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MODERNISATION AND EXTENSION OF A PYRITES ROASTING PLANT AT BARREIRO

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1. INTRODUCTION

After several years of operation, one of our sulphuric acid contact plants, with a production capacity of 100 tons per day MHS (100 % H_2SO_4) has reached the end of its planned working life.

The raw material used is Portuguese pyrites, the roasting plant consisting of four furnaces, each turning 20 tons per day. There are two hot electrostatic precipitators in brick work. The gas purification section has two towers through which weak sulphuric acid circulates, and four cold electrostatic precipitators for H_2O separation. There is also the drying tower, the four-stage converter and the absorption tower.

After examining the purification and conversion installations, we decided that, by introducing some slight modifications, it would be possible to increase the installed capacity to 150 tons per day, if the sulphurous gases could be brought up to a minimum SO_2 concentration of 10%.

It was thus necessary for each furnace with eight hearths and a diameter of 6.5 m, should be able to roast 30 tons per day of pyrites and produce gases of a 10.5 % concentration at the furnace exit with pyrites cinders containing 2 to 2.5 % residual sulphur in sulphide form. This composition is, in fact, best suited to chlorinating roasting, before the blast furnace stage.

After considering the integral plan for using the products derived from the pyrites, we aimed to recover the waste heat from the sulphurous gases for raising steam. In this regard, we had had very good results in another factory belonging to our group.

2. POSSIBLE SOLUTIONS

Before continuing, we should like to review the likely solutions to our problem of obtaining sulphurous gases of the desired concentration of 10.5 % SO_2:

2.1 - Sulphur combustion
2.2 - Use of fluidised bed furnaces
2.3 - Recycling system

2.1 - Sulphur combustion

If the heat of conversion is included, a high yield accompanied by a good production of steam (1,150 kg/t MHS at 45 kg and 250°C) is obtained or, if the steam expended during sulphur fusion is deducted, 1,000 kg/t MHS is produced. As sulphur was cheap at the time the problem was being considered, this solution was of interest from the economic point of view in the light of the relatively moderate investment which would be needed.

However, this would have necessitated a shut-down of the furnaces, the hot electrostatic precipitators, the purification towers and the cold electrostatic precipitators. Although the latter were not ready to operate, they could be repaired economically.

2.2 - Use of fluidised bed furnaces

Another solution consisted in replacing the existing hearth furnaces by fluidised bed furnaces, the steam production of which is about 950 kg/t MHS, and therefore better than that obtained in the normal hearth furnaces (600 kg/t MHS), taking steam at 45 kg/cm2 and 250°C.

This solution has the following disadvantages:

1. Heavy investment. Neither the furnaces nor the hot electrostatic precipitators can be used.
2. Difficulty of utilising the pyrites cinders, because of the high **arsenic** content of the Portuguese pyrites, the average composition of which are indicated in Table I below.

TABLE I

Mines	Fe	S	As	Cu	Zn	Pb
S.Domingos...	41,0	45,5	0,54	1,05	1,75	0,67
Lousal	41,4	44,8	0,41	0,61	1,55	0,66
Aljustrel ...	39,9	45,5	0,41	1,26	3,08	0,67

For many years the aim in roasting cuprous pyrites was to derive maximum profits from the sulphur content by transforming it into SO_2 and by producing copper sulphate, giving it a maximum solubility in order to separate it by simple washing.

The strong competition of very cheap elemental sulphur obliges us at the present time to utilise completely all the possibilities in the pyrites, and we thus obtain in addition

a) iron oxide from the pyrites cinders and
b) heat for the production of steam.

Roasting thus becomes an operation designed to produce SO_2 and the maximum usable heat energy, thus decreasing losses in the process; whilst the pyrites cinders are prepared in such a manner as to afford maximum yield in the succeeding operations designed to extract their metal content. This process can therefore be considered as the initial phase in the overall metallurgical treatment of pyrites.

The arsenic content of pyrites cinders is of fundamental importance for the steel industry, and the maximum admitted is 0.08 %. As far as hearth furnaces are concerned, there is no difficulty in meeting this specification, but this is not the case with fluidised bed furnaces. In the latter, about 80 % of the arsenic is fixed in the cinders. There are specially constructed furnaces for roasting in two stages, where the arsenic can be distilled, leaving a maximum residue in the cinders of 0.1 % if the pyrites have from 0.2% to 0.5% arsenic and if the average does not exceed 0.35 %.

With fluidised bed furnaces, the devaluation of the cuprous pyrites cinders, resulting from a lower yield from the solubilisation of the copper should also be borne in mind.

The "fluidised bed furnace" solution cannot be considered in our case, as the average arsenic content of Portuguese pyrites exceeds the maximum admitted amount (0.35%) mentioned above. So far, we do not know of any fluidised bed furnaces which give entire satisfaction when using Portuguese pyrites cinders for the steel industry.

2.3 - Recycling system

After making calculations relating to the new operating conditions for the furnaces, we observed that there was an excess of heat which would cause the temperature to rise above the levels which can be tolerated by the metallic parts of the furnaces.

It was therefore necessary to deduct this excess of heat, thus limiting the capacity of the furnaces and preventing us from attaining our objective, i.e. 30 tons per furnace. The problem was resolved by recycling a part of the sulphurous gas issuing from the furnaces after cooling it to about 400°C in waste heat boilers. It was more logical to recycle the gases after de-dusting in the hot electrostatic precipitators, but the latter could not accommodate the planned increase in the volume of gases. After selecting a suitable flow of gas, this absorbs the excess heat given off in the furnace and transmits it to the boiler in the form of calorific energy to increase steam production.

3. - RECYCLING SYSTEM

This system is currently used to regulate temperatures inside fluidised bed and turbulent layer furnaces. At the time of drawing up our plans, we did not have any concrete results on its application to hearth furnaces.

The main advantage of the process lies in the fact that the specific production of steam can be increased and can reach levels of 800 to 900 kg/t of 100% H_2SO_4, expressed in steam at 45 kg/cm2 and 250°C, when the temperature of the exit gases from the boilers is 350°C. Moreover, losses of heat through defective insulation of the furnace, the boiler and the gas collectors is avoided. Thus steam production by the three processes (sulphur combustion, fluidised bed furnaces and hearth furnaces) is more or less equal, and this nullifies the disadvantage of the one or the other.

The distribution of calorific energy involved in the combustion of pyrites in hearth furnaces is usually as follows:

sulphurous gas	65%
cooling air	20%
various losses (cinders, radiation, etc.)	15%

One could thus improve the heat recovery yield by trying to decrease the losses.

Only 50% of the heat carried into the cool air from the shaft and arms is used in the exchanges where water is heated up to 200°C. If this air were re-circulated into the furnace instead of the cool air used for combustion, 20% of the heat present in the furnace would be completely used up. This system has long been in use in blende furnaces.

We have learnt that one installation using pyrites is now in operation. Other losses can be also lessened if the insulation is designed satisfactorily.

Another advantage is the increase in specific capacity of the furnaces (kg of sulphur/m^2 of surface of the bed), because it becomes possible to control excess temperature.

There are also the following advantages :

Greater uniformity of distribution of the temperatures through the various hearths of the furnace , with elimination of the usual areas of excessive heat. Higher concentrations of SO_2 can be obtained, for the increase in temperature which results no longer creates a problem. Since the temperatures in the hearths can be controlled with great precision, incrustation can be retarded, and this decreases the number of times each hearth has to be cleaned out and thus affords more regular operation. Wear on the teeth also decreases as a result of a better thermic system.

In our particular case, the planned production of steam was 720 kg/t MHS at 45 kg/cm^2 and 250°C, bearing in mind that the hot electrostatic precipitators require an exit temperature from the boilers of an average of 400 to 420°C, corresponding to 82% of the heat utilised at an exit temperature of 350°C.

Because of production requirements we had to anticipate the start-up of the plant. The planned modifications to the form and slope of the teeth, as well as in respect of the number of rotations of the shaft, have not so far been considered. The operation of recycling in two of the four existing furnaces has increased steam production from 520 kg/t to 630 kg/t MHS. This result is in conformity with our calculations.

When we started up the recycling system, we regulated the furnaces merely by blowing air into the lower hearth by means of the ventilator which is inserted there. We had no difficulty in reproducing the system of temperatures obtained with normal control. In the hottest hearths of the two furnaces with which we experimented we obtained temperatures of 850 to 880°C. These were too high for our type of pyrites, for they require a very considerable amount of work to maintain the furnace in good working condition.

After introducing the recirculation gases into the third hearth, temperature decreased to 820 to 830°C, the entry temperature of the gases into the boiler having decreased from 800° to 770°C, as planned.

We tried to verify whether the arsenic carried in the sulphurous gases was fixed by the Fe_2O_3 present in the last hearths of the furnaces. We recycled the sulphurous gases through the seventh hearth for 48 hours. The arsenic content at the centre was raised from 0.08% to 0.21%.

However, recycling through the upper hearths does not affect the residual arsenic content, for there is practically no Fe_2O_3, as can be observed by analysis of the sulphur content of the pyrites to be treated. The amounts found in samples taken from the various hearths are indicated in Table II.

TABLE II

	HEARTHS			
	1	2	3	4
% S on entering the hearth	100	76	67	62

In these hearths, we mainly observed the liberation of the sulphur atom according to the reaction

$$Fe\,S_2 \longrightarrow Fe\,S + S$$

which corresponds to 50% of the sulphur present.

In one way one can say that only after this stage does Fe_2O_3 begin to form.

4. MODIFICATIONS MADE TO THE FURNACE

Since the flow of sulphurous gases was to be increased by a maximum of 23%, it was necessary to examine the gas exit sections.

For the recycled sulphurous gases we planned inlets into the 3rd, 5th and 7th hearths of the furnace. For the roaster air blown in by the ventilator, we designed inlets in the bottom hearth.

Between the furnace exits and the boiler there is a dual purpose chamber for

a) trapping some of the dust arising from the decrease in the speed of the gases, and
b) completely burning the atomized sulphur distilled by the pyrites in the first and second hearths of the furnace.

The metallic part of the interior of the furnace, the arms and the teeth, have undergone modifications. The percentage of chrome in the metal alloy used has been increased to prevent too rapid a corrosion due to the higher working temperatures (850°C instead of 750°C, as mentioned above).

To improve the distillation of lead, pyrites were admitted directly into the third hearth. At present, we obtain levels of 75 to 82% lead distilled, instead of about 50% before.

5. - WASTE HEAT BOILERS

Portuguese pyrites, with high arsenic and lead contents, give rise to the formation of extremely hard incrustation in the boiler tubes which is difficult to eliminate. For this reason, when selecting a boiler we have to choose a type affording easy cleaning of the tubes.

In 1950, at the time of the installation of the first boiler in this factory, we chose a type with horizontal water tubes with cast iron protective jackets, for we were then still unaware of the nature of the incrustation. Cleaning was carried out by blowing air through the tubes. The boiler, which worked at an effective pressure of 18 kg/cm2, became very easily blocked by the incrustation which sometimes completely closed down the whole nest of tubes.

This experience led us to construct in another works and in collaboration with a German firm of specialists, a vertical boiler with double gas tubes and with mechanical cleaning, working at 45 kg/cm2.

This solution is very satisfactory and we already have two boilers which have been working in this manner for nearly 3 years, without any serious problems having arisen.

The greatest obstacle to be overcome was that of the mechanical cleaning, for the construction of the apparatus was very difficult, the tubes requiring to be 8 m. long in view of the size of the piping. However, the problem was solved satisfactorily, and our two cleaning installations are now working fairly well.

At the time of modifying the roasters, in order to facilitate the construction of the cleaning installations we planned to have the boilers divided into two flues, which has had the effect of reducing the height of the boiler by half.

Apart from the heat from the sulphurous gases, we also recover part of the heat from the cool air from the shaft and arms of the furnace. This recovery allows us to raise the temperature of the water up to 200°C before its entry into the boiler.

5.1 - Description.

We have had the two boilers constructed independently of each other, because it seemed advantageous to us to be able to isolate one boiler completely for repairs or inspections, without disturbing the operation of the other.

Each boiler is coupled to two furnaces. The gases pass through the two vertical flues forming the boiler, from top to bottom through the first, and from bottom to top through the second. Between the two flues, in the upper part of the boiler, there is a stainless steel regulator which lets the gases through without cooling them. The temperature of the gases at the boiler outlet are regulated easily and efficiently - a most important point for the good working of the electrostatic pricipators.

Each of the main pipes is formed by nests of double tubes bound together at their ends by oval holders. The gases circulate inside the tubes of least diameter (93 Ø) and the water circulates in the space left between these tubes (fig.1).

The length of the tubes is about 4,600 mm. The first flue is formed by 7 nests of 10 tubes, and the second by 6 nests of 10 tubes. This difference in the number of nests serves to maintain the speed of the gases roughly equal in the two flues. In fact, the average speed is about 11.4 m/s in the first flue and about 10.2 m/s in the second.

5.2 - Incrustation

The most difficult and, as yet, unresolved problem, in our opinion, is the incrustation of the tubes.

Portuguese pyrites produce excessively hard and adhesive incrustations in the flues, and this makes cleaning very difficult. This incrustation consists mainly of arsenious anhydrides. The following are the details of an analysis of the incrustation in parts where the gases are hottest and also where they are coolest.

	Gas Inlet	Gas Outlet
Gas temperature.......	750°C	360°C
H_2SO_4.................	2.0	3.0
SO_3	9.0	12.6
SiO_2	3.3	2.6
As_2O_3.................	41.1	39.3
PbO	16.3	9.6
ZnO	0.3	0.3
Al_2O_3.................	1.1	1.1
Fe_2O_3.................	20.0	24.2
	93.1	92.7

On the basis of this analysis we may especially observe the existence of sulphuric acid, which could not be present if the system $SO_3 + H_2O$ ......H_2SO_4 was in balanced operation, for the temperature necessary for the formation of sulphuric acid (200°C under our conditions), is much lower than that of the wall of the flue (256°C).

We attribute the formation of this acid to the action of some compound acting as an oxidising catalyst of SO_2, giving rise to the formation of SO_3 in high localised concentrations. The latter combines with the steam present in the gases and forms sulphuric acid at temperatures exceeding 256°C.

The acid would react with oxide and form sulphates, which, having a bigger volume, would compress the incrustation and make it very hard. This explanation is hypothetical, and we have been unable to confirm it.

5.3 - <u>Cleaning of the tubes</u>

Because of the incrustation formed, we needed a mechanical system of cleaning enabling us to maintain the tubes sufficiently clean to guarantee efficient transmission of the heat.

The system of cleaning adopted comprises four shafts guided by several sockets placed in the tubes. This sytem is very rigid and does not give rise to much vibration (fig. 2). At the end of the shafts there are cleaning heads with blades which, when rotated, open up and scrape away the incrustation. The efficiency of the blades is, of course, greater the higher the speed of rotation of the cleaner shafts. Unfortunately, the vibration does not allow us to exceed 500 r.p.m.

However, the cleaning is satisfactory and the boiler can operate for a year with constant production of the same quantity of steam. The cleaning is carried out once or twice per day.

Despite the mechanical cleaning, incrustations of about 5 mm thickness continue to form, and it is necessary to eliminate them each year. There is therefore an annual shut-down of the boilers for total cleaning.

This cleaning is carried out firstly by means of a high-speed rotating device with a special cleaning head. This eliminates most of the incrustation adhering to the tubes. When the incrustation reaches a certain degree of moistness, the cleaning is stopped and the process is continued with a 20% solution of caustic soda (60°C), which attacks the incrustation and completely cleans the flue.

This system of cleaning has been a complete success.

We have observed no traces of corrosion in the boiler in any of the inspections we have carried out.

5.4 - Performance statistics

The following are some of the characteristic performance statistics of the boiler :

- Heating surface		175 m^2
- Gas flow		6,100 N m^3/h
- Inlet temperature		750°C
- Outlet temperature		
1st flue		460°C
2nd flue		345°C
- Transmission factor		
1st flue		21.5 Kcal $h^{-1}m^{-2}{}^{o}C^{-1}$
2nd flue		22.7 Kcal $h^{-1}m^{-2}{}^{o}C^{-1}$
- Gas speed		
1st flue	- inlet	13.4 m/s
	- outlet	9.5 m/s
2nd flue	- inlet	11.0 m/s
	- outlet	9.4 m/s
- Reynolds Value		
1st flue	- inlet	12,000
	- outlet	13,000
2nd flue	- inlet	17,000
	- outlet	18,000
- Theoretical Temperatures		
1st flue	- water temperature	256°C
	Temperature of the iron tube	
	- interior	257.4°C
	- exterior	258°C
	Temperature of the incrustation	
	- exterior	292°C
	Average temperature of the gas	586°C
2nd flue	- water temperature	256°C
	Temperature of the iron tube	
	- interior	256.6°C
	- exterior	257°C
	Temperature of the incrustation	
	- exterior	272°C
	Average temperature of the gas	407°C

- Steam production per unit of surface area	9.5 $kg/m^2/h$
- Flow of steam per hour for the boiler	1,650 kg/h
- Steam production per ton of acid	550 $kg/t/H_2SO_4$

HANDLING OF THE PYRITES CINDERS

All pyrites users know the difficulty of avoiding atmospheric pollution from the dust arising from handling pyrites with an insufficient moisture content (6 to 8% water is the minimum suitable level).

We have planned and designed an installation for our factory which, in view of the good results obtained, we describe below.

This installation consists essentially of a chain conveyor, a dampening worm conveyor and a skip (fig.3).

The furnace cinders are discharged at a temperature of 500°C onto the chain conveyor by gravity. We have placed a sieve with apertures of 30 mm in the chute connecting the furnace to the conveyor, in order to prevent large sized lumps entering the conveyor, as this could affect its operation adversely. Initially, this grill had a vibratory movement which we subsequently decided was not necessary. The chain conveyor is cooled by fresh water, the temperature of which must not exceed 40°C. The flow of water is considerable, 400 m^3 per day, and is used in another factory as reaction water.

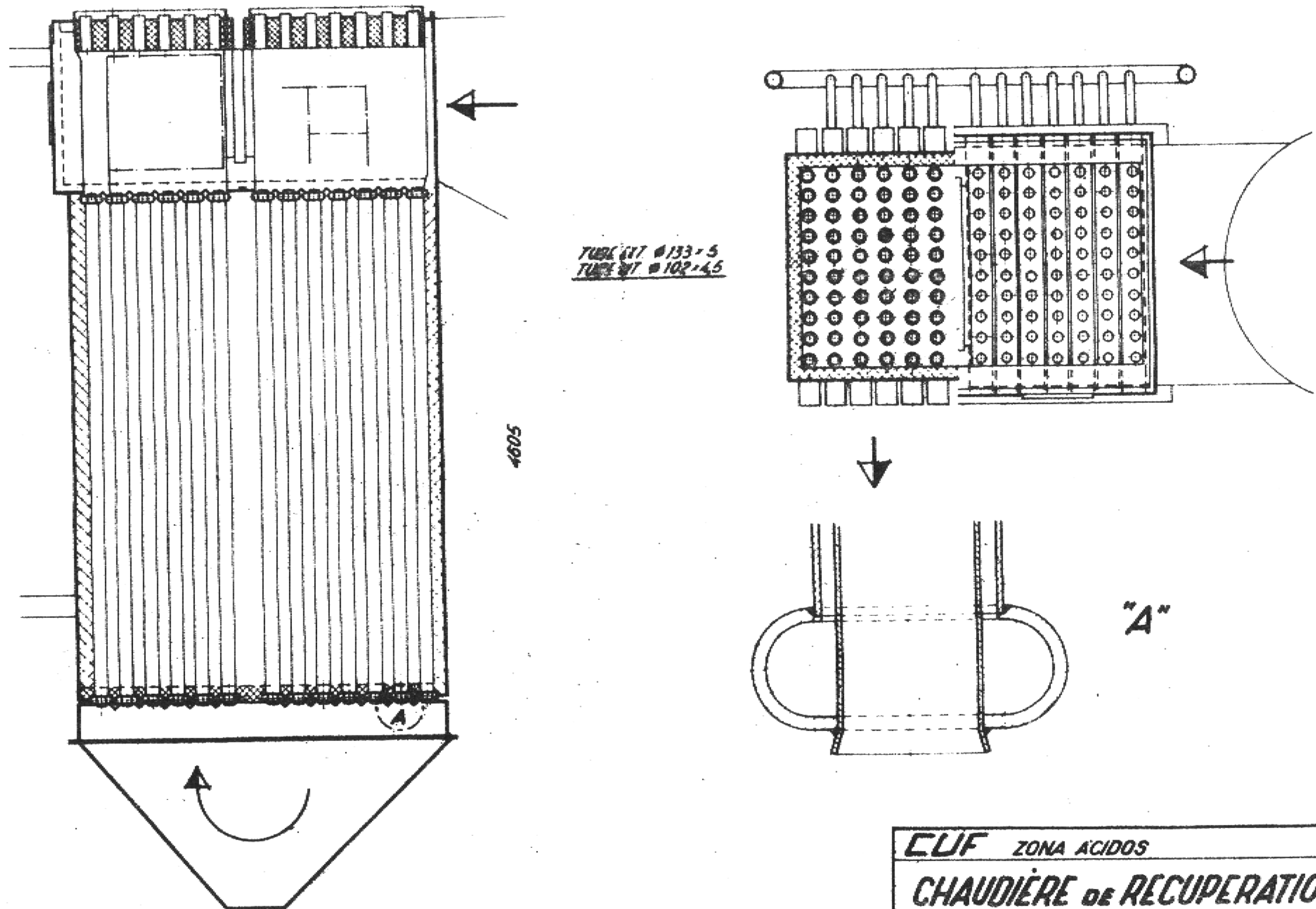
With regard to the construction of the conveyor, it was not at first completely water tight and this led to corrosion in places. After this was rectified, there were no further difficulties.

The conveyor discharges the pyrites cinders onto a dampening worm conveyor. An additional worm conveyor is in reserve. The design of this dampening worm gear was very carefully made. The envelope is lined with anti-corrosive ceramic bricks mortared together with a special cement. The pyrites are conveyed forward by means of variable angle blades in special anti-corrosive steel.

Experimental economic study of the materials for the parts in contact with the moistened pyrites showed that mild steel, which is normally used, is not the most economic material, although its cost per kg is ten times less. We also made a study of the sprinklers, the total flow of which is controlled by a rotameter to ensure suitable moistening, bearing in mind their working pressure (1.8 kg/cm2) and the angle of the cone of the jet.

From the moistening worm conveyor the cinders are discharged into a small tank, the lower aperture of which has a trap valve governed by the skip itself. When the skip is in its lower position, the trap valve is open. When the skip moves away the trap valve is closed to prevent the pyrites falling through on to the ground. The movement of the skip is governed by a clockwork mechanism which is suitably regulated so as not to exceed the carrying capacity of the skip bucket.

The skip discharges the cinders into a large tank, from which they are transported by hopper wagons (Fig. 3).



CUF ZONA ÁCIDOS

CHAUDIÈRE DE RECUPERATION

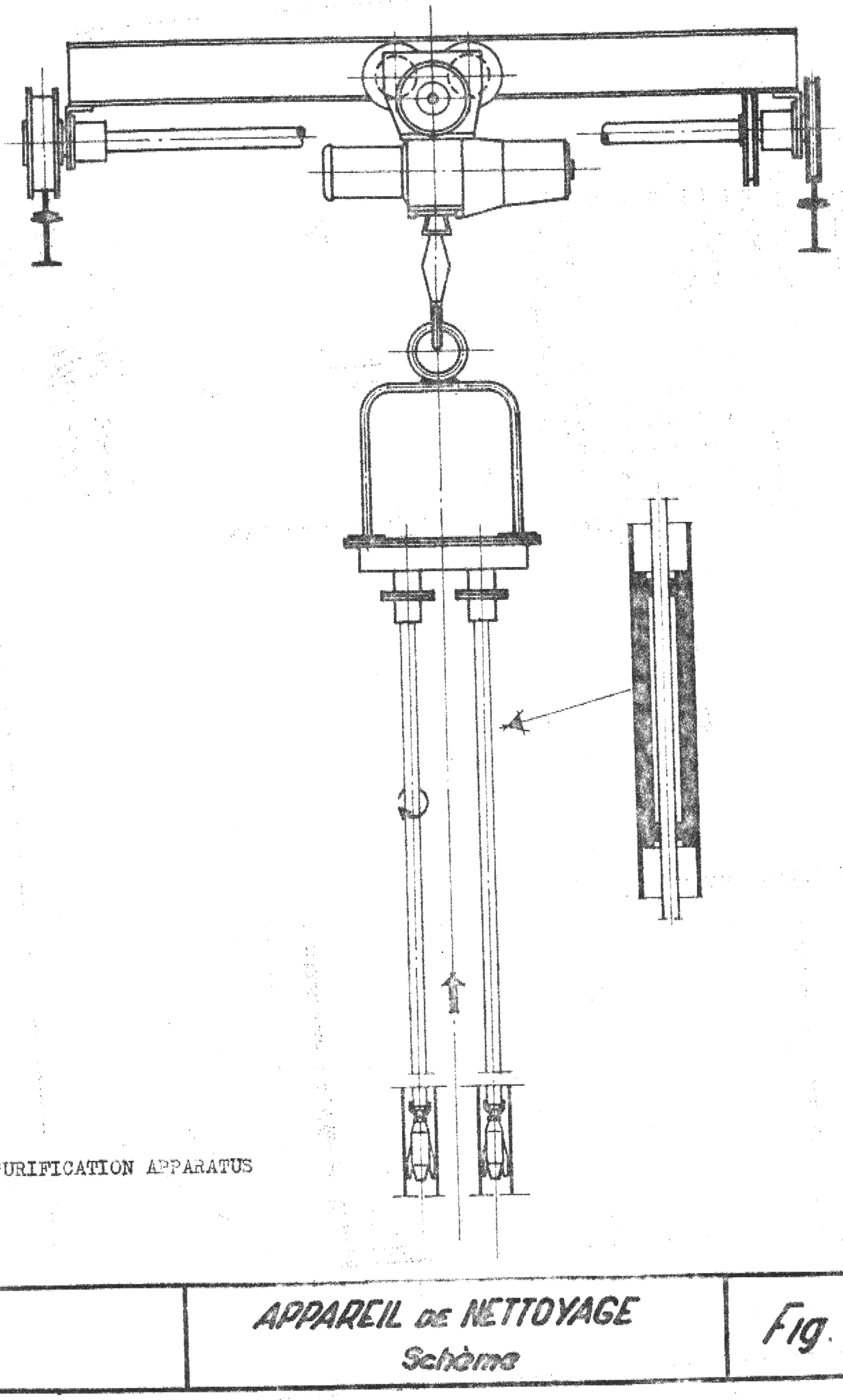
RECUPERATION BOILER

Schème

fig. 1

Z. ACIDOS

BARREIRO



PURIFICATION APPARATUS

APPAREIL DE NETTOYAGE

Schème

Fig. 2

Z. ÁCIDOS

BARREIRO

HANDLING OF PYRITES CINDERS

1 FOUR 30 tpj
30 tons/day furnace

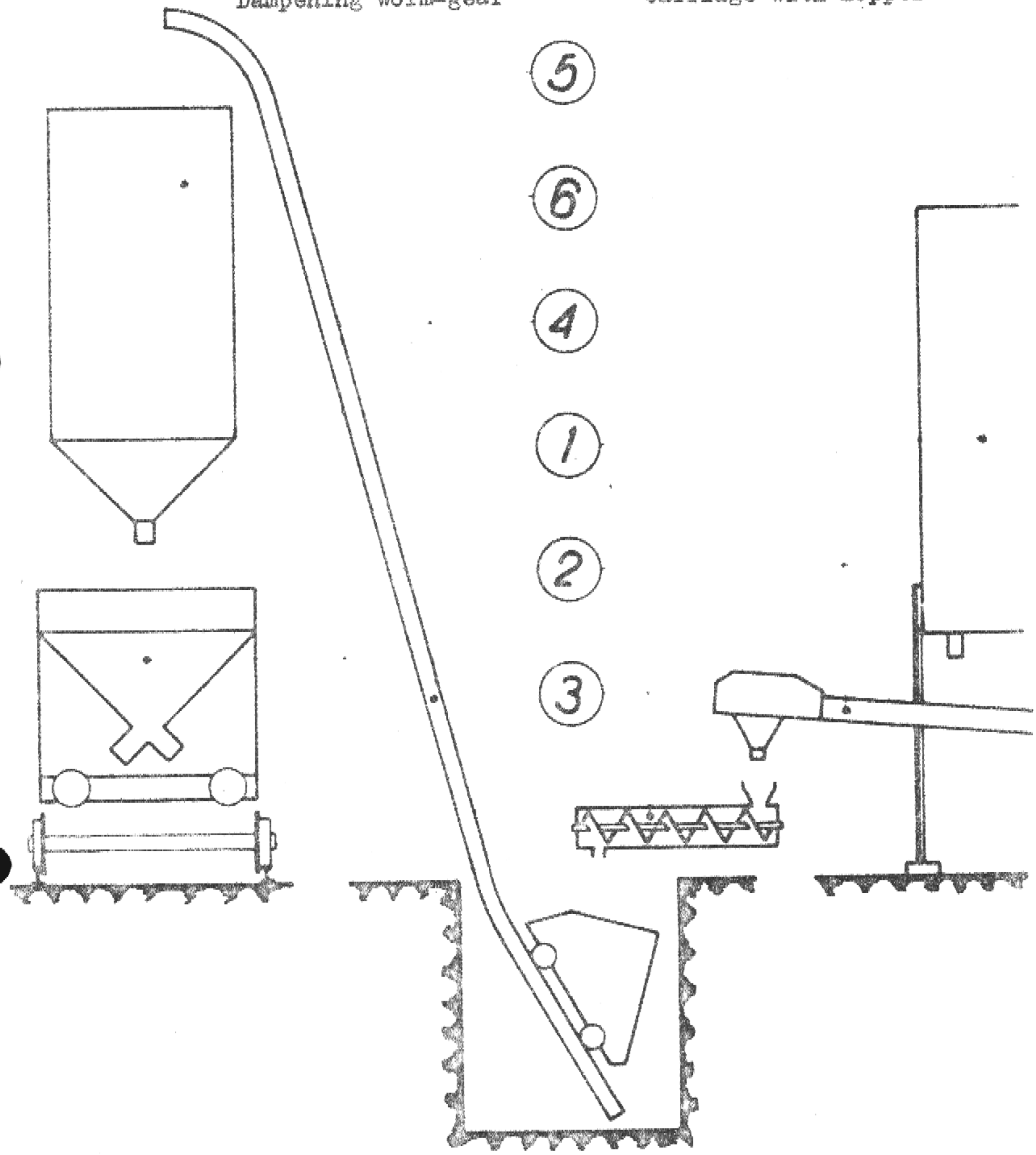
2 TRANSPORTEUR À CHAINE
Chain conveyor

3 VIS HUMIDIFICATEUR
Dampening worm-gear

4 SKIP
Skip

5 SILO
Silo

6 VAGON À TREMIE
Carriage with hopper



MANUTENTION DES CENDRES DE PYRITE

Fig. 3