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## THE POSSIBILITIES OF THE CONTACT PROCESS FOR THE MANUFACTURE OF SULPHURIC ACID.

by Etablissements Kuhlmann.

### FOREWORD.

Superphosphate manufacturers have always paid a good deal of attention to the evolution and progress of sulphuric acid manufacture.

On the one hand, their industry is the most important consumer of this acid. In France the percentage of consumption has been as follows:-

70% in 1929, peak production of superphosphate (2,140,000 tons)  
33% in 1938, (for a production of 1,170,000 tons)  
50% in 1948, (for a production of 1,400,000 tons).

On the other hand, the value of sulphuric acid included in the cost price of one ton of stored superphosphate usually represents about 40% of the value of this fertiliser.

For this reason, in addition to studying the problems of the manufacture of superphosphate and its further treatment, superphosphate manufacturers will find the problems of sulphuric acid manufacture of interest.

### FRENCH DATA.

(a) Raw Materials. The opinion in regard to the manufacturing process depends in the main upon the raw materials and, in this connection, it would be useful to recall the situation obtaining in France:-

In 1948, 150,000 tons of pyrites was produced. The imports for the manufacture of sulphuric acid amounted to 700,000 tons of pyrites and 18,000 tons of sulphur. In addition, 32,000 tons of blonde (32% of sulphur) was roasted.

The other raw materials were negligible. In France, for example, the consumption of spent oxide amounted only to 4,000 tons whilst Great Britain draws about 20% of her total production of sulphuric acid from these spent purification materials.

(b) Basic price. As the economic conditions of the different countries are by no means balanced, there exist numerous disparities in price which would render the interpretation of certain data difficult. For this reason we recall, in the following, the value of the principal basic elements in France on January 1st, 1949.

The KWH cost about 6 to 7 frs according to district;  
A ton of fuel (fines for the boiler) cost 3,000 frs per  
ton ex mines; i.e. 20 times the price of 1938.

One man-hour cost 135 frs;  
 Price of 1 kg of lead was 165 frs; after starting off at 5.20 frs. in 1939 and 77 frs. on January 1st, 1948, it reached a maximum of 181 frs. and then fell rapidly.

Ordinary pyrites with 48% sulphur, which was worth 325 frs. per metric ton delivered to works in 1938, cost, during 1948, 3000 frs. and finally 5600 frs.

As to sulphur, last year its price was 22 U.S. Dollars per ton of 1016 kgs, f.o.b. Galveston (freight about \$8.75). By way of example, this price can be compared with that of Spanish pyrites (basis 48% sulphur) which was worth 42/7 per ton f.o.b. and 45/6 on January 1st of this year.

### LEAD CHAMBERS AND CONTACT PLANTS.

It is well known that in the United States the contact process has, for many years, been exclusively employed for new plants. To our knowledge and, according to the "Industrial and Engineering Chemistry", only 5 small acid plants of manufacturers in the South of the United States have been constructed on the principle of lead chambers. The same periodical reports that some of the disused chambers have been replaced by Mills-Packard chambers.

It is equally well known that during the war Great Britain met her requirements by constructing exclusively contact plants, all based on the use of sulphur, for obvious reasons: simple and rapid construction and safe sea route.

In France it is obviously superfluous to look for a similar effort during the war period. The few plants built before enemy occupation were also contact plants (especially two units of 100 tons each) in order to obtain the necessary concentrated acid and oleum.

It may, however, be of interest to give the following figures of a single French Company which roasted 200,000 tons of pyrites year in and year out.

Towards 1929 the respective production of contact and chamber acids was in the ratio of 1 to 3; in the course of the critical years for the fertiliser industry this ratio came very close to one; in 1948 it was 2 to 3, without making an exception for the results vitiated by war events which have particularly affected lead chambers. In two of the plants which at present produce 100 tons each of monohydrate per day, 1 : 3 and 1 : 5 respectively by contact, modernisation is under consideration with a tendency to abandoning the lead chambers; one of the projects is already being executed and comprises a contact unit of 150 tons per day, fed by a flash roaster.

In France the necessity for a rapid repair of damaged plants has in numerous cases led to the rebuilding of chambers stripped of their lead with only the general skeleton standing. But it is significant that Companies, basing themselves in the main on the manufacture of fertilisers to the exclusion of chemical products, have decided to build contact plants on finding everything razed to the ground, or even in such cases as quoted above.

### CONTACT PROCESS.

Such a change which, in a very general way, gives preference to a catalytic process is, in the first instance, prompted by a feeling of prudence. Because it is a matter of experience that, when sulphuric acid production is slowed down owing to agricultural crises, the running of the lead chamber plants is the first to be affected, as contact acid, the transport of which is in addition cheaper, finds a customer more readily on account of its high concentration and purity.

Numerous indeed are the industries which, after having been satisfied for a long time with chamber acid, freed from arsenic or purified, have gone over to the use of contact acid which ensures a greater safety in running and very often a considerable economy in production costs as well as an improvement in the quality of their products.

To build a contact plant is tantamount to taking out an insurance, and the example of French industrialists to whom we have referred, proves that the corresponding "premium" has not been regarded too onerous, having regard to investments and the cost of production of an acid destined for the production of commodities which definitely require that quality.

It is, however, outside our scope to set down here a detailed comparison of the processes in question or to propound the merits of one against the other.

After having stressed, in general, the tendency borne out by facts we consider it more appropriate to mention some special cases and some very particular possibilities of the contact process.

#### THE CASE OF SULPHUR.

The moment sulphur is at the disposal of the manufacturer as a raw material the contact process becomes indispensable on account of its simplicity.

This, it will be noted, has been the conclusion of our English friends who have at their disposal world known specialists for the construction of lead chambers. The excellent manner in which the problem of war has been solved is adequate proof of the soundness of their choice.

#### THE CASE OF GASES VERY RICH IN SO<sub>2</sub>.

We propose to touch only very lightly on the exceptional case of works which have at their disposal concentrated or even pure sulphurous acid, usually obtained by enriching gases which are too low in their SO<sub>2</sub> content to be directly transformed into sulphuric acid. We know from experience that this is not a purely theoretical case, and it would be appropriate to mention that only the contact process can benefit from enriched gases by means of a special and very simple catalysis. In practice it is possible to utilise gases with an average content up to 25% of SO<sub>2</sub>, without having recourse to air, enriched with oxygen. We call attention to the fact that this special problem has been described by M.G. Bachelard in the March number 1939 of "Industrie Chimique".

#### THE CASE OF GYPSUM.

The use of natural sulphate of lime (anhydride or gypsum) requires exceptionally favourable conditions in order to be a paying proposition (proximity of coal mines; extensive and homogenous layer of gypsum) and an adequate production capacity (at least 80 tons of monohydrate per day, together with an approximately equal quantity of cement). That is why, to our knowledge, less than 10 plants work according to the contact process.

Incidentally, it would seem to us a matter of interest to note the remarkable possibilities of the contact process. When using gypsum, the gases have a very low content of sulphurous acid: 4% SO<sub>2</sub> with about 7 - 8% of oxygen, introduced by an air current as the gases of the reduction furnace are devoid of oxygen. In less favourable conditions it is possible to maintain the catalysis in autoreaction. Besides, in the Mediterranean climate it has been possible to obtain all the production of oleum without a cooler.

## THE CASE OF METALLURGICAL GASES.

What we have just said about the gases from gypsum applies of course, also to the corresponding metallurgical gases. This is of interest to Superphosphate producers seeing that they are generally compelled to utilise or even to "mop up" the production of acid corresponding to these gases.

From the technical point of view it has to be observed that it is sometimes possible to combine with the treatment of normal roasting gases that of gases with a lower content than that mentioned above, or of gases generated intermittently, in such a manner as to be able to use them in a contact plant. We know of concrete cases, using gas from Dwight-Lloyd roasters or water-jacket furnaces.

## RECUERATION OF REACTION HEAT.

The heat caused by oxidation of sulphurous gas is very carefully eliminated in all processes except in the contact process, such elimination constituting a total loss.

In the catalysis, on the contrary, one operates with a temperature higher than  $400^{\circ}$  C, and it was possible to give thought to the recuperation of the 22.6 Kg cals., generated by the formation of one molecule gramme of sulphuric anhydride.

Actually the technical expert has, in the first instance, to compensate for losses by radiation and to reserve a margin for auto-reaction: he draws upon a portion of the  $31^{\circ}$  rise in temperature which normal burner gases undergo when 1% by volume of  $SO_2$  is converted into  $SO_3$ , in order to transfer to the cold gases entering the heat exchangers a proportion of this heat. But, in addition, one has to watch that the exchanges of heat are carried out in such a manner as to combine the difficulty of obtaining the greatest speed of reaction at the various stages of catalysis with the necessity of terminating this reaction at a sufficiently low temperature for a favourable equilibrium. It is only on this condition that it is possible to maintain a yield by catalysis of more than 98%, a point which is very important for countries in Europe with few raw materials.

Thus it is explained that in the treatment of normal gases the catalysis itself is responsible for the disposal of the calories generated by oxidation.

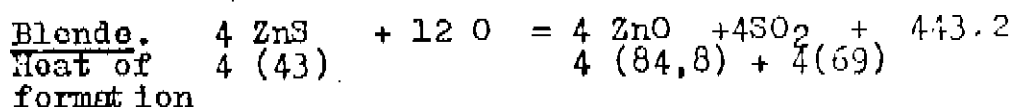
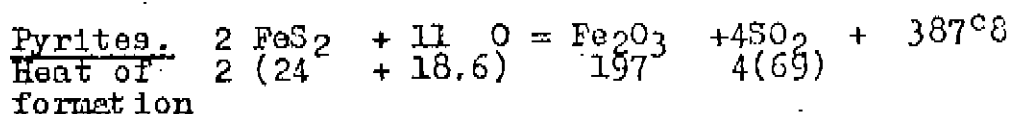
But matters are certainly different if one has rich gases or hot purified gases at one's disposal. This is the well known case of contact plants fed by a sulphur furnace. There is then co-ordination or even imbrication between the recuperation of heat, liberated by catalysis, and that resulting from combustion of sulphur.

May we recall that the idea of this last mentioned recuperation has been described in detail in 1938 by Frédéric Kuhlmann in his memorable patent in regard to the catalytic oxidation of sulphurous gas.

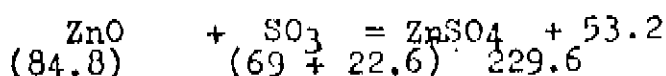
The combustion heat of ores remains the most important and the most attractive recuperation since roasting gases have a high temperature. Let us recall in this connection that the combustion of sulphur liberates 2,200 calories per kilogramme, that of pyrites about 1,455 and the combustion of blende 1,108 calories.

As compared with sulphur it has to be observed that the oxidation heat of the metals, contained therein, is anything but negligible and, if the roasting of the blende is carried out in such a way as to form a definite proportion of zinc sulphate, additional heat is generated.

Apart from impurities the released heat is as follows:



To this has to be added for zinc sulphate:



The blende less rich than pyrites (32% S against 48% S) liberates less calories when burning. But for the same quantity of monohydrate produced, the blende will liberate, even without sulphating, more calories than the equivalent quantity of pyrites. From the foregoing figures it will be seen that, per ton of monohydrate, (assuming a sulphur yield of 90% in the two cases) pyrites theoretically releases 1,100 calories and the blends 1,225 calories. But as the loss by radiation is more pronounced with blends, the roasting of pyrites is more advantageous.

However, in practice, and in spite of the considerable progress made in the removal of dust entrained by roasting gases, the loss by radiation and various other factors is such that only direct concentration in the gas flues, which is accompanied by other limiting factors, has been practiced until the appearance of roasting by suspension. (I)

The steep rise in fuel prices revived the idea of using recuperating boilers instead of furnaces of the usual type. But the damping of such installation is very difficult, and we consider that the need for not too great a reduction in the temperature of the gas, admitted to the Glover, in order to preserve an appropriate denitrating and concentration of chamber acids, does not permit of recuperating more than 250 kgs of water vapour per ton of monohydrate produced.

But the contact process is exempt from this limiting factor and, in the numerous installations of flash roasting, there is no apprehension of lowering the recuperation gases from the recuperating boilers to 300°.

Thus it is possible to recuperate 0.7 tons or even more than one ton of water vapour per ton of monohydrate in the case of blends and up to 1.5 tons with pyrites.

This very appreciable recuperation of water vapour (or motive power) shows the importance of plants equipped with flash roasters, based on the contact process.

It can even be said that such installations, normally using flotation pyrites, remain advantageous even in the case where difficulties of supply would render it necessary to employ ordinary non-flotation pyrites, such as the pyrites from Rio.

R. HERVET.

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(I) It is understood that we have disregarded contact plants with sulphur furnaces for which the recuperation of heat is greatly facilitated and reached about 1 ton of water vapour per ton of monohydrate.