

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).*

THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

AGRICULTURAL COMMITTEE

1, AVENUE FRANKLIN D. ROOSEVELT

PARIS (8^e)

TEL. BALZAC 57-25

SECRETARY,
R. M. COLLINS

CENTRAL OFFICE

32 OLD QUEEN STREET

LONDON, S.W.1.

TEL. WHITEHALL 7262

ARCHIVES

September 1951.

LE 264

TECHNICAL MEETINGS 1951

Paper No. 5.

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 It must not be published prior to that date and, in any case, it must not be published without the permission of the author.

PRODUCTION OF SULPHURIC ACID FROM HYDROGEN SULPHIDE BY A WET RECOVERY PROCESS.

by Dr. Schuringa, Albatros Superfosfaatfabrieken N.V.

(May, 1951.)

INTRODUCTION

During the technical meetings at Milan in 1949 we raised the question whether delegates had any experience in the production of sulphuric acid direct from hydrogen sulphide. The answer was negative.

Since then a study has been made of this possibility which resulted in the construction at the Albatros Works, Pernis of an installation with a production capacity of approximately 40 tons of 84% sulphuric acid from hydrogen sulphide on the wet contact principle. The hydrogen sulphide is supplied by the Shell refinery which is situated next to the Albatros factories.

It goes without saying that the world scarcity in elemental sulphur is also felt in the Netherlands, although the use of sulphur in the Netherlands is low in comparison with the United Kingdom, France and Belgium, owing to the fact that sulphuric acid is only produced from pyrites.

In 1950 imports of sulphur amounted to 3000 tons, whereas the total production of sulphuric acid (100%) amounted to approximately 450,000 tons. On the other hand, some 200,000 tons of 78% acid were imported from Belgium, mainly on behalf of the superphosphate industry. The latter requirements cannot be met at the present moment.

It will, therefore, be understood that a study was made of the possibilities of processing hydrogen sulphide, as derived from coal and oil, direct. Natural gas is found in the Netherlands, but it contains very little sulphur. Within our knowledge, the first contact plant based on H₂S was built at the El Segundo Refinery of Standard Oil in the United States in 1936. Since then, installations of various types have been constructed.

TECHNICAL POSSIBILITIES

Various methods are used for the removal of H₂S from coke oven gas or refinery gas; i.e. dry processes (hydrated iron oxide, activated carbon) and wet processes. The latter can be sub-divided into processes in which hydrogen sulphide is discarded, and processes with recovery of H₂S.

Without enlarging in detail on the various techniques we list below the processes most in use. The means of absorption are put in brackets:

1. Girbotol process (mono-, di-, or tri-ethanolamine)
2. Shell phosphate process (tri-potassium phosphate)
3. Alkazid process (a.o. sodiumalanine)
4. Phenolate process (sodium phenolate)
5. Vacuum carbonate process (sodium carbonate)
6. Also used is the Thylox process in which sulphur as such is recovered. A neutral solution of a sodium thioarsenate is used. The absorbed hydrogen sulphide is oxidized by bubbling air through the solution. The oxidation is catalyzed by the arsenic compounds. Sulphur as produced by this process is not suitable for the production of sulphuric acid because of its impurity and its high percentage of arsenic.

It is possible to produce sulphuric acid in various ways from concentrated hydrogen sulphide. The oldest method used is the roundabout way via sulphur. In the original Claus process hydrogen sulphide is passed over iron oxide or bauxite with half the molecular quantity of oxygen. In more modern installations half of the H_2S is burnt to SO_2 . H_2S plus SO_2 in molecular proportion 2 : 1, yield sulphur when passed over bauxite.

Should one wish to avoid this roundabout production via sulphur three other processes are possible. In burning hydrogen sulphide an equivalent quantity of water is formed. Should it be desired to produce a 98% acid this water should be removed by cooling towers before the gas is oxidized in the normal way, but in that case preheating of the gas before it reaches the converter is necessary. In case 80 - 82% sulphuric acid is strong enough, the apparatus may be greatly simplified as the washing and cooling of the combustion gas is no longer required. The drawback in this process is the cooling tower, as under direct condensation the dreaded persistent acid mists are created. This difficulty can be overcome by placing electric mist precipitators behind the condensation towers.

Finally, it is possible to use a normal chamber or tower plant for the conversion of combustion gases from H_2S .

TECHNICAL AND ECONOMICAL ASPECTS

In deciding what method of processing sulphuric acid from hydrogen sulphide should be preferred in certain cases, the following factors must be considered:

- (1) Distance between hydrogen sulphide source and sulphuric acid processing plant.

Especially in the oil industry it will frequently occur that the location of the refineries is a long distance away from the sulphuric acid processing plant - at any rate if the percentage of sulphur in the crudes is so high that the production of sulphuric acid exceeds the refineries' requirements. As a rule, in such cases sulphur will be produced despite the unfavourable output of the Claus system. Often sulphur has to be removed at the wells to prevent corrosion of the crude oil pipelines. The production of sulphur also offers certain advantages in case the production of H_2S is not continuous; sulphur can be stocked, whereas no stocks can be made of H_2S . It is undesirable to stop production of a sulphuric acid factory that processes directly from hydrogen sulphide.

- (2) The desired acid strength.

If an acid stronger than 80% has to be produced, wet recovery and chamber systems are of no use. Is the processing of

sulphuric acid carried out locally and the hydrogen sulphide production of a continuous nature, the cheapest method would be the one of direct combustion followed by washing/cooling chambers. The Netherlands State Mines have constructed a 98% acid plant with an annual production capacity of 20,000 tons for the processing of hydrogen sulphide from coke oven gas.

If an acid of approx. 80% suffices - which is generally the case as far as the superphosphate industry is concerned - either a wet recovery process or a tower system with direct combustion will be used.

(3) Installations' output.

Older Claus systems guarantee a sulphur recovery of approx. 85%, whereas the more modern Claus methods guarantee a 90-92% sulphur recovery. The output of the various types of contact installations using hydrogen sulphide is almost equal to that of an ordinary contact installation that processes from sulphur, i.e. approx. 97%

(4) Steam production.

It is interesting to compare the steam productions of the various systems. Per ton of manufactured monohydrate this amounts to:

1,5 ton	from:	flash roasting pyrites
0,9 ton	"	sulphur
1,3 ton	"	H ₂ S

Interest and depreciation of higher investments required for monohydrate installations, built to process from H₂S rather than from sulphur, are largely compensated by the higher production of steam. A major percentage of the steam obtained by flashroasting is known to be compensated by the considerably higher investments and the cost of power for grinding.

In using the European Claus system 2 tons of steam are obtained per one ton sulphur; the American system (Girdler Corporation Process) guarantees a production of one ton of steam to one ton of sulphur produced.

(5) Investments

We are roughly stating the proportions of the investments for the various systems. Taking a basic investment of 100 for a factory processing from sulphur, investment for a wet contact installation processing from H₂S should be 110, and for a dry contact installation (98% acid) 120. If one prefers a Claus installation, total investment should be 140. Calculations are based on equal production.

A comparison with chamber systems is more complicated as proportions fluctuate according to the magnitude of production. For a small production capacity (up to 15,000 tons per annum of 80% acid) investment should be 115; for a larger production capacity (50,000 tons per annum of 80% acid) it should be 100.

SHORT DESCRIPTION OF THE ALBATROS PLANT

Transport of Gas

The Shell Works concentrate the H₂S from refinery gas according to the Shell process (potassium phosphate). The gas is, under pressure, led to the Albatros plant through pipe lines over a distance of approx. 1500 metres.

The fact that H₂S is highly poisonous together with the fact that part of the pipe line passes over public grounds,

has given rise to deliberations as to whether these pipe lines should be constructed above or below ground. In the end a double walled pipe was constructed underground in sloping position and fitted with a special apparatus for drainage of any water of condensation.

An extensive number of safety measures has been provided in the entire plant. If in certain circumstances no more gas could be drawn off, the gas would automatically be pressed back to the furnaces of the refinery.

Burner and Heat-Exchanger.

The burner is a sheet iron oven, lined with firebricks. As a safety measure, explosion valves have been constructed. The combustion is started by oil ignition. The combustion gases are cooled in a heat-exchanger. Per one ton of 78% sulphuric acid one ton of steam (18 atmospheres) is obtained.

Converter.

Before entering the contact furnace, which is of the normal shelves system, the gas is cooled by pre-heated air in order to prevent condensation. In the converter the same precautions are taken. Contact mass of the Vanadium type is used.

Absorption system.

After conversion of the gases they are led to a steel absorption tower. The tower is lined with acid-proof bricks and has "acidur" stoneware filling. The tower is sprayed with part of the acid produced. Maximum strength of the acid produced is 86%.

The problem of the acid mist which, once formed, cannot be removed by wet absorption, is solved by a wet Cottrell precipitator which is placed behind the absorption tower. Between absorption tower and wet Cottrell a humidifier is provided for.

The grounded electrodes are rows of vertical plates. The high tension is generated by a new type of generator as developed in Germany on a semi-conductor rectifier basis, with a power of 7,8 KVA.

The efficiency of the electrical treater is approx. 100%. No sulphur trioxide is lost through the stack.

Costs of Production.

The installation is operated by one man only. The chief of the chamber plant supervises operations.

Costs of production are practically met by the value of steam produced, which is put at 15/- per one ton of steam.

According to Dutch standards, production costs, excluding interest and depreciation, amount to about 14/- per ton acid produced.

Engineering

The installation was constructed by Chemiebau, Niedermarsberg.