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

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A NEW TECHNIQUE IN THE MANUFACTURE OF
SULPHURIC ACID.

by Pietro Guareschi, Professor at the University of Genoa.
(July 1949)

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Summary.

Classical and intensive methods for the production of sulphuric acid from nitrogen oxides, whose chemical process has been interpreted by Lunge and Berl, are mentioned. A new intensive process, using nitrogen oxides, where the cycle of chemical reactions is quite different is then analysed and advantages are enumerated for this process compared with the former.

In this process there is no gaseous phase reaction $2NO + \frac{1}{2} O_2 \rightleftharpoons N_2O_3$ of the Lunge and Berl type but the oxidation of SO_2 takes place at the expense of the oxidation reducing process between nitrous and nitric compounds in liquid phase only.

This reaction is favoured and made possible at all by the presence of persulphuric radicals to be easily determined in the sulphuric acid with high nitrose contents.

Description is made of the complete cycle of reactions wherein the presence may be noted of compounds with higher oxygen contents than for the normal Lunge and Berl cycle.

Description is also made of a plant for the practical operation of this cycle.

During the last thirty years the sulphuric acid industry has made steady progress with the application of the intensive chamber process (Moritz, Mills-Packard) and of the packed tower system (Opl, Larison, Petersen).

The reaction in these processes does not differ greatly from the standard pattern. There are some variations in constructional details but the theoretical cycle for the formation of sulphuric acid has not undergone any change. For all systems operating mostly in the gaseous phase the theory of Lunge and its derivations can be applied.

It may be noted that Lunge has given the most rational explanation of the oxidation cycle of sulphuric acid and this theory, modified by Berl, is still the most largely accepted to-day.

However, for a process working in the liquid phase only, this theory cannot be accepted.

The process we are now going to consider differs from the aforementioned classical systems by new conceptions having both a theoretical and practical significance offering two principal advantages:

- 1) a small volume of reacting elements and consequently a high production per unit;
- 2) a low consumption of the oxidiser.

These two factors are of great importance in as much as they reduce capital and working costs.

In our process the nitrous gases are employed for the oxidation of sulphur dioxide into sulphur trioxide, but all reactions occur in the liquid phase and theoretically, during the cycle, nitrous gases are not generated.

Technicians will understand that this fact has a very great importance in the practical as well as the scientific field, in as much as it calls for a thorough examination of a reaction, the parallel of which is not easily to be found in inorganic chemistry.

Indeed, it is not to be excluded that this reaction might be described as a bimolecular one in liquid phase. The velocity of oxidation, also for enzymic reactions, according to Schulze's law, is proportional to the concentration of the catalyst in the dispersed systems:

$$\frac{dx}{dt} = K C N_2O_3$$

As we are going to prove, the presence of persulphuric radicals in the molecules of the nitrous compounds is evident.

The oxidation velocity of SO_2 is proportional to the radical $(SO_4)_2$

$$\frac{dx}{dt} = K_1 C (SO_4)_2.$$

Consequently it was necessary in such a case to have recourse to reactions in the liquid phase; two different reactions should be considered:

- 1) a very rapid one, the oxidation of sulphur dioxide by reduction of the nitrous gases;
- ii) the other, a rather rapid one, regarding the re-oxidising of the nitrous gases and of which the well-known equilibrium constant has been determined by Bodenstein. It is therefore easy to understand why in the chamber plants and similar systems the whole cycle of production is based on the reaction having the lowest velocity

This fact explains the necessity for all systems working in the gaseous phase to have towers of large volume and low gas velocity in the system, strictly to attain the lowest velocity.

Before considering the practical application of the process, which is capable of giving a high production per unit together with a low consumption of oxidiser, we shall briefly consider its theoretical basis.

The above formula, which was given by us several years ago (1), shows how an increase in the concentration of the nitrogen oxides with a valency of at least 3 represents the reaction in the liquid phase. This phenomenon is not connected with the formation of nitrous products but with nitric compounds combined with sulphuric acid.

Two practical considerations follow, the explanation of which is given on the basis of the above theory:

- 1) the higher the concentration of the nitrous-nitric compound in the circulating nitrose, the greater the transformation efficiency and the lesser the consumption of the oxidiser;

2) By an increase in the concentration of nitrous compounds in the nitrose expressed as N_2O_3 , the nitric radicals also increase. The resultant acid, which contains highly oxidised persulphuric radicals, cannot be called nitrosylsulphuric acid.

It ensures a greater efficiency of transformation and a greater velocity of oxidation with a maximum content of nitric radicals in the nitrosulphuric molecule.

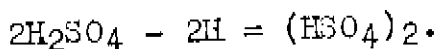
In order to reach an efficiency approaching to the theoretical value, nitrogen ^{valencies} cannot go below 3, but it is better to have a valency of 5. For this reason the reaction must always remain in the liquid phase. Anyway, there must be absolutely no development of nitrous gases reduced by SO_2 .

In this process where the concentration of the nitrogen oxides, termed N_2O_3 , is never below 10 - 14% by volume but can, on the contrary, be very high, there is, theoretically, no production of gases, but only a transition from trivalent to pentavalent nitrogen and vice versa, always in liquid phase, as a nitrosulphuric compound.

This process shows, without doubt, such a reaction and, having regard to its velocity, it explains the more intensive production of sulphuric acid in the packed towers, a production which can reach 300 kg/m^3 .

Hantsch and Berger have, in fact, made an interesting study of certain nitrogen peroxide compounds. They have investigated reactions of perchloric acid with nitric acid, obtaining a series of perchlorates of hydronitric acidium $(ClO_4)_2 N(OH)_3$, where the chlorine, as in all the perchlorates, has a valency of 7.

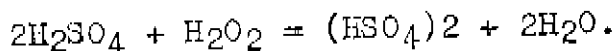
It is well-known that powerful oxidisers, i.e., anode oxidation process; the peroxides of hydrogen and sodium etc., can transform the sulphuric acid into persulphuric by a subtraction of two atoms of hydrogen:



Persulphuric acid being not known in a free state, only its salt may be considered, for instance ammonium persulphate.

Replacing the ammonia group by the monovalent group $O-N(OH)_4$ a compound having an orthonitric acidium radical $N(OH)_5$ is obtained. By analogy, in the structure with Hantsch's perchlorate of nitracidium, the highly oxidised compound formed by contact with the nitric and nitrous gases is called orthonitracidium.

The same reaction is obtained with sulphuric acid and H_2O_2 :



The persulphuric acid can be experimentally determined in this reaction. Consequently in the complex molecule there is nitric acid with one molecule of water.

Several tests have confirmed the conceptions given above.

We will not consider here in detail the theoretical treatment of the strongly oxidised nitropersulphuric acid. In this process the reaction velocity is given by the presence of the nitracidium radical whose oxidation and reduction velocity are very high.

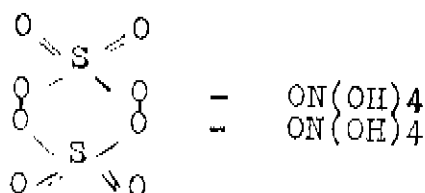
During the reduction in the presence of sulphur dioxide the nitrous gases are always instantaneously oxidised. For this reason the relationship between SO_2 and the sulphurnitric compounds must be the lowest, allowing for normal operations.

The reaction occurring between nitrose and sulphurous gases is therefore a reaction where the nitrose, in the presence of air-oxygen, maintains its composition unaltered, without the development of any nitrous gases with persulphuric groups acting as oxidising agents. (2)

Experience gained on this subject has shown:

- 1) the presence of the persulphuric group in the nitrose having a high content of nitrogen compounds rated as N_2O_3 ;
- 2) a high development of oxygen in the reaction between the nitrose and ferrous sulphate;
- 3) a high development of oxygen during the hydrolysis of the nitrose.

From these laboratory tests the possibility arises of obtaining, by the nitrous vapours formed with sulphuric acid, water and oxygen (from the atmosphere) a compound having a high grade of oxidation, namely the following polymerized compound: $(SO_4 \cdot NO(OH)_4)_2$ with following molecular structure:



In the above formula the acid persulphuric radical can be seen. The presence of the persulphuric acid can be demonstrated by following chemical test:

- 1) when the nitrose reacts with a solution of manganese sulphate in the presence of silver nitrate or sulphate, the manganese salt becomes transformed into permanganic acid or permanganate; with the nitrose from our Fossano and Vercelli plants, the reaction is very definitely positive;
- 2) when benzidine (paradiphenyldiamine) in an acetic solution (0,2 gr of benzidine in a 20% acetic acid solution) comes in contact with the nitrose it becomes a beautiful green-blue, i.e., the characteristic colour of persulphuric acid. In the presence of nitrous-nitric groups sodium acetate should be added.

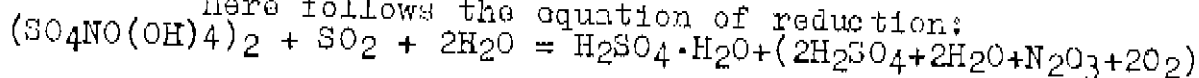
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The first treatment of the nitrose was effected by ferrous sulphate; other treatments followed with SO_2 and other metals, such as mercury, obtaining in a Bunte burette a high percentage of oxygen, absorbed by potassium pyrogallate. Other gases were first absorbed in the alkaline solution.

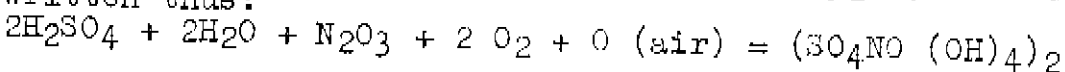
In the tower processes the exchange reaction which always occurs in the liquid phase, can be expressed by the following equation. The oxidation velocity will be proportional to persulphuric ions:

$$\frac{dx}{dt} = K, C(SO_4)_2$$

Here follows the equation of reduction:



As for the action of the air (oxygen) this equation can be written thus:



We do not wish to dwell further on theoretical conceptions assisting in the explanation of the interesting results obtained in this process for the production of sulphuric acid.

The liquid phase reaction permits the following to be obtained:

- 1) a high efficiency of transformation of the sulphur (over 99,9%);
- 2) Continuity of operation also by considerable variation of the capacity;
- 3) High productivity and hence towers and apparatus of small volume;
- 4) Low consumption of oxidiser;
- 5) The complete discarding of the Gay Lussac. Only those nitrous vapours are recovered which escape owing to the nitrous tension;
- 6) Reduction of the cost of plants in respect of ordinary installations;
- 7) low maintenance cost.

Of great importance is the possibility of being able to operate in the liquid phase only with the employment of a very low concentration of gas in SO_2 (2 - 3%). This is very useful for the recovery of sulphurous gases in the metallurgy of copper, zinc, etc. Also employing a Lammig mixture where there are wide variations of concentration during their combustion, in the liquid phase and of the presence of nitrous products, oxidation to the maximum, gives best operating conditions.

The following scheme is very simple:

the specific production can reach 300 kg/m^3 of sulphuric acid at 100%. The reaction rate for every section is constant; as there is no development of nitrous gases as in the ordinary systems, theoretically the reaction can take place only in a tower or chamber where, by means of the packing, the contact between sulphurous gases and the nitropersulphuric acid can be more easily accomplished. Heat of reaction is eliminated by cooling the circulating acid.

The process is based on the following plan:

the sulphurous gas after having been freed from dust enters the denitrating tower which is constructed with acid resisting and refractory material.

The denitrating tower is fed with nitrous sulphuric acid coming from the absorbing apparatus. Since this acid has a concentration much higher than that which is to be produced some water must be added.

The feed is distributed in the tower by means of a spraying system. This tower provides only for denitration.

The denitrated acid which comes from the tower is cooled in a tubular cooler and is then collected in tanks from where it is either conveyed to storage or to some other destination.

Since there is an excess of heat carried by the gas or liberated in the reaction, an apparatus is provided for the removal of this excessive heat, consisting of a pump and a feed tank, in order to circulate the denitrated acid within a closed circuit.

The sulphurous gases, after denitration, pass on to the reaction cycle proper. This system is formed by four sections, connection between them being in series and in parallel. The reaction apparatus is characterised by a rapid reaction of great intensity

and with a heavy circulation of nitrous acid in closed circuit. In the first reaction apparatus SO_3 hydration water is introduced.

The acid produced in the system is introduced into the first sector of reaction as well as in the second, third, etc., in parallel and is collected at the end of the system. A part of the nitrous acid goes to the denitration tower tank.

The sulphurous gas is drawn off by means of a fan, placed between the two sections of the scrubber or filter tower. The latter is employed particularly for the recovery of particles of acid, carried by the currents of gases and from nitrous gases developing by the tension of the nitrose.

The attached flow-sheet gives a precise idea of the construction.

The industrial operation of this process represents an important advance in the manufacture of sulphuric acid.

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- (1) P. Guareschi - On the lead chambers reaction
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 - (2) P. Guareschi - Paper presented to the Congress of Industrial
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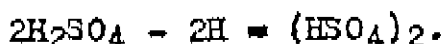
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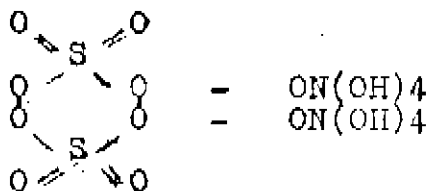
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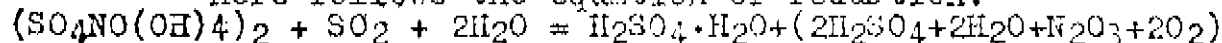
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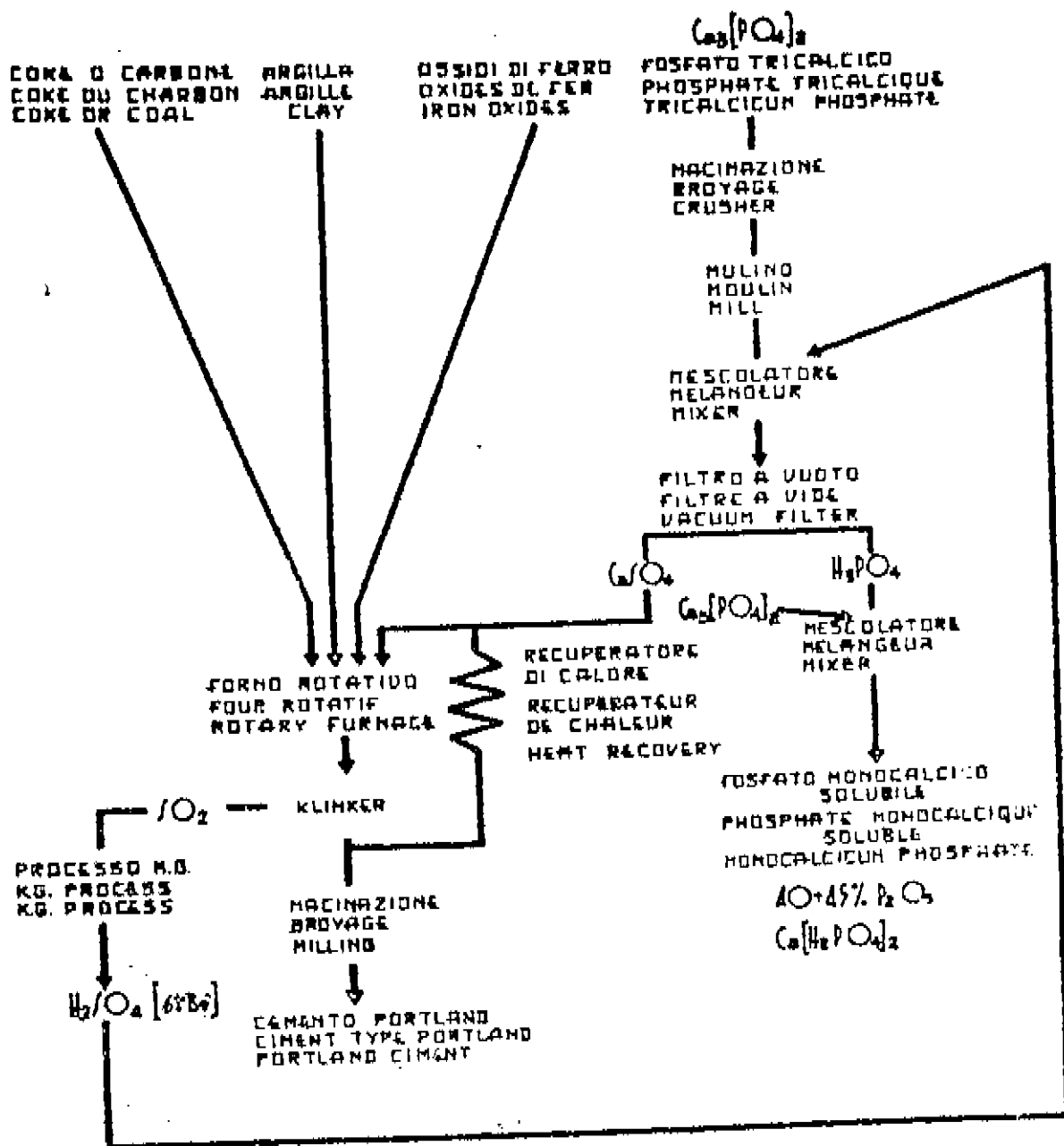
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