

ISMA* Technical Meetings

Landskrona, Sweden
2-4 September 1947

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

On the acid-forming Reactions of the Lead-Chamber Process, bySven and Rolf Nordengren.

Up to now the theories of the lead chamber process have exercised a very small influence on the manufacture of sulphuric acid, which for about a century and a half has been allowed to continue as well as it could without the aid of a true scientific explanation of the main reactions of the process. Only in the last fifteen years, when the building of lead chambers had practically ceased, has some light been thrown on the process itself.

Even if a considerable amount of sulphuric acid is nowadays being produced in contact and tower plants, and no new chamber systems are being built, a still better understanding of the chamber processes would undoubtedly be of value. A very great number of chamber plants are still working in the superphosphate industry. The cheapest acid for this industry is now being obtained from modern tower plants but even for the development of such plants further investigations in the field of theory should be of great interest. There is, further, a certain demand for smaller and more compact units able to be erected without great costs, for it seems to be a waste of material that such huge buildings should be needed for such a small production of sulphuric acid, as say, 100 tons a day.

These are no new ideas. We need only refer to the Schmelde-Klencke process which, even if it made no ultimate progress, at least showed the possibility of a very high increase in production per cubic space.

There is another side to this problem. If the production per cubic metre could be considerably increased it would perhaps be possible to utilise wastegases with a low content of sulphur dioxide, at the same time obtaining the sulphur free of cost and cleansing the atmosphere of gases poisonous at least to trees and crops in the vicinity.

The safest way to progress in this direction seems to be the study of the most important reactions of the process, the acid-forming reactions. The intention of this paper is to point out certain facts, which have in no way been overlooked by the scientists recently, dealing with these problems, but which, nevertheless, seem to require still more attention.

The main reactions of the lead chamber process, as now known, can be concentrated in a table suggested by W. J. Müller (table I).

The reactions are divided according to the phase or phases in which they occur.

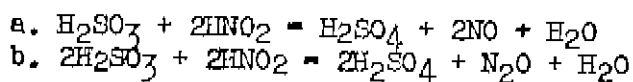
In the liquid phase we have the hydrolysis of the nitrosyl-sulphuric acid. Only its main reaction appears in the table. The nitrous acid, formed at the hydrolysis, will without fail be decomposed to a certain degree so that, dissolved in the liquid phase, all oxides of nitrogen and even a very small amount of nitric acid will be present although this content will be kept very low by reason of the nitrogen

oxide, NO, which is liberated in the liquid phase.

The second reaction of the liquid phase is the main acid-forming reaction of the lead chamber process. After absorption of SO₂ in the liquid gas phase (reaction III) sulphuric acid is formed in the liquid phase at a reaction in which act the product or products received from the hydrolysis of the nitrosylsulphuric acid,

Two questions have arisen with regard to this formula. The first is: Does the sulphur dioxide react as SO₂, or as sulphurous acid, H₂SO₃? It is known that a gaseous mixture of SO₂, N₂O₃ and water vapour does not react, or reacts only to a very slight degree, without a liquid phase. It has been believed therefore that the process must occur either at the interphase liquid gas or in the liquid phase. Even if the latter is far more probable it still leaves open the question whether SO₂ reacts in hydrated or unhydrated form.

The second question is: Does nitrous acid, HNO₂, itself, or one of its decomposition products, act as oxidizing agent? It is now generally believed, after the work of Abel and fellow workers, that the oxidation is done by the nitrous acid itself according to the following gross equations:



In a more concentrated sulphuric acid the reaction "a" will predominate. Abel has come to the conclusion that the primary process is as follows:



The radical HNO may either form NO with HNO₂ or react so that 2 radicals form N₂O.

There is, however, a third question which would especially interest a sulphuric acid expert in the industry. What gives rise to the chamber mist? Can this mist be due to the small quantities of sulphur trioxide and eventually to arsenic trioxide coming in with the gases from the burners? It seems improbable that the water, introduced into the chambers, even if finely sprinkled, would be able to form such a mist. This is where certain research work, done already about 25 years ago by Sven Nordengren, but hitherto unpublished, might be of some interest.

This investigation attempted to show how known quantities of NO₂(N₂O₄) and SO₂, respectively N₂O₃(NO + NO₂) and SO₂ would react in the presence of superfluous water. Sulphur dioxide, nitrogen monoxide and oxygen were produced in pure forms, carefully dried and then brought together in a glass pipette with valves at both ends, and the quantity was measured in such a way that there was a slight under-pressure in the pipette.

When the gases were mixed oxidation took place to NO₂(A, trials 1-6) or to N₂O₃(B, trials 7-13). The quantity of SO₂ was sufficient for a reduction to N₂O in both cases.

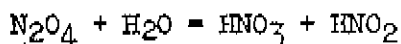
Except for a vivid colouring showing the oxidation process, nothing occurred, only a very small spot of crystals, apparently lead chamber crystals, appeared on the inside of the pipette. No mist whatever

was visible even if the pipette was left for 24 hours.

One end of the pipette was now placed below the surface of distilled water and the valve at this end was opened. The water entered rapidly into the pipette and rose to about $1/3$ of its length. Instantly the gas volume over the water surface was filled with a dense mist. This mist existed simultaneously with the colour. After a few seconds the colour faded and disappeared, but a white mist still remained. The mist was absorbed by the water leaving a colourless gas over a colourless liquid in the pipette.

The analysis of this liquid showed that sulphuric acid had been formed in both cases, considerably more, although not quite twice as much, in series A compared with series B. There was further found in the solution a quantity of un-oxidized SO_2 and nitrous acid, but very little nitric acid.

In the trials marked C (14 and 15) a quantity of nitric acid was introduced with the water in the pipette, corresponding to the amount that should have been formed if the N_2O_4 of the series A had reacted with water:



and a quantity N_2O_3 corresponding to the nitrous acid was formed as gas in the pipette. It will be seen that the production of sulphuric acid was reduced so far that only a small quantity of the nitric acid could have taken part in the reaction.

In the trial marked D(16) the mixture of nitrous gases corresponds to series A, but no SO_2 was introduced in the form of gas. A few drops of water were let into the pipette and brought to reaction with the gas mixture which corresponded, or nearly corresponded, to NO_2 . When this reaction had taken place more water was introduced in the pipette and in this water the same quantity of SO_2 was dissolved as was introduced in the form of gas in the series A. The result was a reduced production of sulphuric acid.

In the trial marked E(17) the pipette was filled only with NO and SO_2 and the same amount of nitric acid as in series C was introduced with the water. The production of sulphuric acid was very small.

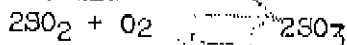
The trials F(18 and 19) show the result when a quantity N_2O_3 as in series B was made to react with a quantity of water until the colour disappeared, after which SO_2 was introduced as gas. This resulted in a reduced production of sulphuric acid.

The visible mist and the analyses of the different trials seem to support the interpretation that a considerable part, perhaps the main part, of the reaction takes place over the surface of the liquid, although sulphuric acid is, doubtless, also formed in the liquid itself. This will in no way contradict the opinion that the sulphuric acid is formed in a liquid phase if the mist is formed before the sulphuric acid is produced. It seems also probable that the reactions in the gas volume are the first to occur and that the oxidation process in the liquid mainly comes later. This would indicate that the first reduction of the nitrous compounds took place in the gas volume and that a further reduction followed afterwards in the solution.

Keeping to the series of trials and with no reference to the conditions in the lead chambers, this question can be raised: What is the origin of the mist?

There seem to be only two answers to this question:

Either, sulphuric acid is formed in the gas phase in a direct way from gas compounds, as indicated in the theory of Lunge, abandoned long ago, or, the primary mist must be caused by the small amount of SO_3 present according to the formula



The quantity of SO_3 present will indeed be very small but if, for instance, gases from a pyrites furnace are released and meet the moisture of the atmosphere the mist will be clearly seen. When the water streams into the pipette, part of it will rapidly evaporate saturating the atmosphere with water vapour; and SO_2 and water will form very small drops of sulphuric acid dispersed in the gas phase.

If this explanation be true the rest is easy. The drops will absorb more water vapour and take up SO_2 and nitrous compounds, and more sulphuric acid will be formed according to the formulae of table I. Part of the nitrous gases will react with the liquid itself mainly forming nitrous acid, because even if the composition was NO_2 from the beginning a quantity of NO will be formed during the oxidation process in the mist. At the reactions in the liquid, N_2O will partly be formed, as shown by Raschig long ago.

The results obtained by the trials in the pipette seem to be contradictory to certain experiments made by Sven Nordengren and published in the handbook by Lunge-Waesser on sulphuric acid. Nitrous gases, SO_2 and water vapour were mixed continuously in a glass chamber which could be kept at a fixed temperature. Above the boiling point of water no sulphuric acid was formed but, as soon as the temperature was lowered to about 100°C and water was being condensed on the walls of the glass chamber, the sulphuric acid process started. There might be a possibility that, as the gases went rapidly through the glass chamber, the small drops of sulphuric acid of molecular size had insufficient time to grow to visible size and, charged electrically, would not precipitate on the walls of the chamber.

Another objection could be raised on account of the investigations made by Szegő who has pointed out the large increase in the vapour tensions with the increasing curvature of small particles. Against this objection stand the practical results of the trials.

The question then arises if the experience gained at the trials can be said to represent the conditions in the lead chambers in such a way that conclusions can be drawn regarding the chamber process. There is one fact common to both cases: The mist, the existence of which in the lead chambers has received no reasonable explanation. An experiment was recently made to investigate whether the mist would appear if sulphuric acid of about 55°Bé was introduced into the pipette. The mist appeared even in this case although to a lesser degree. When water is sprinkled into a chamber, conditions will appear very similar to those in the glass pipette only the surrounding gases will be more diluted. Possibly each drop will be surrounded by an atmosphere in which still smaller drops of sulphuric acid containing nitrosylsulphuric acid will be dispersed. There are certain facts favouring this possibility besides the existence of the mist. If the drops were not protected by the mist, nitrous acid would be formed in the drops.

and a larger quantity of N_2O would be formed. If the formation of sulphuric acid depended on the surface of the original drops then the old method of introducing steam would possibly give a better result than if water were sprinkled into the chamber, as the condensed drops arising from the steam would be smaller and consequently have a larger total surface.

There seem to be certain grounds for the assumption that in lead chambers sulphuric acid is formed in two ways. Primarily SO_2 , present in very small quantities in the chambers, gives rise to small drops of sulphuric acid, and in this dispersed liquid phase, as well as on the chamber walls moistened by the mist, a secondary formation of sulphuric acid takes place. Although the quantity of sulphuric acid formed in the secondary way is, in quantity, the most important, the sulphuric acid formed primarily is indispensable to the whole process in the chambers. In tower systems the acid, primarily formed, is partly, although not totally, replaced by the circulating acids.

In the discussion following the reading of this paper the opinion was expressed that the chamber mist had probably only a very small significance in the chamber process; in the lead chambers the sulphuric acid was mainly formed at the walls. The authors of the paper were of a contrary opinion. They have asked permission to add the following paragraph to their paper:

"At the Landskrona plant a Peterson tower is placed after the chambers but before the Gay-Lussac towers. As the quantities of sulphuric acid and water going on to and leaving the tower are known and also the proportion between sulphuric acid and water in the mist immediately before the tower, the amount of sulphuric acid formed in the tower can be determined separately from the amount of mist condensed in the tower. At one time the total production of the system was determined as follows, (100% H_2SO_4 in 24 hours):

2 Glover towers	4,7 ton
Lead chambers	83,1 "
Petersen tower, production	25,3 "
" " condensed mist	13,4 "
	<hr/> 127,0 ton.

The large quantity of condensed mist in the Peterson tower clearly shows that a considerable part of the production in the chambers is due to the mist."

TABLE I.

Reaction phase	Type of reaction	Reaction equation	Place of reaction
Liquid	Hydrolysis	I- $\text{SO}_5 \text{NH} + \text{H}_2 \text{O} = \text{H}_2 \text{SO}_4 + \text{HNO}_2$	Glover, Chambers, production towers.
	Oxidation	II- $\text{H}_2 \text{SO}_3 + 2 \text{HNO}_2 = \text{H}_2 \text{SO}_4 + 2 \text{NO} + \text{H}_2 \text{O}$	
Liquid-gas	Absorption	III- $\text{SO}_2 + \text{H}_2 \text{O} = \text{H}_2 \text{SO}_3$	-
	-	IV- $\text{N}_2 \text{O}_3 + \text{H}_2 \text{O} = 2 \text{HNO}_2$	-
	-	V- $\text{N}_2 \text{O}_3 + 2 \text{H}_2 \text{SO}_4 = 2 \text{SO}_5 \text{NH} + \text{H}_2 \text{O}$	Gay-Lussac and partly Glover, chambers, production towers.
	Disabsorption	VI- $\text{NO}_{\text{sol}} = \text{NO}_{\text{gas}}$	Glover, chambers, production towers.
Gas	Oxidation	VII- $2\text{NO} + \text{O}_2 = 2 \text{NO}_2$	Everywhere in the system

TABLE II.

Trials	Gas quantities 0,760 mm				Introduced into the liquid		Found in the solution				
	Series	No	O2	NO	SO2	H NO3	SO2	H2 SO4	SO2	H NO2	HNO3
A		1	28,16	54,34	84,48	-	-	0.3231	0.0305	0.0240	-
		2	28,18	50,37	84,55	-	-	0.2918	0.0513	0.0271	-
		3	27,62	55,24	82,86	-	-	0.2542	0.0779	0.0424	0.009
		4	28,81	57,65	88,45	-	-	0.3060	0.0510	0.0260	-
		5	28,15	56,34	84,48	-	-	0.3039	0.0470	0.0185	-
		6	27,96	55,93	85,88	-	-	0.2806	0.0515	0.0205	-
B		7	14,07	56,28	84,43	-	-	0.1684	0.1231	0.0265	0.001
		8	14,07	56,26	84,43	-	-	0.1828	0.1234	0.0113	traces
		9	14,21	56,93	85,28	-	-	0.1741	0.1149	0.0199	-
		10	14,14	56,56	84,84	-	-	0.1705	0.1271	0.0131	-
		11	14,04	56,18	84,27	-	-	0.1838	0.1304	0.0103	-
		12	13,97	55,89	85,84	-	-	0.1716	0.1186	0.0203	-
		13	14,07	56,27	84,40	-	-	0.1933	0.1239	0.0075	-
C		14	7,00	27,98	84,05	-	-	0.1002	0.1704	0.0366	0.09
		15	7,00	27,98	84,05	-	-	0.1010	0.1528	0.0201	0.07
D		16	27,84	55,68	-	0.2611	0.1045	0.1340	0.0053	-	-
E		17	-	28,14	84,43	-	-	0.0160	0.2188	0.0173	-
F		18	14,07	56,23	84,43	-	-	0.1268	0.1635	-	-
		19	14,07	56,23	84,43	-	-	0.1353	0.1500	0.0206	0.009