International Fertilizer Industry Association

ISMA* Technical Meetings

Paris, France

25-27 September 1951

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

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

AGRICULTURAL COMMITTEE
1, AVENUE FRANKLIN D. ROOSEVELT
PARIS (8E)
TEL. BALZAC 57-25

SECRETARY: R. M. COLLINS

CENTRAL OFFICE
32 OLD QUEEN STREET
LONDON, S.W.1.
TEL. WHITEHALL 7262

LE 292. September 1951.

TECHNICAL MEETINGS 1951.

Paper No. 11. CONFIDENTIAL

This paper will be presented at the Technical Meetings in Paris on September 25th and 27th, 1951. It must not be published prior to that date and, in any case, it must not be published without the permission of the author.

NOTES ON THE RUNNING AND STABILITY OF A SULPHURIC ACID PLANT - KACHKAROFF SYSTEM.

by R. DEGHELT.

The choice of the process to be adopted by a fertiliser manufacturer, who wishes to install a sulphuric acid plant, is somewhat difficult. He is guided by considerations of the cost of installation, output, consumption, and also of facilities in regard to running and maintenance, elasticity and stability.

In regard to these latter points it seemed to us of interest to submit the results of our experience, extending over almost one year, with a plant installed at Brest, according to the Kachkaroff process, and put into operation in July 1950.

This unit has been erected under the KACHKAROFF/MATIGNON patent for the intensive manufacture of sulphuric acid, according to the process and technique of Mr. Salsas Serra.

The plant has a production capacity of 40 tons per day of sulphuric acid, expressed as mono-hydrate.

In its entirety the plant comprises:

- 4 Moritz furnaces of 7.5 tons with electrostatic dust precipitator;
- 2 Glover towers in parallel;
- the actual Kachkaroff system composed of four steel towers, of which
- the "first section" tower is in steel, lined with refractory bricks and filled with Raschig rings. Circulation of acid in the upper portion is by a series of distributors;
- three towers are in steel without lining, empty (with the exception of the last, which contains packing in the lower section), where atomisers project the acid in the form of mist.
- finally, two Gay Lussac towers.

A battery of coolers controls the temperature of the circulating acids. It goes without saying, that there are pumps for moving the acid, a fan, tanks and all the usual accessories.

We do not propose to recapitulate the whole theory on which the Kachkaroff process is based and which by now is well known. It is common knowledge that, according to this theory, the formation of H_2SO_4 takes place in the liquid phase and that its velocity is the more pronounced the greater the concentration in N_2O_3 in relation to SO_2.

This has led to a circulation of a very concentrated acid, rich in nitrous products, in the four K. towers, in a very rapid cycle and in a closed circuit. The concentration of nitrous products, however, is limited by the tension of nitrous vapours which again are a function of the temperature and strength of acid.

The aim to be attained is evidently a complete oxidation of SO_2 and a satisfactory recuperation of nitrous products. For this it is necessary to ensure a stability of reaction, i.e., according to the Kachkaroff theory, to obtain such that the proportion of SO_2, initially transformed, remains constant in each of the sectors. When this equilibrium is achieved, it is observed that the chimney of the plant emits only a little white smoke.

When the reaction takes place towards the top, i.e., when it is more active in the first sections of the apparatus, the smoke becomes orange-coloured; there is a visible loss in NO_2. The reaction has terminated too quickly, the oxidation has been too rapid, and the equimolecular proportion $NO + NO_2$ has been disturbed at the expense of a less well absorbed NO_2.

With the inverse hypothesis, reactions take place in the last sectors of the apparatus, and the smoke remains white. In this case it is known that there is a formation of intermediary compounds, resulting in losses in nitrous products in the form of NO_2. There is then an excessive consumption of nitric acid.

The rôle of the supervisor of the plant consists, therefore, of avoiding a displacement of reactions, i.e., of maintaining the concentration and the temperature within the fixed limits. These limits are very narrow + or - 2° centigrade and + or - 0.1 degree Bé.

And yet, the equilibrium is very easily obtained and, in spite of the very unfavourable working conditions, such as lack of current for 18 consecutive hours, very heavy thunderstorms etc., considerable displacements of reactions have rarely been observed.

It is the conception of the plant itself which enables the supervisor to control the concentration and the temperature of the circulating acid, that is, in fact, the nitrous tension and the tension of water vapour.

First of all, the reduced dimensions of the plant limit the heat exchanges with the exterior and reduce the influence of atmospheric conditions.

On the other hand, the cycle of circulation of the acid is rapid, since 40 cubic metres of acid are pumped at a delivery rate of 60 cubic metres per hour. Almost the total quantity of the acid, circulating in a closed circuit, passes into the cooler and, by varying the delivery of the cooling water, the temperature is easily regulated.

Nevertheless, as the working conditions of the superphosphate industry have forced us to limit our production, at times, to a third of the total capacity of the apparatus - it should be noted lead chambers could attain such a low limit only with difficulty - we have been induced during cold spells to eliminate the cooling water and observed a falling-off in temperature of the order of 10° centigrade.

The reactions were then transferred to the farthest units of the apparatus, a fact which we detected by the presence of a small quantity of SO_2 of the gases entering the Gay Lussac tower (up to 0.1%) and by the exaggerated loss in nitrous products. In order to compensate these losses it was necessary to introduce 4 times the normal quantity of nitric acid during several days.

This additional supply of nitric acid could be considerably reduced, or even eliminated, by taking the precaution of compensating the fall in temperature by dilution of acid to limits compatible with a satisfactory resistance of the iron.

In this way, after a stoppage of manufacture lasting 18 hours, due to lack of electricity, and after the temperature of the gases, leaving the first tower, and of the circulating acid had diminished by 10° centigrade, the equilibrium of the temperature has been established twenty hours after commencing operations and the equilibrium of reactions has been established immediately after dilution of acid, without the necessity of introducing an additional quantity of nitric acid.

It is just as easy to regulate the concentration of the circulating acid as the temperature under normal working conditions. In view of the fact that the acid is weighed every two hours and the water is distributed at the top of the first tower by a system of four nozzles, pierced in such a manner as to ensure a delivery of 40 to 100 litres each, we have noticed a deviation of not more than 0.2° Bé.

The temperature and the strength of the circulating acid being regulated, the equilibrium of the reactions depends, in addition, on the nitrous tension, i.e., on the concentration of nitrogen oxides.

Experience shows that, all things being equal, deviations of the order of 4 grammes per litre (circulation acid contains about 100 grammes per litre) do not interfere with the running of the apparatus.

But if the great volume of the circulation acid is taken into account - and this volume explains the remarkable inertia of the apparatus - it is observed that such a variation in content corresponds to a very considerable quantity of nitric acid.

4 grammes per litre in 40 m^3 represent 160 kgs of N_2O_3, hence 260 kgs of pure HNO_3 or about 500 kgs of 36° Bé nitric acid.

From the above observations important deductions are obtained:

(1) When nitric acid is introduced into the circuit of the K manufacturing towers, but not into the denitration tower, there is no difficulty in supplying them in a discontinuous manner, for example, 60 kgs in 1 hour, three times a day.

(2) The effects of losses in nitrous products make themselves felt only when they exceed 160 kgs, calculated as N_2O_3 and have to continue for a long time before attaining a dangerous limit. Temporary causes, such as change in the composition of the gases during the cleaning of the furnaces, have no repercussion on the equilibrium of the reaction.

Finally, a satisfactory recuperation of the nitrogen oxides depends also on a well-conducted denitration.

This denitration is important, as, independently of the recuperation in the Gay Lussac towers, the Glover towers must receive a portion of the circulating acid (strong nitrous acid containing about 100 grammes per litre of N_2O_3) corresponding to the production, in the Kachkaroff towers, of about 75 to 80% of the total production (which is obtained at the outlet of the Glover tower).

In the first months of production, when operating at a low rate, we only obtained a satisfactory denitration by allowing a certain dilution of the acid in the Glover, the strength of which did not exceed 57.5o Bé.

The recuperation in the Gay Lussac was nevertheless satisfactory.

Actually, we get better results and a total production in 60° Bé acid by utilising our two Glovers in the following manner:

The gases traverse them in parallel, the acids are circulated in series, the first Glover receiving all the acid for denitration (production of Kachkaroff, make up acid from the Gay Lussac tower) and, in addition, a certain quantity of the acid of the closed circuit; and the second Glover receives the acid coming from the first (with the exception of the quantity circulating in close circuit).

As the acid in the Gay Lussac towers is only renewed by one fifth every hour, the sprinkling of the second Glover is reduced to about 1 m3 per hour, which permits of using to the best advantage the temperature of the gases.

The homogenous mixture, coming from the first Glover and circulating in the second, has a medium nitrous content (25 grammes N_2O_3 per litre) diluted to 58° Bé. The reaction is very intense at the top of the tower and engenders much heat, which ensures a rapid denitration, whilst the heat carried by the gases to the bottom of the tower ensures concentration.

CONCLUSIONS.

We must obviously underline that our observations are the result of a somewhat short experience, seeing that the plant has been operating for barely a year.

Nevertheless, it is indisputable that the Kachkaroff process permits of the installation of units enjoying a remarkable immunity against all causes of interference of short duration. This stability affords a great facility of exploitation. Errors by supervisors can be readily remedied, even after several hours; it is possible to face stoppages of 24 hours etc.

The recuperation of nitrogen oxides is also favoured and, as a matter of fact, our consumption of nitric acid, calculated in monohydrate, in relation to monohydrate sulphuric acid, decreased to about 0.70%, the apparatus operating at less than half its capacity.

The recruiting of the staff was easy. Ordinary workmen, chosen from the most skilful and intelligent, but without special training, made excellent supervisors.

A single workman can run the whole apparatus without difficulty. Of course, a furnace hand ensures the smooth running of the furnaces. During the day one workman spends a few hours on cleaning.

The starting up gave rise to no incidents and equilibrium was attained in 8 days, counting from the introduction of pyrites into the furnaces.

The change over from one manufacturing cycle to another presents no difficulty. An unforeseen cut in current, incidents in the running of the pumps, stoppages for various reasons, interfere only slightly with manufacture.

Summarising, it may be said that the apparatus is easy to run and of great stability.

---------oOo--------