difficulties referred to above.

4.1.2. Purification plant with added acid

In this case, the first question to be answered is what concentration of acid should be used in the purification plant. To avoid the danger of deposits resulting from dilution or concentration, a strength of 60% was chosen as representing a minimum solubility.

With reference to the calculation of arsenic for the acid produced in the purification plant and the values shown in graph No.5, we find that the quantity of acid to be added in the purification plant is 600 kg 100% H_2SO_4 or 1000 kg 60% H_2SO_4 per hour. However, since there are high supersaturations of arsenious anhydride, we work in practice with an As_2O_3 concentration which is 50% higher than its solubility, and therefore the quantity of acid is reduced to 670 kg 60% H_2SO_4 per hour.

4.2 Cooling the gases

Gas cooling is carried out in two stages. In the first stage the gases are cooled in the first tower chiefly by evaporation of the water in the recirculating acid which brings about a slight reduction in the enthalpy of the gases. In the second stage the more rapid cooling of the gases initiates condensation of the water vapour while at the same time the enthalpy of the gases declines more rapidly. This means that more of the gas cooling must be effected in the second tower.

For calculating the rate of cooling of the gases we made use of the double film theory, since the cooling is achieved by heat and mass exchanges between the gaseous and the liquid phases.

We give in the Appendix a summary of the theory we used for the calculation.

The calculated values and the values found under practical conditions are given in Table I.

A study of the values shows that there is good agreement with those found in practice and confirms that this method may be used to investigate the cooling of gases.

TABLE I

			theoretical		practical
			initial	350°C	
No.1 Tower	gas temperature	initial	350°C		370
		final	113	105	118
	acid temperature	initial	80	40	74
		final	90	70	85
	final saturation of gas		0,084	0,044	--
% H ₂ SO ₄		60%		61.2	
No.2 Tower	gas temperature	initial	110		118
		final	50		48
	acid temperature	initial	38.5		41
		final	50.0		49
	final saturation of gas		0,045		--
	% H ₂ SO ₄		5		6

5. Removal of hydrofluoric acid

It is essential to remove all hydrofluoric acid in a contact plant because it poisons the catalyst. We have therefore given this matter particular attention.

A determination of the fluorine content of the gases before the system was modified gave the following values:

on leaving tower No.1 - varying between 57 and 126 mg/Nm³

on leaving the cold

precipitators - varying between 2.6 and 46 mg/Nm³

kg SO₄H₂/
1kg As

kg SO₄H₂/
100%/1kg
As

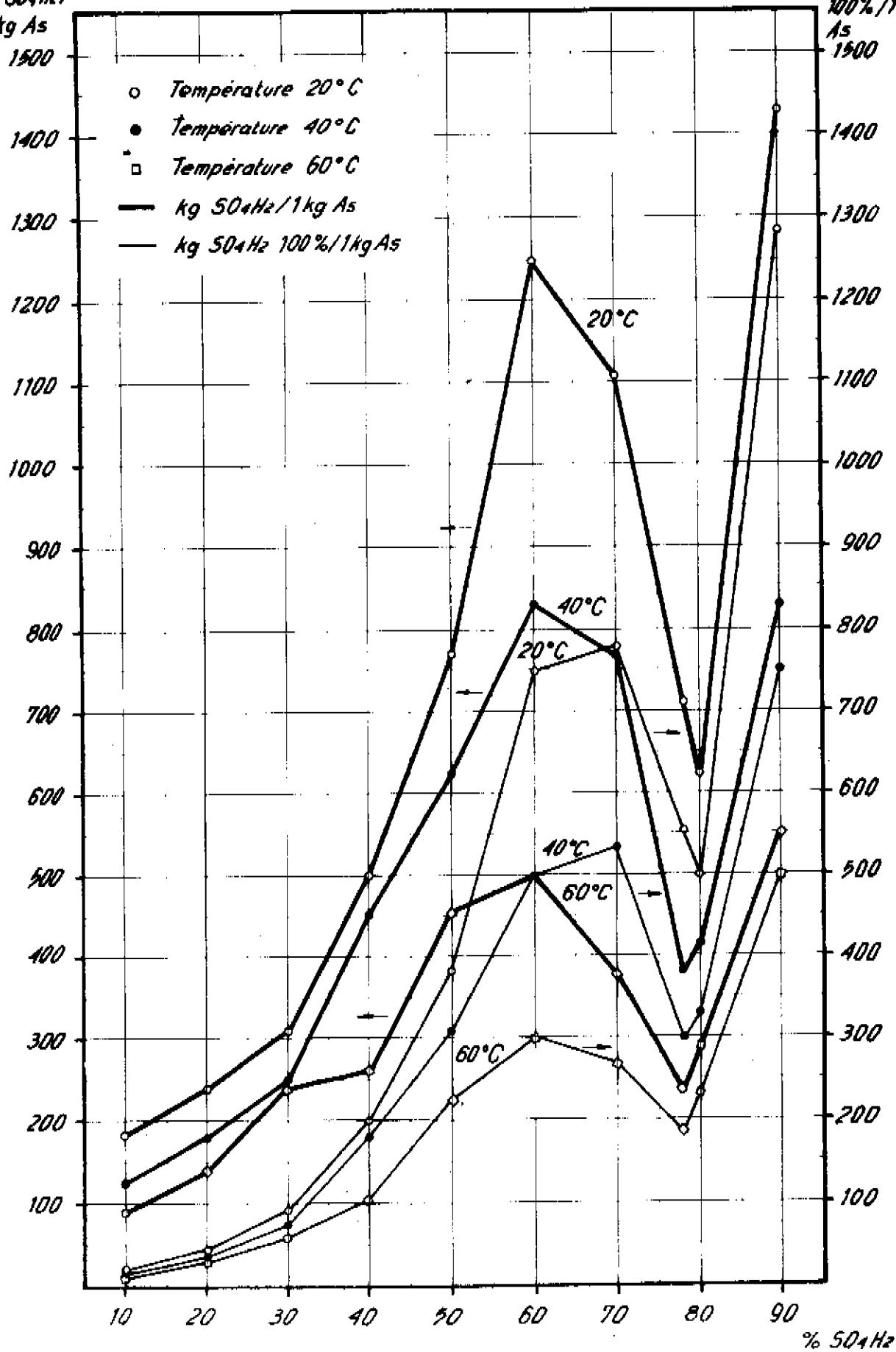
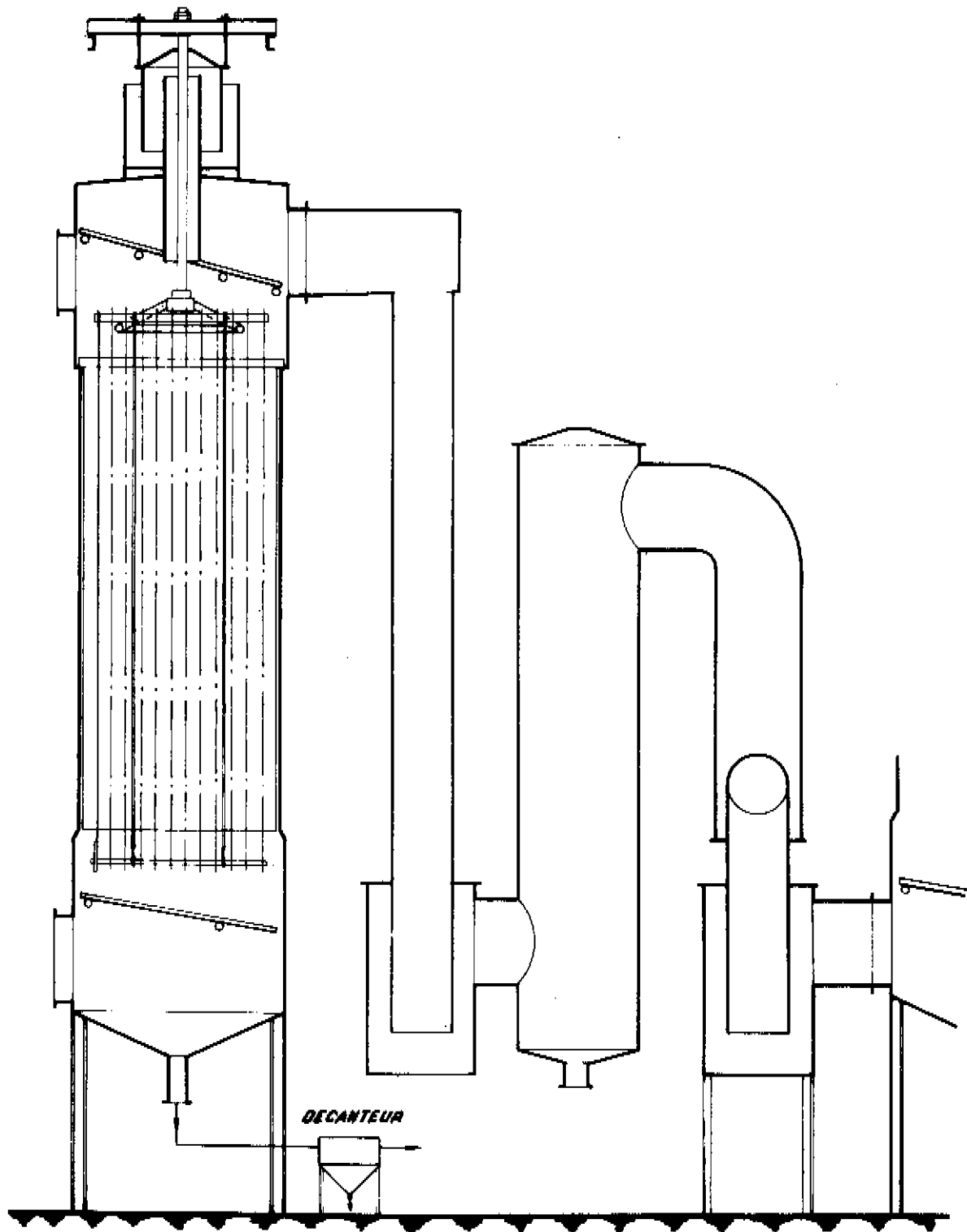


Fig. 5



ÉLECTROFILTRE DE GAZ HUMIDE

Fig. 6

The variation in the amounts found is due to the heterogeneity of the pyrites.

We based the procedure we adopted for the removal of hydrofluoric acid on its extreme solubility in water.

We tried a number of systems but the most efficient was to spray the water at high pressure (7 kg/cm² (=99.5 p.s.i.)) in an M type Peabody scrubber with a capacity of 50 l/h which was installed in a collector just before the cold precipitators. An analysis of the gas on leaving the cold precipitators showed that it no longer contained any hydrofluoric acid after the scrubber was installed.

The use of this extremely simple system enabled us to remove the hydrofluoric acid content of the gases completely. If this method is compared with other methods, for example, towers with glass wool packing, it is seen to be both simple and cheap, although it has the drawback that it does not protect the packing of tower No.2 against attack by hydrofluoric acid. The hydrofluoric acid which is extracted at the same time as the sulphuric acid by the cold precipitators is probably precipitated as insoluble lead fluoride.

6. Acid-mist removal - When the gases leave the purification system they entrain an appreciable amount of dilute acid in the form of fine droplets. This is removed in lead precipitators with two runs at different voltages. Fig. 6 is a diagram of the precipitator which has the following operating data :

Gas volume	1.11 m ³ /s
mean gas temperature	30°C
operating voltage	
1st run.....	37 000 V
2nd run.....	30 000 V
power per m ² of discharge electrode	
1st run.....	11.54 A/m ²
2nd run.....	23 A/m ²
power per m ² of collecting electrode	
1st run.....	50 A/m ²
2nd run.....	100 A/m ²

mean intensity of field

- 1st run..... 3300 V/cm
- 2nd run..... 2700 V/cm
- specific surface area per field..... $180 \text{ m}^2/\text{m}^3/\text{s}$
- free vertical surface..... $2 \times 3.02 \text{ m}^2$
- gas speed..... 0.185 m/s
- Total retention time..... 48 s

The acid collected contains sludges which are separated in the sedimentation tank before the acid is fed into recirculation in tower No.2.

The accumulation of sludges at the electrodes is such that the chambers must be cleaned out once a month.

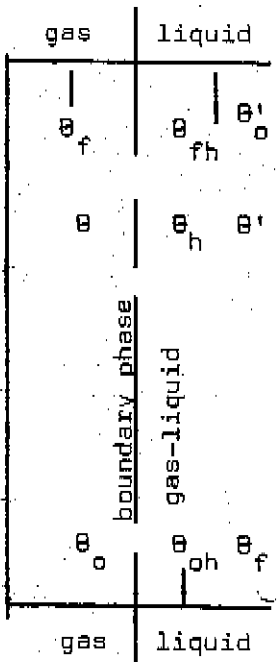
With the passage of time it is noticed that the power of the precipitator falls although it is working with higher voltages. It is believed that this power reduction is due to the formation of a film of lead sulphate which acts as an insulator and consequently reduces the electrical field.

Appendix

1. Theory used for calculation

1.1. Symbols used

Let us consider a tower with counter-current flow where :



- θ_o = initial temperature of gases
- θ_f = final temperature of gases
- θ = temperature of gases at any point inside the tower
- θ'_o = initial temperature of liquid
- θ'_f = final temperature of liquid
- θ' = temperature of liquid at any point inside the tower
- θ_{oh} = temperature of boundary phase where gases enter
- θ_{fh} = temperature of boundary phase where gases leave
- θ_h = temperature of boundary phase at any point within the tower
- θ = throughput of dry gas

L = throughput of liquid

S = proportion by weight of vapour contained in dry gas (kg water vapour per kg dry gas)

S_h = proportion by weight of vapour corresponding to the adiabatic saturation point

C_h = specific moist heat, i.e. quantity of heat required to raise by 1°C the mass unit of dry gas and the water vapour it contains

C_L = specific heat of dry gas

λ = latent heat of vaporization.

1.2 Hypothesis used for calculation

Two hypotheses were considered for this calculation:

- the temperature of the wet-bulb thermometer equals the temperature of adiabatic saturation.
- in a given straight section of the tower the boundary phase is at the temperature of adiabatic saturation which corresponds to the gas conditions existing in the same section.

On the basis of this hypothesis, temperatures θ and θ_h are expressed by the following equation:

$$(S_h - S) = C_h (\theta - \theta_h) \quad (1)$$

i.e., the quantity of heat given up by the gas is exactly equivalent to the quantity of heat needed to vaporize the liquid.

1.3 Heat exchange equation for the liquid film

If h'_c is the coefficient of heat exchange for the unit of volume dV of the tower, the quantity of heat absorbed by the liquid will be: $d_q = h'_c a (\theta_h - \theta') dV$.

This heat will cause a change in temperature such that:

$$d_q = L C_L d\theta'$$

Integrating the two equations we have:

$$h'_c a (\theta_h - \theta) dV = L C_L d\theta'$$

or

$$\frac{h'_c a}{L C_L} V = \int_{\theta'_0}^{\theta'} \frac{\theta_h - \theta}{\theta_h - \theta'} d\theta' = I_L \quad (2)$$

The calculation of the integral I_L implies a knowledge of the functional relationship between θ_h and θ' .

1.4 Relationship between θ_h and θ'

A comparison of thermal conditions at the bottom of the tower and at any straight section will enable us to derive an equation which together with equation (1) will enable us to define conditions at any point in the tower.

The quantity of heat given up by the gases will equal the quantity of heat absorbed by the liquid, plus the heat consumed in vaporization.

We thus have:

$$G C_h (\theta_0 - \theta) = L C_L (\theta_f - \theta) + G \lambda (S - S_0) \quad (3)$$

Since:

$$S - S_0 = (S - S_h) + (S_h - S_0)$$

we have by equation (1) :-

$$S - S_0 = \frac{C_h}{\lambda} (\theta_h - \theta) + (S_h - S_0)$$

and substituting in equation (2) we then have:-

$$G C_h (\theta_0 - \theta) = L C_L (\theta_f - \theta') + G \lambda \left[\frac{C_h}{\lambda} (\theta_h - \theta) + (S_h - S_0) \right]$$

hence:-

$$S_h = \left(S_0 + \frac{C_h}{\lambda} \theta_0 - \frac{L C_L}{G \lambda} \theta_f' \right) + \frac{L C_L}{G} \theta' - \frac{C_h}{\lambda} \theta_h \quad (4)$$

This equation makes it possible to establish a relationship between θ' and θ_h if we know the partial vapour pressure of the liquid corresponding to saturation as a function of the temperature, and if we take an arbitrary figure for the final temperature of the liquid θ_f' .

Knowing the partial pressure at saturation and the temperature, we can plot the curve $S_h(\theta_h)$. To obtain the different operating values, it is merely necessary to draw the straight lines $S_h(\theta_h)$ for the different values of θ' (which we shall regard as a parameter.)

The intersection of these straight lines with the curve $S_h(\theta_h)$ will enable the corresponding values for θ_h and θ' to be found.

If we assume a linear relationship between θ_h and θ' , we obtain the following equation:

$$\theta_h = C \theta' + D \quad (5)$$

by using these values.

1.5 Determination of I

Equation (5) enables us to resolve the integral I_L

$$I_L = \int_{\theta'_0}^{\theta'_f} \frac{d\theta'}{\theta_h - \theta'} = \int_{\theta'_0}^{\theta'_f} \frac{d\theta'}{(C-1)\theta' + D}$$

$$= \frac{1}{C-1} \lg \frac{(C-1)\theta'_f + D}{(C-1)\theta'_0 + D}$$

since

$$I_L = \frac{H' c_a V}{L C_L}$$

we have

$$\lg \frac{(C-1)\theta'_f + D}{(C-1)\theta'_0 + D} = \frac{(C-1)h' c_a V}{L C_L}$$

In this equation all the quantities are known except the value for θ'_f . We therefore give an estimated value for θ'_f and carry out the determination and compare it with the arbitrary value. Should they be very different, a new arbitrary value is taken and the calculation will be worked over again until an acceptable agreement is obtained.

1.6 Equation for heat exchange for the gas film

The equation will be

$$dq = \frac{h_c a}{c} (\theta - \theta_h) dV$$

where $\frac{h_c a}{c}$ = coefficient of heat exchange for the unit of volume of the tower

The quantity of heat given up by the gas will be:

$$dq = -G C_h d\theta$$

If we take these two equations as equalling each other, we have

$$h_c a (\theta - \theta_h) dV = -G C_h d\theta$$

or if we take

$$\alpha = \frac{h_c a}{G + C_h}$$

we have $(\theta - \theta_h) dV = -G C_h d\theta$ (6)

In this case there is no possibility of establishing a relationship between θ and θ_h ; it is however possible to consider $(\theta - \theta_h)$ as a function of volume.

In the case of the first wash tower where the difference $(\theta - \theta_h)$ is large and changes a great deal, we must admit that this relationship is exponential. In the case of the second tower where this difference is approximately constant, we may consider the relationship as linear.

In the case where the relationship is exponential, we have

$$\theta - \theta_h = A e^{-BV}$$

where $V = \theta$ at the base of the tower

$V = V_t$ at the top of the tower

We therefore write equation (6):

$$A e^{-BV} dV = -d\theta$$

or integrating

$$\frac{A}{B} (1 - e^{-BV_t}) = \theta_0 - \theta_t$$

In the case of a linear relationship, that is to say,

$$\theta - \theta_h = AV + B$$

we write equation (6):

$$\propto (AV + B) dV = -d\theta$$

or integrating

$$\propto \left(\frac{A}{2} V_t^2 + B V_t \right) = -(\theta_f - \theta_0)$$

DISCUSSION

Mr. V. HENRIQUES (Portugal) : The purification of gases in a sulphuric acid factory using pyrites as its raw material is a subject which has been neglected in the literature. The importance is, however, very great for if the purification system does not function properly, it generally leads to trouble in the drying, absorption and catalysis stages.

Impurities which are not eliminated during the purification process cause pollution of the absorption acid, poison the catalyst and considerably decrease its vanadium content, and even cause obstruction of the towers. Under our working conditions, we have been led to adopt the following general arrangement: elimination of dust by electrostatic precipitators, cooling and partial scrubbing of the gases in a packed tower, and final elimination of acid droplets in cold electrostatic precipitators. In order to use the acid produced during purification for the manufacture of superphosphate, we use a highly concentrated acid in the first tower. We are thus obliged to make an external addition of acid, in order to obtain the total elimination of arsenic. Elimination of the hydrofluoric acid is achieved before the passage through the electrostatic precipitators. We have carried out a study of the circulation of the tower acid, using the double film theory, and we have obtained satisfactory agreement between theory and practice.

Mr. L. BARR (Sweden) : Mr. Henriques describes how his company has modernised an old roaster gas contact acid plant. His paper is useful in defining the different factors we have to face in contact acid production. Although the equipment used contains nothing new or unique, the approach to designing the arsenic removal by using arsenic solubility curves is especially interesting. The paper provides us with an example of how the two production factors, labour and capital, can sometimes be reduced by the same action. By making the purification system simpler, not only is the maintenance cost reduced, but also the investment cost when building new metallurgical contact acid plants. We see from p.1 of the paper that one of the stated objects of the study was to reduce the number of towers. Why should we not amend this to "to reduce the amount of apparatus in

general" ? And here the question arises: how far can we go without sacrificing any sulphur? The common practice in Sweden is similar to the modified plant described here, although I am not certain that we dissolve all the arsenic. Nevertheless, I have often thought that we overdo it, when we design purification systems: the different pieces of equipment, in a system like that described in the paper, overlap each other considerably in respect of the main functions of dust removal, cooling, scrubbing, mist removal, etc. It ought to prove more economic if this overlapping of functions could be decreased. Of course, this general topic concerns all process industries, but its significance for metallurgical contact acid plants in the fertiliser industry is obvious. This is not only because we are the heaviest acid consumer, but also because we do not really need a very pure acid. In fact we mix dirty drip acid with the very clean contact acid and claim that this increases the fertilising properties of our products.

What remains to be considered, therefore, as Mr. Henriques pointed out, is how to prevent the heat exchangers and converters from losing their efficiency and how to make a continuous operation certain. The problem of making a metallurgical contact acid plant cheaper to operate and build is of special interest for those who are choosing between pyrites and brimstone as a raw material. Sulphur burning contact plants are not likely to become any simpler.

I should like to ask Mr. Henriques two questions. Firstly, if he were to build a completely new contact plant using the same pyrites and having the same pollution restrictions, would he build it like the modified one he describes in the paper, or does he think that with the experience he has now obtained, he could take a further step towards reducing maintenance costs or investment costs, or both?

My other question concerns the wet electrofilters.

Mr. Henriques states on p. 8 that the sludges are separated from the drip acid collected in the filters. Does he do this to recover foreign matter which has a market value - selenium, for instance?

Mr. HENRIQUES: With regard to the first question, I can say that we are going to employ a similar system in a new factory. We shall have two towers, one for cooling and one for scrubbing. Maintenance costs are not very great in such a system.

With regard to the second question, we do in fact have a plant for the recovery of selenium in the sludges.

Mr. O. JENSEN (Denmark): Have you tried using plastic pipes, particularly polypropylene pipes in the circulation system of the dirty acid? I think you would find that scaling in such pipes was very slight, compared with lead pipes.

Mr. HENRIQUES: In our particular case, the use of P.V.C. pipes is not possible, because the working temperature is very high and the resistance of such pipes would not be sufficient. I think it is a good solution for the second tower, but in our particular case our problem concerns the price of this material, because plastic pipes are much dearer in Portugal than lead pipes.

Mr. JENSEN: I think polypropylene piping could easily stand high temperatures up to 90° - 100° C. I do not think your temperature in the first tower is more than 80° - 90° C.

Mr. HENRIQUES: Yes, this is correct, but we have no experience with this subject.

Mr. A. GEORGIU (Greece): What is the acid content in the first scrubbing tower, in view of the fact that a considerable evaporation of water takes place in this first tower, thus assisting the formation of large droplets because of the presence of arsenic?

Mr. HENRIQUES: In the first tower we used a 60% acid.

Mr. GEORGIU: We have the same problem in Greece, but for us it is much more serious, because Greek iron pyrites contains three times more arsenic than that which you use: ours contains 1.8% As. We work with a much lower concentration, i.e. 15 - 20%, with a view to making use of the largest possible amount of steam. Have you tried working with acid concentrations of less than 60%?

Mr. HENRIQUES: Yes, we have also worked with concentrations of 10 to 12% - not lower, because we wish to avoid the crystallisation of lead sulphate - and we have also worked with higher concentrations, in order to be sure of not crystallising the arsenic. This has worked very well. The elimination of the arsenic is total. The arsenic content in the acid produced is about 0.8%.
