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                DEVELOPMENT AND EVOLUTION
        OF THE KACHKAROFF PROCESS IN FRANCE.

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        The principles, application and the latest improvements
in the Kachkaroff-Matignon process for a simultaneous
production of sulphuric and nitric acids have already been
described (Ref. 1 and 2).   In spite of the considerable
advantages which might have been expected owing to the fact
that nitric acid was being used progressively to complete the
action of sulphuric acid and even to replace it in the
production of certain fertilisers, this process has not made
much progress seeing that the first installation in France
has not yet been completed.

        On the other hand, the intensive manufacture of sulphuric
acid alone, a special case of the mixed process, has greatly
developed during the last few years, particularly in France,
where four installations are actually operating with very
satisfactory results thanks to the improvement in the
apparatus employed and the technique applied in the course of
their erection.

        The essential characteristic of the Kachkaroff process
is the use of nitrous sulphuric acid of a feeble nitrous
tension in support of the reactions in the liquid phase, in
spite of the fact that its content in nitrous compounds is
considerably higher than that of the acid circulated in the
other intensive processes.

        In the mixed process, this characteristic allows of a
simultaneous absorption of SO_2 and nitrogen oxides and its
adaption to the manufacture of sulphuric acid alone; although
it has not permitted of the complete elimination of the Gay
Lussac towers, as envisaged by Kachkaroff, the volume of
these towers has been less than that of a lead chamber system.

        The use of sulphuric acid with an increased density and
nitrous content has allowed of the construction of a large
portion of the apparatus in ordinary steel without lining.
The reaction chambers with the exception of the first which
is completely or partly lined with acid-resisting bricks are

constructed in unprotected sheet iron in the form of vertical cylinders placed in the open on a concrete platform.

These apparatus have been tested for more than two and a half years and we are of the opinion that their present form and arrangement which includes some slight variations, can be considered as final.

The entire apparatus (see figure No. 1) consists of one or two towers of the Glover type placed in series or in parallel, of three to five chambers or towers of reaction either completely packed with Raschig rings with a static distribution of acid or completely empty or partly packed and equipped with centrifugal atomisers to distribute the acid in the form of a mist and, finally, of two standard Gay Lussac towers.

The elimination of all packing in our first apparatus has not given satisfactory results in spite of the high degree of fineness of the atomised acid and this was partly due to the unsatisfactory distribution of the gases in the cylinders the diameter required for obtaining a satisfactory atomisation of the acid being too large in relation to the flow of gas. As the production capacity per volume unit of the empty towers was considerably lower than that of the packed towers, the towers of the first installations were completely packed with rings the dimensions of which decreased towards the top, those of the upper layer being 20 or 30 millimetres, and, finally, the mechanical atomisers were eliminated.

Nevertheless, the complete packing of the towers represents a very heavy expense and diminishes considerably the useful volume necessary for the re-oxydisation of NO. In the more recent installations we have, therefore, combined atomisation and packing in such a manner as to obtain a satisfactory distribution of the gases and to ensure the re-oxydisation of NO necessary for the acceleration of the simultaneous absorption which is a characteristic of the process.

In the latest installations we have equipped one portion of the towers with a partial packing of Raschig rings, at times limited to a layer of one metre in depth, the acid being distributed in a very fine mist which penetrates even the inside of the packed portion. The results obtained were excellent and we are applying this procedure to the new installations now in course of construction.

The use of ordinary steel without protection for the construction of reaction chambers, gas and acid pipes, coolers, etc. has resulted, particularly in the first months of operating the installations, in some incidents due to local corrosion.

Nevertheless, it has been ascertained that the average wear and tear was absolutely negligible and that the corrosion was due to accidental causes which, generally speaking, can be foreseen and avoided.

In the reaction chambers the acid mist condensed on the walls and the circulating acid ensured an efficacious protection by the formation of a very thin layer of basic

sulphate of iron.   A blow or an excessive speed of the acid
on the sheet iron may facilitate corrosion by preventing this
layer from forming or by making this protective layer disappear.

Another cause for wear and tear is an accidental dilution
of the acid at a spot where it is not sufficiently renewed, as
for example in the gas tubes at the side of a joint which is
not air-tight and which allows moist air to enter.   Sometimes
the wear and tear has appeared at the seam of an unsatisfactory
welding or in a faulty iron sheet but all these accidents are
not serious and can be readily repaired during operation.

In short, the satisfactory behaviour of ordinary steel
without protection is, in our process, much superior to that
of lead in the standard chamber system the average wear and
tear being less than 0.05 millimetres per annum.

The advantages of the use of this material as compared
with the first Kachkaroff installations erected in Italy are
as follows:-

(a) Much lower inital establishment costs;

(b) Considerable decrease in the consumption of
electricity and water for cooling purposes.

THEORY OF THE PROCESS

We have already described the theory of the Kachkaroff
process.   Kachkaroff is of the opinion that the reaction of
the formation of sulphuric acid occurs entirely during the
liquid phase and that it depends upon the absorption of SO_2
and of the separation of the NO formed, i.e., the diffusion
of the SO_2 and NO molecules separating the liquid and gaseous
phases across the intervening layer.

The formation of sulphuric acid in the liquid phase is
as follows:-

(I) $(SO_4. H (NO) H_2O)2 + SO_2 = 3 H_2SO_4 + 2 NO$

according to Kachkaroff, the compound of the first expression
is a hydrated nitrosyl sulphate of which the extended formula is

$$SO_2OH - N - N - SO_2 OH$$
$$OH \nearrow | \quad | \searrow OH$$
$$OH \quad O \quad O \quad OH$$
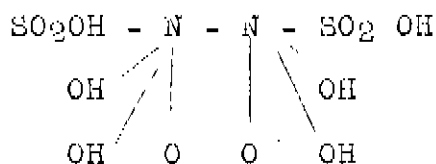
Reaction (I) is bi-molecular which is in accordance with
the laboratory work and the industrial results obtained by
Kachkaroff.   Hence is described the speed of reaction

$$\frac{dx}{dt} = K C_{N_2O_3} \times C_{SO_2} = K (a - x) (b - x)$$ which gives
on integrating

$$Kt = \frac{1}{a - b} L \frac{b(a - x)}{a(b - x)};$$ and as the nitrous
concentration of the acid is practically constant, it is
possible to write it as follows:

$$\frac{dx}{dt} = K\,a\,(b - x)$$ which gives on integrating

$$Kat = \frac{b}{b - x}$$

For the same volume of gas taken in, i.e. once the system has been established, the equation is

$$\frac{b}{b - x} = Ct_0, \text{ i.e. } \frac{C_{SO_2}\text{ Initial}}{C_{SO_2}\text{ final}} = Ct_0.$$

which means to say that

(1) the fraction of the absorbed SO_2 will be constant and independent of the initial SO_2 content.
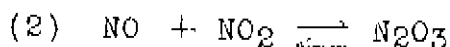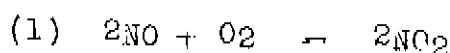
(2) the production capacity will be proportionate to this content.

As to the influence on the speed of reaction of the nitrous concentration of the acid which is practically a constant factor, Kachkaroff makes no distinction between the total nitrous content of the acid and that which is sometimes called active nitrous content (Ref. No.3) and which depends upon the degree of dissociation of the nitrosyl sulphuric acid. It is true that Kachkaroff introduces into his theory a new compound, an acid hydrated nitrosyl sulphate of which, unfortunately, we do not know the theoretical bases nor the marginal stability in more or less dilute sulphuric acid. In any case, the extended formula of this compound, as propounded by Kachkaroff, makes nitrogen appear as pentavalent which seems to us little probable.
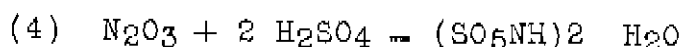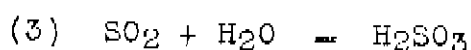
We have given to this theory a different form whilst maintaining the bi-molecular character of the fundamental reaction.

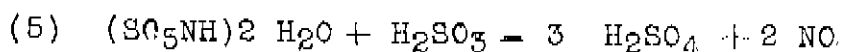The reactions which come into play are as follows:
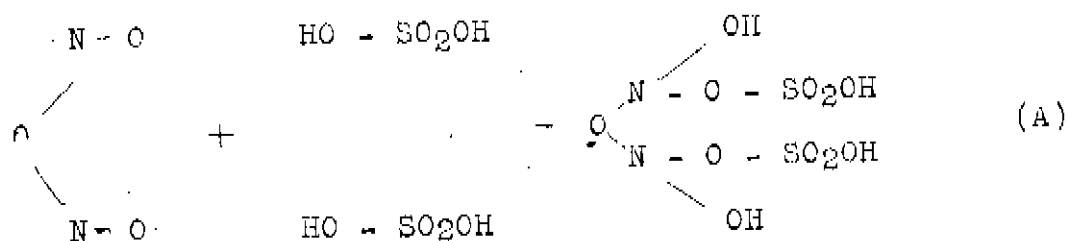
(a) In the gaseous phase:

(1) $2NO + O_2 \rightarrow 2NO_2$

(2) $NO + NO_2 \rightleftharpoons N_2O_3$

(b) In the intermediate layer

(3) $SO_2 + H_2O \rightarrow H_2SO_3$

(4) $N_2O_3 + 2 H_2SO_4 \rightarrow (SO_5NH)_2\ H_2O$

(c) In the liquid phase:

(5) $(SO_5NH)_2\ H_2O + H_2SO_3 \rightarrow 3\ H_2SO_4 + 2\ NO$

The hydrated nitrosyl sulphuric acid formed by reaction (4) is a product by the addition of sulphuric acid and nitrous anhydride.

$$
\begin{array}{ccc}
\text{N - O} & \text{HO - SO}_2\text{OH} & \\
\diagup & & \\
\Omega & \qquad + & \\
\diagdown & & \\
\text{N - O} & \text{HO - SO}_2\text{OH} &
\end{array}
\qquad
\begin{array}{c}
\qquad\qquad\text{OH} \\
\diagup \\
\text{N - O - SO}_2\text{OH} \\
- \text{O} \\
\text{N - O - SO}_2\text{OH} \\
\diagdown \\
\qquad\text{OH}
\end{array}
\qquad\text{(A)}
$$

this compound has a pronounced oxidising power and a certain stability which corresponds entirely to the acid employed in the Kachkaroff process according to the technique we have evolved and which establishes an optimum ratio between the density and the nitrous content of the circulation acid in the towers.

Contrary to what has been said in regard to the other intensive processes and as we have even confirmed, the speed of reaction in the Kachkaroff process is not proportional to the degree of dissociation of nitrosyl sulphuric acid SO_5NH measured by the nitrous tension of the supporting acid but to a certain factor which depends both on the density and nitrous content of the acid, i.e. on the content of the acid in active nitrose in a sufficiently stable form which, according to our ideas, corresponds to the compound (A).

The hydrolysis of nitrosyl sulphuric acid is expressed as follows:-

$$SO_5NH + H_2O \rightleftharpoons H_2SO_4 + HNO_2$$
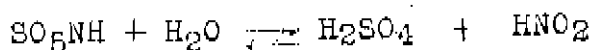
but the acid HNO_2 decomposes rapidly

$$2\ HNO_2 \rightarrow NO + NO_2 + H_2O$$
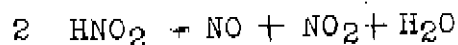
and in order to maintain an active nitrous content of the acid it is necessary for the nitrous concentration of the gases to be very high.   This, for example, is the case with the Petersen process (Ref. No. 3).

In our opinion hydrolysis of SO_5NH occurs in two stages:

(6) $2\ SO_5NH + H_2O \rightleftharpoons (SO_5NH)2\ H_2O$

(7) $(SO_5NH)2\ H_2O + H_2O \rightleftharpoons 2\ H_2SO_4 + 2\ HNO_2$
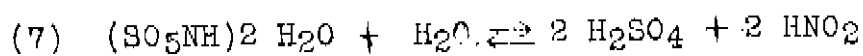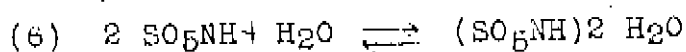
of which the first characterises our process.

The speed of oxidation of sulphurous acid, reaction (5) depends upon the degree of hydrolysis (6) but it is understood that hydrolysis cannot be completed without the appearance of the second stage (7) with partial denitration of the acid and an increase in the nitrous concentration of the gases.

Our technique consists, therefore, of maintaining the ratio between the density and nitrous content of the circulation acid within the theoretical limits of the hydrolysis (6) but with a sufficient margin to make the final regulation of the afore-mentioned ratio easy and to ensure a smooth running of the installation. (See figure 2).

If we consider the intermediary curve between the two limits which practically corresponds to the optimum degree of hydrolysis we are able to complete the Kachkaroff theory on the

influence of the nitrous content of the acid on the speed of oxidation of the sulphurous acid, the factor "active nitrous content" being represented in our process by the different points of the optimum curve.

In our process the influence of the temperature of the acid is somewhat small as it varies between rather narrow limites - 40° to 60° - Nevertheless every appreciable variation in temperature must be set off by an adequate variation in another factor - generally speaking, the water content of the acid is acted upon so that the degree of hydrolysis remains constant.

We have, therefore, the two essential factors of the oxidation speed of Sulphurous acid - SO2 concentration of the gases which determines within certain limits the concentration of the sulphurous acid in the liquid phase and the active nitrous content of the acid - which allows us to calculate the characteristics of an installation and the operating conditions for a given production.

The other factors which have to be taken into account serve in our process only to determine the characteristic parameter of each installation.

According to the form and dimensions of the reaction chambers the distribution of gases and rate and nature of packing and the manner of distributing the acid one arrives at obtaining a certain active contact as between the gases and the acid which allied to the total volume of the installation gives the factor of efficiency of the apparatus. This is how we have been able to attain a considerable reduction in the volume of the circulating acid for a given specific production by combining the partial packing of the chambers with the distribution of the acid in the form of a very fine mist as we have described above.

Nevertheless this factor or parameter remains constant for each installation and tends to become the characteristic of our process where the influence of purely chemical factors is essential.

Moreover, in regard to the reactions in the gaseous phase, the characteristic parameter of the installation plays a preponderant role. Although the mass of the nitrogen oxides circulated with the acid ensures to a high degree the oxidation of sulphurous acid it is indispensable to re-oxidise NO and to recuperate it as completely as possible before releasing the gas into the atmosphere.

We have already said that the simultaneous absorption of the sulphurous gas and nitrogen oxides was the essential characteristic of the K.M. process of which the intensive manufacture of sulphuric acid alone was a special case. In order to obtain this simultaneousness Kachkaroff has used sulphuric acids very rich in nitrosyl sulphuric acid but of such density that the nitrous tension of these acids is almost nil.

The application of his process made Kachkaroff see that it was necessary to utilise acids a little more dilute than he had envisaged and this in order to avoid abnormal reactions with loss of nitrogen oxide and to terminate as completely as possible the oxidation of SO2. Thus he had to add to the

first apparatus erected in Italy a small Gay Lussac tower following his reaction tower.

The studies and experiments wo have made in regard to the optimum ratio of density and nitrous content of the acid has led us to diminish still a little further the density of the acids with a given nitrous content and consequently to equip the installation with two small Gay Lussac towers in order to bring about a methodic recuperation of the nitrogen oxides contained in the residual gases.

It is known that the recuperation of the nitrogen oxides requires that the latter should be absorbed in the equimolecular proportion of NO - NO_2, an absorption which is almost quantitative.

In the lead chamber apparatus where the free volume is considerable the oxidation of NO to NO_2 at the end of the apparatus takes precedence over the oxidation of SO_2 in such a manner that under normal working conditions there is in the released gases a small proportion of SO_2 and there is also a slight excess of NO_2 which is not retained in the last Gay Lussac. On the other hand, in the K. process as in the other intensive processes, when the oxidation of SO_2 is almost complete the NO is still predominant over the NO_2.

As we have already said at the beginning of our paper, we have applied in the latest installation in France a combination of packing and atomising by improving upon the technique thanks to the obtaining of a very fine mist and the fact that the partial packing is arranged in such a manner that it can be penetrated by the atomised acid. Thus the simultaneous absorption of nitrogen oxides is accelerated by the uninterrupted presence of acid mist and gases arrive at the inlet of the first Gay Lussac with a nitrogen oxide content of less than 5 grammes of N_2O_3 per cubic metre.

In figure 3 it is possible to see, compared with the Petersen process, the curves representing the SO_2 content of the gases and of nitrogen oxides circulating in the apparatus.

When studying these curves it is possible to realise that these two processes are essentially different. It is the use of a circulation acid of a density invariably higher than 61° Bé, which may at times exceed 64° Bé, and a correlative nitrous content between 5 and 10% N_2O_3 which is the essential cause of this difference and which has permitted of the choice of a simple, economic and resistant apparatus which constitutes a fresh progress in the manufacture of sulphuric acid through the intermediary of nitrogen oxides.
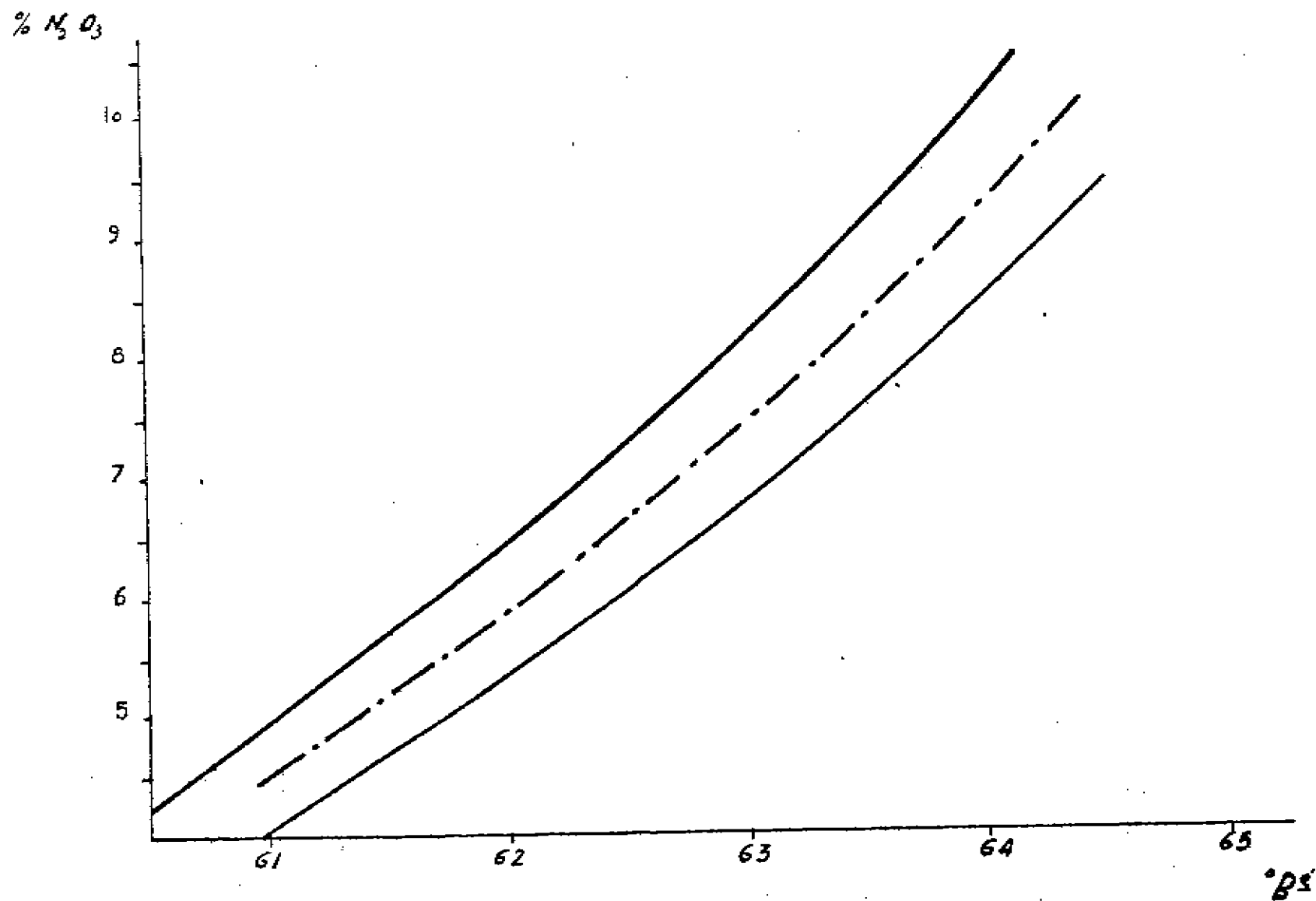
FIG. 1

PROCÉDÈ KACHKAROFF - SALSAS SERRA -

- Schéma géneral -
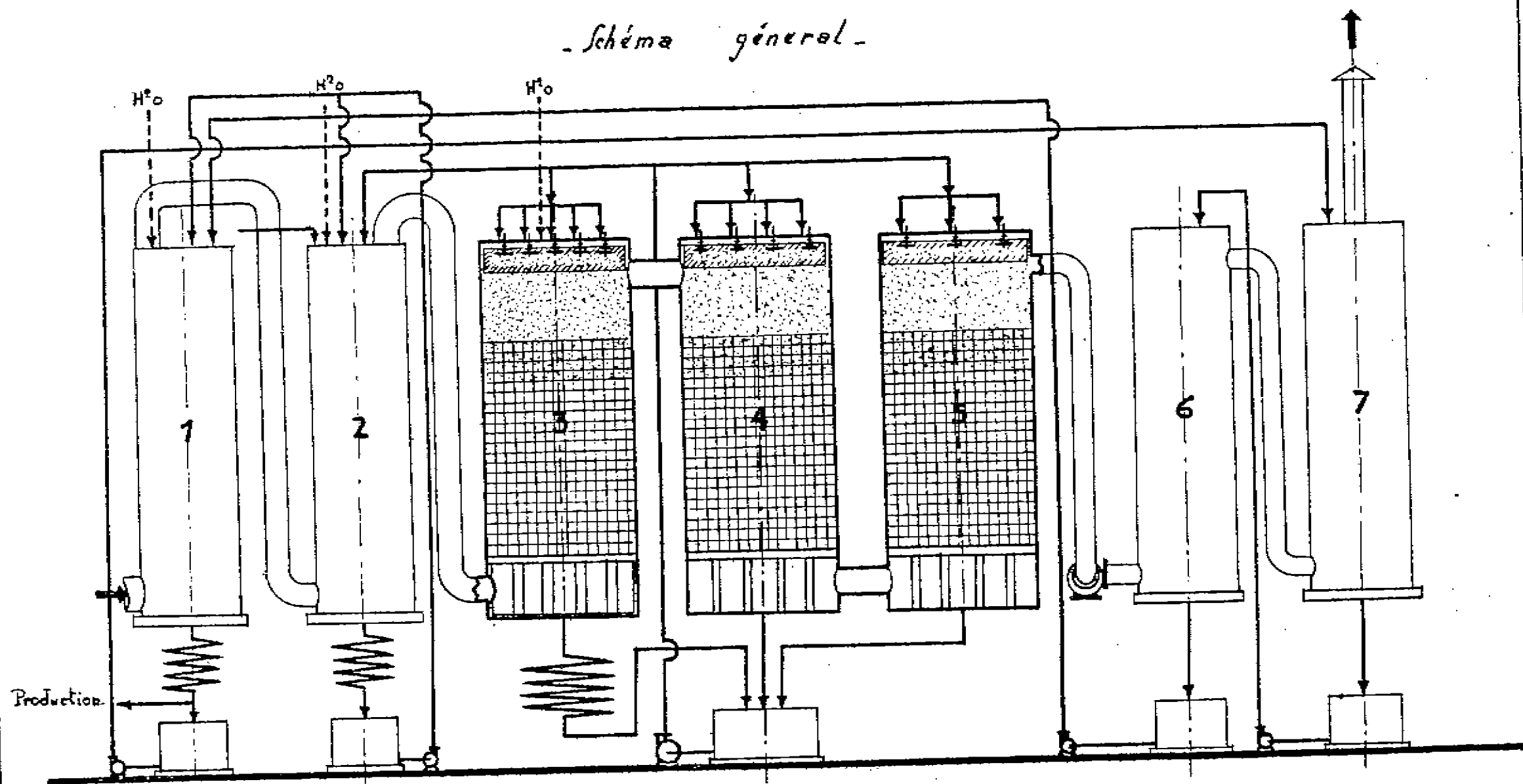
1 et 2 Tours de Glover - 3.4 et 5 Tours de reaction - 6 et 7 Tours de Gay Lussac.

FIG. 2.

_ PROCÉDÈ KACHKAROFF - SALSAS SERRA _

% N_2O_3

_ Rapport entre densité et nitrosité de l'acide _

Fig. 3 — Composition des gaz Procédés Petersen et Kachkaroff-Salras Serra.