# I GAS PRODUCTION

The interrogation of Dr. Sebel (Engineer in charge of gas production) and Dr. Jeltsch (Chemist in charge of $H_2S$ removal) was carried out by Hollings, Weir, Odell and Hopton on April 22nd and 23rd, 1945. Additional information was obtained by C.A.F.T. about the same time and by Ellis and Morley on May 16th. Newman interrogated Oberingenieur Ohler, Dr. Schroeter, Dipl. Ing. Stingl and Obermeister Heuer on May 14th and 15th, 1945, in regard to the detailed operation of the slagging gas producers (abstichgeneratoren).

## Gas Production

Water gas for $NH_3$ and methanol synthesis and for $H_2$ production was made in three distinct ways. The bulk was still made on water gas generators, of the usual design, working a cycle and using oven coke, and the rest was divided between Winkler generators, using $O_2$ and grude coke, and slagging producers, using $O_2$ and oven coke, or Rohschlacke (refuse from the Brassert generators). A rough summary of the plant can be seen in the following table:

| Type | No. of Units | Unit Capacity M3/hr Gas | Normal Output from Plant M3/hr. H2+CO |
|---|---|---|---|
| "Pintsch-Drehrost"<br>"Pintsch-Brassert" | 10 | 5,000 )<br>10-12,000?) | 240,000 |
| Winkler | 1<br>4 | 40,000 )<br>80,000 ) | 55,000 (Limited by<br>(oxygen available;<br>(a second Winkler<br>(ran to make<br>(producer gas for<br>(power. |
| Slagging producers | 6 | 15,000(coke)<br>8,200<br>(Rohschlacke) | ?<br>30,000 |
| Pintsch producers | 10 | ? | Not used |

## Water Gas Generators

The original generators were of an old Humphreys and Glasgow design built by Pintsch (now referred to as "Drehrost-generatoren"), but most of them had been modified by Brassert (now referred to as Pintsch-Brassert-Generatoren). Very little attention was paid to this plant, as it was old and contained little novel. Only a few of the generators were seen, and as a number of changes had been carried out on various generators it was difficult in the short time available to get any clear idea of how many generators included each modification or indeed what was the effect of each modification. The following notes are therefore very incomplete.

All generators had concentric ring rotary grates, but whilst some were brick-lined others had jacket boilers. They had an I.D. of 3 m, so that the stated output of 10,000 to 12,000 $M^3$/hour must be considered very high and possibly in error. They were enabled to achieve high outputs without clinker troubles by extracting ash with a high coke content (50% C), the theory being that troublesome clinker could not form if ash were not allowed to accumulate in high concentration; the carbon in ashes was not lost, as it was used on the slagging producers. At least some of the generators actually in use were hand-operated.

The fuel used was oven coke, made from bituminous coal, and brought by rail from the Ruhr, a distance of 275 miles. The daily consumption of coke was 3,000 T/D.

We were told that until very recently the Winkler generators, using oxygen and local brown coal or grude coke, were more expensive to run than the coke water gas generators, despite the high cost of coke after its long haul and this had been the reason for the continued existence of the old method of gas manufacture. Only in the last years of the war, apparently, had the cost of Ruhr coke become high enough to make the Winkler generator cheaper to run. We do not know how far these arguments include considerations of the high capital cost needed for a new plant, remembering the old generators were in existence.

Winkler Generators (Site 279 on Works plan)

These generators were built in 1929-31 and since then have been subjected only to minor modifications. Since more modern installations were seen elsewhere (e.g. Zeitz) the plant was not covered in much detail. They have been used to gasify both dried brown coal and "grude" coke (brown coal low temperature coke), and have been used for the manufacture of power gas, producer gas for $NH_3$ synthesis and water gas. In recent years the fuel has been almost entirely grude coke, with one Winkler run to make power gas and one run to make water gas. Shortage of oxygen limited the plant output of water gas to one Winkler.

The principle of the Winkler generator is well known: particulate fuel was used, the most suitable size being 3 mm diameter, with less than 10% above 5 mm and the blast of air alone (when making power gas) or of a mixture of oxygen and steam (when making water gas) was sufficient to make the fuel "dance" or boil. As a result very high outputs could be obtained from a given cross-section in comparison with orthodox water gas generators.

There were five Winkler generators in all; the oldest and smallest one had an output of 40,000 $M^3$/hour water gas for a cross-section area of 12 sq.m. and the other four each had an output of 80,000 $M^3$/hour water gas for a grate area of 25 sq.m.

The change over from dry brown coal to grude coke probably took place because of the increased demands of hydrogenation for dry brown coal, thus causing a limitation of drying capacity, and also because of the availability of grude coke from various neighbouring brown coal L.T. carbonization plants, set up primarily to recover tar from the coal. Both fuels were quite satisfactorily gasified, although dry brown coal gave a higher $CH_4$ content of synthesis gas. The fuel was fed into the side of the conical base by four screw conveyors.

All the generators originally had stationary grates, over which swept a rotating water-cooled arm, to remove ash through an opening on one side. The blast passed through this grate. In recent years however the small generator (1943) and one large generator (1944) were modified and the grate and rotating arm eliminated, the oxygen and steam mixture then being added through tuyeres entering the side of the conical base; this successfully eliminated all shut-downs for repairs of the rotating arm, although by then the earlier rather serious troubles due to leaks from the arm, had been much reduced; more important however, it was claimed that the modification had reduced the consumption of fuel and oxygen by about 10%, although no reason was given. The grateless generator was fitted with two screw conveyors at the base, which could be run intermittently to remove that ash, foreign material, etc., which was not blown over and had collected at the base. A grateless generator has been installed at Brüx.

In operation of generators with grates, only about 10% of the ash was withdrawn at the base through screw conveyors; the remainder passed overhead. It was possible to run for 1 to 2 weeks without these screw conveyors, large material merely collecting slowly on the grate. The overhead ash contained 50 to 55% carbon and had a maximum size of 0.3 to 0.4 mm. It could either be returned to the generator or burnt on boilers; it had also been used as an active carbon for the dephenolation of effluents.

The blast, when making water gas, consisted of a mixture of 40 to 50% oxygen with 60 to 50% steam. About two-thirds of the oxygen was blown through the bed and one-third, mixed with 20% steam to prevent explosions in the tuyere main, was blown through tuyeres into the gas space about 3 to 4 m above the bed, with the object of gasifying carbon in dust entrained in the gas and cracking any tar and hydrocarbons. The original design had the top half of the generator enlarged to a bulb, designed to give a longer time contact for these reactions, but in later designs this was eliminated and the straight cylindrical portion heightened to give the same effect; the reason for the change was given as capital cost. Some of the generators at Leuna still had these bulbs, but some had not; the exact number of each was not obtained with any certainty. In all later plants the straight-sided generators were installed, e.g. three at each of the Brabag plants at Böhlen, Magdeburg and Zeitz, and five at Brüx (but including one grateless type as mentioned before). The most detailed account of this design is given in the report on Zeitz. Three such generators were also built by I.G. at Ludwigshafen for Japan, designed to work on a grain size mineral coal of particularly active character.

The whole generator was brick-lined and no trouble was obtained with clinker. The fuel bed temperature was about 900°C, but this depended on the nature of the fuel. The bed depth was about 1 m. and had a back pressure of about 0.5 m. water gauge.

With less reactive fuels, such as bituminous coal derivatives, the Winkler generator was said to be much less satisfactory. Much higher bed temperatures had to be used and the $CO_2$ in water gas was high.

Typical performance figures were given as follows:-

| | | Water Gas | | Power Gas | |
|---|---|---|---|---|---|
| | | Dry Brown Coal | Grude | Dry Brown Coal | Grude |
| Gas Analysis | % $CO_2$ | 19 | 20 | 10 | 11 |
| ($H_2S$ free) | % CO | 38 | 38 | 22 | 27 |
| | % $H_2$ | 40 | 40 | 12 | 7 |
| | % $CH_4$ | 2 | 1.5 | 0.7 | 55 |
| | % $N_2$ | 1 | 0.5 | 55 | |
| Net C.V | T.cals/M | - | - | 950 | 956 |
| Fuel | kg/$M^3$ | 0.625 | 0.50 | 0.335 | ? |
| Oxygen | $M^3/M^3$ | 0.25-0.26 | 0.25-0.26 | nil | nil |
| Steam | $M^3/M^3$ | 0.39 | 0.375 | nil | nil |

Typical analyses of the fuels, not necessarily corresponding with the above figures, were

| | Dry Brown Coal (dry basis) | Grude Coke (dry basis) |
|---|---|---|
| C | 61.1 | 68 |
| H | 4.7 | 2.0 |
| O | 17.0 | 2.2 |
| N | 0.1 | - |
| Volatile S | 3.3 | 1.3 |
| Ash | 13.8 | 26.5 |
| $H_2O$ | (6.0) | (2.0) |

The major thermal losses were as carbon carried away as dust and as sensible heat carried away in the water gas at about 900°C. The flue gas was passed through a cyclone to recover any coarse dust, was cooled to about 200°C in a waste heat boiler, and passed through a hydraulic seal; it was then dedusted in a direct contact water washer and a Theisen disintegrator. It was stated that unsuccessful attempts had been made to build recuperators and heat exchangers in the top of the generator, presumably to preheat the blast.

To avoid explosions when using oxygen-steam blasts it was essential to get good mixing; on the Winklers it was present practice to mix at a minimum distance of 30 to 40 m. from the point of entry into the generator, with several bends to promote turbulence.

<u>Slagging Producers</u> ("Abstichgeneratoren")

The original slagging producers at Leuna were three Würth producers, using coke breeze, "ashes" from the water gas generators or simply coke, blown with air only to make producer gas for $NH_3$ synthesis; the producers were completely brick-lined and ash was removed as molten slag. Steam or oxygen could be added as conditions permitted.

Owing presumably to brickwork failures the Würth type was replaced by another, in which the whole of the lower part of the producer was water-cooled. There were six of these producers, five of I.G. design and one by Pintsch. One had been built during the war. The producers were blown with oxygen and steam and the capacity of each unit was 15,000 M3/hour of substantially nitrogen-free producer gas.

The producer was built of 1/2" to 5/8" iron plate, having a diameter of 2.5 metres at the tuyeres and 3.8 metres higher up, with the inside diameter of the brickwork 1.7 metres at the tuyeres and 3.3 metres at the top. The total height was 7 m. above the tuyeres and the fuel bed was 4 m. deep above the tuyeres. Only the top part, above the fuel bed, and the lower part, below the tuyeres were brick-lined; the rest was bare metal. In five generators the producer was water jacketed but in the last one built the jacket had been omitted and the metal was cooled merely by trickling water down over the outside. This modification had been carried out as the result of a serious accident on one of the old type; a piece of clinker became lodged just above a tuyere and as a result the incoming oxygen caused a very high local temperature, which burnt a hole in the jacket; the producer became flooded and quenched and before it was noticed oxygen had broken through, causing a serious explosion in the gas mains and gas coolers. This could not happen with the latest design; it was said that there was no trouble with evolution of steam as the water merely became warm.

It was very difficult to make power gas on these producers, using air only; the difficulty was presumably insufficiently high temperature to permit slagging, owing to heat abstracted through the generator walls, since the old brick-lined Würth producers could be run successfully on air.

When making producer gas, a mixture of oxygen and steam was introduced at the tuyeres and a temperature of 1,700°C was obtained, although the exit gas temperature was only 400°C. Limestone could be added to act as a flux for the liquid slag. Depending on the fuel, slag was run off at intervals of 20 to 60 minutes. One method of slagging was to run the liquid slag first into troughs, where any iron sank (and was dug out at intervals), and then into cold water: another method was to tap off molten iron from the extreme bottom of the generator and molten slag from a tap somewhat higher.

A wide variety of fuels could be used, but Rohschlacke (refuse) containing 50% carbon, from the Brassert generators was normally used. The fuel should be above 30 mm. and could be as large as 1 to 2 feet. When using metallurgical coke it was common practice to add 3% of limestone and 20% of solid slag from previous working to assist in the formation of slag. When using coke the blast mixture was 35% $O_2$ and 65% steam: when using Brassert Rohschlacke the mixture contained 50 to 58% $O_2$ and 50 to 42% steam.

Typical operating figures were:

| | | Brassert Refuse | Grude from Deuben | Met. Coke | Met. Coke with $CO_2$ |
|---|---|---|---|---|---|
| $CO_2$ | % | 9.7 | 5.4 | 6.8 | 3.0 |
| CO | % | 66.5 | 62.4 | 61.4 | 92.5 |
| $H_2$ | % | 22.9 | 31.2 | 31.0 | 3.0 |
| $CH_4$ | % | 0.0 | 0.0 | 0.0 | 0.0 |
| $N_2$ | % | 0.9 | 1.0 | 0.8 | 1.5 |
| $H_2S$ | $g/M^3$ | 2.7 | 13 | 4.3 | 2.2 |
| $O_2$ | $M^3/M^3$ $H_2$+CO | 0.347 | 0.276 | 0.262 | 0.310 |
| $H_2O$ | $kg/M^3$ $H_2$+CO | 0.207 | 0.266 | 0.346 | nil |
| $CO_2$ | $M^3/M^3$ $H_2$+CO | nil | nil | nil | 0.258 |
| Fuel | $kg/M^3$ $H_2$+CO | ? | 0.80 | 0.490 | 0.530 |
| Carbon | " $H_2$+CO | ? | 0.482 | 0.424 | 0.460 |
| Fuel Analysis | C % | 45-50 | 54 | 86.8 | 87.2 |
| ash | % | 55-40 | 16.9 | 9.1 | 11.8 |
| $H_2O$ | | 0 | 22 | 1.8 | 1.0 |

The figures in the last column are interesting; here steam in the blast was replaced by $CO_2$, resulting in a very high content of CO in the gas made.

Smaller slagging producers were available and used for testing various fuels and various methods of running.

## Pattenhausen Generator

This generator was not inspected, although the installation was seen from a distance. The principle of this generator was that all the heat of reaction was added in the form of highly preheated steam at about 900°C. A large excess (fourfold?) of steam was used and gasification of dry brown coal proceeded at about 600° to 700°C, a temperature only possible with a highly reactive fuel. We gathered that the plant was not a great success and certainly no other units had been built, although the original one started up in 1937.

## Oxygen Plant

This consisted of Linde-Frankl units of conventional design and was not studied in detail. There were 9 units in all, having a total capacity of 23,700 $M^3$/hour of 98% $O_2$, the two oldest units producing 1,900 and the other seven 2,850 $M^3$/hour. The actual output over the five years 1938-42 averaged 22,000 $M^3$/hour 100% $O_2$. A somewhat smaller quantity of nitrogen was also recovered, and used before the war approximately equally for purging and for $NH_3$ synthesis: during the war a drop in $NH_3$ output caused less $N_2$ to be used for the latter purpose; the maximum capacity of pure $N_2$ was 32 to 36,000 $M^3$/hour, limited to that obtainable from four units.

The energy consumption varied from 0.5 to 0.6 KWH/$M^3$ oxygen, averaging about 0.55 KWH/$M^3$ 100% oxygen. With the cost of power at 1.1 to 1.2 pfg/KWH, the cost of oxygen was said to be 1.6 to 2.0 pfg/$M^3$; 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 50 $M^3$/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

## $H_2S$ 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 g/$M^3$ S (or 1 to 1.5% $H_2S$); it was purified by alkacid in two stages: after the coarse purification it contained 2 g/$M^3$S and after the fine purification it contained 150 mg/$M^3$ S.

The liquor normally used was a solution of sodium glycocoll, $NH_2.CH_2.COONa$, of S.G. 1.17, containing 200 g/l, calculated as $Na_2CO_3$ or 45 g/l calculated as nitrogen (these two figures indicate the presence of some $Na_2CO_3$ as such). It was a selective solvent for $H_2S$, so that for example with a gas containing 20% $CO_2$ and 2% $H_2S$ it would remove nearly all the $H_2S$ but only about 2% $CO_2$. The absorbers of the coarse purification each had a diameter of 3 m for a gas rate of 20,000 $M^3$/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/$M^3$ liquor in the coarse purification and 150 kg/$M^3$ liquor in the fine purification. The mixture of $H_2S$, $CO_2$ and steam leaving the regenerator was condensed at 50° to 60°C, to reduce the $H_2S$ content of the condensate, and the $H_2S$ was finally burnt in a Claus kiln; the recovered sulphur was eventually used to make $H_2SO_4$.

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, $CH_3.CH(NH_2).COONa$, but this also dissolved $CO_2$; it was used at Leuna only for purification of tail gases from hydrogenation. This liquor could be used for $CO_2$ removal, when its capacity (in the same concentration as used for glycocoll) was 25 $M^3$ $CO_2$/$M^3$ liquor, the steam consumption being 120 kg/$M^3$ liquor; over 95% removal of $CO_2$ was possible.

## Active Carbon Process

The whole of the Pintsch-Brassert water gas, containing 3 to 4 g/$M^3$ S, together with a varying fraction of Winkler gas, was purified down to 1 to 2 mg/$H_2S$/$M^3$ 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°C and then steamed. Air or oxygen was added to the inlet gas, so that in effect $H_2S$ was oxidized to sulphur, which was left on the charcoal; $NH_3$ 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° in the absence of air. The polysulphide solution was then distilled at 2 ats, with a top temperature of 111°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 $H_2S$ removal contained 250 mg. organic sulphur/$M^3$. This was converted to $H_2S$ in the CO conversion plant, and this $H_2S$ was almost completely removed during the removal of $CO_2$ and CO.

## CO Conversion

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

$$CO + H_2O \longrightarrow CO_2 + H_2$$

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 $NH_3$ and $H_2$ contained 3 to 4% CO, whilst converted gas for methanol contained 30% CO. The catalyst was $Fe_2O_3$ with 6 to 7% $Cr_2O_3$.