

quantity of nitrogen was also recovered, and used before the war approximately equally for purging and for  $\text{NH}_3$  synthesis: during the war a drop in  $\text{NH}_3$  output caused less  $\text{N}_2$  to be used for the latter purpose; the maximum capacity of pure  $\text{N}_2$  was 32 to 36,000  $\text{M}^3/\text{hour}$ , limited to that obtainable from four units.

The energy consumption varied from 0.5 to 0.6  $\text{KWH}/\text{M}^3$  oxygen, averaging about 0.55  $\text{KWH}/\text{M}^3$  100% oxygen. With the cost of power at 1.1 to 1.2 pfg/ $\text{KWH}$ , the cost of oxygen was said to be 1.6 to 2.0 pfg/ $\text{M}^3$ ; a separate set of figures were given, stating this cost to be made up of 60% power (the above figures give only 41% at most), 30% amortisation and 10% labour, repairs, etc.

A small quantity of krypton was also made as a by-product. The capacity was about 30  $\text{M}^3/\text{month}$ , containing about 75% krypton, with the impurities mainly oxygen.

#### Documents in Connection with Gas Production

The following documents give additional information:

- (1) Drawings of the Winkler generator, which had been deposited at Bottendorf, were taken by the U. S. Navy team.
- (2) Files relating to the Winkler plant were collected by Mr. Hopton from engineer Sauer's office and placed with the official documents.
- (3) Leuna report 837, entitled "10 Jahre Sauerstoff-Vergasung in Leuna" by Sabel, dated 15.9.42, was arranged by Dr. Morley to be sent to London through the Military Governor of Merseburg.
- (4) Leuna report 916, entitled "Jahresbericht der Stickstoff und Sauerstoff - Fabrik und Nebenbetriebe 1938-42" by Koppe, dated May 1944, was arranged by Dr. Morley to be sent to London through the Military Governor of Merseburg.
- (5) A drawing of the slagging producer was obtained by Mr. Ellis and placed with the official documents.

#### $\text{H}_2\text{S}$ Removal

Two methods were used: an Alkacid process, purifying Winkler gas and the old active carbon process, purifying Pintsch-Brassert generator gas and some half-purified Winkler gas.

#### Alkacid Process

Winkler gas contained 15 to 20  $\text{g}/\text{M}^3$  S (or 1 to 1.5%  $\text{H}_2\text{S}$ ); it was purified by alkacid in two stages: after the coarse purification it contained 2  $\text{g}/\text{M}^3$  S and after the fine purification it contained 150  $\text{mg}/\text{M}^3$  S.

The liquor normally used was a solution of sodium glyccoll,  $\text{NH}_2\text{CH}_2\text{COONa}$ , of S. G. 1.17, containing 200 g/l, calculated as  $\text{Na}_2\text{CO}_3$  or 45 g/l calculated as nitrogen (these two figures indicate the presence of some  $\text{Na}_2\text{CO}_3$  as such). It was a selective solvent for  $\text{H}_2\text{S}$ , so that for example with a gas containing 20%  $\text{CO}_2$  and 2%  $\text{H}_2\text{S}$  it would remove nearly all the  $\text{H}_2\text{S}$  but only about 2%  $\text{CO}_2$ . The absorbers of the coarse purification each had a diameter of 3 m for a gas rate of 20,000  $\text{M}^3/\text{hour}$ , and contained 7 to 9 bubble-cap trays. The gas/ circulating liquor ratio was 500 in hot weather, rising to 1,500 in cold weather. In the regenerators direct steam and indirect steam were both used, the steam consumption being 80 kgs/ $\text{M}^3$  liquor in the coarse purification and 150 kg/ $\text{M}^3$  liquor in the fine purification. The mixture of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and steam leaving the regenerator was condensed at  $50^\circ$  to  $60^\circ$  C, to reduce the  $\text{H}_2\text{S}$  content of the condensate, and the  $\text{H}_2\text{S}$  was finally burnt in a Claus kiln; the recovered sulphur was eventually used to make  $\text{H}_2\text{SO}_4$ .

Iron was used for the cold parts of the Alkacid plant, brick-lined iron for the regenerator, aluminium for the indirect heater and hot pipes, and an aluminium-silicon alloy, called Silumin or Alpax, for the pumps. No appreciable corrosion was experienced at Leuna.

An alternative solvent was sodium alanine,  $\text{CH}_3\text{CH}(\text{NH}_2)\text{COONa}$ , but this also dissolved  $\text{CO}_2$ ; it was used at Leuna only for purification of tail gases from hydrogenation. This liquor could be used for  $\text{CO}_2$  removal when its capacity (in the same concentration as used for glyccoll) was 25  $\text{M}^3$  liquor, the steam consumption being 120 kg/ $\text{M}^3$  liquor; over 95% removal of  $\text{CO}_2$  was possible.

#### Active Carbon Process

The whole of the Pintsch-Brassert water gas, containing 3 to 4 g/ $\text{M}^3$  S, together with a varying fraction of Winkler gas, was purified down to 1 to 2 mg/ $\text{H}_2\text{S}/\text{M}^3$  in the active carbon process, which had been in use for 20 years. Raw Winkler gas could not be used in this process because its high sulphur content caused excessive temperature rise.

The carbon was prepared from brown coal carbonised at  $900^\circ$  C and then steamed. Air or oxygen was added to the inlet gas, so that in effect  $\text{H}_2\text{S}$  was oxidized to sulphur, which was left on the charcoal;  $\text{NH}_3$  was also added to the gas to act as catalyst. After passing gas for about 10 days the sulphur was extracted with ammonium sulphide solution at  $40^\circ$  in the absence of air. The polysulphide solution was then distilled at 2 ats, with a top temperature of  $111^\circ$  C; the vapours were condensed and used again, whilst molten sulphur and water separated into two layers at the bottom of the still and were run off separately. It was stated that the still effluent was not obnoxious.

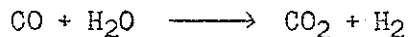
This process apparently was widely used in Upper Silesian plants: it was, however, unsuccessful on coal gas at Huls, because of gum-forming compounds.

### Organic Sulphur

Gas after H<sub>2</sub>S removal contained 250 mg. organic sulphur/M<sup>3</sup>. This was converted to H<sub>2</sub>S in the CO conversion plant, and this H<sub>2</sub>S was almost completely removed during the removal of CO<sub>2</sub> and CO.

### CO Conversion

The plant in which the water gas shift reaction was carried out was seen but not inspected in detail.



It was an old plant, working at atmospheric pressure. The development work on this process has been done at Oppau and an account is given in the report on that target. Converted gas for NH<sub>3</sub> and H<sub>2</sub> contained 3 to 4% CO, whilst converted gas for methanol contained 30% CO. The catalyst was Fe<sub>2</sub>O<sub>3</sub> with 6 to 7% Cr<sub>2</sub>O<sub>3</sub>.

II. AMMONIA SYNTHESIS

This section was not discussed in much detail, as the plant was old and largely out-of-date. A much better knowledge of I. G.'s latest ideas could be obtained from a visit to the  $\text{NH}_3$  synthesis plant of the Ostmarkische Stickstoff Werke at Linz, Austria, or at least from a study of the designs and drawings, which were carried out by Oppau; the plant at Linz commenced operation in 1940.

General

The gases received were catalysed gas i.e. water gas, which had been subjected to CO conversion with steam over brown oxide; part of the gas, ex Winkler and water gas generators, had low  $\text{N}_2$  and CO, and eventually went as  $\text{H}_2$  mostly to hydrogenation; another part had low  $\text{N}_2$  but higher CO and eventually went to synthesis of methanol and iso-butanol; a third part, ex water gas generators, had high  $\text{N}_2$  and low CO, and eventually went to  $\text{NH}_3$  synthesis. It was possible to compress and purify these three gases in three parallel streams, but it was also possible under certain conditions to unite the gases for  $\text{NH}_3$  and  $\text{H}_2$  into one stream of low  $\text{N}_2$ , the necessary  $\text{N}_2$  being added to  $\text{NH}_3$  synthesis gas after compression and purification had been completed; such  $\text{N}_2$  came from the Linde-Frankl oxygen plant.

Staff Interviewed

Dr. Paul Koppe, chemist in charge of H.P. Division, and Dipl. Ing Martin Rabes,  $\text{NH}_3$  synthesis and  $\text{O}_2$  plant engineer, were interviewed on May 12th and Dr. Koppe alone on May 16th.

Compression

The compressors were contained in at least five buildings. They were 5-stage horizontal machines, some of old design; they were driven by steam gas engines and electricity and had capacities respectively of 3,300, 10,000 and 15,000  $\text{M}^3$ /hour catalysed gas and the total installed capacity was 660,000  $\text{M}^3$ /hour, although the maximum rate used was about 550,000  $\text{M}^3$ /hour. A complete list of machines was obtained by U. S. S. B. S. The first three stages of compression brought the gas up to 25 ats. at which pressure  $\text{CO}_2$  was removed by water washing. The last two stages brought the gas to the final pressure of 250 ats: the original plant design pressure of 200 ats. had been raised as the result of revision of ratio of test pressure/working pressure. Additional compressors were used to compress part of the gas to 25 ats. to cover the gas removed in  $\text{CO}_2$  removal.

It was stated that no oil emulsion trouble was experienced in the CO Removal Plant at Leuna and, therefore, a particular point was made to interrogate the compression plant engineers - Ober Ing Gleitz and Ober Ing. Weissenfels on the subject of lubrication.

Superheated steam oil of 320° C Flash point, 50-55° Engler viscosity at 50° C and 0.01-0.02% asphalt content is fed to the steam cylinders of the main steam engines. These machines take steam at 15 ats. and 320° C and discharge either to the LP steam system or to condensers. Oil is

extracted from the steam before it reaches the condensers and is heated to 90°C and cleaned and dewatered in a centrifuge. The cleaned oil is mixed with a machine oil of 3° Engler viscosity at 50°C and is used as make-up oil to the compressors. It has a flash point of 230°C, a 50°C Engler viscosity of 22-30° and a 100°C Engler viscosity of 3-4°. This latter property is considered to be particularly important.

A compressor of 16,000 M<sup>3</sup>/hour capacity uses about 2.2 kgs/hour of lube oil.

There is a catchpot of 500 mm diameter and 4 M long immediately after each compressor and this is blown every two hours. At the inlet to the CO Removal Plant there is a further catchpot 600 mm diameter and 10 M long for each 100,000 M<sup>3</sup>/hour of gas for collection of oil and condensate.

In order to avoid condensation gases are never allowed to cool below 30°C. In the third stage of compression, gas temperature may be as high as 48-50°C. Piston rings are made of material in the pearlitic state with long graphitic inclusions to hold the oil to the surface of the ring.

The Leuna engineers gave the following general data on lube oil consumption in compressors:

TABLE 1A.

<u>Pressure</u>  ats.	<u>Lube Oil Consumption</u> grms/1000 M <sup>2</sup> swept surface of	
	(a) <u>cylinder</u>	(b) <u>piston rod</u>
2.5	1.9	7.0
11.0	3.25	10.0
28	7	17.5
70	20	25.0
170	20	-
250	20	-

### CO<sub>2</sub> Removal

The largest absorption towers were 2.4 m. I.D., but there were 60 to 70 old ones of 1.4 m. I. D. They were packed with ceramic rings; Leuna had never tried bubble plates. A rose-type distributor was used and with a constant water-rate there was no trouble with mal-distributions; they had tried re-distributing water half-way down the tower, but this had brought no advantage. There was no chlorination of circulating water and no trouble with algae. The exit gas contained 1.5% CO<sub>2</sub>.

Water from the towers was let-down in one stage through Pelton wheels. The let-down gas contained 93% CO<sub>2</sub>. Part of this was used as an inert gas and part in the ammonium sulphate plant, the rest being blown to atmosphere. No urea was made at Leuna and only a little dry ice, and this only for internal use: no dry ice could be sold, because of the difficulty in eliminating the smell, said to arise from organic sulphur compounds originating in the Winkler generators.

I.C. 7370

The let-down water was used for gas-cooling at the CO conversion plant before being sent for regeneration. This was done to eliminate O<sub>2</sub> from catalysed gas, which in the presence of H<sub>2</sub>S and H<sub>2</sub>O was said to cause corrosion in the gas compressors. This system had been used for 15 years, with no corrosion.

#### CO Removal

This plant used copper liquor at 250 ats. The liquor contained only carbonate, with no formate (last used 1925). It was regenerated at a maximum temperature of 40°C, using a vacuum in two stages, ending at 160- to 200 mms. Hg. absolute pressure.

They had not used refrigeration of the liquor, as cooling below 5°C caused deposition of ammonium carbonate. No vapour pressure curves were available.

There was no difficulty in controlling the cuprous/ cupric ratio. An automatic measurement of cupric, depending on the colour, was used.

There was said to be no difficulty with sludge deposition of any sort. Dr. Koppe ascribed this to the low temperature of regeneration. The oil separators on the 5th stage delivery of the compressors were very simple but were said to be very effective; they consisted merely of a pipe dipping into a forging, with the gas outlet at the top.

Let-down engines for power recovery from copper liquor were used, but only old-type machines were seen.

#### Final NH<sub>3</sub> Make-Up Gas Purification

Gas leaving the CO removal plant was washed with NH<sub>3</sub> liquor, to reduce the CO<sub>2</sub> content from 0.04% to <1 mg/M<sup>3</sup>. Active charcoal (to remove organic sulphur poisons) had never been used.

#### NH<sub>3</sub> Synthesis

The capacity was originally 1200 T/D NH<sub>3</sub>, but according to I. G. staff, even after extensive repairs lasting 10 months, only 1000 T/D NH<sub>3</sub> could be made in the future.

The gas circulating system was conventional. Exit gas from the converter was cooled first in a water cooler and then in a cold exchanger before entering a condenser refrigerated by evaporation of liquid ammonia. Liquid NH<sub>3</sub> was condensed out of the gas and unconverted gases returned to the converter via the cold exchanger and a circulator. Liquid NH<sub>3</sub> was let down from a catchpot after the refrigerated condenser. If ammonia gas could be used as such, part of the make of liquid ammonia was used for refrigeration purposes; otherwise the NH<sub>3</sub> gas from the refrigerator was re-liquefied and returned to the refrigerator system. Under the former method of working, the yields of gaseous and liquid NH<sub>3</sub> were approximately equal, averaged over the year. Make-up gas entered the circulating system at a point between the converters and water-coolers; this gave a minimum water content in the gas returned to the converter.

The plant was arranged as a number of separate gas circulating systems. The first system consisted of a number of units in parallel, each taking make-up gas containing 1% Argon +  $\text{CH}_4$ ; the circulating gas in this system contained 4 to 6% Argon +  $\text{CH}_4$  and the  $\text{NH}_3$  content of the gas rose from 3-4% to 8-10% during passage through the converters. Purge gas from this system was used as make-up to another system working with circulating gas containing more impurities. In turn, purge gas from this system was used as make-up for the next, and this procedure was repeated until, in the final system, the inert content of the circulating gas was some 20-30%.

### Circulator

A point of interest was use of a centrifugal circulator at Leuna, drawings of which were obtained. It was stated that at the Ammonia plant at Linz this type of circulator had been adopted throughout. It was reported that this circulator ran perfectly satisfactorily with a routine dismantling every 3 months for examination of bearings.

The machine is an ordinary electric driven centrifugal pump totally enclosed in a high pressure vessel in a way similar to that used in the oil industry for dealing with hot-oil pumps. The difference is that the electric motor is also enclosed. This means that there is no gland problem but there is instead a bearing lubrication problem, which is said to be much easier to overcome. For a capacity of 80,000  $\text{M}^3/\text{hr}$ , the forging containing the circulator is about 14 feet long and about 2 feet internal diameter. The machine was built so that, if the pump did not have the required performance, the number of stages could be increased. The use of such a pump for the circulation of gas on hydrogenation plants was not considered practicable because of the great difficulties of ensuring the proper lubrication of the bearings in the presence of hydrocarbon vapours.

### Catalyst

This was the usual iron-type catalyst, promoted with alumina and potassia and sometimes a little lime. Preparation was as follows: 19 kgs of small pieces of Swedish iron (or sometimes charcoal iron during the war) were placed in a shallow water-cooled iron pan, 50 cm diameter and 15 cm deep. Pure oxygen was then played on it after ignition by a "Zundkirsche"; after 10 minutes 1 kg of the promoter was added to the now molten mass and the oxidation completed in another 20 minutes. The mass was poured on to an iron pan and allowed to cool, when it was broken up and screened. Material between 5 and 12 mms was used in the converters, whilst the fines were remelted.

The promoter was made by dissolving 16 kgs pure  $\text{Al}_2\text{O}_3$  and 4 kgs  $\text{KNO}_3$  in 2 litres 60° Baume  $\text{HNO}_3$  and 2 to 4 litres water; this was boiled and cooled to a solidified cake. Sometimes a little lime was also added.

The final catalyst had the composition; 97%  $\text{Fe}_3\text{O}_4$ , 2.5%  $\text{Al}_2\text{O}_3$ , 0.16% S and 0.03% C, with a bulk density of 2.0. No sample was obtained.

It was said that this was the same recipe as for the so-called Mittasche catalyst, except that the latter contained more lime; the Mittasche catalyst was better for water-containing gases, but the I. G. catalyst was to be preferred for the dry gases used at Leuna. The same catalyst was used at Leuna for the SYNOL process.

Catalyst removed from the converters was re-fused in an electric furnace and was said to be as good as the new catalyst.

About 30 T/D N ( $\approx 36$  T/D  $\text{NH}_3$ ) was made per converter, containing 6 T catalyst. The normal life was about one year if purge gas from methanol and iso-butanol entered the system, even with a guard converter; thus about 2000 T  $\text{NH}_3$  were obtained per T catalyst. With no methanol purge gas longer life was obtained.

The poisons in methanol purge gas were said to be oxygen-containing substances, such as  $\text{CH}_3\text{OH}$  and  $\text{R}_2\text{O}$ . The sulphur content of make-up gas was said to be  $< 0.1$  mg S/ $\text{M}^3$ .

#### Converters

Converter design had by no means reached finality, and both Leuna and Oppau had tried out a number of designs.

The normal design used at Leuna was as follows. An internal interchanger was fitted under the catalyst, contained in tubes, touching one another for good heat transfer, and narrowed down at the bottom, for fitting into a tube plate. The incoming gas passed up over the outside of the interchanger tubes and over the outside of the catalyst tubes, cooling the catalyst and so maintaining a more favourable temperature gradient; the gas then passed down through the catalyst and then through the interchanger tubes.

In another type which had been tried the catalyst was cooled, not by being placed in tubes, but by placing tubes in the catalyst bed. The cooling gas passed through these tubes, which were either in the form of hairpins passing up and down the catalyst, or in the form of tubes carrying a central leg, up which passed the gas after carrying out the cooling in passing down the annulus.

More fundamental changes in design had been carried out at Oppau: they had built one or two "stalls", both with internal and with external interchangers, but Dr. Koppe said they had encountered constructional difficulties; such converters had inter-tray cooling with cold gas, as in a hydrogenation stall.

Leuna had not carried out any fundamental research on catalysts or on the kinetics of reaction: this had all been done at Oppau.