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

MAXIMUM ENERGY RECOVERY IN A SULPHURIC ACID UNIT WITHIN A FERTILIZER PRODUCTION COMPLEX

By R.F. BARUT, T.C. LE and L. LONG
Heurtey Industries

A result of the world's growing fertilizer needs has been a tremendous increase in production associated with higher production unit capacities.

Rising energy costs call for the maximum recovery of available calories and their use within integrated production facilities.

The trend toward the production of phosphate fertilizers on phosphate rock mining sites, i.e. in countries which often have energy problems, further increases the interest of solution making it possible to economize energy in the form of fuel-oil or electricity.

Phosphate fertilizer and complex fertilizer production plants will be designed, to an increasingly greater extent, to include the production units normally situated upstream, i.e. sulphuric acid and phosphoric acid units. It is in fact simpler to transport sulphur than to transport sulphuric acid.

We shall take the example of an integrated plant of the type commonly found, including the following three basic units :

- sulphuric acid unit using sulphur
- wet-process phosphoric acid unit
- NPK granular fertilizer production unit

A sulphuric acid production unit based on sulphur and using the contact process generates highly exothermic reactions. The installation can operate only if the calories produced are removed.

The two basic reactions of the process are :

- the sulphur combustion reaction :

$$S + O_2 \longrightarrow SO_2 + 70.5 \text{ kcal}$$

  This reaction is carried out in the sulphur furnace where liquid sulphur is burnt in the presence of air. During normal operation, the combustion gas temperature is about 1000° C.

- the sulphur dioxide conversion reaction :

$$SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3 + 22.6 \text{ kcal}$$

  This is a balanced reaction the best speed of which is obtained at a gas temperature of about 430° C.

  This reaction takes place in the converter where the gases go successively through several catalyst beds, and it is necessary to cool them between each passage over the catalyst.

In the so-called "single absorption" process or the air dilution process, cooling can take place in the following manner :

- Between the sulphur combustion furnace and the converter :

  a waste heat boiler allows the gases to be cooled from 1000° C to 420° C

- Between the first two passes of the converter :

  it is possible to use the available calories to superheat the steam produced in the waste heat boiler

- Between the other passes :

  cold and dry air will be injected in order to cool and dilute the gases and, hence, increase the conversion efficiency. The gases leaving the converter are then cooled to 190° C in an economizer which preheats the boiler water before they enter the absorption tower.

In the "intermediate absorption" process, the injection of dilution air is eliminated, but an additional economizer is used to cool the gases before their entry into the intermediate absorption tower.

A sulphuric acid unit is thus a major source of thermal energy. This energy finds its use in the unit itself, but also in the other units of the fertilizer production complex : phosphoric acid unit and NPK fertilizer unit.

We shall show that a suitably designed recovery system enables such a complex to be self-sufficient from the energy standpoint, and even to be a supplier of energy to the exterior.

Steam and Electricity Production

For its operation, the complex requires :

- Electric power, which is of great importance because in the example given further a power of about 9,300 kW is necessary for a NPK 17-17-17 production complex of 1,500 tpd capacity with a 650 tpd capacity P_2O_5 unit and a 1,800 tpd capacity H_2SO_4 production unit ;
- Low-pressure steam, which represents a major part of the flow produced for heating requirements, in particular for the concentration of the P_2O_5 unit and for boiler water degassing ;
- medium-pressure steam, in a smaller proportion, intended mainly for sulphur fusion.

Given the high temperature levels (between 400 and 1000° C) of the gases in the H_2SO_4 unit, it is desirable for the steam produced by this unit to be at high pressure and high temperature.

For reasons of flexibility and safety, the blower of the H_2SO_4 unit will be driven by a steam turbine.

The rest of the HP steam will be used to supply a turbo-alternator and possibly a boiler feed turbo-pump.

As the steam used within the plant is in most cases at low pressure, the above-mentioned turbines will be of the back-pressure type, a solution involving a low initial capital outlay and easy operation.

Medium-pressure steam requirements, which are relatively moderate, are taken from the turbo-alternator during normal operation.

The appended steam diagram shows the different steam production elements in a H_2SO_4 unit, as well as the turbines mentioned above and the three HP, MP and LP steam networks. Note will be made of an auxiliary boiler, provided in order to allow independent plant starting on steam and also to ensure the uninterrupted operation of the fertilizer and phosphoric acid units in case of a short shutdown of the H_2SO_4 unit. The auxiliary condenser makes it possible to balance steam production and consumption without water losses.

Upgrading of available energy

The amount of calories and the temperature levels being fixed for a given H_2SO_4 unit, it is known that the energy which can be drawn is expressed as $W = \Delta H \times Qv$ in which ΔH is the enthalphy difference between the superheated HP steam and the LP steam at the exhaust of the turbines and Qv the HP steam flow generated by the waste heat boiler.

It is possible to increase W by increasing both ΔH and Qv.

1. Increasing $\Delta H = H_1 - H_2$

In order for this difference to be as large as possible, one attempts to increase the value of H_1, i.e. the characteristics of the HP steam, by increasing the superheat temperature and pressure. In fact, for sulphuric acid units, the amount of heat available for superheating the steam is rather limited so that one remains within the 400 to 430° C range. On the other hand, it is possible to increase the HP steam pressure within limits consistent with the possibilities of boiler design. In recent years, there has been a constant increase in the design pressure of waste heat boilers in H_2SO_4 units. This design pressure has been raised from 25 to 30 Ata, and then to 45-55 Ata and, in the past 2 years, 60-70 Ata.

For its part, Heurtey Industries installed, in 1973, a fire tube boiler of 50 Ata for a 1,500 tpd capacity H_2SO_4 unit, a water tube boiler of 52 Ata for a 1,700 tpd unit and, finally, a fire tube boiler of 67 Ata for a 1,800 tpd unit (see figures in appendix).

Raising the boiler design pressure to 100 Ata should present no difficulty for water tube boilers and should be achievable in fire tube boilers, at least for certain boiler manufacturers equipped with suitable production facilities.

However, the increase of ΔH will also be obtained by lowering the H_2 enthalpy of the LP steam. The pressure of 3.5 Ata, sufficient for the concentration of phosphoric acid by the vacuum evaporation processes and for various other plant heating needs, can be regarded as a reasonable value.

2. Increasing Qv

The second factor upon which depends the recovery of energy W is the steam flow Qv. Its increase is favoured by the adoption of a high pressure for the HP steam because it is known that the latent heat of vaporization decreases as steam pressure increases. However, Qv can also be increased by supplying the first economizer with the hottest possible water, which is obtained by degassing the boiler feed water at a pressure which is relatively high, but which remains compatible with the steam pressure of the LP network.

Results of studies on recovery energy upgrading

Systematic studies were carried out on the upgrading of recovery energy in order to determine the maximum amount of HP steam and the maximum electric power obtainable from different H_2SO_4 units capacities ranging from 500 tpd to 2,000 tpd. As an example, we are giving three curves representing the steam flow Qv and the power W available at the terminals of the alternator as a function of the HP steam pressure at the exit of the superheater for three H_2SO_4 production capacities : 500 tpd, 1,500 tpd and 1,800 tpd.

The electric power W indicated is generated in the turbo-alternator by part of the HP steam of the waste heat boiler, the other part of this steam being intended for the turbine driving the blower of the H_2SO_4 unit. In every case, the LP steam network is at 3.5 Ata, i.e. assumed to be intended for the supply of the NPK and phosphoric acid units.

We are giving below, as an example, figures relative to the case of a fertilizer production unit including :

- a 17-17-17 NPK fertilizer production unit of 1,500 tpd
- a phosphoric acid unit producing 650 tpd P_2O_5 at 54 % concentration
- 1,800 tpd H_2SO_4 unit
- the corresponding utilities

Consumption values are :

- MP steam	5 tph
- LP steam	
process units	71 tph
utilities	14.5 tph
- electric power for entire plant including boiler feed pump	9,300 kW

Our study indicates that, after a certain HP steam pressure, the above requirements are covered entirely by the waste heat boiler and the turbo-alternator unit of the plant. Above this value, at P = 80 Ata for example, it would be possible to export electric power (about 1,000 kW) and LP steam (about 4 to 5 tph). The plant will thus be not only self-sufficient but can also export energy even if its sulphuric acid unit is exclusively captive.

The auxiliary boiler(s) included in the diagram can operate on standby during the normal operation of the plant. It will be used only for plant start-up or for ensuring a certain continuity of operation for the fertilizer units when the H_2SO_4 unit is shut down. This boiler can even be eliminated if the plant is connected to a ~~common~~ power production unit of a large complex.

Economic consequences

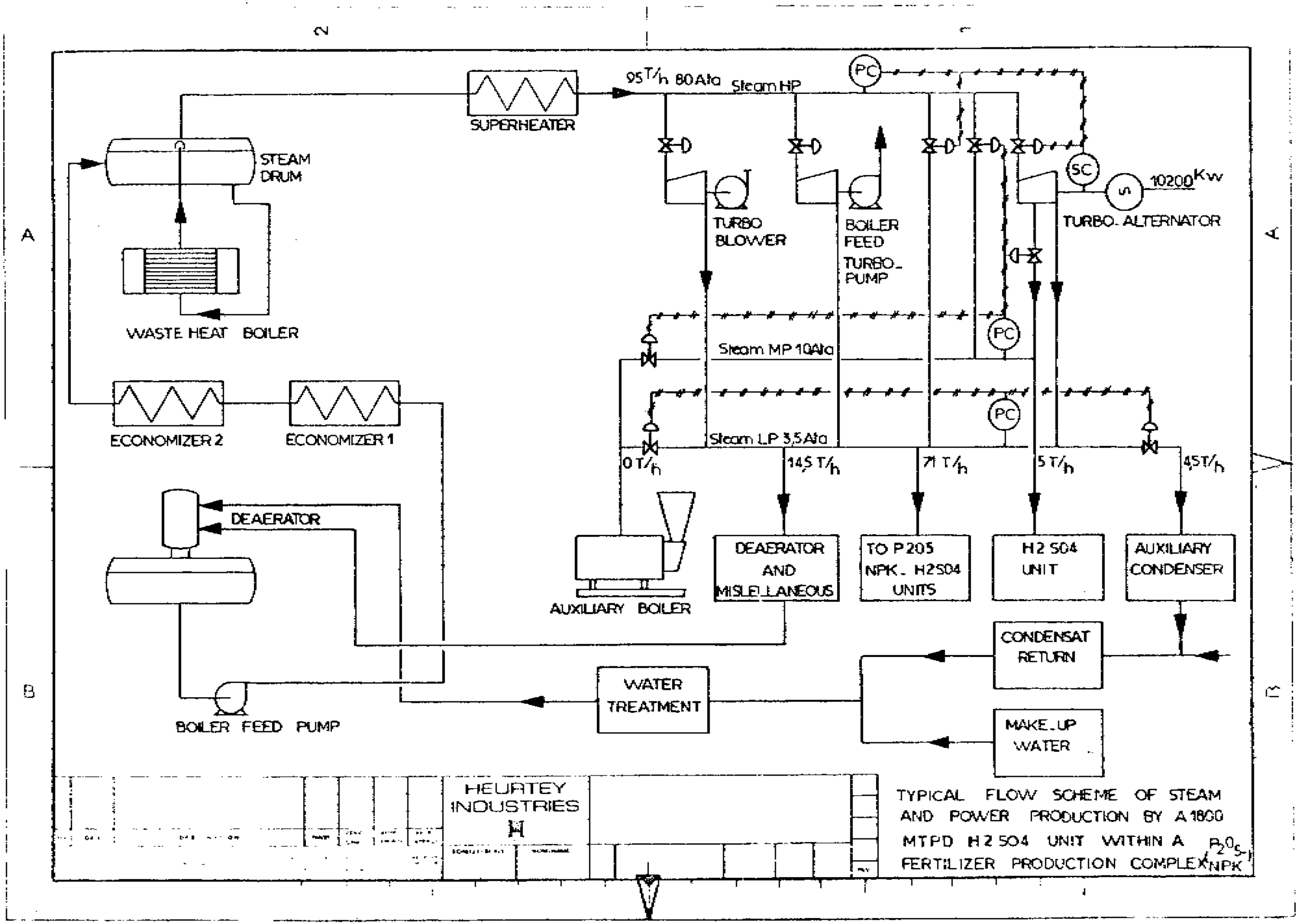
As each plant is a particular case dependent on many factors, such as location, energy supply, operating procedure, and so forth, we are not giving any precise comparison figures. In order to avoid any erroneous interpretation, we shall confine ourselves to pointing out the following :

1. Given the high cost of energy, which can be expected to continue upward, every ton of imported steam and every imported kWh will be of primary importance for plant production costs. For example, economic calculations in France are based on the following cost of energy : 0.035 F/thermie of fuel-oil and 0.10 F/kWh. Under these conditions, every ton of LP steam imported would cost about 175,000 F per year, including the cost of water, and every MW imported would cost 800,000 F per year, considering 8,000 hours of work per year. It is thus desirable, to the extent possible, to make the plant independent as regards energy.

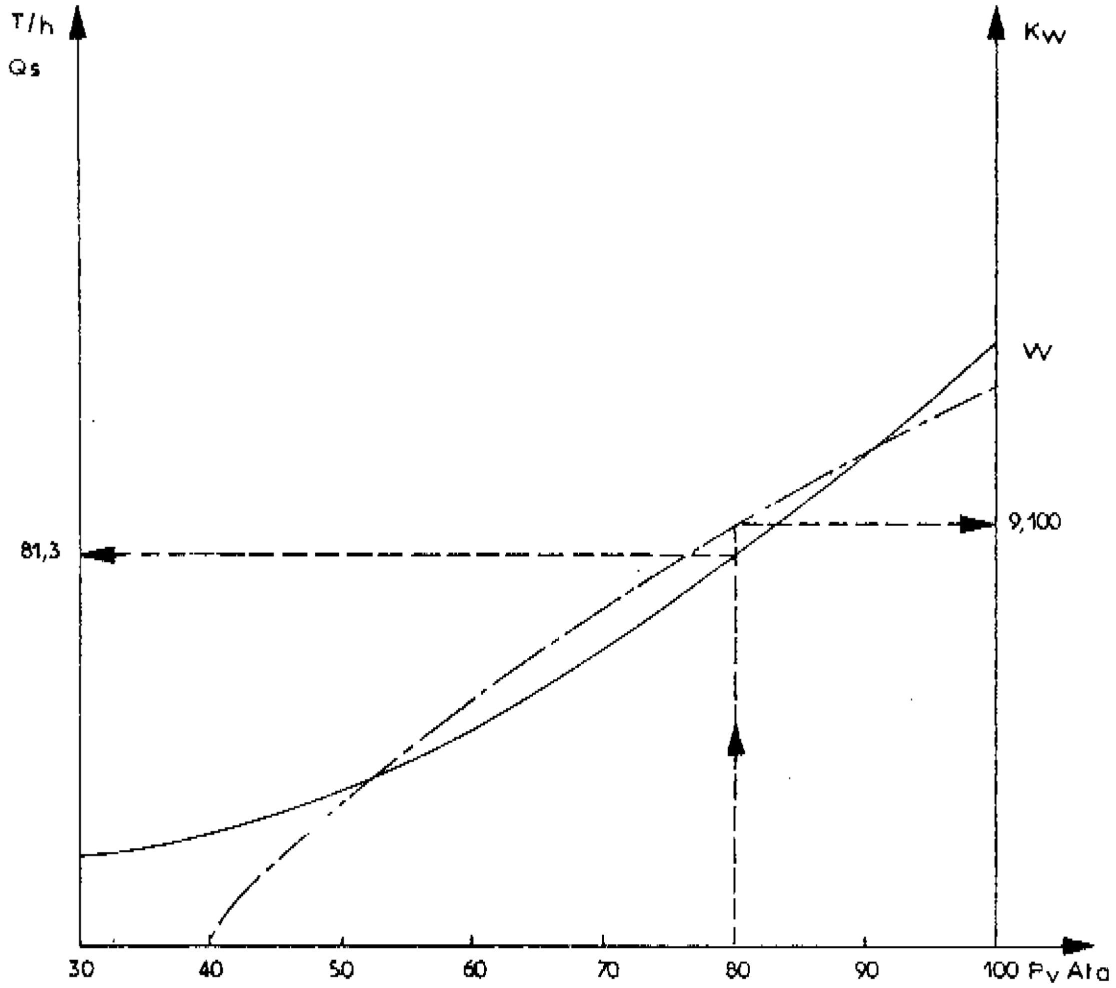
2. Higher energy costs also justify an examination of the possibility of exporting energy by increasing the design pressure of the waste heat boiler and the capacity of the turbo-alternator unit. The additional investment is noticeable only for the boiler, but would be relatively lower for the turbo-alternator and, in any case, the payout will be short if exporting can be continued and invoiced at the prices indicated above.

3. We must still consider the treatment of boiler feed water which becomes more sophisticated when steam pressure is raised. In fact, its economic effects are very small when HP steam pressure must increase from 40 Ata to 100 Ata at the superheater exit. At 40 Ata, it is necessary to demineralize the make-up water, which already makes it possible to obtain good quality wator (resistivity from 200,000 to 500,000 ohms/cm). Beyond 60 Ata, it is necessary to add another ion exchanger column in the form of mixed beds, thereby ensuring water of high purity suitable even for boilers with design pressures in excess of 110 Ata (resistivity higher than 3×10^6 ohms/cm and silica lower than 0.02 mg/l). We see that, in the final analysis, the additional outlay for water treatment is very moderate since it corresponds to the addition of a new resin column, the rest of the water system remaining unchanged.

It is thus possible to conclude that, in the general case, the economic solution is, firstly, higher capacity units and, secondly, the maximizing of energy production.



TYPICAL FLOW SCHEME OF STEAM AND POWER PRODUCTION BY A 1800 MTPD H2 SO4 UNIT WITHIN A FERTILIZER PRODUCTION COMPLEX P_2O_5-NPK



Steam and electric power production versus steam pressure for a 1500 MTPD H_2SO_4 single absortion unit.

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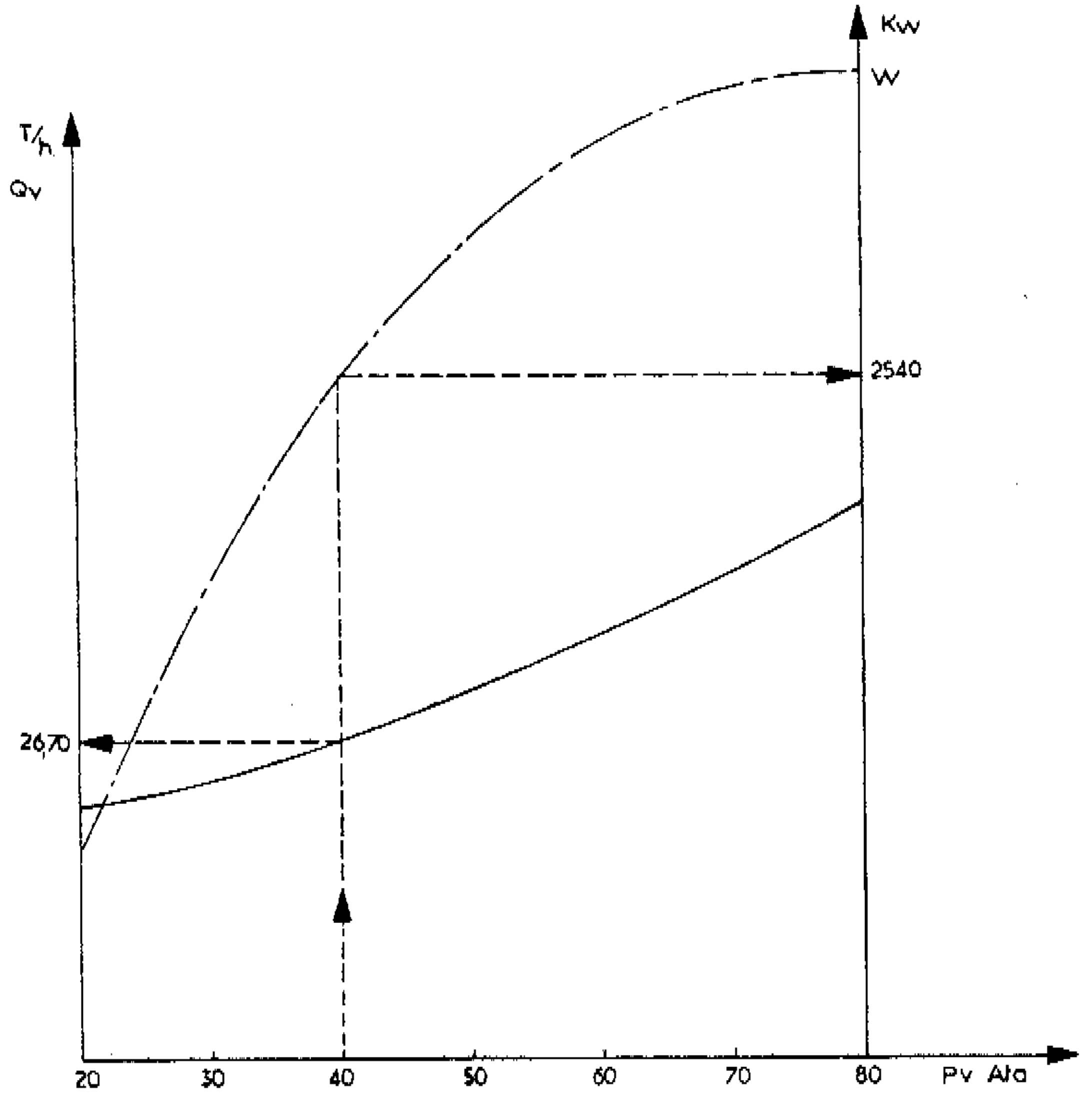
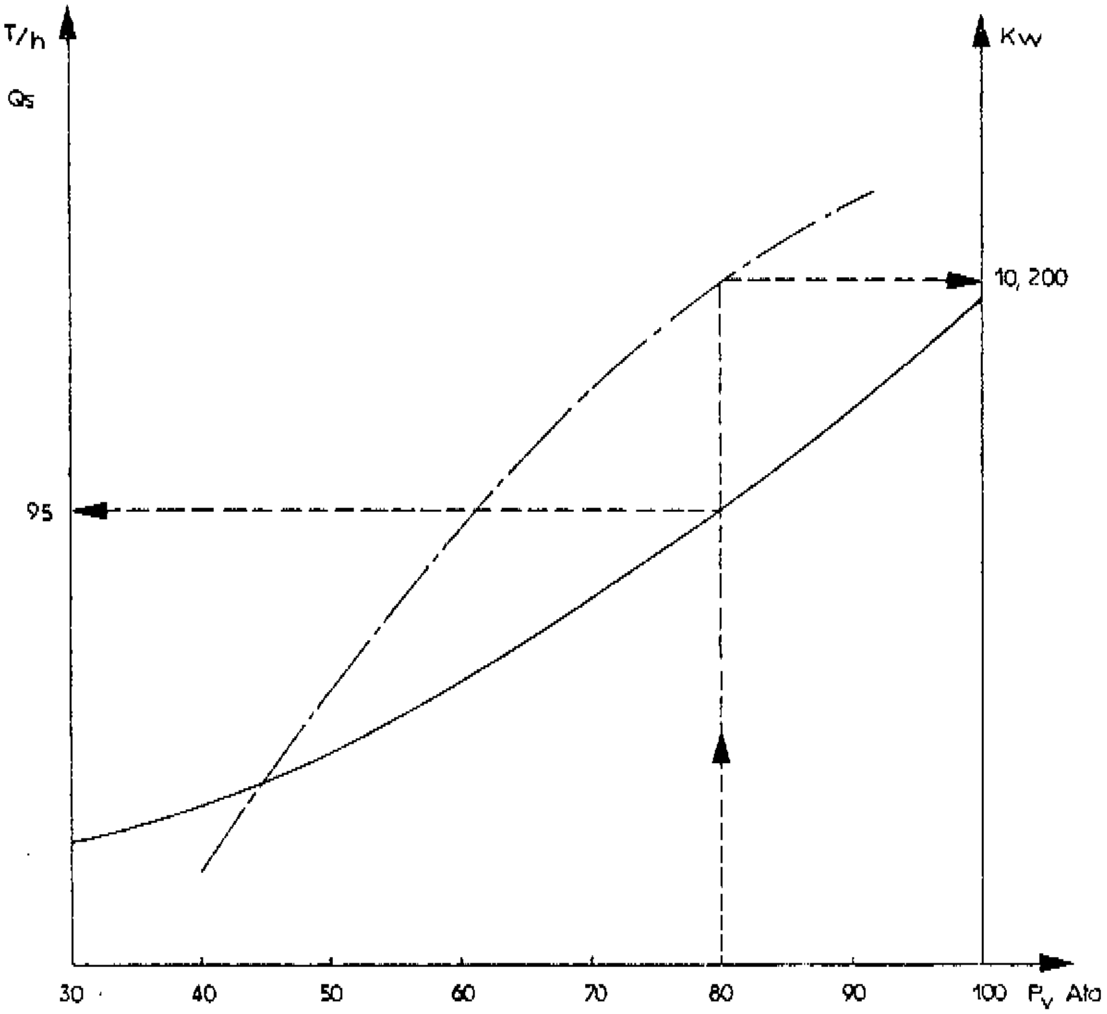
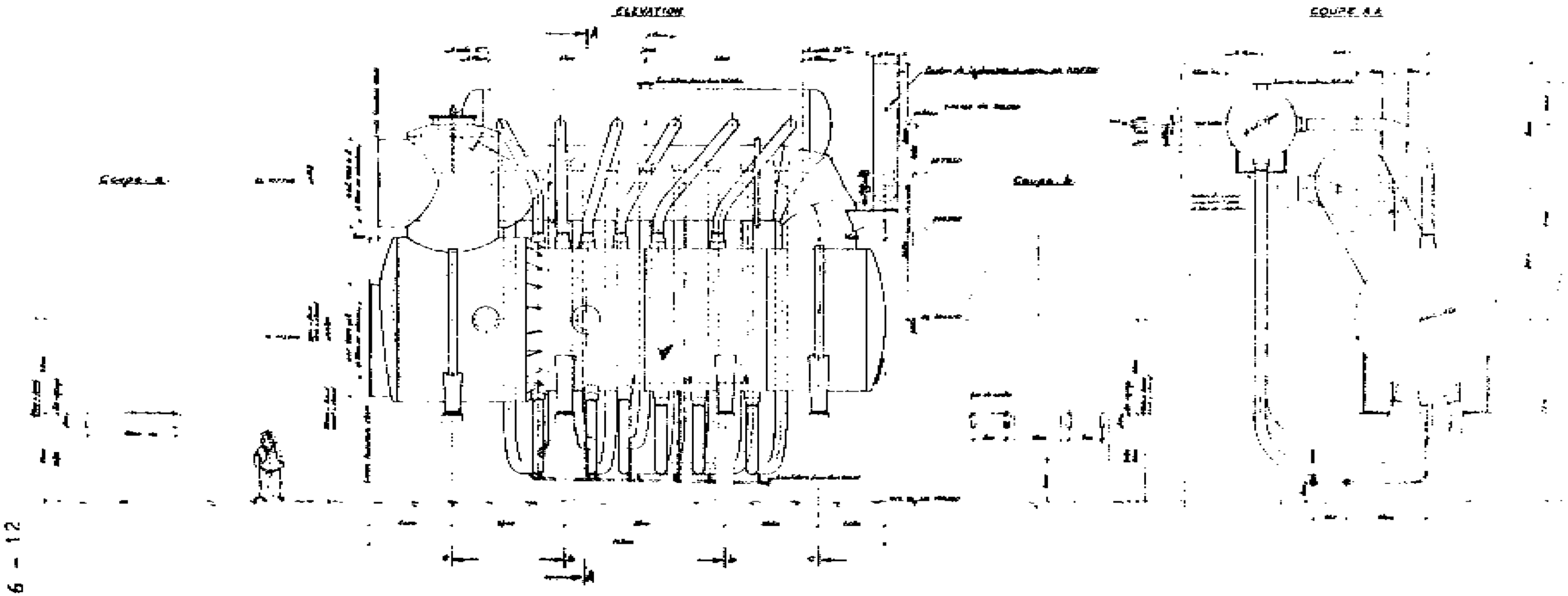


Steam and electric power production versus steam pressure for a 500 MTPD H_2SO_4 single absortion unit



Steam and electric power production versus steam pressure for a 1800 MTPD H_2SO_4 inter.-absorption unit.



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N° Cde HEURTEY [illegible] Z 401 N° Cde CLIENT
N° EQUIPEMENT SG 85-31 Date

C Modif. fondations et mise à jour
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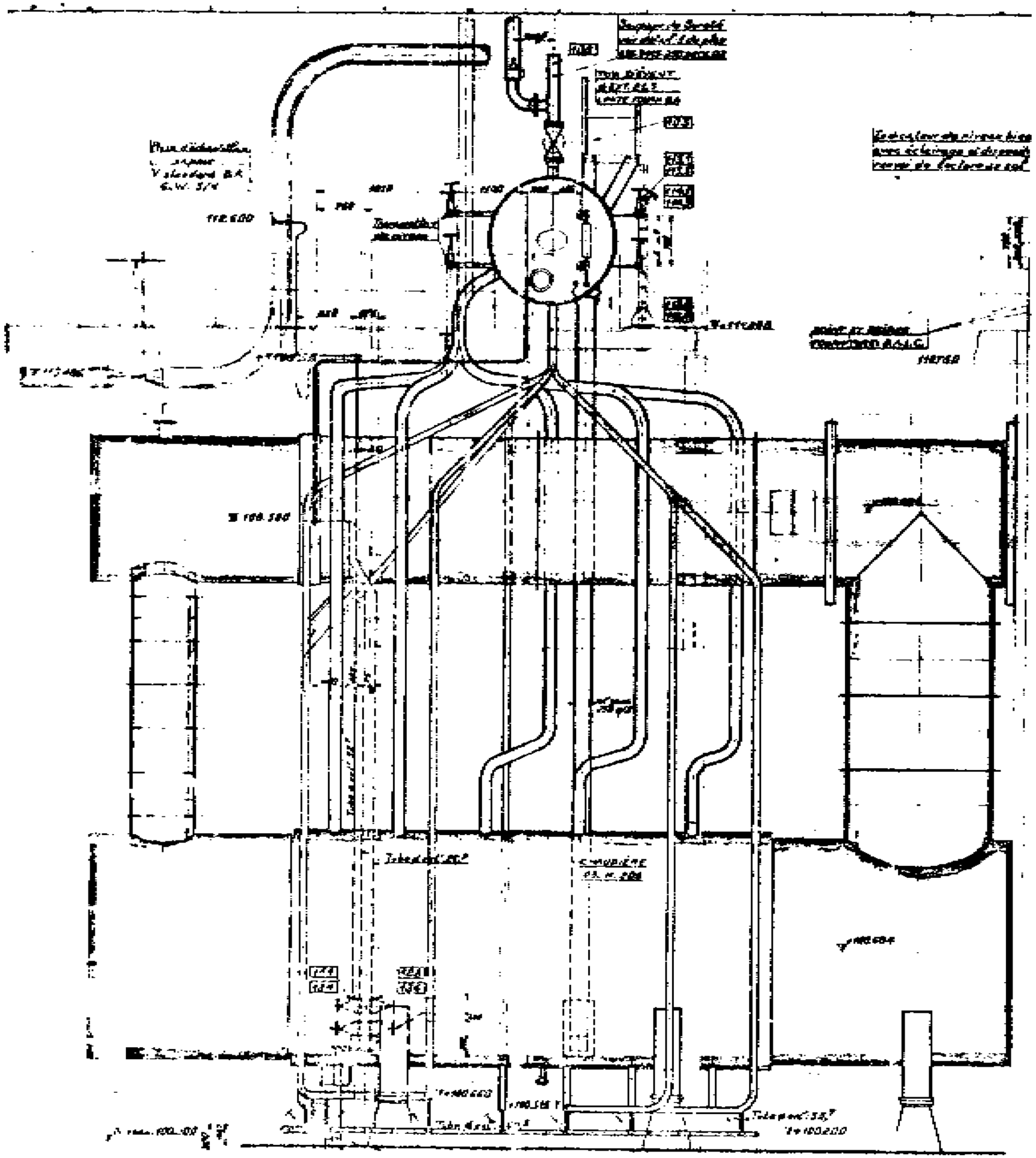

LE PLAN EST LA PROPRIÉTÉ DE LA SOCIÉTÉ

BABCOCK-ATLANTIQUE

SIÈGE SOCIAL 48, RUE LA BOÉTIE PARIS (8e)

NEURTEY COFAZ, LE HAVRE

CHAUDIÈRE DE RÉCUPÉRATION (de l'atelier …)

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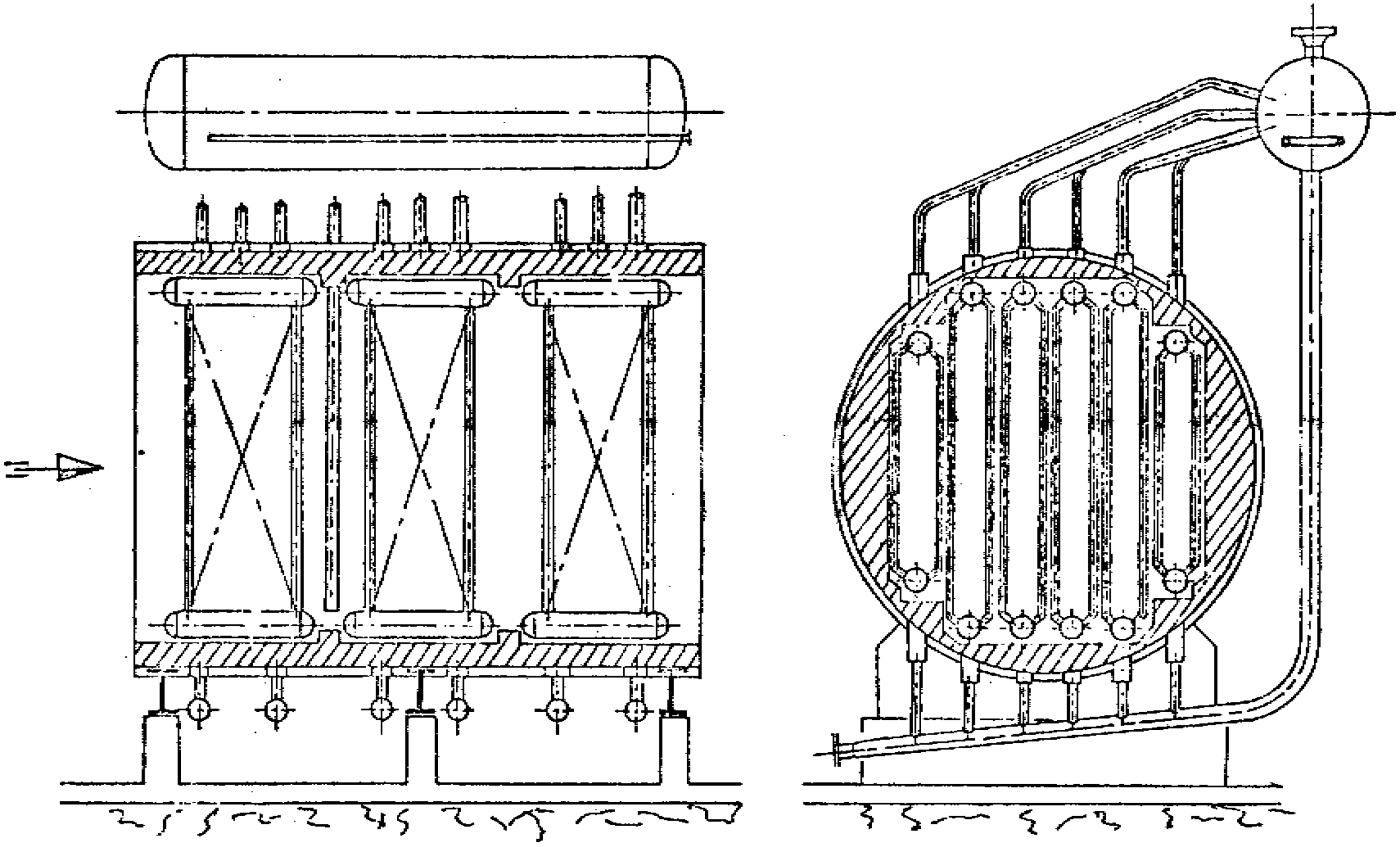
ENSEMBLE DES TUYAUTERIES DANS SES LIMITES DE FOURNITURES



WASTE HEAT BOILER WITH WATER TUBES FOR A 1700 t/d H_2SO_4 UNIT

CONSTRUCTOR A.H. LARDET

DISCUSSION

Mr LE (Heurtey, France)

In our study we concluded that, thanks to a thorough heat recovery, a sulphuric acid plant integrated in a phosphoric acid and complex fertilizer unit enables not only to make the unit energy self-sufficient but also to export part of that energy either as electricity or as steam.

We would now like to add a few additional remarks concerning the pressure and the temperature chosen for the recovered steam.

Although the fatal heat evolved in a sulphuric acid plant is a fixed figure for given capacity and process, owing to the high temperature levels between which heat exchanges occur, it is possible to change the pressure and overheating temperature of the steam within fairly wide ranges.

Indeed theoretically the pressure can be increased to very high levels, 150 atm and more, since the temperature of the inlet gas in the recovery boiler is about 1000 ° C. In practice, in order to avoid using boilers and turbines which are difficult to build and operate, we prefer to limit the pressure to 100 atm. For the overheating temperature of the steam, when we mentioned 400-430° C in our paper, we should have added that this range corresponds to a simple pattern with only one overheater and a large steam production. Indeed theoretically the high gas temperatures would make it possible - to reach the highest overheating temperatures, comparable to those of big thermic power stations, e.g. about 560°C. But there again we prefer to limit overheating to 500° C to remain in the field of non sophisticated equipment.

Summarizing we estimate that it is reasonable to limit the characteristics of the recovered steam to 100 atm and 500°C.

Below these limits the pressure and temperature can be chosen to adjust the production of steam and electricity to the requirements of the whole unit. But we would like to point out that the recoverable energy is the more important as the characteristics of the steam are higher. Of course the investment costs do increase, but, in view of the large fuel saving which all countries have to make, we are convinced that the maximum energy recovery is always profitable and should induce a thorough survey of each case.

Mr LOSTE (S.A. Cros, Spain)

I would like to congratulate you on your excellent contribution to this ISMA conference related to the energy recovery in a sulphuric unit within a fertilizer complex.

This is especially important in these days, when an energy crisis has been developed since the end of last year. All the technical contributions to optimise the recovery of the energy produced in any exothermic chemical processes has to be welcome in our world. Especially in processes such as sulphuric acid manufacture producing massive amounts of energy which can be recovered from gases at high temperature.

To achieve this goal large capacity plants have to be integrated in big chemical complexes and the maximum recovery of the available calories has to be done.

Following this [illegible] S.A. [illegible] has developed a "joint venture " at Huelva with the spanish company E.R.T. to produce P_2O_5. The actual production capacity is (400.000 tons) four hundred thousand tons of P_2O_5 per year.

It consists of 4 lines of H_2SO_4, each one of 1.000 tons per day and 4 lines of H_3PO_4. Additional plants are available to transform partially the H_3PO_4 into intermediate raw materials NPK fertilizer industry, such as M.A.P., D.A.P., T.S.P

In our Huelva P_2O_5 complex a similar scheme for energy recovery has been adopted.

Although the energy recovery system could be different in each particular case, and I agree with you that many factors can determine the optimum solution, I would like to ask you the following question : Have you made studies to determine from the economical point of view, considering the investment and operational costs against the value of the energy recovered, what would be, today, the relationship between the H_2SO_4 plant capacity and the optimum designed steam pressure ?

Mr. LE

We made this study fairly systematically on a number of cases, as we indicated in our paper, units from 500 t to 2.000 t/d. We found that the higher the capacity, the higher the energy recovery. This is due to the fact that, when dealing with a high capacity, the equipment installed has always a better efficiency. In any case the recovery question becomes increasingly up-to-date since the energy cost keeps on increasing.

Regarding the question of the optimum pressure for a given size we feel that, in practice, there is no optimum pressure; this is related to the investment costs on the one hand and to the amortization that one must calculate according to the cost of energy. It was found that, when the pressure is increased, the steam output recovered increases and, at the same time, the thermal potential of the steam increases, so that it is possible to produce more thermal energy.