Screen Analyses (Cont.)

	Raw Coal	Coal Dust	Coal Paste*
Over 0.5 mm	74%	5.2%	1.0%
" 0.3 "	83%	15.0%	3.8%
" 0.2 "	88%	27.3%	10.3%
" 0.1 "		55.6%	27.2%
" 0.06 "	97%	73.0%	53.0%

*) Paste analysis is based on benzol-insolubles in the paste.

Gelsenberg has 6 coal stalls working at 700 atm., while the 7th coal stall is in construction. The stalls deliver a letdown of 18 to 20% asphalt, 20 to 24% benzol-insolubles, and 62% ash in the benzol-insolubles.

B) Centrifuge department.

In 6 lines and 1 reserve line the letdown is delivered to the centrifuge department. After running through an air cooler the letdown of each stall separated in the centrifuge department flows through a water cooler into the letdown vessel. The letdown gas is washed in its own condensate, which is pumped back, and added to the hydrogen. At 200°C the letdown flows through the Eckhardt-meter and enters the letdown vessel. The thinning oil is then added. The centrifuge oil mixture is proportioned by an automatic regulating device. The centrifuge department is well laid out, allowing ample space and efficient equipment layout. The existing operating laboratory makes a very good impression. There are 60 centrifuges with 3 circulating systems, 2 of the circulating systems serve 22 machines each and 1 system 16 machines. In addition, 2 centrifuges may be separately fed from a 100 m3 tank for experimental purposes. The initial pressure in the circulating systems is maintained by an automatic regulating device. Added centrifuges are indicated by a simple device, which has been in satisfactory operation for some time. There is a balanced damper in the residue outlet pipe of the centrifuge. One end of this is a plate flap, which takes up the entire cross section of the line, the other end is a rod with a white disk on its end. When the flap is closed the rod points downward and remains steady. When there is fluid flowing in the line the flap is depressed. The disk rises and assumes an oscillating motion. The position and motion of the disk indicates the volume of the discharging residue.

Simplex pumps with an average capacity of 100 m3/h are used exclusively in the centrifuge department. However, a centrifugal pump has been in operation for a short period for experimental purposes. Pump packing lasts about 3 to 4 weeks. Screens are introduced into the circulating systems and at the centrifuges from time to time to catch pieces of coke. Throughout the past year heavy catchpot oil instead of cylinder oil has been successfully used for lubrication of centrifuges. The following figures indicate the operation of the centrifuges:

Temperature	160 - 170°C
Initial Pressure	1.2 - 1.5 atm.
Nozzles	1.9 mm

Throttles (orifices)	11 - 12 mm
Centrifuge mixture	14 - 15% insolubles with 62% ash
Centrifuge oil	10% insolubles with 60% ash
Residue	35% insolubles with 61 to 63% ash
Centrifuge mixture production	110 - 120 m^3/h
Production/centrifuge	3.2 - 3.3 T/h
Centrifuges normally in operation	36 machines (average for March)
Centrifuges added monthly	37 machines (average for March)
Centrifuges shut down monthly because of unsatisfactory operation	43 machines (average for March)
Centrifuges flushed	Normally 140 to 150/day

The large number of centrifuges flushed is extraordinary. It is impossible to say if this is due to the high ash content of the letdown insolubles or the low temperature at which the centrifuges are operated. It is proposed to operate the centrifuges at 200°C experimentally. The reason for the low temperature is the desire to run the letdown Eckardt-meters at a temperature not exceeding 200°C, because severe wear is expected at higher temperatures. Furthermore the oil loss (high middle oil content) should be kept low.

In Gelsenberg it was noticed that the number of centrifuges flushed increases at the start of a coal stall.

C) Kiln operations. (Low temperature carbonization)

The kiln department has 12 kilns with horizontal preheater coils. In these an increase in pressure is indicated by an alarm device. The injection is controlled by an automatic regulating device.

Output/kiln - 2.8 - 3.2 T/h
Kiln efficiency - 78 - 80%
In operation - Normally 9 kilns
Temperature °C - 530 in the kiln drum
Steam at 2.5 atm. - 200 kg/h
Oil content of the kiln residue - Less than 1%
Kiln gas m3 - 45/m^3 kiln residue

To relieve the high pressure (residual coal) up to 500 tons of letdown monthly are run to the kiln department.

The kiln residue is taken away by belt conveyors and centrally screened. The coarse product is taken to storage and the fine product sold to steel works.

It is extraordinary that since 1939 no drum has been changed in the kiln department. This is probably due to the ribs in the drums, which are periodically renewed (welded on) and by the use of round milling particles by means of which impact and scraping against the drum walls is avoided. Each welded-on rib is 180 mm long, followed by the next rib with a play of 1 cm between them. Each rib is 8 mm high and 40 mm wide. The distance between adjoining ribs is 50 mm, so that there are 111 rows of rib in a length of 3 meters. The material used for these ribs is Goronit, which contains 20% chromium, 2% nickel and 0.5 to 1.5% molybdenum. No catalyst is added in the kilns.

/S/ Dr. Steffen

Hydro. Works, Pölitz A.G.

KCBraun/MC/jw

7-31-1946

T.O.M. Reel No. 78
PP. 73-75
Bag No. 4
Target No. 30/4.13

T-71

MINES

COAL PREPARATION AND RESIDUE OPERATIONS AT HYDROGENATION WORKS SCHOLVEN A.G. (VISIT OF 27 APRIL 1944)

A) Coal preparation. Scholven uses washed nut and fine coal from the Zweckel mine. The hydrogenation coal contains 4½% ash and 10% water. From the lower bin into which the coal is discharged from the bucket cars, the coal is taken to the high bins by a bucket elevator.

From here it is crushed in 2 hammer mills of 50 and 100 T/h capacity, respectively. After the crushing the coal contains from 50 to 70% of pieces larger than 1 mm. The mill hammers must be changed about every 1,500 hours.

Four systems serve for further milling and drying. Each system has a Hilpurg-scale, a ball mill, a screen, a Lurgi-filter and a tube mill. Besides the milling, the drying is also done in the ball mill, which is provided with Wistra-burners. The air required for combustion is circulated in the ball mill after the addition of steam. Each system is run at a capacity of 23 - 30 T/h. After the ball mill, the coarse grain is separated in the screen and returned. It contains about 32% of coal larger than 1 mm. The analysis of the mixture of coal and Lurgi-dust shows only 10% of coal above 1 mm. The catalyst is added just before the coal enters the tube mill. This consisted formerly of tin oxalate, but is now a blast furnace product rich in tin oxide. To this is added 0.03% by weight of tin, based on coal. The paste contains 0.5 - 1.5% of grain over 1 mm.

The plant, while not so well laid out as Gelsenberg, makes a favorable impression from an operating point of view. At present it supplies 55 T/h of coal to five 300 atm. coal stalls. The disintegration in these is between 87 and 91%. Catalyst II, consisting of ammonium chloride made into a 20% paste with pasting oil, is added in Converter I.

B) Centrifuge department. The coal stalls produce hourly from 55 to 60 tons of letdown. There are 51 machines in the centrifuge department, served by 3 circulating systems with 13 centrifuges each and 1 circulating system with 12 centrifuges. A new group of 13 centrifuges is proposed for the 7th coal stall. The following figures serve to show the character of operations in the centrifuge department:

Temperature	180 - 210°C
Initial Pressure	1.2 - 1.6 atm.
Nozzles	1.9 mm
Orifices	5.5 mm
Centrifuge mixture	15% insolubles with 28% ash
Centrifuge oil	9 - 10% insolubles with 18 - 20% ash
Residue	37 - 39% insolubles with 42 - 44% ash
Centrifuge mixture production	85 m^3/h
Production/centrifuge	3.5 T/h
Centrifuges normally in operation	28 machines
Centrifuges flushed	18 machines/day

Particularly noticeable is the low number of flushed centrifuges and the low ash content of the insolubles in the centrifuge mixture, the latter is due to the catalyst used.

Particularly praiseworthy are the scale-containers which receive the letdown and also the excellent results in the use of centrifugal pumps for the transportation of the centrifuge mixture. Two centrifugal pumps of 60 m3 capacity have been in operation over a considerable period and show very little wear. The shafts of these pumps run in hardened bushings 5 mm thick. These are sealed off by a split stuffing box. The packings of 4 Sola-cords have a running time of about 2 weeks. The pressure behind the centrifugal pumps is 3 atm.

C) Kiln operations. (Low temperature carbonization)

This department has 12 kilns, of which 8 are in the old and 4 in the new section. Preheaters have been successfully used for the first time in the new kiln section. The kiln residue is taken away by 2 spiral conveyors and burnt in the power plant. Experiments are being made for further dehydration with centrifuges.

D) Pitch granulation. One of the kilns is used for topping of the letdown. The hot kiln residue is taken through a cooler and a storage vessel to a steam heated container provided with a mixer. From there it is taken to the pitch granulating department at a predetermined constant temperature.

The fluid pitch, subdivided into 8 small streams, here falls into water troughs arranged alongside of each other, each 10 cm wide and 20 m long. The pitch solidifies in water to strings of lead pencil thickness. At the lower end of the sloping troughs the strings run into a screen and the water is separated and pumped back. Then the strings of pitch are taken to railroad cars by a belt conveyor, where they break into pieces 2 to 5 cm long when dropped into the cars. These still contain about 2% water. The water content is controlled by the temperature of the fluid pitch at the point of its entry into the water. The plant is very simple and efficient.

/S/ Dr. Steffen

Hydro. Works, Pölitz A.G.

KSBraun/MG/jw

7.X.1945

T.O.M. Reel No. 78.
Bag No. 4.
Target No. 30/4.13
pp. 58-68

T-72

BUREAU OF MINES

Pölitz, April 14, 1944.

REPORT ON COAL PREPARATION AND SPRAY-GRAIN (SPRITZKORN)

Summary. In March the spray-grain quantity of 26 T/day was considerable. Its cause must be attributed to poor coal grinding. The grinding fineness of the coal particles, even those below 1 mm is reduced with a rising volume of spray-grain and lowers the hydrogenation ability of the coal. A reduction, or possibly a complete elimination, of the spray-grain quantity must therefore be obtained.

The poor coal grinding is due to the overloading of the grinding units in buildings 270 and 271. Of the two systems in building 270, each consisting of a hammer mill and a disintegrater, only one is operated, even with a daily production of 1,600 T. Under these conditions approximately 400 T/day of coarse grain are caught in the shaking screens in building 271 and delivered to the roll-stands. The overloading of the roll stands has the effect that their product contains up to 40% coarse grain, which is not screened out. Even if a part of this is reduced in size in the tube mills the proportion of spray-grain is still large.

Recommended process.

1) For better grinding it is necessary that, with a production of more than 1,200 T/day, two systems be operated in building 270. One reserve system will again be available as soon as the two newly ordered hammer-mills will be in operation.

2) For the elimination of the spray-grain a dry screening in building 271 must be introduced instead of the present wet screening, which causes unavoidable oil losses and gives a product which cannot be used. In any case the coal must be screened after the roll stands. For this purpose the products of all roll stands must be transported to either one of the two shaking screens now on order for the fifth coal stall. The coarse grain caught on these screens amounts to about 2% of the coal and is removed from the system.

Procedure.

1) Spray-grain quantity and coal thru-put.

For the past 11 months the daily thru-put of dry coal and the daily quantity of spray-grain were plotted on comparable curves. (see appendix) These show that the spray-grain quantity is dependent upon the coal thru-put. With a daily coal thru-put of 800 T, it amounted to 0.1% by weight of the coal in May and November, 1943. It therefore amounted to less than 1 T/day. With a thru-put of 1,200 T/day in September and November, 1943, and January, 1944, 4-14 T/day of spray-grain were obtained, amounting to 0.4 to 1.1% by weight. The large fluctuations may be explained by the fact that the largest part of the spray-grain is returned to the tube mills and repeatedly measured. In September, 1943, and February, 1944, with a thru-put of 1,600 T/day, 10 and 23 T/day, respectively, of spray grain or 0.6 and 1.5% by weight, respectively, were obtained. The respective figures are shown in Table A.

Table A.

Spray Grain Quantity and Coal Thru-put

Date:	Thru-put in T/day	Spray grain in T/day	Weight in %
14-17 of May, 1943	800	0.6	0.07
7-14 of November, 1943	850	0.9	0.10
20-24 of September, 1943	1,150	7.0	0.60
20-26 of November, 1943	1,150	4.0	0.35
13-20 of January, 1944	1,250	14.0	1.10
8-15 of September, 1943	1,550	10.0	0.65
10-20 of February, 1944	1,550	23.0	1.48

2) Coal preparation.

In order to determine the cause of poor coal grinding with rising thru-put the individual units of the coal preparation plant must be examined for their efficiency. For this purpose 3 operating periods B, C and D with a varying thru-put are chosen and evaluated, based on the screen analyses. Each evaluation was based on 5 days in which the production was constant. Of the available analyses those coming closest to the average values are used. In addition, an operating period E with a thru-put of 680 T/day of dry coal is shown as an example of particularly good grinding. The screen analyses are reproduced in the curves in diagrams B, C, D and E. (See appendix).

Table B.

Coal Grinding with Varying Thru-put

Case	B	C	D	E
Time	19-23 July, 1943	3-8 Sept., 1943	14-18 Febr., 1944	14-19 Febr., 1943
Coal thru-put, T/day	1,110	1,660	1,520	680
Coal thru-put, T/h	45	65	65	30
Spray grain quantity, T/day	1.5	5.3	22	0.19
Coal grinding:				
Weight in % larger than 1 mm:				
Of Wet coal + catalyst	63	69	66	72
After hammer mill	44	45	51	16
After disintegrater	34	29	39	15
After dryer	7	13	28	11
After roll stand	23	22	40	2
After shaking screen	15	8	10	16
Systems in operation in building 271	3	4	4	2
Systems in operation in building 270	1	2	1	1

a) Hammer mill and disintegrater.

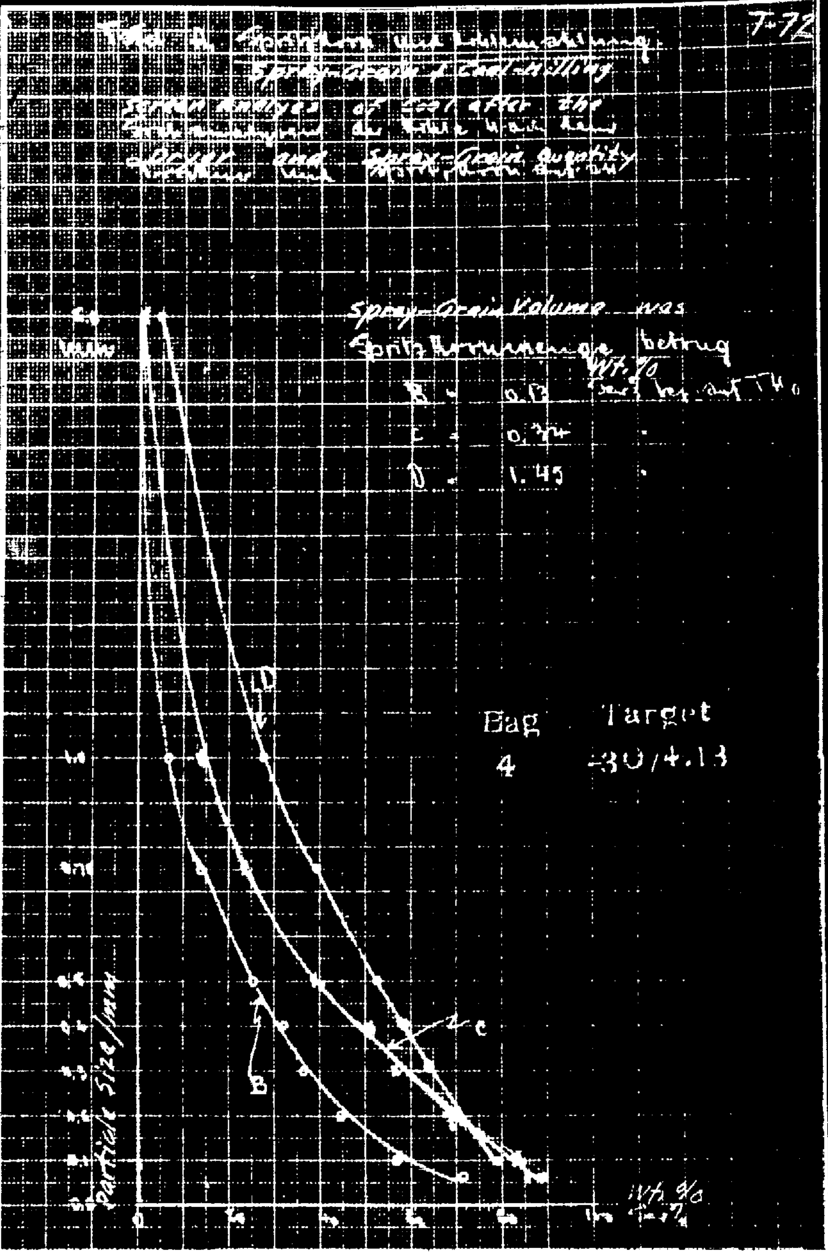
The pre-crushed coal, after the addition of the catalyst, is sent to the hammer mill and disintegrater in succession. (see flow sheet of coal preparation) The hammer mill, capacity 125 T/h, is expected to crush an estimated 90 T/h of coal from a grain size of 0 - 20 mm to a finished product of 0 - 3 mm, containing spray-grains up to 6 mm, after the installation of special screens. The disintegrater has a capacity of 60 T/h of coal. Two systems, each consisting of 1 hammer mill and 1 disintegrater, are available. The third system consisting of 2 hammer mills is on order and is expected to go into operation at the start of the fifth coal stall. The screen analyses show the following:

The pre-crushing is the same with a low and a high thru-put. Approximately 30 to 35% of the coal is reduced to a grain size below 1 mm in this operation, as may be seen in comparing cases C and E in Table B.

The efficiency of the hammer mill is very much dependent upon the thru-put. With a load of 30 T/h the milling is excellent and reduces 50% to below 1 mm (case E), against 19% with a load of 45 T/h (case B). With a load of 65 T/h the milling is poor, (the rest of the report is missing)

KCBraun/MC/jw

7-31-1946



Hydrierwerke Pölitz A. G.
Stettin-Pölitz

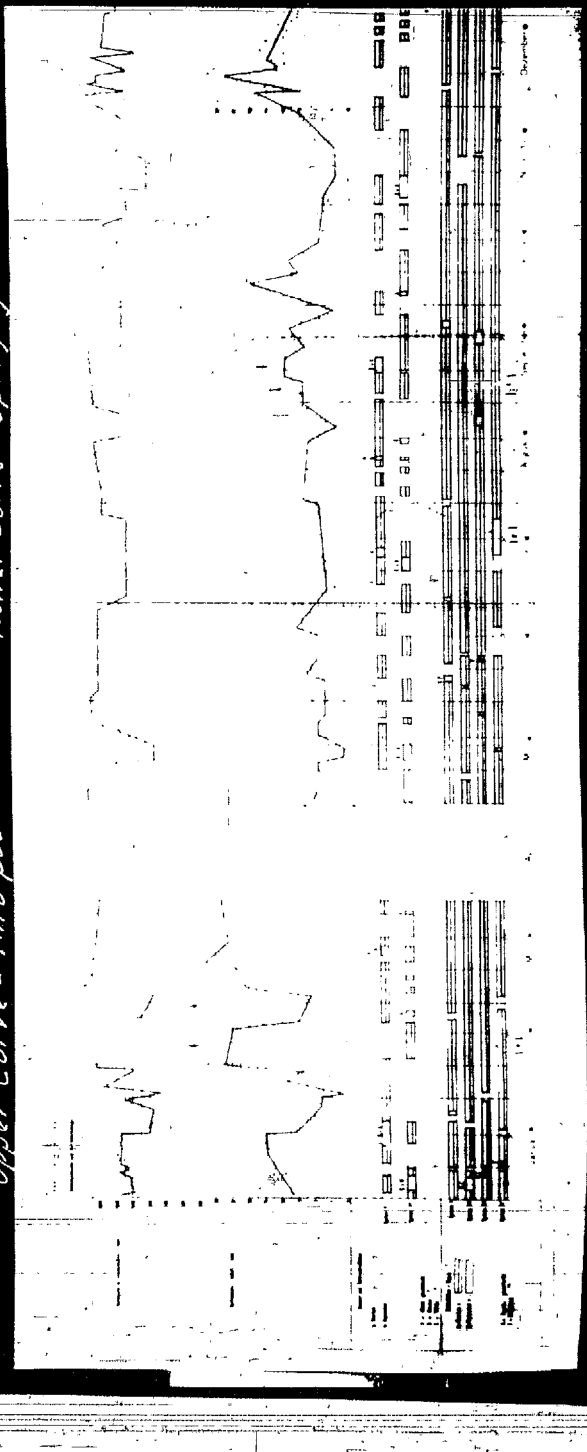
DIAGRAM "A"

DIN-Format A 4 (210 x 297mm)

00067

DIAGRAM "F"

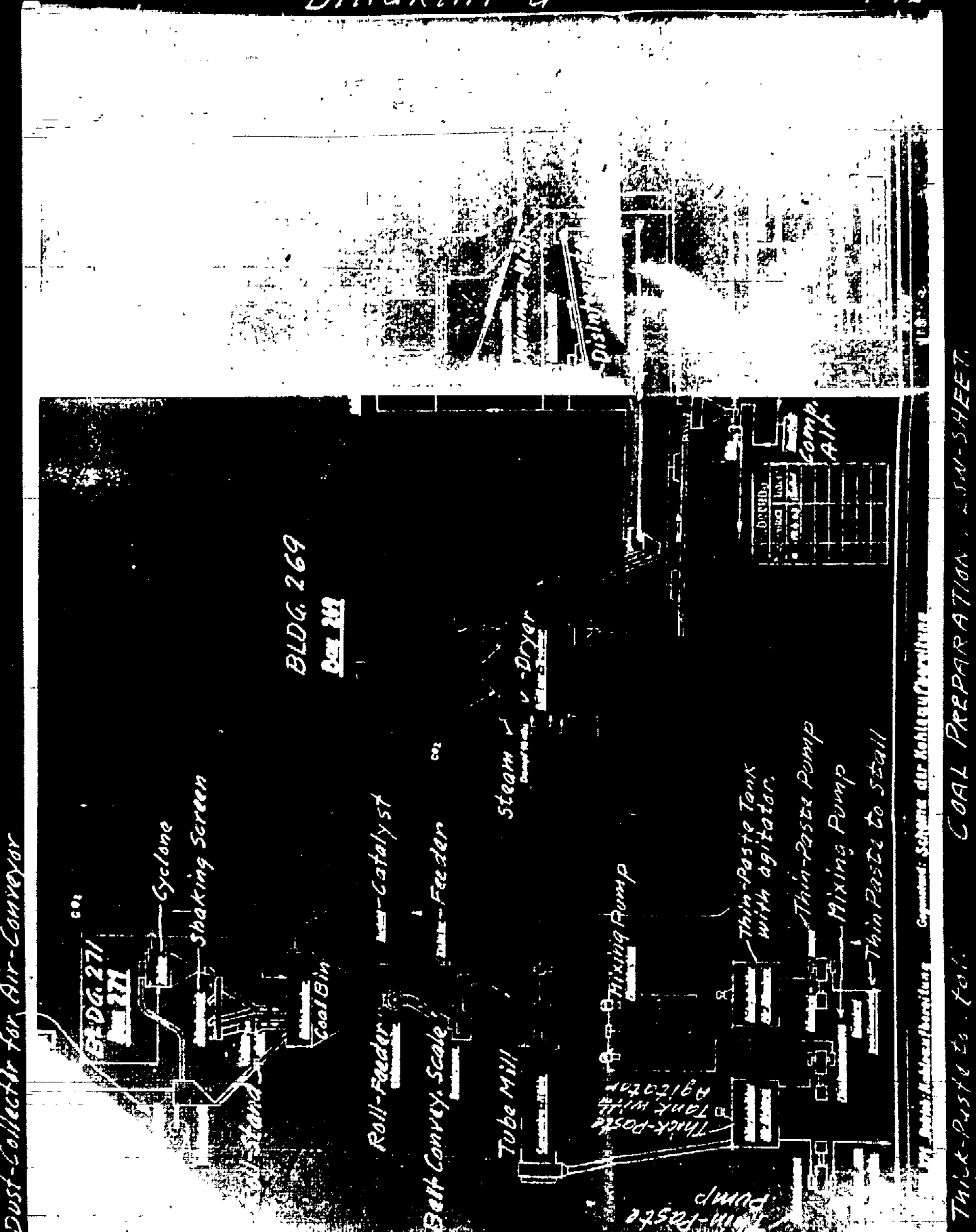
T-72



Upper Curve = Thruput

Lower Curve = Spray-drain.

DIAGRAM "G"



Thick-Paste to tail

COAL PREPARATION, FLOW-SHEET.

T.O.M. Reel No. 9 **BUREAU OF MINES LOUISIANA, MISSOURI** T-73

pp. 297 - 303

Scholven, Dec. 4, 1941.

(Also presented in Reel 164,
frames 436-442.)

GAS CIRCULATION IN THE 700 ATM. HYDROGENATION STALL
FROM THE STANDPOINT OF INSTRUMENTATION.

Communication by Eng. Schappert at the conference of
Dec. 4, 1941 in Ludwigshafen a. Rh.

A simplified scheme of gas circulation is shown in Fig. 1, in which the Stettin relationships of:

Circulation gas pumps

Stalls, including catchpots

Oil scrubbing

were retained. Several stalls are usually connected in parallel in a gas circuit, and oil scrubbing mostly serves a number of aggregates. One may not exceed certain dimensions of circulation gas pipe lines, e.g. the 120 mm lines with 700 atm operations, and the pipe lines are therefore laid in parallel, with a preference for a ring arrangement (Ringschaltung). Circulation gas pumps are short circuited in the bypass, to take up by a suitable regulation of valves the excess stall gas or to give some off in case of deficiency. The principle of this simplified connection diagram, however, is always applicable:

The principal pressures of the system are under continuous observation, mostly by recorded. The absolute pressures P_1 and P_4 are first of all of interest to us as being the maximum and the minimum pressures.

The pressure difference $P_1 - P_4 = \Delta P_4$ is maintained with a differential recorder. This pressure difference has an upper limit in the production of the gas circulation pumps and is directed towards the stall with the greatest pressure difference, so as not to use excessive amounts of electric power. It may be mentioned that the gas circulation pumps were originally designed for a pressure difference of 100 atm. but have however been later converted to 70 atm., and it must be decided whether they should not again be rearranged for 75 or 80 atm on the strength of the present discussions.

Obviously, the pressure difference of all the stalls is of importance and it depends mainly on the thruput, unless irregularities, such as obstructions and crustformation have caused higher pressure differences. This pressure difference may be determined either directly as differential pressure, or else by the determination of the two absolute pressures of the stall inlet and outlet, and plotted on a diagram.

The stall intake valve offers a variable resistance and is throttled the less, the higher the pressure difference of the stall. For this reason, the pressure P_2 of a many-stall system may itself fluctuate with the different pressure differences of the stalls, the pressure P_3, at the outlet of every stall is practically the same, because oil scrubbing offers a definite resistance and the suction side of the circulation gas pumps also works at a constant pressure.

We may therefore calculate two pressure differences which are of interest:

1) ΔP_1 the principal resistance on the pressure side of the circulation pipe line must be in the inlet valve, as well as in the fittings and flanges. As a rule, the differential pressure of the inlet valve was found to amount to 10 - 15 atm. to permit the cold gas to flow into the converter with sufficient over-pressure. For this reason, the cold gas at the inlet into the converter has an excess pressure of 20 - 25 atm. Should this excess pressure be suddenly reduced to half its amount, the amount of inflowing gas will also be suddenly greatly reduced, until a proper opening of the cold gas valve will again furnish the necessary amount of cold gas. The wish to be able to observe regularly this pressure difference of the inlet valve is therefore clear. Thus, e.g., Pölitz has planned for some time to locate a differential manometer at this place.

2.) The other pressure difference of almost equal importance, ΔP_3 combines information on the suction side of the circulation gas and especially the oil scrubbing, which also consists of a number of aggregates, like the stall installation. The difference in pressure of the individual washers is compensated by the inlet valve, and one may, naturally, go only so far with this type of regulation since otherwise an increase in this differential pressure would proceed at the costs of the stall pressure, which is of determining value for the supply with cold gas. Even if not utterly vital to record this difference in pressures, it would still be desirable to evaluate it continuously from the absolute pressures P_3 and P_4 to permit noticing changes as they are just produced. Pölitz records this differential pressure of the whole scrubber system, including the gas coolers for weeks before any trouble actually occurs when suspecting irregularities in the flow relationships from greater variations in temperature in the circulation gas cooler than anticipated. This increased differential pressure was not the cause of any operational difficulties, because the total differential pressure of the pumps could still be greatly increased (up to 100 atm.). Never the less, the fact of this increase in the pressure difference indicates the formation of some deposits, even though but slight ones. It may therefore be well to recommend Stettin to foresee making measurements at least whenever plugging up with gas hydrates or ammonium carbonate is possible.

To permit a rapid and certain determination which one of the two parallel circuits is becoming plugged up, one might measure the different paths with throttling dampers, or else, wherever electrical connections permit current measurements, to determine the electrical resistances of the paths. Attention must then be paid to the water continuously injected into the circulation. It is unnecessary to measure accurately its amounts and it is sufficient to obtain comparative information. One may also bear in mind to have the throttling valves connected in a way to permit their occasionally being dismantled and inspected.

It would be advisable to locate close together the differential pressure manometer for ΔP_3 as well as the throttling valves for the two paths. The man who has charge of the pressure difference will then be in position to differentiate between the normal variations in pressure which may also be produced by regulations at the stall from variations resulting from obstructions. Measures required in the two cases are the reverse: in the first case of real pressure rises the by pass valve must be opened, while in case of plugging up the differential pressure pipe line from the circulation pump must be used which may be capable of blowing out the obstruction.

Diagram II shows the pressure relationships of the gas circulation in the 3 and 4 converter stalls. The load on a four converter stall is 1/3 higher than of the three converter stall, and as a result the pressure difference must be round 50% higher, neglecting the fact that the intake mass need not be 1/3 greater.

In these examples the pressure difference of the circulation pumps was 55 atm.

With a pump capacity of	70 atm.
there is therefore a reserve of pressure of	15 atm.
The 55 atm. are divided as follows:	
1) circulation pressure pipe line	2 atm.
2) circulation suction pipe line and oil scrubbing	6 atm.
The pressure differences of the stall may vary between	18 and 32 "
at the intake valve between	29 and 15 "

The shaded surface indicates in all cases P_2, i.e. the pressure difference between the inlet and the outlet of the stall, and that pressure difference is in turn subdivided into:

the upper single-hatched surface representing the pressure difference between

heat exchange + preheating.

the middle double-hatched surface, representing the converter pressure difference.

and the bottom single-hatched surface of the pressure difference of the return path of the heat exchanger + cooler + catchpot.

This leads us to two important viewpoints:

1). The inlet pressure of the stall is increased by the pressure difference of the converters, because the cold gas is to some extent short circuited in the converters.

2). The stall which has the lowest resistance, therefore with the greatest net pressure (Vordruck) is, as a result of this high net pressure in a less favorable condition with respect to the partial pressure of hydrogen, than stalls with higher resistance.

We may summarise by saying:

The normal equipment of the 700 atm. stall must have the following pressure measuring instruments:

for absolute pressure of the pressure and suction sides of the

circulation pump,

circulation differential pressure

differential pressure of each stall,

which is entirely satisfactory to meet the ordinary operation needs. However to meet cases such as have been met in Pölitz for the first time of sudden plugging up of circulation additional recording instruments are suggested:

1). for measurements of pressure difference of the inlet valves of each stall,

2). for measuring the pressure difference of the total scrubber unit,

3). An eventual addition of 1 throttling damper in each parallel branch of the gas circulation,

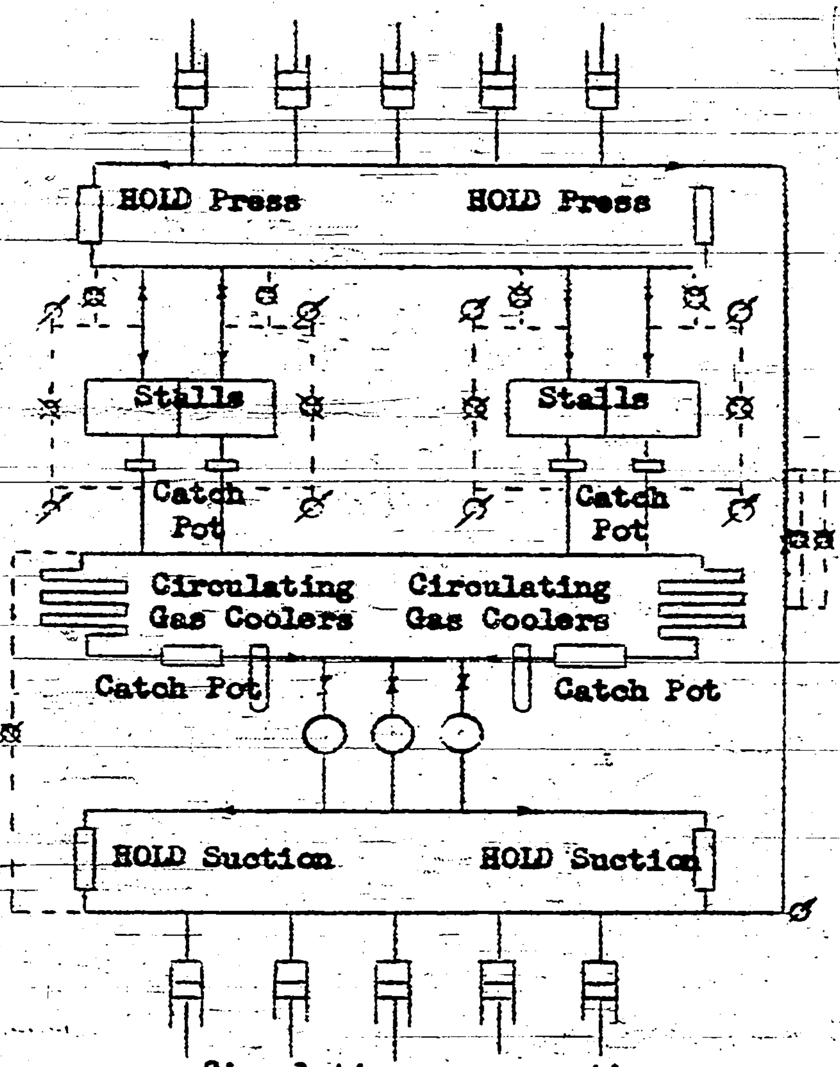
4). to measure the pressure difference of the circulation double, with two instruments based on different principles, e.g. with an air operated and a flask differential manometer.

/s/ Schappert

Sternberg

/jw

CIRCULATION PUMPS PRESS.



Circulating pump, suction.

Fig. 1

PRESSURE DISTRIBUTION IN 700 ATM. CIRCULATING GAS

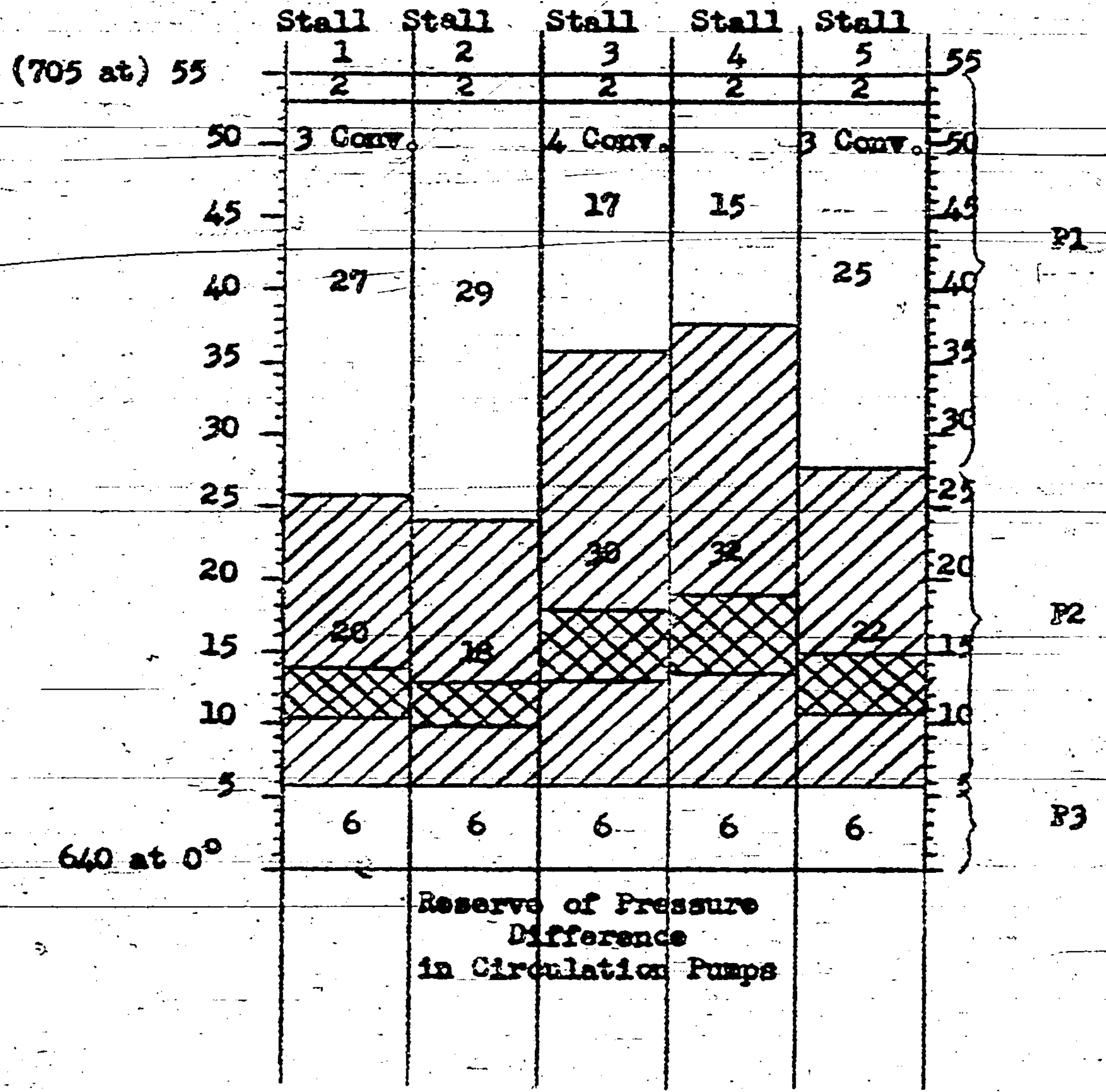


FIG. 2

T.O.M. Reel No. 167 U. S. Bureau of Mines T-74 130
Hydro. Demon. Plant Div.

Frames 23-43

Scholven, March 22, 1944.

High Pressure Experiments, Leuna 1.

A paper by Schappert presented at the colloquium, March 24, 1944

3. PREHEATER PROBLEMS IN THE LIQUID PHASE WITH SPECIAL CONSIDERATION OF THE HEAT PUMP

I am in position to report to you the preheater problems in the liquid phase with a consideration of the heat pump. The heating of our liquid phase outlet product, primarily coal paste, and in particular raising the maximum heat in a gas preheater, is a principal problem in a hydrogenation plant; in the last 2 years there have been some very unpleasant surprises produced by materials, and as a result these very problems require our particular attention today. I may therefore present to you first the development to the present state of heating the coal phase, and follow it up by showing whether the thermal pump may be introduced into hydrogenation, and how this may be done.

The principal units with which the intake feed is heated in the large scale production are the tube-bundle heat exchange apparatus, usually spoken of as the heat exchangers, and the hairpins. These basic units occur always in the subsequent drawings in a schematic presentation which may be foreign to some of our co-workers, and I will show you (figure 1) a hairpin as so represented. The bundle of tubes is inclosed in a high pressure shell and consists of some 200 small tubes of 14 mm inside diameter which are fastened into bundles above and below. We shall not discuss here the technical details, such as their closer bunching on the outside. The feed to be heated, i.e. the coal paste and hydrogen circulates around the tubes. The product leaving the converter, and which must be cooled, passes through the tubes, i.e. hydrogen and the distillate in a counter-current to the paste. To make it more clear, the heat exchangers will be shown in the future separately, with the forward pass in front of the convertors and the return pass of the same heat exchanger behind the converter. The maximum heat is introduced in a gas heated preheater, which consists of a large number of such hairpin elements. The hot combustion gasses give up their heat to the strongly preheated paste and hydrogen which flow through the tubes. The low pressure flue gases do not transmit heat as well to a surface of the same size, as the paste high pressure hydrogen flowing on the inside, and therefore the outer surface is greatly increased by the addition of fins. It may be mentioned here in passing that one such hairpin for 700 atm. weighs around 7 te and costs around RM25,000.

I shall not give you the heat transfer equation with the help of which dimensions of our heat exchangers have been determined, but would like to point out one factor, namely the viscosity, which is of the utmost importance for the heat transfer of our products at a tube wall surface and from that surface. The peculiar behavior of viscosity of coal paste at first caused us great difficulties. The curve, figure 2, shows the typical changes of an approximately 50% coal paste, that is one containing 42% pure coal. The coal paste viscosity behaves entirely normally up to about 150° when determined under normal pressure. The viscosity drops rapidly with the temperature. Above this temperature, however, viscosity rises again rapidly, and reaches a maximum at about 320°, and the height of this maximum could not be measured with the instruments at our disposal. The shape of the curve has been determined by Dr. Hupfer by computations from heat transfer experiments under pressure. The minimum, as well as the maximum, are shifted under high pressure towards the higher temperatures. At any rate this behavior of the coal paste is a disturbing influence to heating to such an extent that such a paste can only be used up to around 300°. This phenomenon is to be traced to the well known swelling property of the particles of coal. The volume of individual coal particles increases upon heating and the surrounding oil film becomes thinner until it finally breaks and the individual particles rub against each other. The very viscous paste will plug up the small space between the individual tubes, and the unit will have to be shut down.

Prior to constructing the first industrial stall in Scholven, unfavorable experiences of this kind have been already obtained in small scale experiments at Ludwigshafen, and we have entirely avoided heating the paste by heat exchange with the distillate.

Scheme 1, Figure 3. This scheme shows the coal stall 300 atm. at Scholven, and also the 700 atm. Gelsenberg stall. Only the operating gas is heated up in the so-called gas heat exchangers. The preheater is explained in a temperature diagram, Figure 4. The stall consists in most cases of 4 converters and 1 hot catchpot. The HOLD and the distillate are cooled in 1 water cooler each, the HOLD to about 200°, the distillate to about 40°. The gas circulation pump circulates the feed after washing it in an oil scrubber, not shown in the scheme, and is made up with fresh gas. Some of the make up gas acts as a cold gas.

The temperature diagram of the preheater, figure 4, shows how paste and gas are heated to the reaction temperature. The flue gases circulate countercurrently with the paste, and only in the last pass concurrently.

We can see in the heat flow diagram of the stall, figure 5, with what amounts of heat one has to deal in such industrial stall units. Around 20 x 10^6 kcal enter the converter. The heat of the reaction inside the converter is around 7 x 10^6 kcal, so that the total sensible heat introduced into a converter is around 27 x 10^6 kcal. Heat losses consist first of all of the circulating heat of the heat exchangers, also of the heat still contained in the HOLD at 200°, and with which the HOLD enters the kiln for further operations. Additional amounts of heat which are shown dark in the residue are heat losses. Of these we have the heat of the HOLD absorbed by water or air coolers, where it is cooled from 440 to 200°. Furthermore there is the heat remaining with the distillation mixture at 328° which is removed in the final cooler and finally the radiation losses of the individual high pressure units (converters and heat exchangers).

The amount of heat, 7.8 x 10^6 kcal, to be added to the paste in the preheater, referred to 16 te of pure coal to be treated in the stall, will give us an efficiency 7 - 65% of the specific heat requirements of this process, which is equal to 750,000 kcal/te of pure coal or 1.5 x 10^6 kcal/te of gasoline.

What are the temperature changes in such a high pressure tube (figure 6)? I have removed a hairpin from the hottest part of the last pass; the temperature diagram shows that the circulation gas had here a temperature of 578° and the paste was at 380°. Where we too know in addition to these temperatures also the temperature transfer coefficients, namely those of the circulation gas to the tube wall and of the tube wall to the paste, the changes in temperature could be calculated, as has been done on the left for a clean tube 90 x 171 in size and at the right for a tube with 10 mm thick incrustations. The incrusted tube has a considerably hotter tube wall and the temperature drop within the tube wall itself is much flatter, that is less heat is being transferred. It may be mentioned here that the N10 steel used as fin material for 700 atm. are rather independent of strain in comparison with the effects of hydrogen at a wall temperature of only 520°. This fact is relatively new and we allowed ourselves to base our designs for 5 years on 560° wall temperature, as a result of which this new limitation to 520° produced many headaches. Up to the beginning of the year we considered our problem primarily to be the reduction of the actual heat consumption, while now a second problem was created namely the lowering of the wall temperature of the hairpins, without however increasing the present number of hairpins.

Additional viscosity experiments have shown that a thinner paste does not possess the second rise in viscosity, but at most a small increase in the region of the rise, which does not exceed the viscosity found at about 100°. This result offers possibilities for a new process which has been introduced in Pölitz.

Figure 7. A thick paste with 54% total solids is broken up into two partial streams, one of which is thinned out by the addition of pasting oil to 43%, producing an average concentration of 47 - 48% total solids. The thin paste, which is the larger component, may be heated readily to the reaction temperature in the heat exchangers. It must however be mentioned that in the production of thin paste and thick paste high speed turbo mixing has been successfully introduced, and we may now operate up to the limit of the 43% concentration of the thin paste, which is important for the economy of the process. The thick paste is either preheated to the reaction temperature in the preheater or else is mixed at a slightly lower temperature with the thin paste, and both streams are mixed together to the so-called mixture proportion. This division of the paste into 2 streams offers the further advantage of greatly reducing the pressure difference in the preheater, which favors the hydrogen partial pressure in the converter. The heat flow diagram, figure 8, shows that the efficiency of heat exchangers has been increased in comparison with the Scholven-Gelsenberg scheme, which reduces correspondingly the load upon the preheater. The actual heat delivered by the preheater amounts to only 330,000 kcal/te of pure coal.

Good results have been obtained using this Pölitz method of operation and there was therefore no objection to providing this method of operation for the Upper Silesian process for gasoline + fuel oil, Figure 9. A better comparison would be obtained by reducing the actual thru-put of 73 te/h to the thru-put of the Gelsenberg and Pölitz stalls of 40 te/h. The heat exchange would be here further increased by heating up the thick paste as well in a bundle heat exchanger to 280°, which is possible for this temperature. Heating the thick paste to over 300° would be impossible in the heat exchanger.

Attempts have also been made to transfer the heat from the HOLD, which has formerly been lost in the cooler, to the thick paste in heat exchangers of our own construction. Such HOLD elements were joined in 20 meter lengths one behind each other and had a cross section shown at the bottom of the figure 9. It may be found however that many technical and operational difficulties have made their appearance, in particular those resulting from the non-uniform production of the HOLD.

The heat flow diagram, figure 10, shows that the heat flow through the preheater has been again reduced. The specific heat still equals about 250,000 kcal/te of pure coal.

Possibilities of further savings in heat as well as reducing the preheater load have not yet been exhausted as long as such large amounts of heat as we find on the heat flow diagrams are still lost in coolers. The heat of reaction produced in the converter is sufficient to heat up the coal paste and we should try to economize heat right at the converter. We have taken so far for granted that the coal paste should enter converter I at 425°. Dr. Pier has shown already at an early date that the use of cold gas as a cooling method should be given up for chemical reasons and that feed itself should be used as the cooling medium. The first practical step in this direction was the use of cold paste. Some facts based on the peculiarities of currents in the converter are here of help. Obviously the same amounts by weight which enter from below must also flow out above. However, this liquid is first made to circulate, as shown by the arrows in figure 11: it is the hot feed movement along the wall downward and becoming mixed with the colder intake feed. The reaction temperature of 440° is therefore reached by mixing the incoming paste at the so-called starting temperature of 425°, and of the return flow at 470°. The return flow carries over therefore the maximum heat. What proofs do we have of this circulation flow, or has it been arbitrarily assumed? It has been found many years ago in Leuna that the coal utilization at the intake of the converter already amounts to some 30%, and at the outlet of converter I it equals to 85%, but rises from 30 to 60% immediately upon entering the converter. This can only be attributed to a mixing effect, and an equally high utilization has been found below, along the wall as higher up.

Accurate measurements of temperature over the cross section of the converter made at Gelsenberg have shown that the temperature along the wall was a few degrees higher than inside. With no return flow the temperature should be lower on the outside than on the inside because of the radiation from the shell.

Dr. Urban has carried out a practical test in Scholven by first introducing cold paste into the converter. The introduction of cold paste from above caused the whole reaction to stop, and the intake temperature in the converter dropped suddenly. The addition from above has therefore interferred with the return flow. When however the coal paste was added from below it was raised without trouble to the reaction temperature. The fact that he made his injection into the second converter did not alter the principle.

The return flow apparently causes irregular currents in the converters but brings the advantage of permitting operation of the converter with a lower intake temperature. It is therefore clear that the large amount of return flow permits a lower intake temperature, than a low return flow. The curve for the minimum converter intake temperature was interpolated to higher thru-puts from the behavior of the inlet temperatures of three and four-converter stalls. This may also be obtained by using a curve based on the law of mixtures, which reproduces the relationship of the return flow from the thru-put. Naturally this curve makes no claims to great accuracy.

One may see that the intake temperature of the converter is no definitely predetermined temperature, and has nothing to do with the reaction temperature. It depends upon the thru-put for any converter type. This is the basis for the different intake temperatures in the large scale and small scale equipment with the radiation losses naturally playing a greater role in small scale equipment. These facts may be used in a variety of ways:

1. The operations are carried in the converter at as low a temperature as is possible from operational reasons; should this require too large a part of the first converter be kept at a too low temperature, a fifth converter can be introduced in a four-converter stall, using the first converter to a certain extent as a preheater converter. This method of operation is at present used in Pölitz with success and the four-converter stall with a preheater converter has somewhat greater yield than the usual four-converter stalls.

2. With too large thru-puts, with which a single converter would require too high an intake temperature, the two first converters can be connected in parallel, which would automatically sink the inlet converter temperature because of the reduced load.

3. Also, a converter with a larger diameter than the other converters can be placed first.

4. Other measures may naturally be used to produce a greater amount of return flow, such as the installation, for instance, of sleeves in the high pressure tube as already had been suggested at an early date by Dr. Anthes and Eng. Goetze.

These measures are not intended to save much heat, because an additional converter would cost several hundred thousand RM, and would never become amortized by a saving in heat of only one - two millions kcal/h. There will however be a great reduction of load on the preheater, because the difficulties are greatest when trying to raise to the highest temperature, and eliminating this necessity will permit an important drop in the wall temperatures.

Should we consider all the different methods based on heat exchangers, which may be used because on the existence of the return flow, such as the cold paste injection or the installation of a preheater converter, the present stage of the heating of a coal stall may be summarized as follows:

The feed can be economically heated by this means to within 40 - 50° of the converter intake temperature. A further reduction of this temperature interval could be produced ~~by~~ further increasing the heat exchange surfaces of the heat exchangers. The gain in heat is therefore economically connected with the installation costs of the additional heat exchangers.

What are the means of bridging this remaining interval in a way to favor the preheater, should this problem arise? First of all, is the thermal pump suited to solve this problem?

I will for this reason briefly repeat the principles of the thermal pump. There are two entirely different processes to produce heat at a higher temperature. The first one is the method previously used almost exclusively, and consists in the utilization of such chemical reactions, mostly combustion reactions, which proceed with production of higher temperature. Our preheaters were throughout operated on these principles. The second principle which has been practically developed only within the most recent times depends on the properties of gases and vapors to become heated up when compressed. The heating proceeds according to the law

$$\frac{T_1}{T_o} = \left(\frac{P_1}{P_o}\right)^{\frac{K-1}{K}}$$

The table, figure 12, shows the increase in temperature at different compression. This requires however the expenditure of mechanical labor which is converted into heat during compression. These processes may therefore also be called mechanical heat production. The law of conservation of energy applies to these methods of heat production as well, and it is impossible to obtain more than 1 kcal of newly produced heat by expending 1 kcal of mechanical work. However, the heat may be brought up from a lower to a higher temperature and this can be done only at the expense of a definite amount of mechanical work, as stated by the second law of thermodynamics. Such arrangements for the transfer of quantities of heat from a lower to a higher level are called thermal pumps. The work expenditure and the work requirements of such thermal pumps are found as follows for air:

One kg. of air is to be compressed adiabatically from 1 atm. to 1.33 atm. which will cause a rise in temperature from 20 to 45°. We may remove from this warm air at some constant pressure p_1 the amount of heat Q_1 = cp $(t_1 - t_o)$ = o.24 x 25 = 6 cal. The work of compression is

$$AL_1 = 427 \times cp\,(t_1 - t_o) = 427 \times 6 \text{ mkg, or } AL_1 = 6 \text{ kcal}$$

In this way by expending 6 kcal of work, 6 kcal of heat have been obtained, as is required by the law of conservation of energy, and it could also be produced by applying brakes to the driving motor, that is without any compressors. It must be remembered however that the compressed air cooled to 20° will still have an excess pressure of 0.33 atm., that it would thus still be in condition to perform additional work. This work could be used to drive the motor, possibly by expansion of the compressed air in a compressed air motor, which will produce the work L_2. For the operation of the compressor, compressed air motor and a driving motor, which together form the thermal pump, we have to supply from the outside an amount of work $L_1 - L_2$.

The amount of heat $\frac{Q_1}{AL} = \frac{AL_1}{AL_1 - AL_2}$

has been thus produced by the expenditure of 1 kcal of work. This value is positive and greater than 1 in all cases, because $L_2 < L_1$. It represents the amount of heat given out by the thermal pump to the outside in the form of usable heat from 1 kcal of mechanical work used up in the drive motor. The question now arises about the origin of the excess of this heat over the heat equivalent of 1 kcal of work used, and how large that is.

The work L_2 of the compressed air motor is smaller during the adiabatic expansion of the compressed air in proportion $T_o : T_1$ than the driving work of the compressor. We have therefore

$$AL_2 = \frac{T_o}{T_1} \times cp \times (T_1 - T_o), \text{ while}$$

$$AL_1 = cp \times (T_1 - T_o), \text{ and we get}$$

$$AL = AL_1 - AL_2 = cp\ (T_1 \times T_o)\ (1 - \frac{T_o}{T_1})\ ; \text{ furthermore}$$

$$\frac{Q_1}{AL} = \frac{cp\ (T_1 - T_o)}{cp\ (T_1 - T_o) \times (1 - \frac{T_o}{T_1})}$$

$$\frac{Q_1}{AL} = \frac{T_1}{T_1 - T_o} = 1 \quad \frac{T_o}{T_1 - T_o}.$$

The excess of heat gained over 1 kcal of heat consumed is therefore

$$\frac{T_o}{T_1 - T_o}.$$

The amounts in the second line of this table represent the total amounts of heat gained with 1 kcal of work used. They exceed the work used from 1 kcal by the amounts in the third line. The latter amounts can therefore only result from the heat present in the operating air before compression and raised by the thermal pumps from t_o to t_1, that is from 20° to 22°, 25°, etc.

In principle this process may also be carried out with steam, and it may be shown that with the two drives, with gas as well as with steam, about the same amount of heat will be produced from 1 kcal of work, when the temperatures are the same. The steam process has the advantage that no expansion motor would be required and that steam would permit to make use of much greater amounts of heat for the same required volumes of the compressor, than with air. The process conducted with steam lets one readily realize that the heat Q_1 required by the thermal pump is to a great extent delivered from the available sources of heat, since every kg. of steam sucked in by the compressor had been first produced in the boiler from hot water by supplying the heat of vaporization. This process can be conveniently represented by the so-called I'S diagram of Mollier, figure 13. One may first of all observe the so-called left and right boundary curves. Underneath this boundary curve is the wet steam region, on the right above is the superheated region and points on this boundary curve represent therefore the saturated steam. These obliquely running lines are isobars, as well as isotherms inside the wet steam region. Only above the limiting curve do isobars and isotherms branch off from each other. The isobars rise with a slight bend on top, while the isotherms rise only slightly toward the right. The process in the thermal pump may be represented therefore as follows:

Steam at 1 atm. and 100° is adiabatically compressed to 2 atm., that is the compression line rises vertically high to the pressure of 2 atm. From here heat will be subtracted from it, at first the heat of superheating until the right boundary curve is reached, and from then the heat of evaporation down to complete liquefaction; the temperature of the cooling medium forms the boundary.

Before proceeding to an example of application of the thermal pump I would like to add the curves of the productivity coefficient $\varepsilon = \frac{T_1}{T_1 - T_o}$ (figure 14) in relationship to the temperature difference $T_1 - T_o$ for different temperatures of heating. We may see that the coefficient rises steeply when the temperature difference becomes smaller, and the coefficient of efficiency itself becomes larger at higher temperatures of heating, than at lower temperatures, while the difference in temperature remains the same.

I will show you in figure 15 a scheme of evaporation of water by means of a thermal pump. The heating will not be done simply by means of electrical resistance, as presented in this picture, where 1 kWh is merely the equivalent of 860 kcal of heat production, or only 1.5 kg. of water, and we will make use of the heat of vaporization present in steam at 100° and make it available at 105° by using a thermal pump. We may obtain at least theoretically an efficiency

$$\varepsilon = \frac{T_1}{T_1 - T_o} = \frac{378}{5} = 70$$

There is produced therefore fifty times greater amount of distillate.

Figure 16 shows the actual appearance of such evaporation installations. The solution to be concentrated in the evaporator is first brought to the boiling temperature, that is 100°, by means of fresh steam. Now the already preheated compressor is put to use. The latter exhausts the vapors from the steam chamber of the vaporizer, compresses them and returns them to the heating body. They are liquefied there and give out their heats of superheating and vaporization. The hot condensate runs into the bottom part of the vaporizer and from there into the preheater where its heat is given up to the feed brought in by gravity from a container at some height. The feed becomes heated to approximately T_1 and after passing through the preheater enters the vaporizer. The condensate of the heating substance cools approximately to the room temperature and runs from the preheater into the storage tank for distilled water. The immediate heat consumption consists practically only in the amount of heat necessary for the original preheating of the vaporizer contents. It plays only a subordinate role in the whole process. The power consumption of the compressor is characteristic for the economy of the whole process.

The heat transfer through the surface separating the condenser and the preheater proceeds freely with but few degrees of heat and the power requirements are therefore theoretically of the order of magnitude of 1% of the heat transferred. They are naturally correspondingly greater during solution with lowering of the vapor pressure. The fact that such units have not nevertheless reached any great practical success and are hardly ever are used in our I.G. works, is to be attributed primarily to the excellent development and operations of the many-unit evaporation equipment. In these, the vapors rising in the first vaporizer are used as a source of heat of the second vaporizer, kept at a lower pressure and which has therefore a lower boiling temperature than the first preheater, so that the first vapors in the heating unit of the second vaporizer become liquefied, and the heat of liquefaction is transmitted to the contents of the second vaporizer. The same amount of steam is developed in the second vaporizer as has been liquefied in its heating unit, and this steam is transmitted to a third vaporizer with still lower pressure and temperature.

We may get directly from the I/S diagram the work to be used for a definite vaporization yield of the thermal pump. The amount of steam, in kilograms, obtained from 1 kcal of work of compression is:

$$G = \frac{1}{AL}$$

Therefore with 1 hph

$$G = \frac{632}{AL} \text{ kg. of water}$$

and 1 kWh

$$G = \frac{860}{AL} \text{ kg. of water.}$$

that is the work of compression of kg. of steam from 1 atm. to 2 atm. is

$$AL = 30 \text{ kcal/kg.}$$

and

$$G = \frac{860}{30} = 28 \text{ kg.}$$

The heat of vaporization at 1 atm. is equal 539 kg. *), and 1 kcal of work requires $\frac{539}{30}$ = 18 kcal of heat.

We now turn to the question whether and to what extent in heating of the other hydrogenation stalls the thermal pump could be introduced. We see that the production coefficient $\varepsilon = \frac{T_1}{T_1 - T_o}$ increases with increasing temperature T_1 and also when the temperature difference $T_1 - T_o$ becoming smaller. A vapor phase stall must therefore be constructed in which the last 10° of heat bridged over normally by means of an electrical resistance heating, will be supplied by a thermal pump. I will show you now two examples (figure 17), the first one a thermal pump in a vapor phase stall and then in a liquid phase stall. The outline here represents a 5058 stall in which the intake temperature into the converter I is at 400° C. We are dealing therefore with an old catalyst. The heat exchanger should heat only up to 390°, and 10°, or 200,000 kcal/h remain yet to be effectively added. The thermal pump, which we have seen to consist of a compressor and an expansion turbine, which must be constructed in our case as high pressure machines may possibly be advantageously installed behind the converter. The compressor in front of the converter would have the advantage of raising the hydrogen partial pressure inside the converter, but would introduce the danger of having some liquid constituents still remaining, and they may do damage in such an arrangement. Computations show that compression of mixture of gas distillates with a compression ratio of 1.05 from 420° to 430° is sufficient to raise the output of the 3 heat exchangers of the stall to the converter intake temperature exclusively through heat exchange. The exhaust engine will then be connected immediately behind the hot heat exchanger in order to win back the maximum amount of energy. It would be profitable to keep the second exchanger as small as possible to transfer only the maximum heating and without the formation of any condensate. As 200,000 kcal/h must be theoretically delivered with electrical resistance heating, the differential production of the compressor and exhaust machines, in this case the thermal pump, would produce only 20,000 kcal/h. This production factor of 10 may naturally be still further raised by making the exchangers still smaller and exhaust at still higher temperatures. Some allowance must however be made for such a heat exchanger in order to overcome other unfavorable heating conditions. An initial preheater is required.

It is more difficult to introduce the thermal pump into the liquid phase. One can think of no machine which would compress a mixture of paste/gas together, and condensate is already present in the return path at any temperature. Moreover the temperature interval to be bridged over is greater in the

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*) Unfortunately no other liquid is known with similar favorable properties as water and with values some 150° C higher than for water.

liquid phase than in the vapor phase. As we have seen it amounts to 40 - 50° with extensive heat exchanging against 10 - 20° in the vapor phase. The thermal pump can find therefore only indirect application in the liquid phase in combination with the auxiliary circuit which is shown in figure 18. This auxiliary circuit, in the use of which either nitrogen or air may be used, is heated by using the highest degree of heat. The maximum of the heat of the distillate is anyway utilized in the heat exchangers and the most suitable heat is the HOLD heat, as well as the heat between the last converter and the hot catchpot which has previously been removed with cold gas. The auxiliary circuit will be heated to 440° by means of these two sources of heat, next compressed in a compressor to 540° for which a compression ratio of 16 will be required, that is from about 10 to 16 atm. This low pressure gas now lowers its heat to 440°, it is exhausted with the same decompression ratio and the nitrogen or the air are cooled to 343°, and is then again heated to 440° in the two coils and recompressed.

What does the preheater itself look like? First of all it has to be constructed with the same number of hairpins as the earlier compressors but without being finned. A jacket is made to surround every hairpin and the hot heating medium circulates through the annular space. The heating medium is under pressure, and the annular space must be of such dimensions that the heat transfer coefficient is higher than in the finned preheater. The maximum heating gas temperature may therefore be lowered, as has actually been done in this case. The maximum heating gas temperature was 540° against 570° and over in the finned preheater with the same number of hairpins.

The production coefficient is no longer as favorable for theoretical reasons as it was in the vapor phase, because one has to work with greater temperature difference as may be also directly seen from the energy balance of the machines, which have been obtained under theoretical conditions. In this stall, as in the vapor phase stall, an initial preheater must be installed for the starting of the stall, because at the start the source of heat from the HOLD is as yet unavailable and heating of the high pressure unit to the required temperature would be too costly with electrical energy. There are naturally some other possibilities to apply the thermal pump in our case. Thus Dr. Donath has suggested to make use at 700 atm. of fresh gas as follows:

It is branched off from the 200 atm. compressor, heated in the last heat exchanger some 200°, and compressed to 700 atm. which will cause it to assume a temperature of 540° and is then used for mixing with the paste-gas mixture heated to 380°.

We have now arrived to the most important question with regard to the thermal pump: Can these high theoretical values be approached, or what may actually be expected from the thermal pump in practice? I have therefore shown again in this table the curve of the production coefficient at T_1 = 800 absolute for a temperature difference up to 250°. One may see that the production factor at low temperature difference theoretically greatly exceeds 20.

What effect will efficiency have and what efficiency may in general be considered? There is first the efficiency of the compressors: η_K. The compressor has a production A_K but gives up only $A_K \times \eta_K$ in the form of heat.

The efficiency η_K is very high and is around 95%. The amount of heat $A_K \times \eta_K$ is delivered to the preheater, but some of it is lost as radiation and some as resistance. Both losses are expressed in the efficiency η_V. It amounts to 72% and consists of two parts, the proportion of the heat transfer and the proportion of the transportation of the fuel gas. The former amounts to 80%, the latter 90%. Thus only the efficiency $A_K \times \eta_K \times \eta_V$ enter into the recovery of work in the exhaust turbine. The efficiency of this machine η_E is 60%. The difference in work amounts therefore to $A_K - A_K \times \eta_K \times \eta_V \times \eta_E$. For further explanation consult the figure.

We may add the following to the curves:

1). The high production figures are strongly affected by the efficiencies of the unit. The upper curve in which only a_K enters into consideration is still high and depends in almost its whole height on the compression of the vapors, since no exhaust machine is used and the whole heat exchange of the system proper never takes place.

2). The bottom curve is flat to such an extent that it becomes no longer important to operate at the lowest temperature differences, if higher differences will cause fewer difficulties; one may obtain therefore only a slightly lower efficiency of the waste heat at lower temperatures.

Were this result the only one available, namely the transfer of 100% more heat during hydrogenation when using the thermal pump than the heat equivalent of the electrical heating used, that is an average efficiency of 2.0, one might be entirely satisfied with the results and think earnestly about applying thermal pumps to hydrogenation.

We have kept so far one fact out of consideration, namely that the thermal pump is driven with an electrical drive which is produced with coal in our case, and we must therefore ask the question: What is the thermal efficiency of electrical energy obtained by us? We have so far tacitly assumed the efficiency of electrical energy to be 100%. This is however by far not the case. To judge this question we use again the I/S diagram. The electrical energy is obtained in counter-pressure turbines. Steam under 100 atm. pressure and superheated to 490°, is expanded adiabatically to 18 atm. The expansion line ends to the right of the vertical, that is the entropy is increased and we get about 1 kg. of steam with around 800 kcal heat contents, an electrical output of around 110 kcal. Steam under 18 atm. with all its high heat contents is still available for heating purposes. With this counter-pressure operation a high efficiency may still be realized depending on how the steam is used. Electrical energy is, however, in most cases produced in so-called condensation installations, specially when there is no use for the exhaust steam. It is also expanded in turbines to a pressure predetermined by the temperature of the cooling water of the condenser. For instance if 18 atm. of steam is used in an expansion turbine and its pressure reduced to 0.05 atm., corresponding to a temperature of saturated steam of 30°, 1 kg. of steam with 525 kcal will be taken out in condensers. The thermal efficiency

$$\eta = \frac{\text{Heat converted into work}}{\text{Total heat}} = \frac{165}{710} = 23\%.$$

Should we consider the efficiency of the boiler as well as other losses, the efficiency of the condensation machine must be set at 21% maximum. Even in our chemical plants which have the highest requirements for heat, a large part of electrical energy must be obtained from condensation engines. Should electrical energy be used for power for the heating with thermal pumps, and the electrical energy produced from coal instead of hydraulically, this electrical energy is produced with a condensation stream and must therefore be used with the poor efficiency of the condensation engines, of 21% maximum.

We have seen above that the high efficiency factor of about 2.0 of the thermal pump is derived from the efficiency of the machines and the heating arrangements. Were the thermal pump to be compared with direct heating, namely with that of our gas-heated preheater, the efficiency factor of 2.0 would have to be multiplied by 0.21, the efficiency of the condensation drives and the total efficiency of the thermal pump drive would amount to 42%, while with our low pressure heating we may count on 65%.

Figure 20 shows how all heat is cooled: that is the heat of the distillation coolers, of the HOLD coolers and the heat given off between the last converter and the hot catchpot. We get waste heat as 10 te/h of steam at 10 atm. and 440°; this is compressed in a turbocompressor to 540°. 1,720,000 kcal/h are transferred in the preheater. The residual steam is utilized in a power engine and we can see that the power requirements of the compressor are not met.

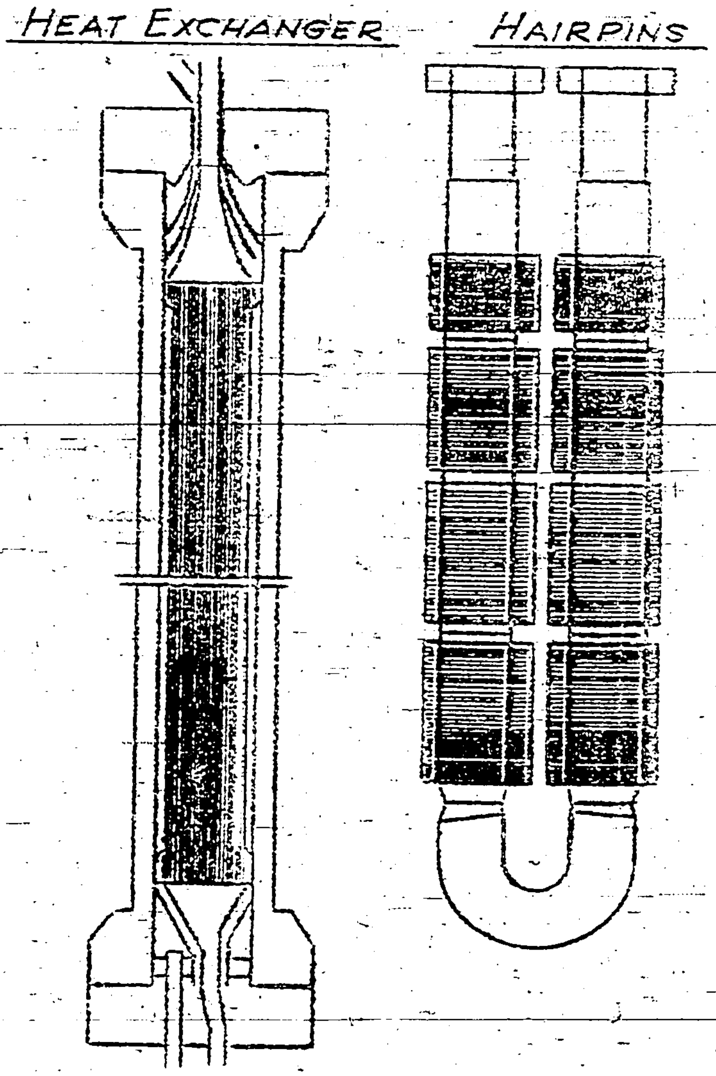
Even if it were possible to increase the efficiency of all expansion machines, as well as lower the heat losses to permit thermal pumps to reach the efficiency of direct heating, and the thermal pumps can be built sufficiently cheaply after sufficient development on large-scale production to permit their actual introduction, there will still remain the question: What is the advantage offered by the thermal pump against the former ways of heating? Such a heat transfer will be markedly more expensive than in our present preheaters, because of the increased engine room installation. In addition, a usual preheater will be required for starting, and the operation preheaters will not have their loads reduced because the same tube wall temperature is maintained at the same surface; we have at most less crust formation by lowering fuel gas temperatures to 540° from 570°. However the present heating may be replaced with pressure heating, possibly by using the principle of Velox boilers, so that even this advantage of the low fuel gas temperatures is lost, while the present efficiency of 65% might conceivably be raised to 75%.

We may therefore summarize as follows:

The use of thermal pumps is in general correct and valuable in economical systems where the power is generated hydraulically and where there is no possibility of combination of heat with power. Thermal pumps will become important in Germany only after all condensation flow is replaced by counter-pressure flow, water power or wind power, after counter pressure flow, outside current, water and air, are introduced for the production of heat. The thermal pump offers no special advantages in application to hydrogenation and will result in a poorer efficiency, and it is therefore too soon to apply the thermal pump raising the temperatures in our hydrogenation stalls, and to consider it more than being merely of general interest.

/S/ Schappert

Sternberg/MC/jw
8-5-1946



HEAT EXCHANGER

HAIRPINS

FIG. 1

VISCOSITY OF COAL PASTE (40% PURE COAL) AT DIFFERENT TEMPERATURES

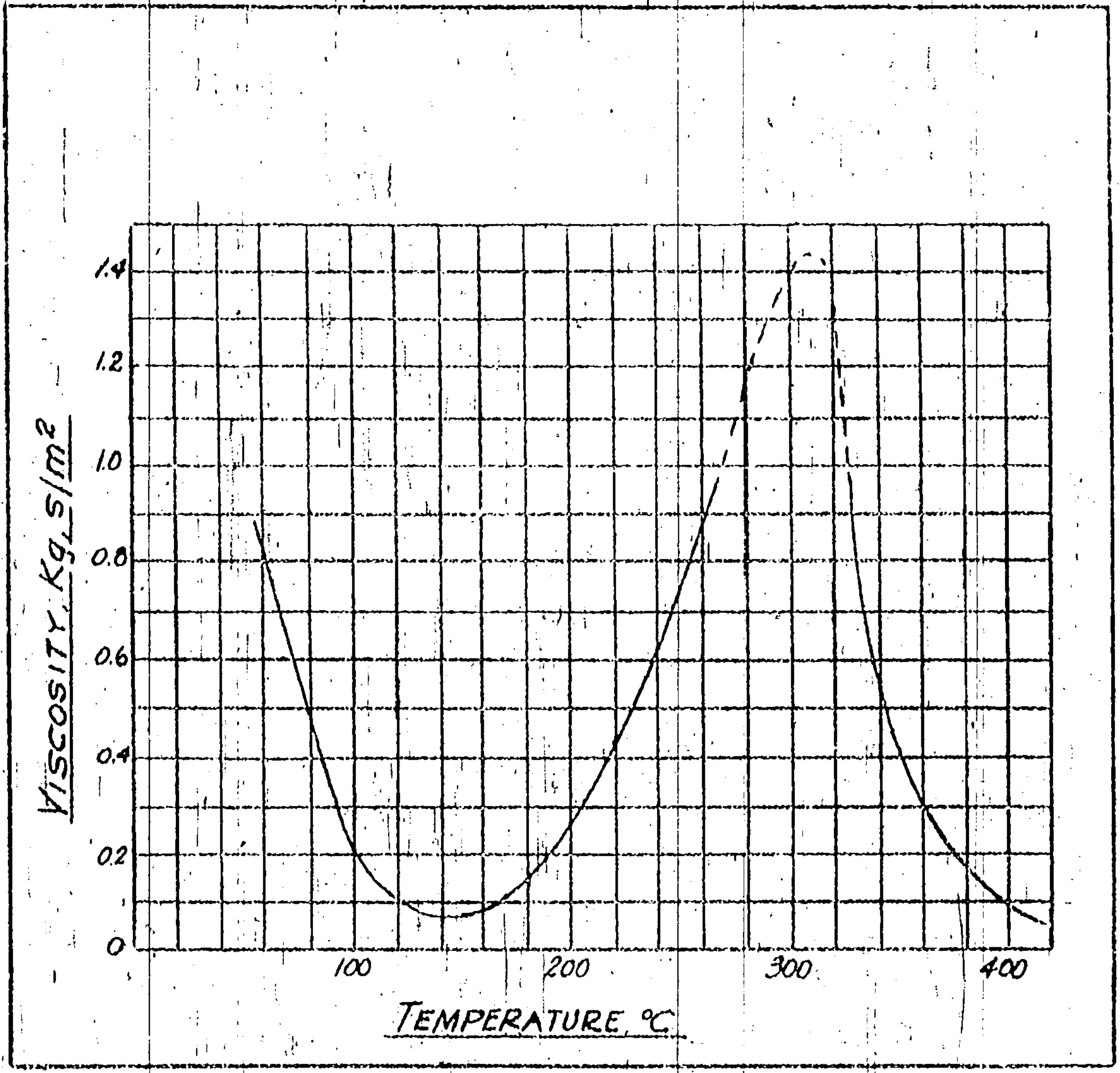
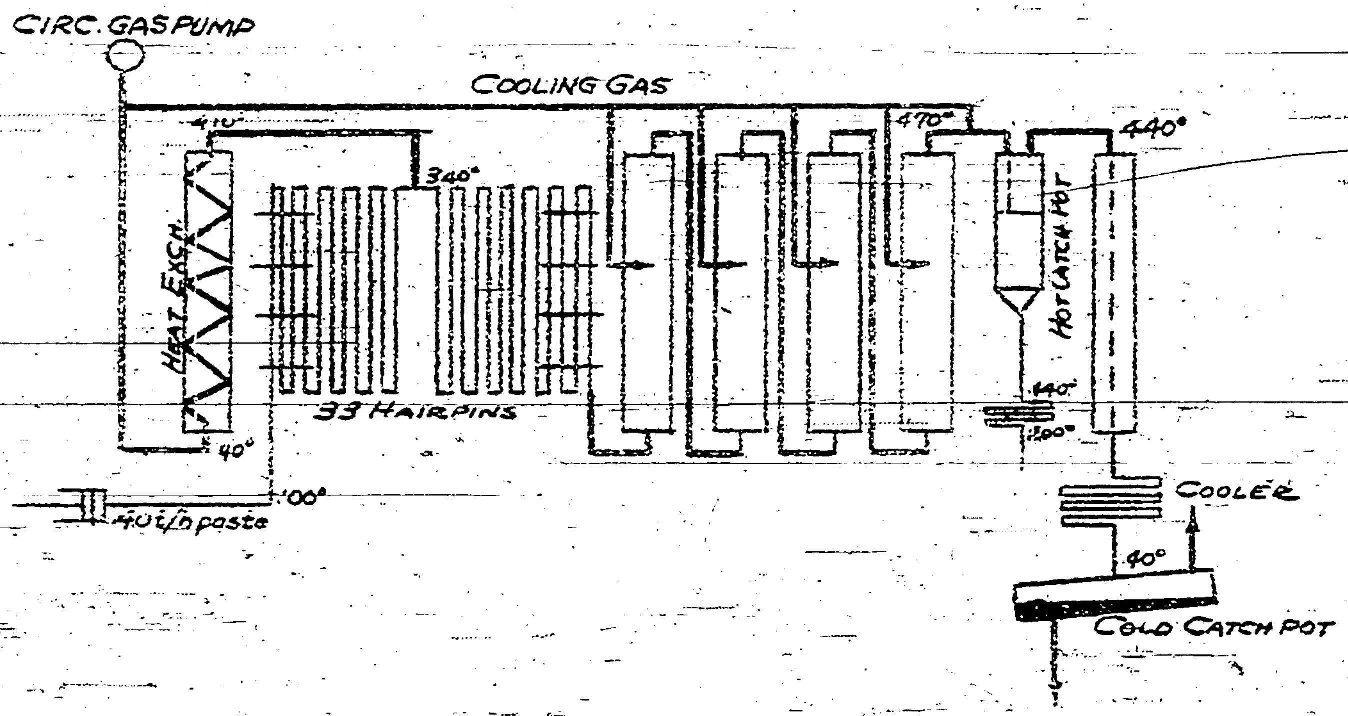


FIG. 2

SCHEMATIC OUTLINE OF THE GELSENBERG & SHOLVEN STALLS



$$\left.\begin{array}{l} 1\ \text{Kg PASTE} = 0.55\ (\text{KCAL}/\text{Kg}) \times (425-100 = 174 \\ 1\ m^3\ H_2 = 0.32\ \text{KCAL}/(m^3) \times (425-40) = 122 \end{array}\right\} = 298\ \text{KCAL}$$

1 Kg PURE COAL GIVES 440 KCAL

1 Kg PASTE (40% PURE COAL) GIVES 176 KCAL

FIG. 3

TEMPERATURE DIAGRAM OF A GELSENBERG AND SCHOLVEN PREHEATER

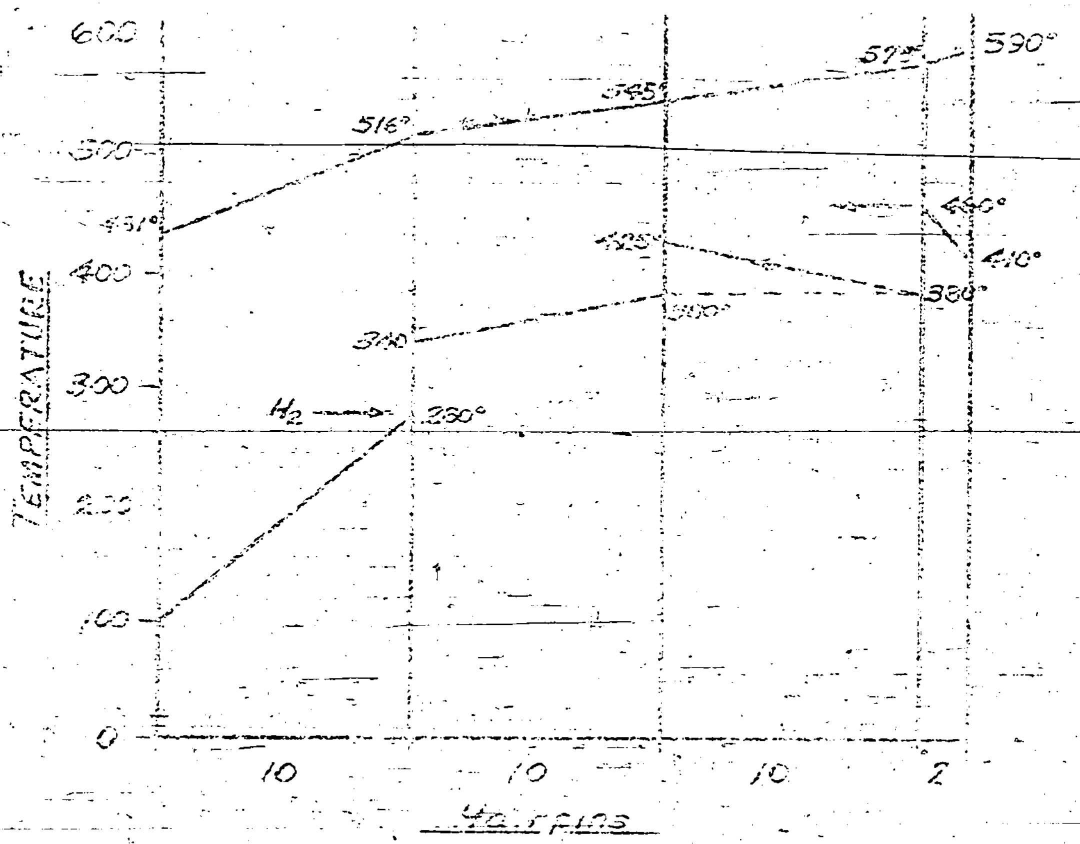
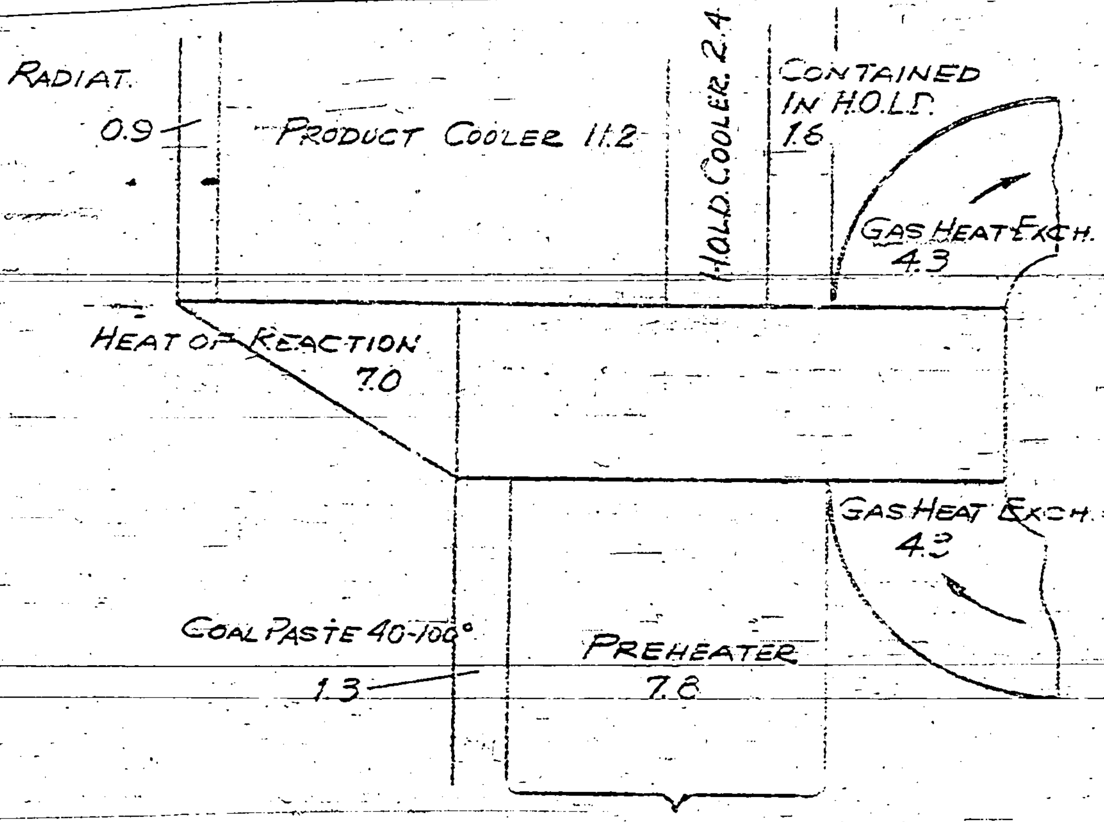


FIG. 4

HEAT FLOW DIAGRAM OF A GELSENBERG COAL STALL IN 10^6 Kcal/h



$Q_{preh.}$ = 300,000 Kcal/te PURE COAL

FIG. 5

THERMAL CHANGES IN A HIGH PRESSURE TUBE 90/171

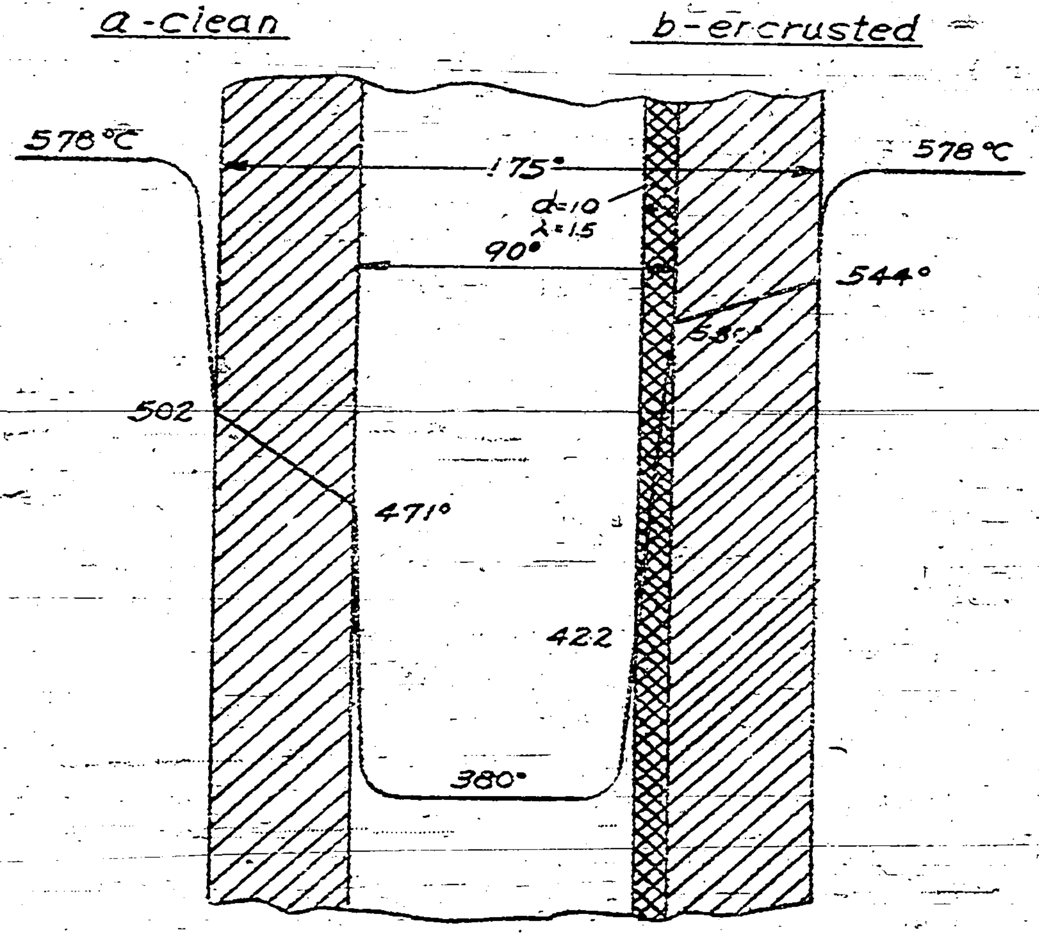


FIG. 6

THE POLITZ STALL

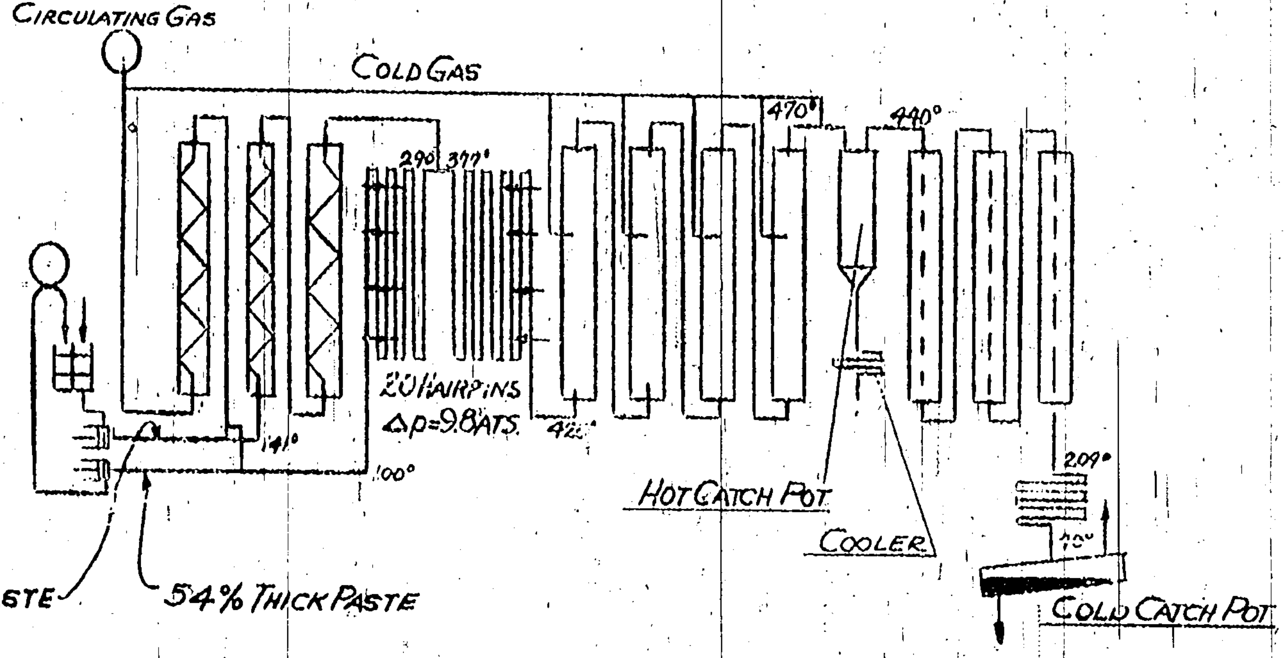
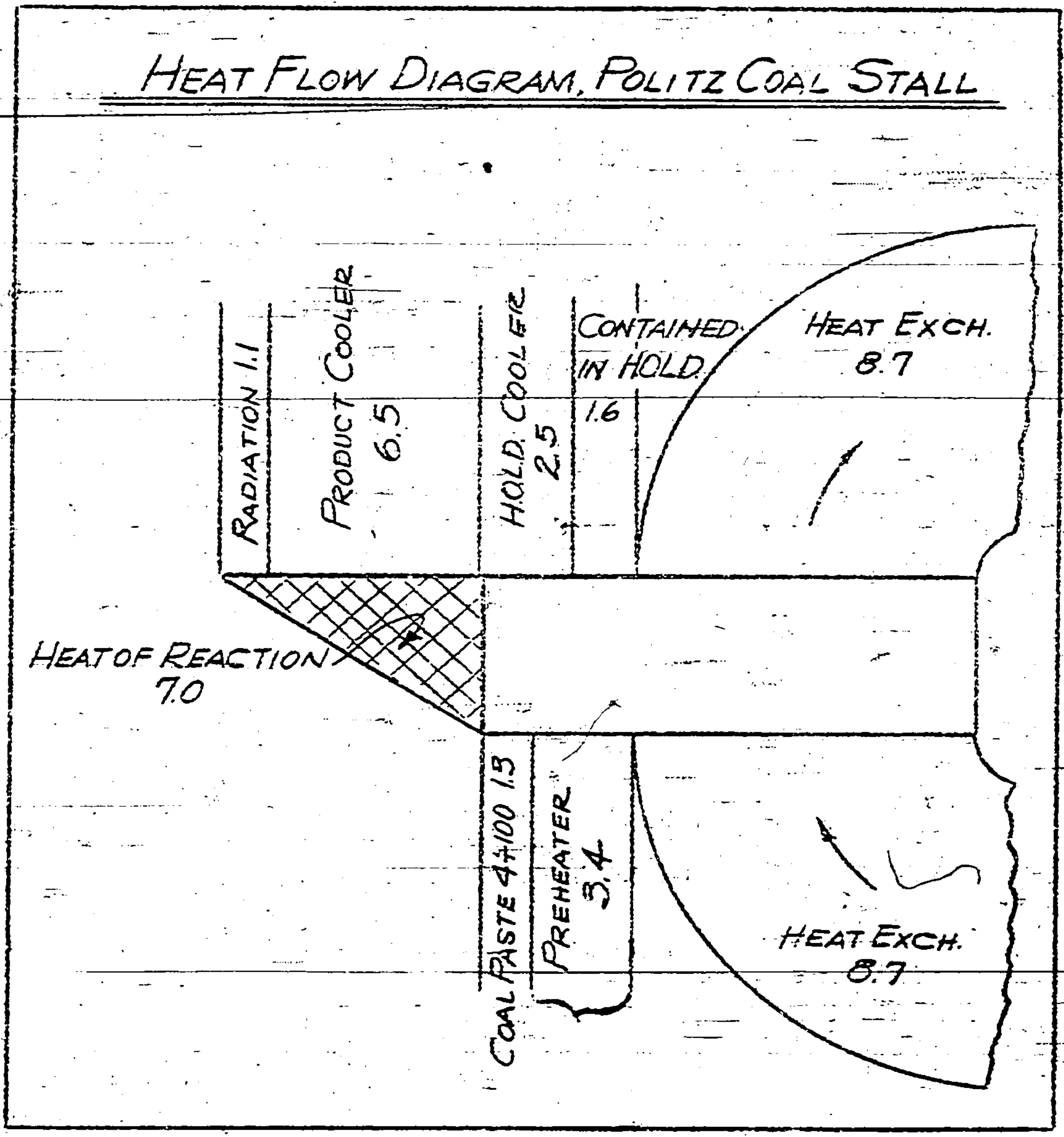


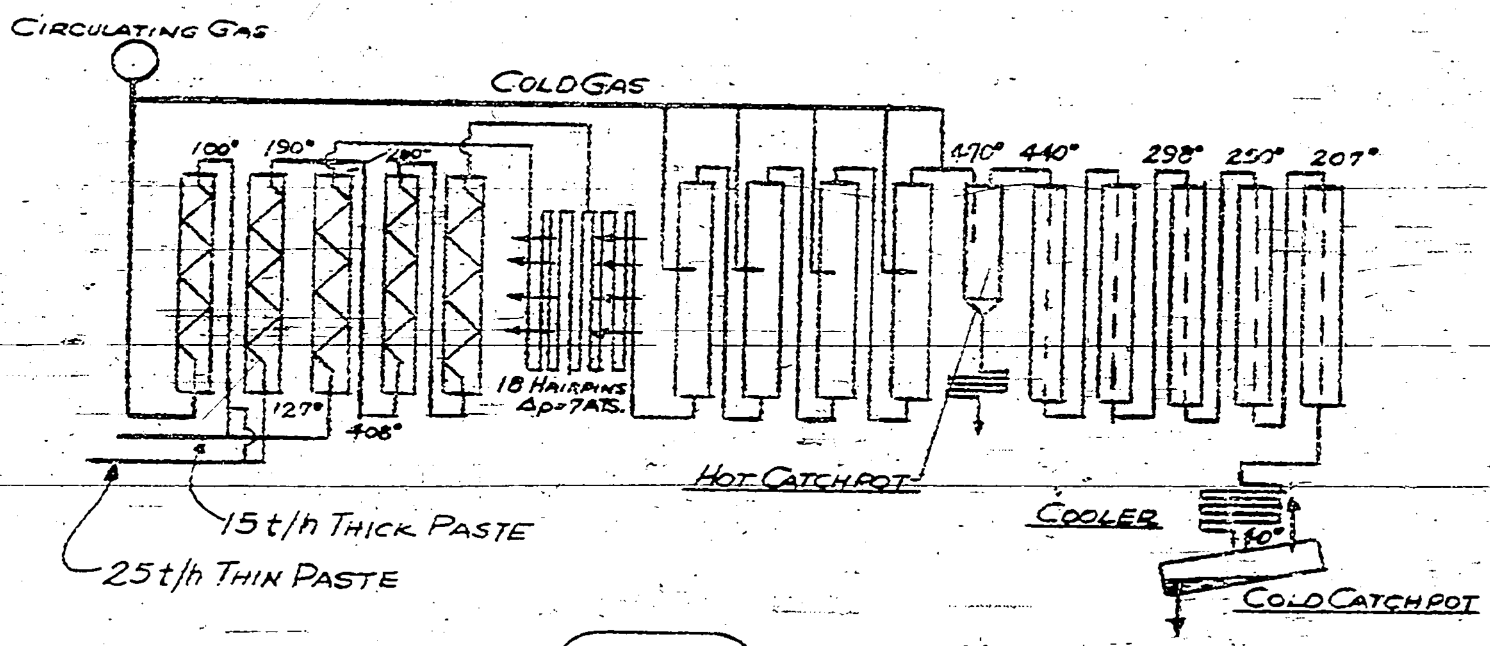
FIG. 7

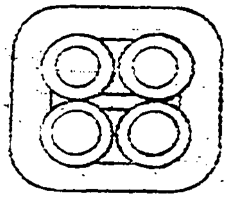


HEAT FLOW DIAGRAM, POLITZ COAL STALL

FIG. 8

SCHEME OF AN O.S. STALL



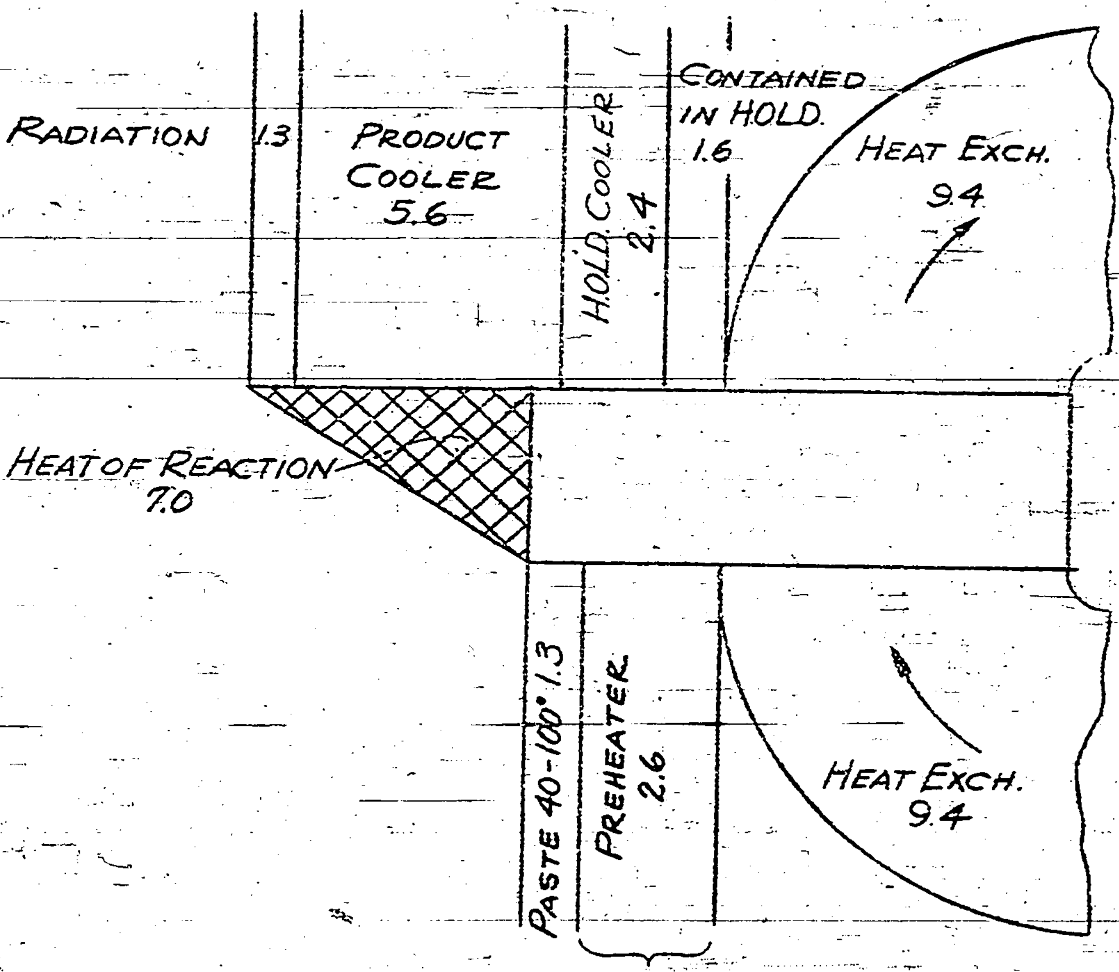


H.O.L.D. EXCHANGER.

FIG. 9

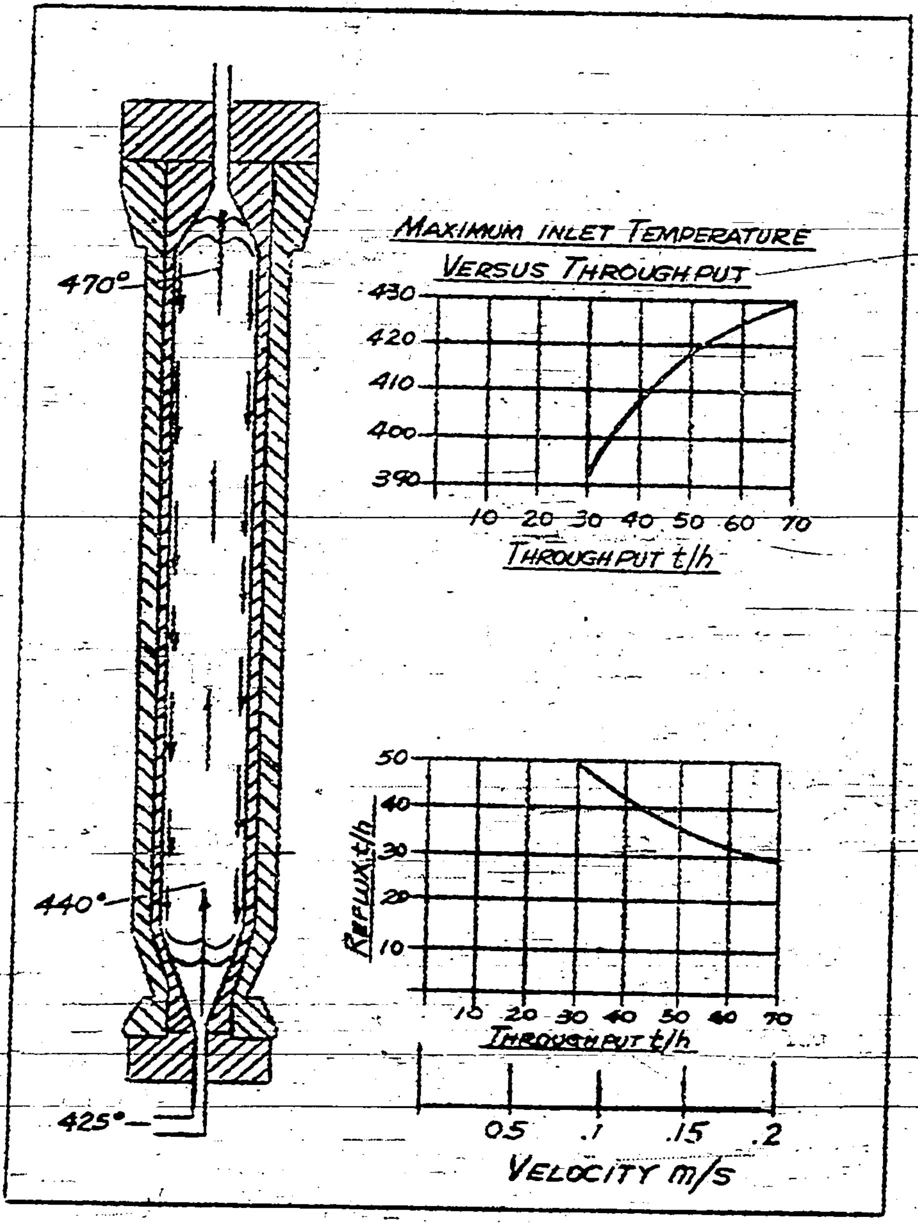
T-74

HEAT-FLOW SCHEME OF AN O.S. STALL IN 10^6 Kg cal/hr.



Q PREHEATER = 270,000 Kcal/t CLEAN COAL

FIG. 10



470°
440°
425°
MAXIMUM INLET TEMPERATURE
VERSUS THROUGHPUT
430
420
410
400
390
10 20 30 40 50 60 70
THROUGHPUT t/h
50
40
30
20
10
REFLUX t/h
10 20 30 40 50 60 70
THROUGHPUT t/h
0.5 .1 .15 .2
VELOCITY m/s

FIG. 11

MOLIER DIAGRAM FOR STEAM

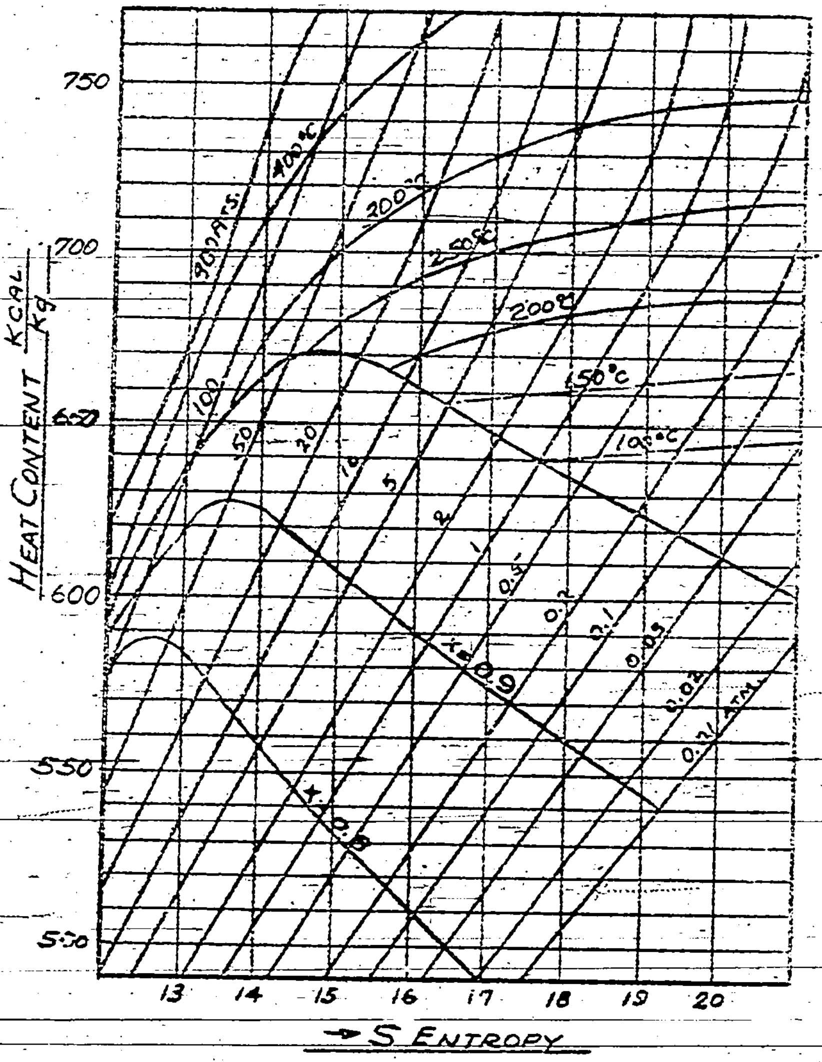


FIG. 13

T-74

THROUGHPUT FACTOR E: VARING WITH THE TEMPERATURE DIFFERENCES T1-T0 FOR VARIOUS HEATING UP TEMPERATURES T1

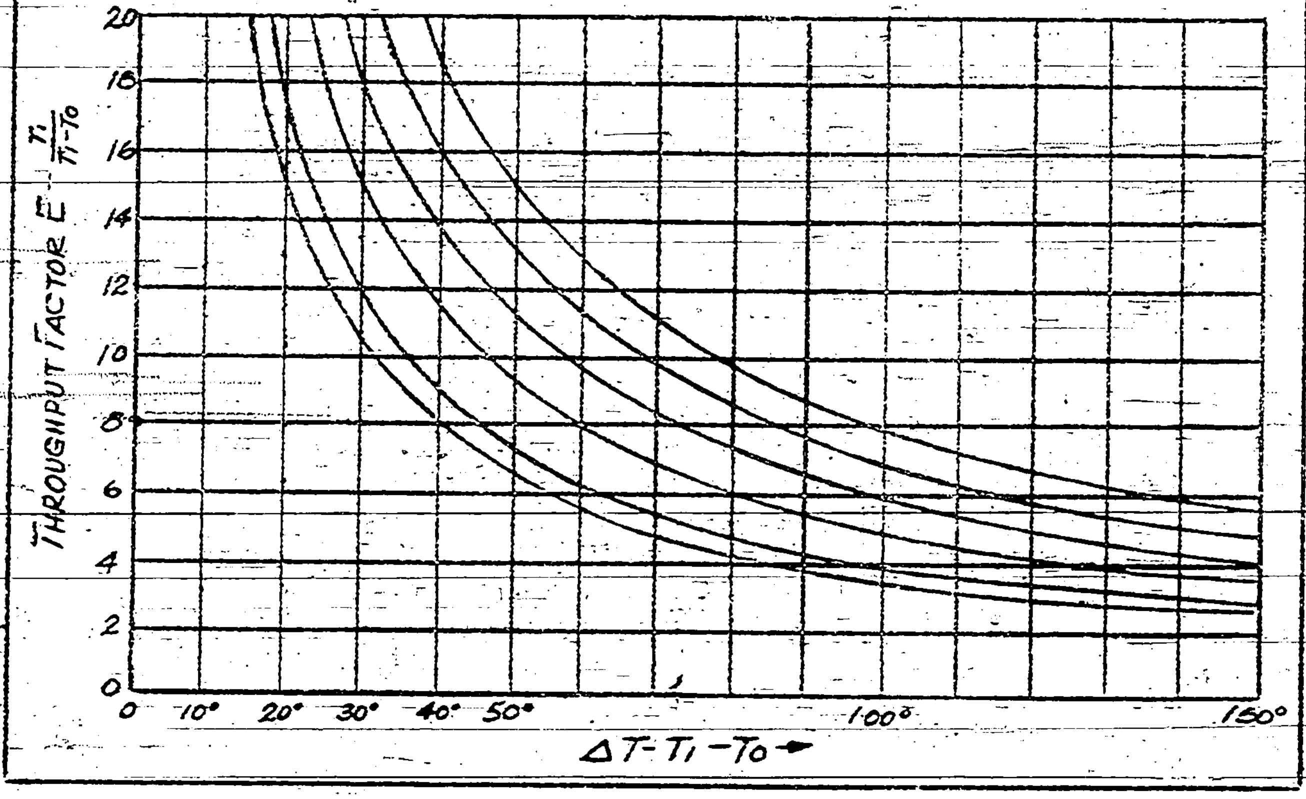
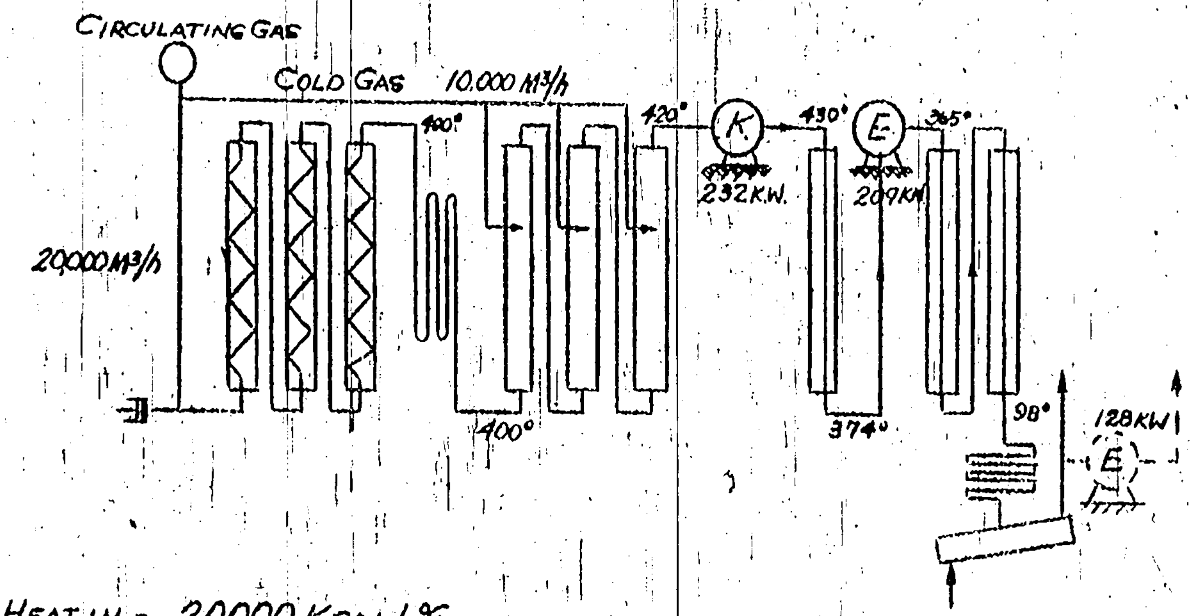


FIG. 14

GAS-PHASE STALL WITH HEAT PUMP



HEAT IN = 20,000 KCAL/°C
HEAT OUT = 25,000 " "
ENERGY REQ'D = 500,000 Kg × 0.12 $\frac{Kcal}{°C\,Kg}$ × 250° = 15×10^6 Kcal
START UP PREHEATER = 1000000 KCAL/h

FIG. 17

BITUMINOUS COAL STALL WITH HEAT PUMP

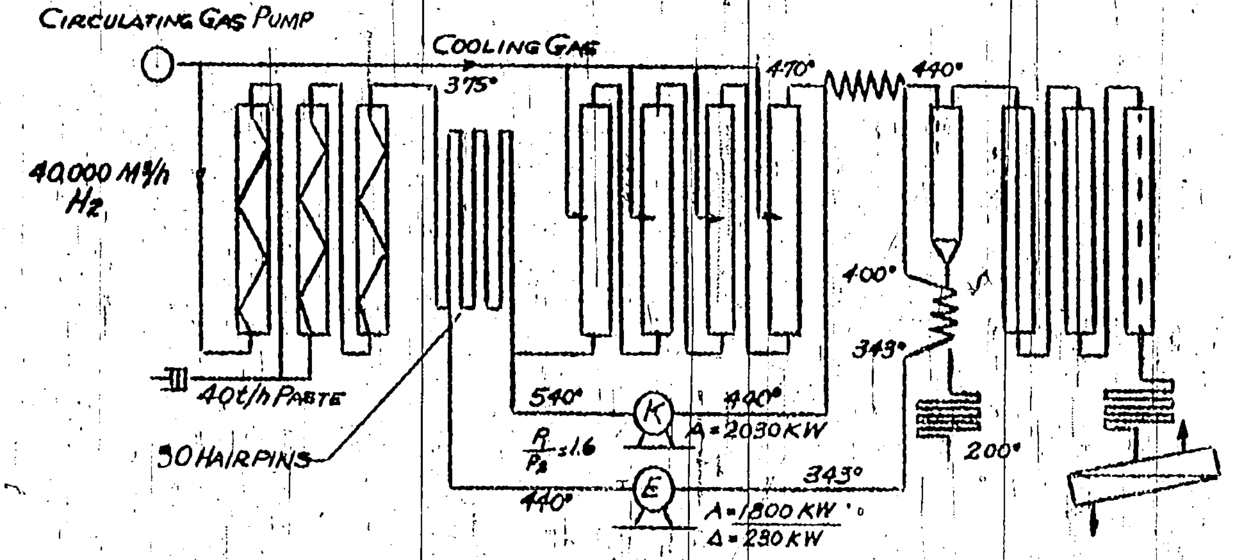
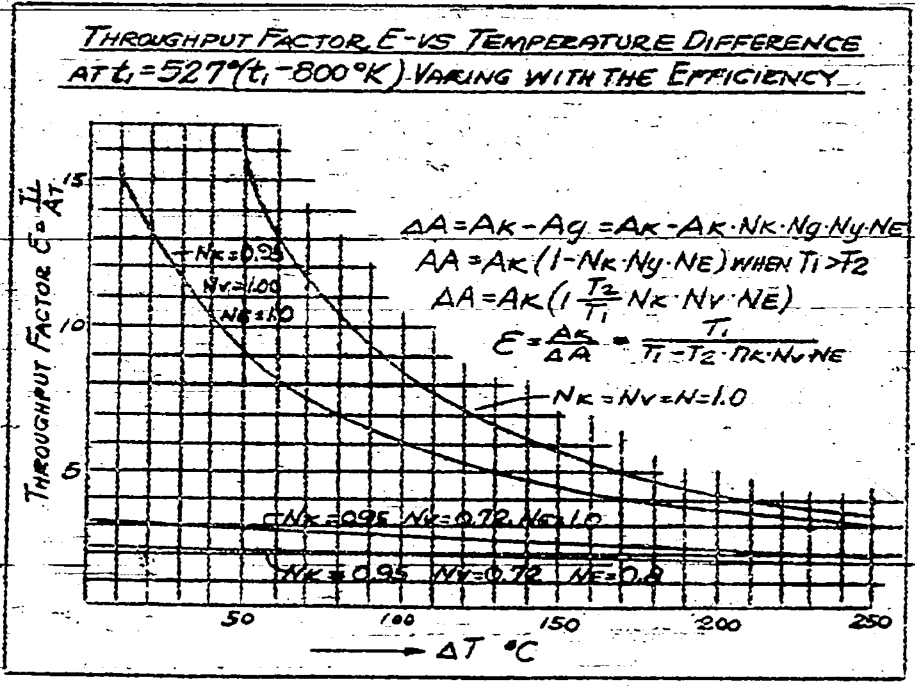


FIG. 18

FIG.19: Changes of Production Coefficient with the temperature difference $t_1 = 527$ ($T_1 =$ 800°C under Consideration of the efficiency.



COAL STALL WITH HEAT PUMP

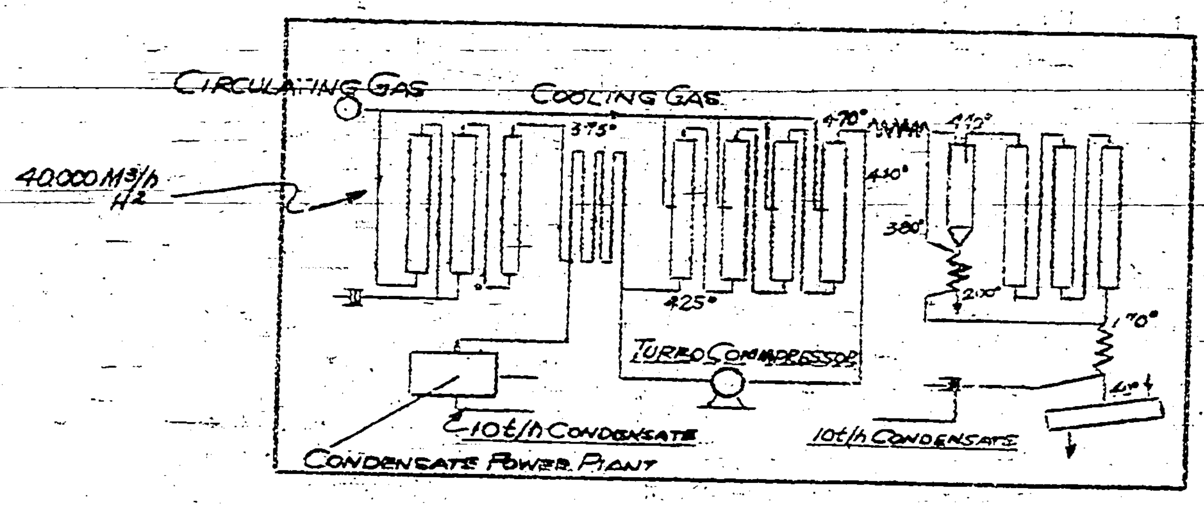


FIG. 20

T.O.M. Reel No. 162
Frame No. 667
pp 865-866

May 19, 1943

High Pressure Test Lu 558

RULES FOR THE CONSTRUCTION OF HYDROGENATION STALLS

The various proposals for general rules can be embodied in the following forms:

1.) Considering that in the future we will still have to count on using pipe bridges in the hydrogenation stalls, the stalls shall be built with closed walls without any openings of consequence. They must be open at least on one side and on the top.

2.) On the open side, and within a distance of up to 30 meters, no working spaces, frequently used traffic aisles, equipment containing inflammable materials, etc., which are not directly connected with the operation of the stall, shall be located.

3.) Working spaces in the immediate vicinity of the stalls (including platforms) must be protected from flares and have ample escape possibilities.

4.) The stalls must be designed for ample wind pressure with the usual safety factor.

5.) The stalls must be designed for an inner static absolute pressure of 300 kg/m^2 with the usual safety factor.

6.) The stability of the stalls, as well as the connection at the head of the high pressure converters, must be such that it can take the horizontal reaction caused by a break in a connecting pipe.

7.) Since, in general, it is impossible to calculate the temporary stresses caused by a hydrogen-air mixture explosion, the reinforced concrete walls or the reinforced concrete skeleton frame must be so reinforced that only a scarring of the walls, which will permit resumption of operations, but no break will occur in such an explosion.

Under present conditions these seven rules embody the measures necessary for sufficient protection of employees.

/s/ Raichle

KCBraun/mc/pkl
8-2-1946

T-76

T.O.M. Reel No. 174
pp. 833-839

Lu, September 27, 1944

CONSTRUCTION OF PREHEATERS WITH HORIZONTAL TUBES

Construction of preheaters for distillation and cracking plants in the oil industry, particularly in America:

Except for one case (de Florenz) all American, as well as other, preheaters for distillation and cracking operate with horizontal tubes.

Also the use of heat transmission by radiation is preponderant here. The recicling of waste gases occurs, but is not the rule. Adjacent to the radiation section a convection section is often built, in which the discharge gases are used for heating the incoming product.

General Arrangement:

In its simplest form, the tube heater consists of a rectangular box with fireproof lining on the walls. The tubes are arranged in a single row along the outer walls and sometimes in a double row on the ceiling. The coldest starting tubes are located in the discharge flue, which is usually arranged for downward flow. While the first mentioned tubes are smooth, that is, without fins, the cold tubes in the discharge flue are usually finned.

From this simplest form, the double preheater with either two or one common discharge flue was developed. One reason was, to provide as large a heating surface as possible within a reasonable space. Another reason was to satisfy the often recurring requirement of two interdependant circulating heating currents, as, for example, the heating of the crude oil and the cracking fraction or alternately, the recicle. (The individual tubes are usually not over 6 meters long.)

Finned tubes were already used in the oldest cracking and distillation coils.

More recently the coils have also been arranged in the center of the heating radius in two rows vertically above each other so that the radiation can reach the tubes from all sides. Each vertical section can then have its cold preheater coil.

Recicling of Waste Gases:

The recicling of the waste gases for reducing the room temperature is occasionally, but not generally, done.

A fine equalisation of combustion to provide as uniformly as possible temperature stresses in the tubes can be achieved by careful calculation.

Reasons for the choice of horizontal preheaters with radiation heating:

1) Can be based only to a very small degree on the oldest cracking plants, such as Bourton, which are directly copied from the steam boiler construction prevalent at that time.

2) The main reason is the simple and cheap construction of the whole preheater, the easy accessibility, cleaning and control of the tubes in operation. In detail:

a) The frame is of simple steel construction in which the tubes are suspended.

b) The tubes are not heated at both of their connecting points, are protected from burning gases, accessible and easy to clean.

c) Ceiling and walls consist of annealed fire-bricks, which are individually suspended from the ceiling and then covered with insulation. Where a cover is required, this consists of simple straight plates. Expensive finned tubes are avoided.

d) The building section is limited to a light roof, usually of corrugated iron, which is intended to protect only against heavy rains.

The use of vertical tubes in the U.S.A. and elsewhere in the oil industry:

Vertical tubes are used in the U.S.A. only in the de Florez cracking process, except for the special construction of Houdry, which really are conduction heat-exchangers and apparently exist only in patent literature, while practical construction follows other lines.

The deciding factor in the de Florez process is said to have been the easier separation and removal of insolubles from the tubes. But radiation heating is also used in these ring-shaped shaft furnaces.

Details of horizontal preheater tubes:

Thru-put:	100 - 5,000 m^3/day
Length:	Approximately 6 meters
Diameter with a capacity of (5,000	bbls./day = approximately 800 T/day = 100/152 mm.

End Closures:

Double bends on each end with specially formed connecting elements. Each tube can therefore be machine-cleaned. Accessibility is very good.

Material:

Originally ordinary carbon steel, was long retained, because operating managers valued the characteristic of the soft steel tubes, inflating before bursting due to incrustation.

Later 46% chromium steel and, because of hydrogen sulfide attack, also alloyed steels, such as V2A. Original construction difficulties have been overcome.

Suspension:

The tubes are individually suspended by heat and scale-resistant steel hangers.

Protection against overloading by radiation:

Since the one-sided stressing of the tubes through radiation at high heat loads has led to difficulties, such as distortion and incrustation, protecting screens have, in part, been placed before the tubes. However, a later construction using radiation from both sides seems more suitable.

Circulation heating:

Is used individually, the rule is simple radiation heating with the use of waste heat for heating the cold oil.

Burners:

Gas, oil or pulverized coal burners (the latter very seldom) are used. Good regulation and control, particularly of the excess air and the temperature, are essential.

Use of horizontal radiation preheaters in hydrogenation in the U.S.A:

Standard Oil has built-in horizontal preheaters with radiation heating in its Bayway and Baton Rouge plants. Tube material is V2A and NCT3. These preheaters have caused no difficulties.

Rebuilding I.G. preheaters:

In considering the problems of rebuilding the vertical tube preheaters, used up to this time by I.G. and the German hydrogenation industry in general, into horizontal preheaters, using the old tubes, any other but radiation heating is eliminated. It seems apparent that the horizontally arranged preheaters must be operated in the same manner as the old preheaters, that is, with circulation heating.

If we visualize such a preheater in a horizontal position and arranged similar to the old there seems to be no reason why the preheater should not operate thermo-technically as well as the old. It must be expected that:

1) The movement of the oil-gas-stream in the tubes will be more uniform than in vertical tubes since the advance of the fluid ahead of the gas in the downward stream is eliminated and thereby also the reason for the more severe wear of the lower bend.

2) That the temperature distribution will be more uniform over the length of the tubes since the present tendency for the hottest gases to accumulate at the top of the preheater is eliminated.

Construction:

Tube Supports:

The difficulty in supporting the long tubes and in their installation and dismantling might possibly be solved by arranging the gas flues vertically and possibly combining a row of tubes in a flue with heat-resistant steel chambers and suspending them as a unit or, possibly even better, support them at the bottom. Each tube bundle so formed would then have to be made removable from one side.

Masonry:

A further difficulty appears in the probability that a new row of specially shaped fire bricks will be required, and that, in general, the masonry and the closure of the heating lines must be changed. ~~In any~~

In any case, a general reconstruction of the preheaters for the horizontal arrangement is required.

/s/ Goetze

KCBraun/mc/pkl

A SUMMARY OF LITERATURE

On Cracking, Preheaters, Heat Transmission and Alloyed Steels.

F = Stress calculations
K = Cracking equipment
M = Metals and heat-resistant alloys
R = Tube-preheater construction
W = Thermo-technical calculations

K Roy Cross, Handbook of Petroleum, Asphalt and Natural Gas

W Industrial Engineering

a) Sidney & C. F. Tate (Foster Wheeler Co.)
"Heat Transfer and Pressure Drop of Liquids in Tubes" 1936, p. 1429

W b) Wilson, Lobo, Hottel: Heat Transmission in Radiant Sections of Pipe Stills. 1932.

W c) C. C. Monrad: Heat Transmission in Convection Sections of Pipe Stills, 1932, p. 505.

K R Nash: "Principles of Motor Fuel Production and Application"

FKMRW National Petroleum News: Many examples.

FKMRW Oil Journal: Many examples.

K Sachanen & Tilicheyev 1929
Chemistry and Technology of Craking. 1932.

Science of Petroleum (Dunstan, Nash, Brooks, Frisard)

K R Volume 4, pp. 2077-2295

W Volume 4, pp. 2175-2207 Heat transmission

F Amsler (H. Windisch), Schaffhausen
Festigkeitsberechnung von dickwandigen Zylindern und Rohren für sehr hohe Drucke. (Stress Calculations of Thick-Walled Cylinder and Tubes for Very High Pressures.)

W Chemie-Ingenieur: Wärmeübertragung durch Strahlung (Heat Transmission Through Radiation)
Vol. I, Part 1, p. 496.

R K Chemie-Ingenieur: Röhrenerhitzer (Tube Heater), Pipe Still
Vol. III, Part 4, P 233.

K Fussteig: Theorie und Technik des Kreckens (Theory and Technique of Cracking.) 1935.

Gröber: Wärmeübertragung (Heat Transmission.)

W Heiligenstädt, Werner: Wärmetechnische Rechnungen für Industrieofen (Thermodynamic calculations for Industrial Furnaces) 2 A 1941.
Strahlung (Radiation) p. 86
Berührung (Conduction) p.74
Röhrbündel (Tube Bundle) p. 79
Uswälzheisung (Circulation Heating) p. 228
Strahlheisrohr (Radiant Heat Tube) p. 226

W Hottel: Wärmetechnisches Handbuch (Handbook of Thermotechnic)

M Hessenbruch: Metalle und Legierungen für hohe Temperaturen. 1940. Zunderfeste Legierungen. (Metals and Alloys for High Temperatures 1940. Scale-resistant Alloys.)

M W Hütte: Ingenieur Taschenbuch (Engineer's Handbook).

R Marder, Motorkraftstoffe (Motor Fuels) pp. 110-117
"Konstruktion der Vorheiser" ("Construction of Preheaters")
p. 259: "Krackverfahren" (Cracking Process)

K Dr. Naphthali, Max "Leichte Kohlenwaszerstofföle" (Light Carbohydrate Oils).

K Rosendahl: Das Kracken von Kohlenwaszerstoffen 1940 (The Cracking of Carbohydrates 1940)

K R Sedlacek: Die Krackverfahren unter Anwendung von Druck 1929 (The Cracking Process Under Pressure 1929)

R Thermann K.: Chemische Apparatur (Chemical Apparatus) 28, 1940 pp. 97, 113, 131

F Windisch H. "Die Berechnung von Kaltgereckten dickwandigen Zylindern und Rohren für sehr hohe Drucke". (The Calculation of Cold-Worked Thick-Walled Cylinders and Tubes for Very High Pressures.)

T.O.M. Reel 145 T-77

pp. 489-490 March 31, 1944

High pressure experiments, Leuna 1

MAXIMUM PREHEATING IN THE LIQUID PHASE

Summary - The old idea of Krönig of operations with CO in the hydrogen is being tested with a view of raising the temperature in the converters. Discussion of CO_2, water gas or O_2-containing decomposition products of the water gas.

Dr. Krönig has tried years ago to reduce the hydrogen consumption in the liquid phase when operating with O_2-rich coals by the addition of a few percent CO to the fresh gas. This CO was supposed to compete with H_2 for the O_2 of the coal, becoming converted to CO_2, which is stable at the relatively low temperatures of the converter. (Water gas equilibrium.) The experiments have been discontinued.

The idea has been since repeatedly expressed to make use of the heat of the reaction of the reaction of oxygen products with hydrogen to raise the preheater temperature in the liquid phase. The following considerations were advanced to stimulate the experiments:

It is known, that in the presence of even a few percent of CO in the fresh gas the temperature of the vapor phase converter rises dangerously, while the increase in the temperature of the preheater and the liquid phase converters amounts to but a few tenths of a millivolt. The reduction of CO with H_2, i.e. the establishment of methane equilibrium (formation of H_2O and CH_4) is relatively slow in the last case, but may be affected by catalysts, as is proven by what happens in the vapor phase. The above equilibrium differs from the usual combustion phenomena with O_2 which must progress much too violently under the high pressure of the converters and produce at least some coking as a result of local superheating. The heats of reactions of the systems which may be utilized for heating are, according to Landolt-Boernstein:

1) Formation of H_2O steam from $(H_2) + 1/2\ (O_2)$ - - - - + 57.1 Cal

2) Formation of CO from $(C) + 1/2\ (O_2)$ - - - - + 29 Cal)
) 96.96 Cal
3) Formation of CO_2 from $(CO) + 1/2\ (O_2)$ - - - + 67.96")

4) Formation of CH_4 from $(CO) + 3\ (H_2)$ - - - + 45.98 Cal

5) $(CO_2) + 4\ (H_2)$ - - - + 39.56 Cal

6a) Formation of CH_3OH (Communication from Tropsch) $(CO) + 2\ (H_2)$ - - + 27 Cal

6b) Formation of CH_4 (by difference, from CH_3OH) - - - - + 18.98 Cal

(To supplement: Water gas equilibrium: $(CO) + (H_2O) = (CO_2) + (H_2) + 9.8/25°$

Reactions 1 - 3, i.e. the introduction of O_2 in to the coal paste, must be excluded by the above. Reactions 4 and 5 deal with the production of the intended reaction velocities and with industrial applications to the process. It must be assumed, that every catalyst which accelerates the formation of hydrocarbons, if added to the paste at the start, will become inactive through deposition of asphalt, for which reason the accelerator of the reaction must be kept separate from the coal paste for the longest time possible.

It appears that in actual operations preheated CO, CO_2 or producer gas must be introduced into converter I (or the last hairpin), to which a catalyst is to be added for the following reasons:

a) Even the regular liquid phase catalyst promotes the reaction: in that case, the pasting of the catalyst in the pasting oil will be found sufficient.

b) Only a metal (of the 8 group) may be considered as a catalyst: in that case, one may advantageously lead the addition gas over iron carbonyl and inject it with or without oil. It will be sufficient to combine only part of CO with the carbonyl.

To introduce the catalyst into the converter:

The additions may well be introduced into the converter through a long tube, inserted into the middle from below, so as to favor the circulation in the converter. Moreover, part of the reaction may take place in the inlet tube itself, transmitting the heat of the reaction through the tube wall.

It is assumed that the reactions of formation of hydrocarbons can be forced.

On the other hand, too rapid a reaction may be moderated by producing intermediate reactions according to the reaction schemes 6a and 6b.

The formation of hydrocarbons from CO or CO_2 may therefore be mastered from the stand point of heat technology, and is well adapted to the solution of the question of maximum preheating.

Sternberg/jw

8-7-46

T.O.M. Reel 162
Frames 886-893
pp.1145-1150

Lu 558 3 May 1943

CONSTRUCTION OF HYDROGENATION STALLS FOR EXPLOSIONS

Ref: Letters from Director Dr. Sauer to Dr. Pier dated 15 March and 19 April 1943, as well as a letter to Dr. Sauer from the Association of Chemical Manufacturers, dated 12 March 1943.

To the questions raised in the aforementioned letters we take the following position:

1. The pressures occurring in Hydrogenation Stalls in Hydrogen Explosions.

The maximum pressures occurring in a totally enclosed space can be fairly accurately calculated. Appendix I and Diagram I indicate these maximum possible pressures and temperatures based on the hydrogen concentration of the mixture with air. For combustion at constant volume and about 32% hydrogen content, a maximum possible static pressure of somewhat over 9 ats. is produced. The inlet passage in the Hydrogenation Stalls is too small to cause a detonation, so that the occurring explosion pressures naturally have a different order of magnitude than is the case with explosives.

It is hardly possible to calculate what explosion pressures occur in practice in the Hydrogenation Stalls, because neither the hydrogen content nor its distribution in the stall at the moment of explosion is known. Even if one tried to solve the problem by a series of simplifying assumptions only static pressure could be determined at best, but not the dynamic stresses and vibrations responsible for the destruction in an explosion, which, for example, are caused by directed gas streams. However it can be assumed with a high degree of probability that the pressures occurring in practice are considerably smaller than the above mentioned theoretical maximum pressure, for the following reasons:

a) The burning gases can escape at the top since the stalls are open there. The escape of the pressure at the front is also possible since the stalls are largely open on that side.

b) It cannot be assumed that the whole stall space is filled with a 32% hydrogen concentration at the beginning of an explosion. This optimum mixture can, at best, be present only in a peripheral zone at the outlet. In the stall explosions which have occurred so far the formed mixture was probably very highly aliphatic, whereby the course of the pressure rise is flatter than with an excess of oxygen and the case in point is rather a rapid burning than a real explosion.

What order of magnitude the absolute pressure still remaining will assume after these considerations are taken can hardly be shown in figures. It was determined, however, thru an inquiry by our Building Division directed to the Building Contractor about the destruction caused by a stall explosion in December 1930 in Me 841, that the explosion pressure in this stall must have amounted to at least 1500 kg/m², as can be calculated from the deformation of the stall and the reinforcing used in the stall walls.

2. Specifications and Rules for the Building of Hydrogenation Stalls.

We, as well as the Association of Chemical Manufacturers, are firmly of the opinion that it is best not to put such rules in writing, because the current adaptation of the construction to the current technical improvements is thereby made more difficult. Furthermore, there is the danger of an unnecessarily heavy construction thru generalization, which would be contrary to the present requirements for the economical use of building space and stall construction materials.

Since, after the letter from the Reichs Ministry of Economics (RWiM) to the District President of Stettin, dated November 27, 1942, the Association is of the opinion that certain rules must be made, we propose the adoption of the following two conditions for the regulation of stall building construction.

a) The calculation of the stalls for simple wind pressure according to the Building Code with the usual safety factors.

b) The calculation of the stalls for an inner static absolute pressure of 300 kg/m² with the usual safety factors.

On the basis of a double wind pressure recommended by Dr. Sauer the fact that in an explosion the stall is under an absolute inner pressure would not be taken into account, so that in this case the stall reinforcing would be in the wrong place.

On the calculation of the stalls for an absolute inner pressure of 300 kg/m² it may be remarked for comparison that it is possible to design the stalls with a wall thickness of 35 cm, as it is generally constructed in its lower section, for an explosion pressure of 600 kg/m² with a reinforcing steel weight of about 70 kg/m³ of concrete, which can still be justified by present demands. On this basis the upper part of the stalls which is mostly built with a wall thickness of 25 cm, could also easily be designed for an absolute inner pressure of 300 kg/m² by using reinforcing necessary to resist the bending moment. Making allowances for the usual safety factors for pressure we can then assume that the stalls would break with a pressure of about 1000 to 1500 kg/m², however, any but a nominal effect of the explosion beyond the stall room could be avoided, as was the case in Leuna.

We should like to recommend, to drop the consideration of the reaction of a freely emerging stream, mentioned in the letter of 19 April 1943 from Dr. Sauer to Dr. Pier under 2) and 3), for the following reasons:

In the largest tubes of 135 mm inside diameter, used at the present time, the reaction in case of bursting at 700 ats. amounts to about 200 tons. Of this, 100 tons act as the component of the force, producing external moments in the converter system.

However, it is practically impossible to give a contractor accurate data on the direction and distribution of this force on the walls. If we assume for instance, that the break in the tube is located in the immediate vicinity of a stall wall, the impact of a stream of 100 tons will be distributed over a smaller surface than at a greater distance. If we assume that the break is, for example, in the middle of the stall (that is 4 m from the wall), and that the stream is widened conically to an assumed angle of 30°, the above mentioned 100 tons could be distributed over a surface of 3.7 m^2, which would still represent an excessive load, even if we assume that the conversion of the kinetic energy into static pressure occurs with a relatively small degree of effectiveness. On the other hand, it must be considered that in case of an ignition of the stream an increase in energy occurs.

If the stalls are calculated according to the foregoing recommendations, a concrete thickness will result such that the wall will stand up without difficulty, at least in a break of smaller lines up to an estimated 30 mm inside diameter, (or by an oblique impact on the wall with correspondingly larger diameter).

3. Explanation of the Stall Explosion in Pölitz in August 1942.

Letter from Dr. Sauer to Hydrierwerke Pölitz of 23 December 1942.

We have made a short test on the behavior of a hydrogen flame with high discharge velocity. Details of this test are recorded in Appendix II. (not available).

From this, the great expansion of the explosion in Stall 15 over the surrounding space can be explained, even without the assumption that a large cloud of an explosive mixture was formed until it was ignited.

The explanation would then be as follows:

When the cold gas supply line on the connecting lines from Converter I to Converter II was knocked off, hydrogen escaped and was immediately ignited on the hot line. Due to the high discharge velocity, the flame was forced into the surrounding space and distributed among a large volume of the atmosphere, accompanied by heavy explosions, (cracking of the flames in test).

Dangerous consequence of such an explosion could be avoided, as in Pölitz, by protecting the surrounding operating equipment from flares. In order to guide the explosion in a distinct direction, the stall walls would have to be built higher than the connecting lines between the converter and the cold gas connecting lines.

This condition might also be met by the arrangement of several nozzles, pointing upward at about 2/3 the height of the converters, thru which high pressure steam could be discharged in case of danger, in order to produce a strong upward draft at the stall and thereby force any explosion flames from the stall to the top.

4. Reinforced Stall Construction In Pölitz.

Letter from Hydrierwerke Pölitz A. G. of 26 March 1943.

The Building Division has recommended changes in the present reinforced stall construction in Pölitz. These are indicated in Appendix III and Drawing Sk 3443. (Not available). They will be discussed with Politz at the earliest opportunity.

(signed) Reichle

KCBraun/pkl
8-6-46

APPENDIX I

La 558 7 April 1943

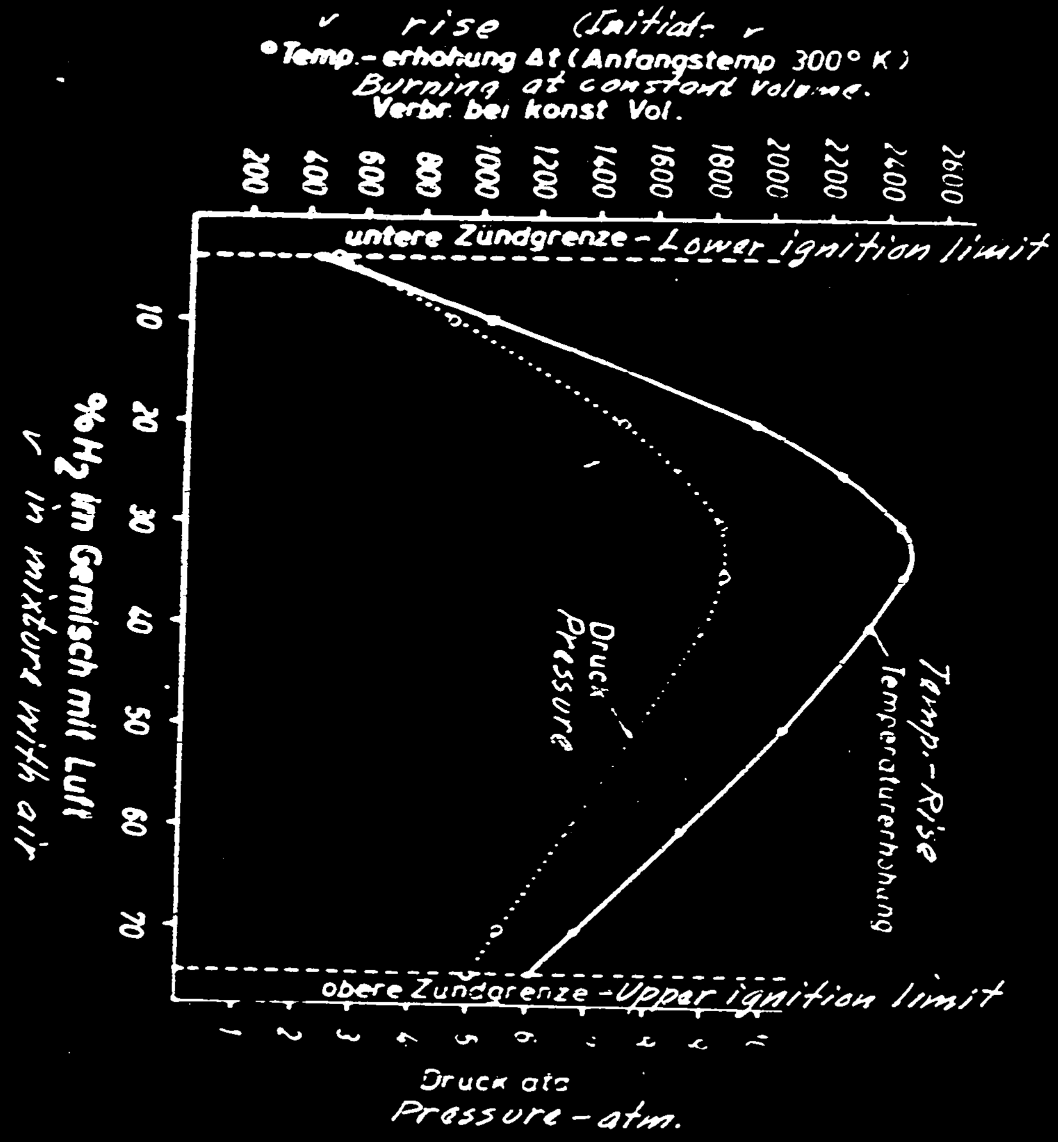
MAXIMUM PRESSURES AND TEMPERATURE IN HYDROGEN EXPLOSIONS

To estimate the possible pressures caused by hydrogen explosions in high pressure stalls due to operating disturbances, the maximum possible temperatures and pressures based on the hydrogen concentration in the H_2-air mixture are calculated (see attached Daigram I). These maximum pressures occur, if the chamber is visualized as fully enclosed, so that the burning gases cannot escape into the surrounding atmosphere. The corresponding temperature calculations for combustion at constant volume have been made at an initial temperature of 300°K (considering dissociation). The maximum pressure possible under these conditions of somewhat over 9 atmospheres occurs with a mixture of about 32% hydrogen content (assuming that the entire gas volume uniformly reaches the maximum temperature). Of course, we are dealing here with static pressures, while the pressure effects caused by directed gas streams cannot be generally determined.

(Signed) v. Rüffling

[illegible]
8-6-46

DIAGRAM I.


✓ rise (Initial ✓
● Temp.-erhohung Δt (Anfangstemp 300° K)
Burning at constant volume.
Verbr. bei konst Vol.
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
untere Zündgrenze - Lower ignition limit
10
20
30
40
50
60
70
% H_2 im Gemisch mit Luft
✓ in mixture with air
Druck
Pressure
Temp.-Rise
Temperaturerhohung
obere Zündgrenze - Upper ignition limit
1
2
3
4
5
6
Druck ata
Pressure - atm.

Appendix II

19 Jan. 1943

THE BEHAVIOR OF A HYDROGEN FLAME AT HIGH EMERGING VELOCITY.

In order to clarify the question, if a hydrogen flame could be extinguished by increasing the emerging velocity, a short experiment was conducted:

A straight tube about 500 mm long and 5 mm I.D. was connected to a tank filled with hydrogen at 130 atm. The tube was fastened horizontally about 150 mm above the ground.

The emerging hydrogen was ignited with the valve slightly open. Subsequent complete opening of the valve had the effect of carrying the flame away from the mouth of the tube. However, it could not be extinguished, but kept on burning with a cracking flame at a distance of about 10 cm. If the valve was throttled the flame returned to the mouth of the tube.

The maximum distance to which the flame may be carried away from the opening, and its spread, is probably dependent upon the shape of the nozzle. In this case no especially shaped nozzle was used but the tube was cut off square.

Appendix III

April 5, 1943

STALL CONSTRUCTION AT PÖLITZ

We would make the following remarks to the 2 plans for reinforcing the stall walls submitted to us.

While the wall surfaces are now stronger, it is essential that the stall supports IP25 remain in position in case of danger. The massive upper inside walkway 1 m wide at + 26.92

can be used for stiffening them. This massive reinforced concrete slab needs only to be correctly reinforced. It is also essential that the wall columns be connected sufficiently strong to this horizontal brace. To prevent the reinforced concrete slabs from being forced out of place in severe wall deformations, we recommend that the corners between the wall slabs be bevel reinforced as shown in attached Sketch 3443. It has been repeatedly shown that a good corner reinforcement is absolutely necessary and that a breaking apart of the walls in an explosion can be prevented only in this way.

The round rod reinforcement of 130 kg/m^3 of reinforced concrete for the walls should be more than ample. Many thin rounds of 8-10 mm dia. will better hold the shattered walls together than the heavier 16 mm dia. rods.

A good anchoring of the concrete slabs to the steel wall beams is more essential. As shown in Sketch 3443, this can be done by stirrups welded to the beams and extending far enough into the concrete.

It is important that the whole structure be so reinforced that all parts will have the same factor of safety against collapse.

T.O.M. Reel No. 5
pp. 198 - 281

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-79

COLLECTED INFORMATION ON THE A-DISTILLATION INSTALLATION AND OPERATIONS
GEISENKIRCHEN-HORST
1939 - 1943

July 14, 1944

Operating year 1939/1940

A-Distillation

1. Operational Characteristics

An atmospheric cone-bottomed still for continuous operations with a tubular heater is used for the separation of the catchpot bottoms into A-middle oil, A-gasoline and heavy oil. The unit is designed for a 32 te/h liquid phase catchpot.

The unit was designed and built by the Foster-Wheeler Company and combines decades of experience of this construction firm, which was a pioneer in the field of distillation. The unit operated with a total heat exchange of the distillate and residues cooling, and is fully automatic. The introduction of a 30 m^3 container in the crude oil line between the furnace and the heat exchanger group was a departure against other installations. This container offers the following advantages:

a) Heat shocks caused by the variations in the converter output and made noticeable in the heat exchangers during cooling were effectively buffered.

b) Variations in the composition of crude product were smoothed out and trouble resulting from them could be discovered on time and remedied.

c) Regulator adjustments were damped and uniform intake temperature into the still was produced.

d) The original purpose of the container to catch the water in the oil has not so far been effectively done. Water is very finely subdivided in the oil and the length of stay in the tank is insufficient (about 1 hour) to cause the separation.

2. Critical Consideration of the Unit.

The unit has so far met the requirements made upon it and has performed satisfactorily in making the distillation cuts. No tests of deterioration have so far been done. There should possibly be more exhaustive investigation of materials, of piping connections, and primarily of the feed oil, to find a properly resistant material which will eliminate in the future many of the changes of the tubes. It would further be advisable to find ways of simplifying the starting and stopping operations, the patch of the distillate and of the residues to the Eckardt volume measuring instruments. The Siemens regulators used in the unit which are built along the lines of the American Foxboro regulators, have so far worked excellently. We have had frequent difficulties with our Eckardt meters for the different products. A possible improvement which could be made would consist in constructing a reflux temperature regulator for a definite required refluxing amount with an arrangement to permit variations of requirements. This might have the advantage of permitting, e. g., a minimum load on the unit with increased refluxing proportion and larger bottom load which would produce a better distillation cut. Conversely, with a lower refluxing proportion a greater load could be realized. The air supply to the firebox through concrete ducts as recommended and used in petroleum refineries has not proven at all satisfactory. The burner orifices become fouled by the abrasion of the concrete walls, and moreover the duct has not been air tight in spite of having been overhauled three times. This represents a considerable loss of pressure in the air supply to the firebox. The unwieldy Pintsch gas pressure regulators will be shortly replaced. The maintenance of the large leather gaskets is difficult. They are leather membranes stitched of four pieces which leak frequently and lead to long repairs. The smaller and more easily supervised Samson regulators are recommended. The safety features for the shutting down of the gas flames have so far been found to perform excellently in many cases. The supplementary fuel introduced into the burners and fed with outside gas (coke oven gas) have not been found satisfactory. Nearly all the burner tips have sintered in the high firebox temperatures and the burner liner is almost completely fused in spite of the best grade of refractory brick insulation. The K.S.B. circulation pumps have worked satisfactorily. The hot oil pumps had at first to be reground, and after a proper packing material for the pipe flanges had been found, the hot oil house, which is a headache in many installations, was kept clean.

It would be desirable to install after the war pure copper gaskets in all the hot parts, such as have been found to perform excellently under similar operating conditions in the petroleum industry. We have so far been able to establish one single instalce of corrosion of pump material in the wear of the centrifugal runner parts of an A-middle oil pump.

3. Operational Results.

The AI unit was started 5/18/1939 with pure tar oil. It received the first batch of catchpot bottoms on 8/5/1939, and since then a mixture of tar oil and coal catchpot product was used in operation, which is the present feed of the A-unit and varies in composition. The unit operated until 11/13/1939, when it was overhauled and replaced by the AII unit. The AI unit was kept in reserve and was started again 5/1/1940 and the AII overhauled. The AII was put again in operation on 6/1/1940, and since that time both units have been operated together.

A total of 149,677 to coal catchpot bottoms & tar oil have been distilled.

Starting with the tar oil represented a difficult operation, since this oil possessed no distillation tailings, it itself being a distillation product intended for reworking in a pipe still. In addition particular difficulties were produced by the high naphthaline contents, everything had to be heated and numerous steam hoses were provided to be used at any spot. The following questions of distillation were studied:

1. The raw product is taken off overhead. It had to be considered whether connections from the temperature compensators of the steam lines reached from the head of the column to the condensers. A static test gave an affirmative result. This method of operation has been used for five days, and then kept.

The distilled middle oil was continuously removed in the reflux containers, and the distillate so produced furnishes at the same time its own reflux. Fears advanced by us were that the packing materials were not satisfactory for such high temperatures (220°C) and should have permitted leaks.

Another doubt concerned the outlet temperature of the cooling water because condensers had to use large amounts of water to avoid too high an outlet temperature. Uncertainties of operations caused by these two factors have caused us to give up this method of operations.

2. The distillate was taken off as a side stream, and since the feed itself had the high initial boiling temperature of over 200°C, and led therefore to no sufficient amounts of lighter constituents, operations were done with an outside reflux. This outside reflux was so selected that its average vaporisation temperature was at least 80 - 100° lower, than that of the side fraction to be taken off, or a middle oil in this case with an average vaporization temperature of 210 - 220°C. Crude benzol was used as a reflux with an average vaporisation temperature of 95°C. Tank-car crude benzol was purchased from one of our concerns, and this product pumped into our reflux. The unit was slowly raised to maximum production, and after the necessary head-temperature was reached, reflux was added to the column. The temperature of the side stream was carefully kept at a constant level and the entrainment of the reflux with the side stream was avoided because of the large difference in the boiling points, so that the reflux could be kept in the unit.

The small amount of distillation residue introduced further difficulties. It amounted to 15 - 20%, and had peculiar properties, in that it had a boiling end point of 360°C, and had therefore a narrow fraction 325 - 360°. In this way the average equilibrium vaporisations temperatures of the crude oil and its residue were very close together, and the still had to be operated very carefully. Large vapor velocities are produced in the tubes of the furnace with the large amounts distilled, with some manifestation of errosion, which resulted in some warping. The damage was not, however, large, and was immediately repaired. 9000 te tar oil were thus distilled with the production of 7100 te middle oil.

DISTILLATION OPERATIONS DURING 1940-1941

pp. 213-214.

Operations: Until March of that year the two A units A 1 and 2 were in continuous operation with an average thruput of 80 - 90%. The units A 3 and 4 were put in operation on March 3 and 5 respectively. These two units have the same average thruput (32 te/h) and the same regulations as A 1 and A 2. They have essential simplifications in the feed supply, and the cooler structures have been altered structurally. The usual difficulties with the regulators had to be overcome when putting A 3 and 4 in operation, and there was additional trouble with the kiln pumps. The production at that time required the preparation of tar-free middle oil in two A installations (A 1 and A 2) and for operations with a tar oil - middle oil mixtures in a third unit (A 4), with one unit only available for reserve when operating with two feeds. This represents a certain limitation against the original intentions, which however was caused less by the equipment than by changes in material through the use of two different A middle oils. The A 1 and A 2 units were accepted after acceptance tests on 7/26 and 7/29/40.

Trouble in Operation.

a) Corrosions.

The feed piping to the A units had to be almost continuously patched and new lengths of pipe put in during the course of the year. Ludwigshafen has found out that it was caused by intercrystalline corrosion by ammonia vapors present in the coal catch pot products. Tar oil corrosion was originally suspected (phenols). The phenomenon has however, also been observed in the gasoline catch pot products, which showed the suspicion to have been wrong. To remedy the trouble the short lengths of pipes of the return bends have been heated in our workshops.

b) Repairs.

The A 1 and A 2 units were shut down on 3/10/41 after almost 2 years of operations, and thoroughly overhauled. No important plugging up of the equipment could be found. A careful examination of the furances showed that the brick work and the furnace tubes were intact. The coolers were strongly slimed and the heat exchangers were equally strongly slimed. The bottoms underneath the feed inlet were greatly fouled.

New Units:

The starting of the A 3 and A 4 units completes the construction step 30 of the A distillation. No additional construction is at present under consideration.

The air supply to the furnaces is through an underground concrete tunnel, which has been found very unsatisfactory (leaks, erosion of concrete) and has been replaced at our costs by a 1200 (meter?) air duct for all the furnaces. The air supply to each furnace is now measured, which permits some determinations of the efficiency and heat balances.

CRITICAL SURVEY OF THE OPERATING YEAR 1940-1941

p. 223

The two units, A 3 and A 4 have been erected and started during the year. Our previous experience with such installations has not made it advisable to make any fundamental changes in the installation.

It has been found necessary to produce for the 7019 stall a middle oil free from tar. The two A units from the two coal catch pot settling tanks are operated with tar-free catchpot oils. All the tar oil produced is sent to the third catch pot, mixed and the correspondingly higher-tar mixture is worked in the third unit. When the 6th coal stall is put in operation, four A units will have to be used, and a reserve of operation will have to be maintained. A small thruput reserve will have to be kept.

Air Duct:

The concrete air duct is again criticized; the section is not translated.

A-DISTILLATION OPERATIONS DURING 1941-1942

pp. 228 - 230

Process: Through the completion of construction program, four A distillation units were available, 3 of which were operated with 100% throughput. The fourth unit served as a reserve unit, to permit making the necessary overhauling and repairs without interfering with the production.

The middle oil cut was kept at 338 - 340°C. Up to 1/19/42 one unit was run on a tar-free feed, and the other on a tar-containing catchpot product, depending on connections at the tank farm. Fuel oil was produced for the first time in 1/30/42, and its quality was perfect from the beginning. Later, one unit was run on fuel oil in 2 operation periods, of one month each.

Changes in Pipe Line: Corrosion phenomena in the feed line were reduced by putting all the feed regulators of the A units in May 1942 ahead of the Eckardt meter, so that, unlike the former Eckardt installations with bends which gave especial rise to leaks, they were placed outside the high pressure range (22 atm) and the pressure was reduced to 10-14 atm.

Corrosion: Damage to the pipeline from the catchpot product required regular replacement twice a month of the pipe lengths and return bends. Observations have taught that corrosion was very much more common in the high pressure region than in the lengths of pipe behind the intake. This result caused the change of location of the intake regulator, mentioned above, permitting other operating parts, such as the Eckardt meter and T pieces (Gabelstucke) to be located behind the intake regulator. Intercrystalline corrosion phenomena were first observed in September 1941 in the middle oil heat exchanger. No special material has been usedthere, no more than in the rest of the middle and heavy oil heat exchangers, and further instances of this corrosion phenomenon were feared in the rest of the heat exchangers. Luckily this remained an isolated case.

Trouble: No production trouble was caused by the operations proper. They were always caused by events on the outside..........

Repairs: The necessary repairs and overhauling had to be made in regular rotation two or three times a year, and were primarily caused by the poor cooling water ....

Frequent repairs were made at the gas pressure regulators with their large leather membrances........

A - DISTILLATION OPERATIONS DURING 1942 - 1943.

Gelsenkirchen-Horst 10/8/1943

Coal Catchpot Product Distillation

Production Methods: Four A units were available during the operating year, of which 3 were operated with about 100% load, while the fourth was kept as a reserve, and was used during the overhauling of the other three units.

All three units were used with the same crude, unlike the earlier years. Foreign oil was always added in the third coal catchpot tank, which also acted as a mixing tank. The off-oils, condensates and both wash oils were always added in tank Q, to produce perfect settling of water and solid particles.

On the suction side, the feed was invariably taken from the mixing tank T. No tar-free oil has therefore been produced during the operating year.

No more fuel oil has been produced this year.

With small variation, the middle oils were cut at 335 - 343°C

The gasoline process, which included routing to refining operations by way of the coal gasoline tank A into the gasoline catchpot was given up in October 1942 for reasons which had nothing to do with distillation. From that time on, the combined gasoline + middle oil were sent to the tank H and introduced into the high pressure as sulfurized feed.

Operating conditions: The level of operations could be maintained high by a biennial overhauling (once in the spring and once in the fall). No large amount of trouble has as yet been met in spite of having the operating units run with 100# load. The units have however a reduced thruput in comparison with the times when first started by no longer being capable of reaching a level of 120% of the nominal capacity. We must find an explanation for it in the fouling of the individual bottoms of the column because of the deposition of some leafy particles, which caused a partial closing up of the silts (Schlitzboden). It was usual in the past to open the bottoms of the columns during overhauling underneath the inlet and free them from the accumulations of residual coal and oil slime. The above mentioned pure rust depositions above the intake have now been discovered, and during the next overhauling in the spring of 1944 a cleaning of all the bottoms must be carried out.

a). Corrosions: Leaks caused by corrosions were this year again the cause of constant replacing of lengths of tubing and of return bends in the common pipe line from the catchpots to the units. Leaks have been found in isolated cases in the middle oil pipe lines as well. The more or less periodic appearance of these leaks is striking and as yet unexplained. The previously tried measures for the prevention of corrosion by tension-free annealing of the tubes previous to their use, has been found to be absolutely insufficient. Beginning with June 1943 a normalising annealing of the tubes, intended since the beginning of the year, could be put in operation. The preventive normalized annealing used by us after discussions with Leuna differs however considerably from the method used at Leuna. The reason for it is in the absence of a correspondingly long annealing furnace. What improvements the normalizing annealing may produce will have to be judged after a longer observation period. The construction with tubes of the EZ material has also been planned. Lengths of tubing of this material have in the meantime been delivered, however flanges of the same material could not be delivered by the Krupps because of damage by bombing. Attempts to provide the EZ tubes with flanges of other material are now in progress.

b). Water........

Repairs: The valves made by the firm Borsig and used in the fuel gas line of the furnace of the distillation unit leaked very frequently and often caused shut-downs for repair.

During the year these valves were replaced with the Audco valves. So far they have been found satisfactory both in respect to staying tight, ease of operation and serviceability.

The furnace burner had to be cleaned in regular rotation of every 6 weeks, because of the oily and slimy deposits formed in the orifices.

During the starting of the furnace of the A i unit the bottom in the radiation zone showed a 12 cm sag. The supporting bar for the bottom tubes in this zone had to be raised. In addition, major repairs were necessitated in the burners of the different furnaces, because the vaults of the burner muffles were cracked. The burner muffles were coated with a stamped mass developed here. The material and the method have been found very satisfactory.

The water meters of the different units were very difficult of access on the roof of the hot oil pump house. All of them have been replaced with meters in the vertical branch of the water line on the outside of the pump house.

Sternberg/pkl
8-15-46

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

T-80

T.O.M. Reel No. 111
Short Report No. 22 by W. Schenker
Tech. Test. Lab. Oppau.

Ludwigshafen, October 27, 1942

THE CALCULATION OF A HIGH PRESSURE HEAT EXCHANGER
(A practical example for instruction purposes)

(Note: This report is so hard to read that some of the data contained in this translation are based on estimates and/or interpolations.)

A. Calculation of an exchanger.

For dimensions see Sketch 1, for assumed values of the product see Table 1.

TABLE 1

		Hot Gas	Cold Gas
Weight of gas	kg/h	13,500	13,500
Pressure	atm.	200	200
Inlet temperature	°C	399	188
Outlet temperature	°C	228	347
Specific gravity at 0°C	kg/Nm^3 *	0.17	0.16
Av. specific heat at inlet	kcal/kg/°C	0.66	0.67
Av. specific heat at outlet	kcal/kg/°C	0.65	0.68
Av. coefficient of heat transfer	kcal/hm °C	0.160	

* Nm^3 = standard m^3 based on 0°C and 760 mm mercury.

a) Calculation from the heat content.

The actual coefficient of thermal conductivity is derived from the heat content of both of the gases and the mean temperature difference between the two gas streams, according to equations:

$$Q_m = (G \times c_{pm} \times t)_m{}^* \qquad 1)$$

$$(\Delta t)_m = \frac{t_3 - t_4}{2} = \frac{t_1 - t_2}{2} \qquad 2)$$

$$k = \frac{Q_i}{F_m \times (\Delta t)_m} \qquad 3)$$

---

* G equals the quantity of gas per tube in kg/h.

* G x c_{pm} equals water value of the two gases.

The results of calculations are given in table 2.

TABLE 2

		Hot Gas	Cold Gas
Heat content at inlet	kcal/h	3,597,000	1,664,000
Heat content at outlet	kcal/h	2,026,000	3,200,000
Heat exchanged, Q_i	kcal/h	1,571,000	
Heat absorbed, Q_a	kcal/h		1,536,000
Heat loss from the heat contents, Q_v	kcal/h	35,000	
Mean temperature difference $(\Delta t)_m$	°C		48.5
Coefficient of thermal conductivity, k	kcal/hm^2 °C		534

In the most favorable case the heat:

$$Q_{max} = G\left((c_p \times t)_4 - (c_p \times t)_1\right) \qquad 4)\ *$$

could be exchanged, or, in this case:

$$Q_{max} = 3,597,000 - 1,664,000 = 1,933,000 \text{ kcal/h.}$$

If

$$\frac{Q_a}{Q_{max}} \times 100 = \phi_1, \text{ efficiency of heating,}$$

and

$$\frac{Q_i}{Q_{max}} \times 100 = \phi_2, \text{ efficiency of cooling} \qquad 5)$$

then

$$\phi_1 = 79.4\%$$

$$\phi_2 = 81.2\%$$

b) Calculations from the heat transmission.

The coefficient of thermal conductivity (Wärmedurchgangszahl) can be calculated with sufficient accuracy from the laws of heat transmission (Wärmeüberganges). If α_i and α_a are the coefficients of heat transfer (Wärmeübergangszahlen) on the inside and the outside, respectively, of the bundle tubes, k_r the coefficient of thermal conductivity (Wärmedurchgangszahl) per running meter of tube, and k the coefficient of thermal conductivity (Wärmedurchgangszahl) per m^2 average tube surface, then

$$\left(\frac{\alpha \times d}{\lambda}\right)_i = 0.036 \times \left(\frac{d}{L}\right)_i^{0.05} \times \left(\frac{3{,}600 \times w \times d \times \gamma \times c_p}{\lambda}\right)_i^{0.79}$$

or

$$\alpha_i = 0.044 \left(\frac{(G \times c_p)^{0.79} \times \lambda^{0.21}}{d^{1.73} \times L^{0.05}}\right)_i \qquad 6)$$

With reference to the external coefficient of heat transfer (Wärmeübergangszahl) it is permissible to place:

$$\alpha_a = \alpha_i$$

With the large ratio in diameters $d_a - d_i$ of the bundle tubes an accurate calculation of the heat exchanged may properly be made by the use of k_r:

$$\frac{1}{k_r} = \frac{1}{\pi} \left(\frac{1}{\alpha_i \quad d_i} + \frac{1}{2\lambda \text{ Steel}} \times \ln \frac{d_a}{d_i} + \frac{1}{\alpha_a \quad d_a}\right) \qquad 8)$$

From this the total exchanged heat Q_w in kcal/h:

$$Q_w = z \times L \times k_r \times (t_1 - t_2) \qquad 9)$$

---

* For different water values change accordingly. Eq. 4)

Where z equals the number of tubes, L the effective length of tube, t_i and t_a the mean temperature of the inside and outside, respectively, of the flowing gases.

However if the coefficient of thermal conductivity (Wärmedurchgangszahl) is based on a m^2 mean surface, then:

$$k = \frac{k_r}{\pi d_m} \qquad 10)$$

and

$$Q_W = z \times L \times \pi d_m \times k \times (t_i - t_a) \qquad 11)$$

or

$$Q_W = F_m \times k \times (t_i - t_a) \qquad 12)$$

In the preceding example the following values are determined:

$$\alpha_i = 0.044 \times \frac{(89.50 \times 0.662)^{0.79} \times 0.160^{0.21}}{0.014^{1.73} \times 6.9^{0.05}} = 1,100 \text{ kcal/hm}^2 \text{ °C} \qquad 6a')$$

$$\frac{1}{k_r} = \frac{1}{\pi} \left(\frac{1}{1,100 \times 0.014} + \frac{1}{2.40} \times \ln \frac{23}{14} + \frac{1}{1,100 \times 0.023} \right) \qquad 8a')$$

$$k_r = 28.4 \text{ kcal/hm °C}$$

$$Q_W = 151 \times 6.9 \times 28.4 \times 48.5 = 1,433,000 \text{ kcal/h} \qquad 9')$$

The deviation from the measured heat exchange Q_1 is accordingly:

$$Q_1 - Q_W = 1,571,000 - 1,433,000 = 138,000 \text{ kcal/h} = 8.8\%$$

The coefficient of thermal conductivity (Wärmedurchgangszahl), based on the mean heat exchange surface is:

$$k = \frac{28.4}{0.0185 \pi} = 487 \text{ kcal/hm}^2 \text{ °C} \qquad 10')$$

and the exchanged heat therefore is

$$Q_W = 60.60 \times 487 \times 48.5 = 1,433,000 \text{ kcal/h} \qquad 12')$$

as per equation (9')

B. <u>Advance calculation of a heat exchanger.</u>

The following values are generally given: G, γ, c_p, λ, t_1, t_3.

Furthermore, d_i, d_a, L, may be assumed from experience or standard Warehouse sizes.

The number of tubes z, is determined by the actual gas volume V_m and a practically assumed gas velocity (w_m). If, for example, V_o and γ_o are based on 0°C and 760 mm mercury (V_o in Nm^3/h), and if we tentatively assume t_2 and t_4 so that the mean temperature drop $(\Delta t)_m$ = 30 - 60°C, then

$$V_m = V_o \times \frac{1.033}{P_m} \times \frac{273 + \frac{3 + t_4}{2}}{273} \qquad 13)$$

$$z = \frac{V_m}{3{,}600 \times w_m \times \frac{\pi d_i^2}{4}} \qquad 14)$$

and

$$G = \frac{Q}{s}$$

Now the coefficient of heat transfer (Wärmeübergangszahl) λ_i can be calculated from equations 6a) or 6), also k_r (equation 8)) and the exchanged heat Q_w (equation 9)). This Q_w may be greater or smaller than Q_i (equation 1)):

$$Q_i = G \times \left\{(c_p \times t)_3 - (c_p \times t)_4\right\} \qquad 15)$$

Now we vary temperatures t_2 and t_4 and repeat the calculation until Q_w and Q_i agree with each other closely enough (a recalculation of k_r need not be made).

If the finally determined end temperatures t_2 and t_4 are not close enough to the starting temperatures t_3 and t_1 of the other medium, that is, if the heat exchange has not gone far enough, the heat exchange surface must be increased. (Contrarily, if the heat exchange surface has been calculated too great, a smaller heat exchange will suffice.)

C. <u>Further suggestions.</u>

1.) The foregoing example refers to a heat exchanger for gases. For the calculation of the coefficient of heat transfer (Wärmeübergangszahl) λ_i, the "Nusselt" equation (equation 6)) was used. This may also be written:

$$Nu = 0.036 \times \left(\frac{d}{L}\right)^{0.05} \times Pe^{0.79} \qquad 6b)$$

where

$$Pe = \frac{3{,}600 \times w \times d \times \overset{\gamma}{\lambda} \times c_p}{\lambda}$$ is the Peclet number.

Since

$$Pe = Re \times Pr.$$

where $Re = \frac{w \times d \times \overset{\gamma}{\cancel{\rho}}}{\eta \times g}$ is the Reynolds number

η = dynamic viscosity kg. sec/m^2

and

$Pr = \frac{3{,}600 \times \eta \times g \times c_p}{\lambda}$ is the Prandtl number, then also

$$Nu = 0.036 \times \left(\frac{d}{L}\right)^{0.05} \times Re^{0.79} \times Pr^{0.79} \qquad 6c)$$

The Nusselt equation, valid for $Re > 10{,}000$, distinctly turbulent flow.

2.) More accurate, and also valid for liquids in turbulent flow, is the Kraussold equation *)

$$Nu = 0.032 \times \left(\frac{d}{L}\right)^{0.054} \times Re^{0.8} \times Pr^{0.30} \qquad 16a)$$

where the heat is transferred from the liquid to the wall,

and $$Nu = 0.032 \times \left(\frac{d}{L}\right)^{0.054} \times Re^{0.8} \times Pr^{0.37} \qquad 16b)$$

where the heat is transferred from the wall to the liquid.

3.) If the external coefficient of heat transfer (Wärmeübergangszahl) of a baffle plate heat exchanger is to be calculated, for example, with gas on the outside and liquid on the inside, it must be considered that, first, there is no pure cross stream on the outside and, second, that the external heat transfer surface cannot be fully utilized because of the eddy currents at the baffle plates.

4.) The compressibility of the gases is not taken into consideration in these calculations for practical purposes; their influence, even at high pressure, amounts to only a few per cent.

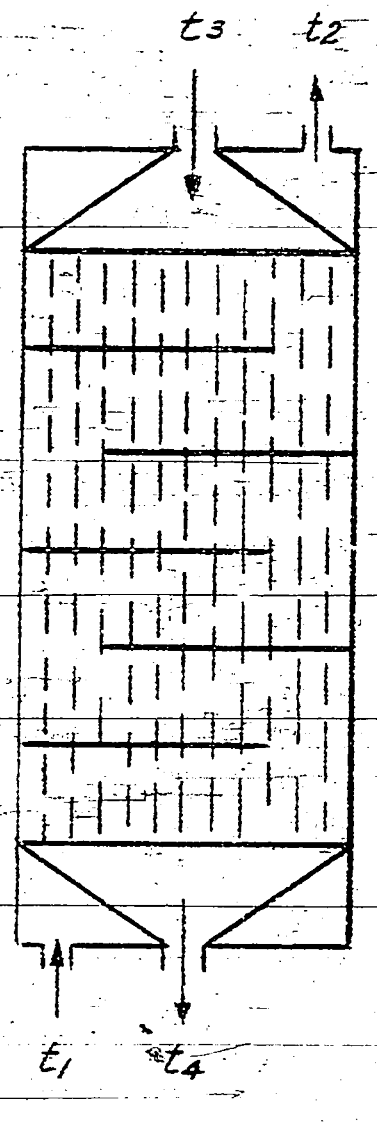
5.) The pressure losses (in gases) have, in general, no important influence, they may, however, be considered in accurate calculations.

6.) The heat loss to the surroundings, which in the foregoing example is indicated from the heat balance (Table 2) as Q_v = 35,000 kcal/h, can be more accurately calculated from surfaces and air temperatures, that is, dimensions and coefficient of heat transfer of the insulation. In the foregoing example this calculation gives 36,000 kcal/h, which practically corresponds to the tabular value. The heat loss here amounts to only 2.2% of the heat exchange, can therefore be neglected.

Braun
~~Sternberg~~/mc/pkl
8-8-1946

*) For purely laminar flow, $Re \leq 2{,}300$, other relations prevail.

FIG. I



Dia. of Tubes = 161/147 mm.
Effective Length of Tubes = 5500 mm.

HIGH PRESSURE HEAT EXCHANGER

T.O.M. Reel No. 3
Target No. 30/4.08
Bag No. 2745
Item No. 8

T-81

August 6, 1946

MONTHLY OPERATING SHEET - "A" DISTILLATION

Gelsenberg Benzine A.G. Operation Control	Distillation	June 1940

Designation	Distillation A_1			Distillation A_2			Dist. A_1 A_2
	m^3	Sp.Gravity	To	m^3	Sp.Gr.	To	To
Cold Catchpot	20.03	0.9750	13 703	19.59	0.9730	11 745	25 448
Reflux			-			-	-
			-			-	-
Throughput			13 703			11 745	25 448
Liquid Phase Gasoline	0.62	0.7180	425	0.85	0.7215	509	932
"A" Middle Oil	12.24	0.9530	8 376	11.43	0.9550	6 853	15 229
Heavy Oil 10^3	6.66	1.0500	4 552	7.15	1.0500	4 286	0 838
Offgas m^3 35.4x10^3 A_1 19.3A_2	0.09	1.7550	63	0.05	1.7750	34	97
Loss % 2.11/0.54	0.42		289	0.11		63	352
Total	20.03		13 703	19.59		11 745	25 448
Liquor 927							
Middle Oil + Gasoline Yield%			64.2			62.6	63.4

Operating Figures

Unit	Furnace Temperature °C			Oil Inlet		Oil Outlet		Flue Gas	Hours of Opr.
	Rad.Zone	Bridge	Outlet	°C	Atm.	°C	Atm.	% CO_2	
A_1	772	545	203	141	4.2	319	-	6.8	684.17
A_2	800	566	230	141	4.0	319	-	-	599.67

Energy Figures

Unit	Elec. Energy KWH 10^3	Fuel Gas m^3	Low Pressure to Col.	Low Pressure to Total	H.P. Steam to	Fresh Water 10^3m^3	Recirculating Water m^3 10^3	Fuel Gas tonne thruput	Low Pres. Steam thruput Col.	Low Pres. Steam thruput Total
A_1	50.0	726.2	389.8	431.3	145	15.9	-	53.0m^3	28.4	31.5kg.
A_2	44.0	633.9	268.6	478.8	130	21.5	270.1	54.0m^3	22.8	40.7kg.

Upper Heating Value 3,244
Lower Heating Value 3,000

T-82

T.O.M. Reel No. 174
pp. 914-921

U. S. BUREAU OF MINES
HYDRO. DEMON. PLANT DIV.

Leuna, May 24, 1937

MEASURING THE VISCOSITY OF PASTING OIL, HOLD AND COAL PASTE FROM SCHOLVEN AND LEUNA HYDROGENATION WORKS

When judging the following determinations one must bear in mind that coal paste has no true fluidity but appears "pasty" at low temperatures. We may therefore not speak of a true "dynamic viscosity" and may only determine "the behavior of coal paste when applying any measurements for viscosity at a definite temperature obtaining values similar to those for purely viscous fluids of known viscosities. The values obtained must be considered as being essentially purely relative."

The measurements were made with a viscosimeter developed by the Leuna control laboratory which was especially adapted for measurement of liquids of high solids content. A disk rotated at about 40 rpm was immersed in the liquid measured. A vertically arranged cylindrical body dipped into the rotating liquid and the moment of rotation exerted upon the cylindrical body by the rotating liquid was determined by electric compensation. The apparatus is standardized by using a liquid of known viscosity. Unfortunately the most viscous available standard viscosity has a viscosity of only 0.1 kg sec/m^2. However, the moment of rotation increases in direct proportion to the viscosity up to this value and the apparatus was standardized in units of rotation moment under the assumption that the viscosity and moment of rotation remained linear. The standardization curve was extrapolated to eight times greater value. Measurements of viscosity of pasting oil and HOLD (figures 1 and 2) could be performed in the usual way. The samples were heated to some definite maximum temperature and the viscosity was determined on cooling at definite temperatures. The HOLD sample contained about 28.5 per cent of solids.

The measurements of coal paste exhibited fundamental difference between the soft coal paste and brown coal paste. The curve in figure No. 3 was obtained by first heating like samples of soft coal paste and brown coal paste to 110° and determining their viscosity, then heating to 160° and measuring the viscosity again during cooling. Such a stepwise heating was done because it was known from previous determinations that the volatilization of some constituents caused a change in the viscosity. The surprising result was now found that with the Leuna brown coal paste both curves combined into a smooth curve without a break, while the coal paste of Scholven was changed very strongly towards higher viscosity values. At temperatures of 160° a change already took place in the soft coal paste, probably caused by the swelling of the coal, as could be verified by the change in the volume of the paste. At Scholven's request 1 per cent ammonium chloride was added to the soft coal paste and the curve No. 3 shows that this results in a new increase in viscosity.

This change in the soft coal paste during heating and the increase of the viscosity starting at a certain temperature caused us to measure viscosities during heating as well. The rotating part with the paste was heated up to a high temperature with gas heat during 1 - 1.5 hours. The characteristic curves were then obtained as shown in figures 4 and 5. The brown coal paste (48.5 per cent solids) invariably showed a lower viscosity at higher temperatures and but a slight difference is obtained during cooling and heating, while with the soft coal paste a certain minimum was reached upon which the viscosity rose. Near the inversion point the swelling of coal must already have happened. Unfortunately all the soft coal paste had been used up during determination of this point and the maximum temperature below which there was no change in the soft coal paste, that is no variation between the heating curve and the cooling curve, could not be determined. Measurements could only be made to 200° because near this temperature the vapors evolved would be ignited by the gas flame used in heating the paste, and moreover the heat developed by the gas flame was dangerous for the mechanism of the apparatus. To test whether the rise in viscosity was primarily due to the swelling of the coal or to the volatilization of the volatile oils, Mr. Schappert has suggested the determination of the solids in the heated oil. When benzol was used as the solvent the percentage of solids before heating was 49.3%, after heating 51.3%, with pyridine as the solvent; before heating 44.5% solids, after heating 48.5% solids.

(TWO PARAGRAPHS ENTIRELY ILLEGIBLE)

We may summarize as follows:

"During heating of paste oil and HOLD the viscosity changes normally with the temperature. With the coal paste, probably as a result of swelling, an inversion point is reached at an elevated temperature."

(The rest of the summary is illegible.)

/s/ Weis

Sternberg/mc/pkl
8-7-1946

I. Pasting Oil, Scholven
II. Pasting, Oil, Leuna

5/12/1937

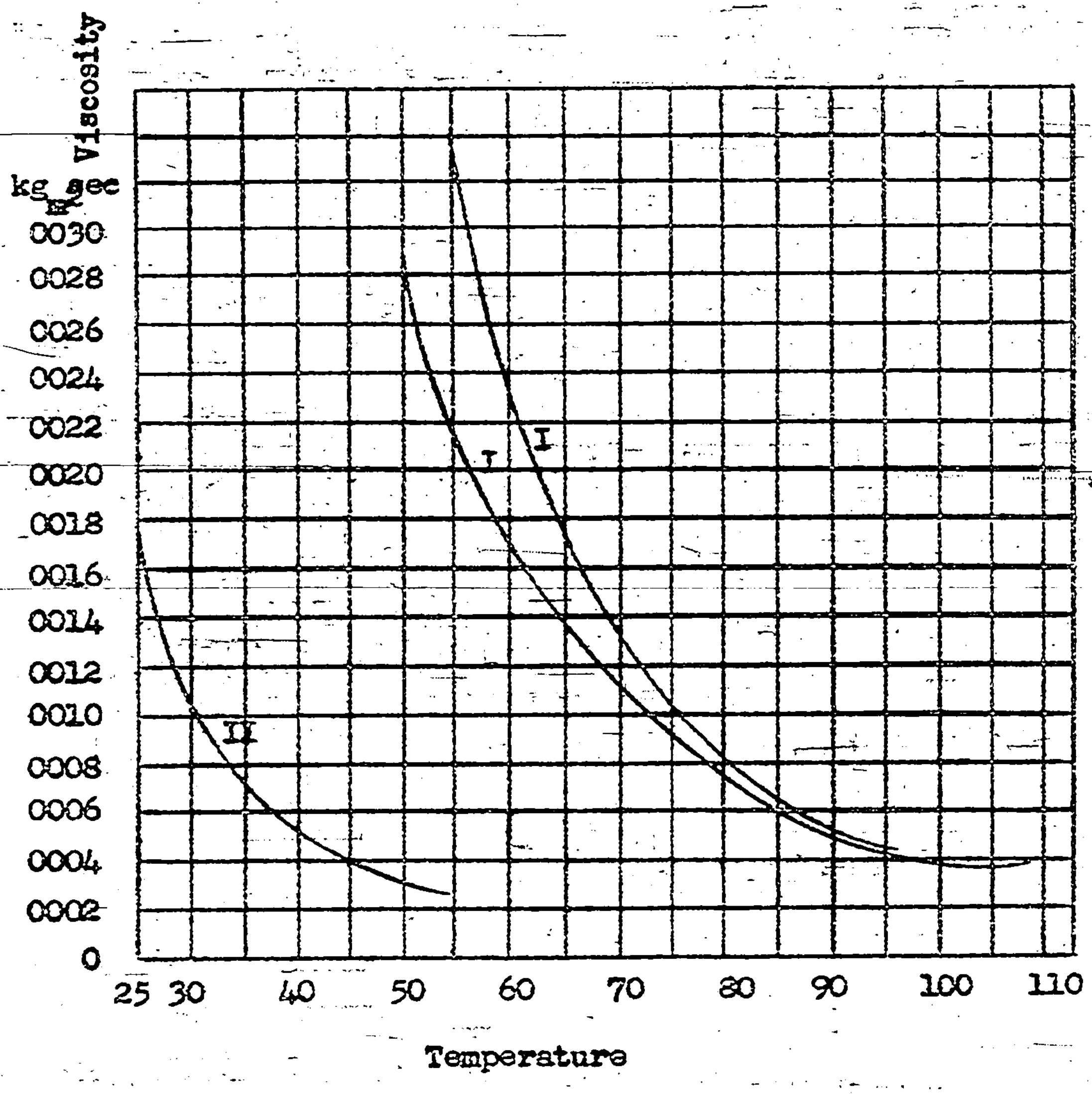


Fig. 1

I. HOLD, Scholven

II. HOLD, Leuna

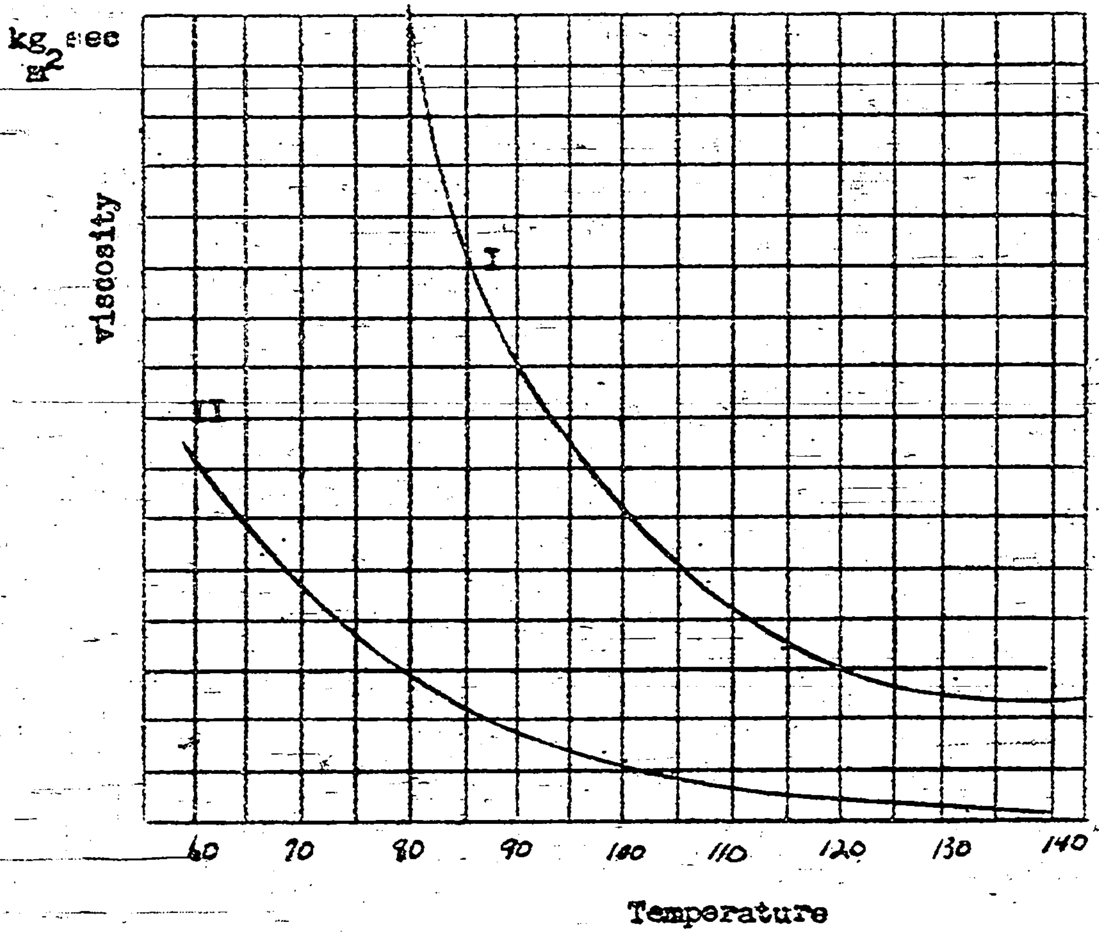


Fig. 2

I. Coal paste, Scholven, pure
II. Coal paste, Scholven, 1% NH_4Cl
III. Coal paste, Leuna

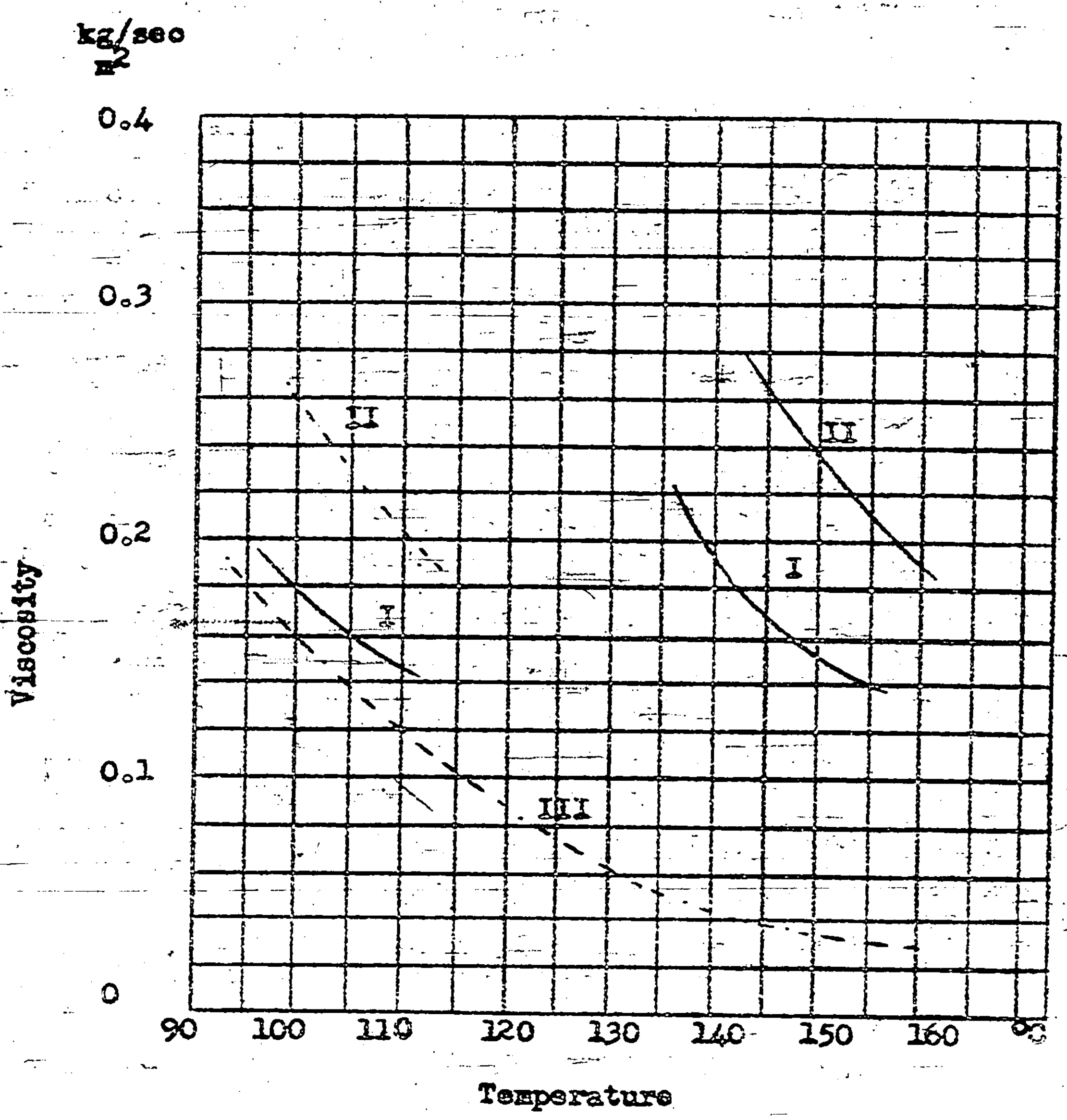


Fig. 3.

T-82

BROWN COAL PASTE, LEUNA, 5/21/1937

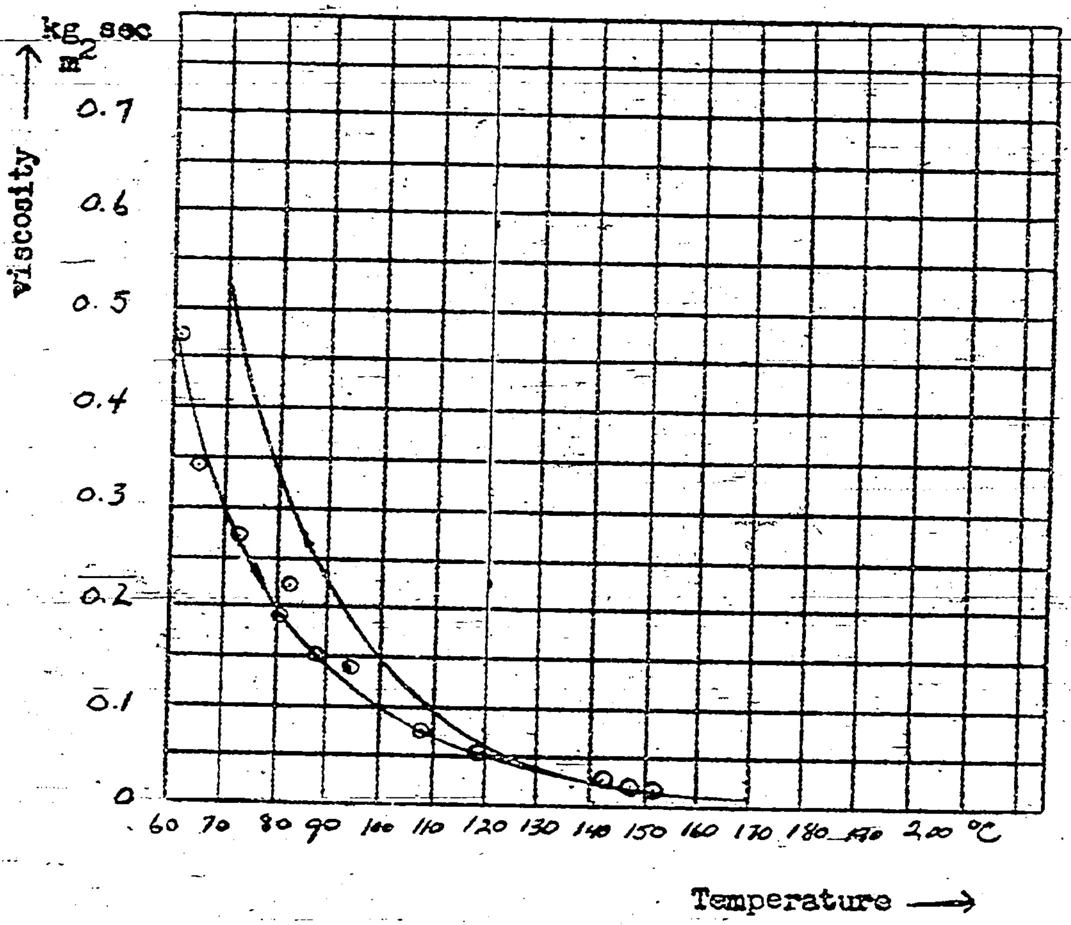


Fig. 4

COAL PASTE, SCHOLVEN

5/20/37

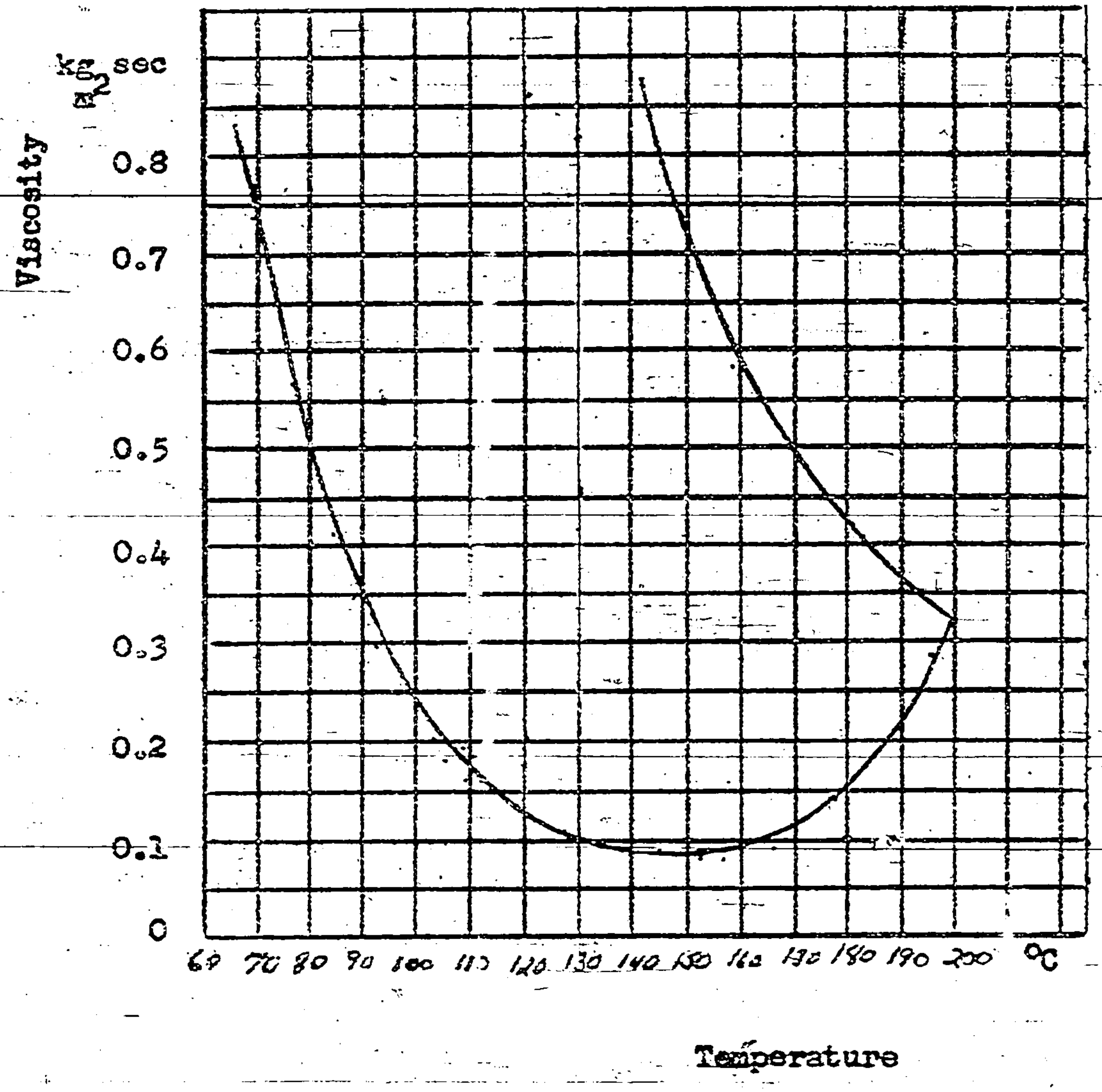


Fig. 5

T.O.M. Reel No. 104
184

Frames 794-806

T-83

U. S. Bureau of Mines

Hydro. Demon. Plant Div.

March 22. 1943

REDUCING THE LOAD ON THE LIQUID PHASE PREHEATERS

SUMMARY

The 700 atm. gas preheater of the soft coal units are mostly equipped with N10 hairpins. The following measures were suggested to increase their life and the safety of operation and while simultaneously producing an appreciable saving in fuel gas:

1. The introduction of a fifth converter for each four-converter stall in which the peak temperature of the preheater is reached.

2. The construction of a gas heat exchanger to utilize more completely the heat still remaining in the distillation mixture.

3. The cold paste method.

4. A few other measures the effects of which however are of less importance.

There is naturally also a great reduction in load when a unit is changed from gas heat exchange to paste heat exchange. for instance in heat exchanging the thin paste. which was done successfully.

Chemical improvements have also been suggested. in particular such which were aimed at reduction in the incrustation.

A. Heat conservation plans.

Table 1 shows the conditions existing in the liquid phase at the individual works during the rise in temperature:

Depending on the kind of heat exchange we may distinguish between four groups: The heat transfer in the heat exchangers rises from 35 per cent in the group I (gas heat exchange in Gelsenberg) to 84 per cent in the group IV (Leuna) where in addition to the total heat exchange there is also a heat recovery from the HOLD.

In Blechhammer where. the same as in Pölitz. the thin paste heat exchange has been foreseen. this percentage amounts to 52 per cent and with the very high thru-put of 70 te/h necessitates the supply of 14.000.000 kcal/h with a 70 per cent efficiency of the preheater. This amount of heat represents the heat of combustion of 1.5 te of oil. with the heat of the reaction of 12.000.000 kcal/h of the same order of magnitude (440 kg/1 kg of the utilized pure coal).

The difficulties met with the N10 material have made it necessary to lower the wall temperatures of the hairpins: Under new conditions, the hottest hairpin of the coal preheater at 700 atm. has a wall temperature of

470° on the inside
485° on the outside

However in Blechhammer these temperatures are about 40° higher because of the required circulation gas inlet temperature of 600° even with the new preheaters, and there is therefore practically no safety margin against the recently established temperature limit for the N10 material of 520° maximum inside temperature.

With the thickness of incrustation of about 10 mm in the hot part of the preheaters at Gelsenberg and Pölitz, the wall temperatures rise about 30 - 50° above those of the unincrusted state. These values have been found with the use of thermocouples and agree fairly well with the computations, on the assumption of heat conductivity of the crust 1.5 kg/°C, m, h.

As far as the reserves of a preheater are concerned the temperature limit of 520° is not yet reached, and the circulation gas temperature may correspondingly be raised with these incrustations, while naturally taking into consideration the blower temperature.

Gelsenberg has in addition greatly reduced the intake temperature in converter I, namely from 425 to 390° which has resulted in a great reduction in the load of the preheater in that way. Only after exhausting these means will thru-put have to be reduced; however computations of economy show that shutting down the stall and cleaning the preheater are more expedient.

It is first of all urgently necessary to bring about a reduction in the load of the preheater, particularly the Blechhammer preheaters. The following means were found best to achieve this purpose, and will be explained numerically on the example of the Blechhammer preheater:

I. The heat exchanger production is increased.

1. By building a gas heat exchanger one may then preheat the inlet gas to 200° which will eliminate gas hairpins. The gain in heat: 3,000,000 cal/h or 150,000 mcal/yr. and stall, so that the additional heat exchanger would be amortized in less than one year.

2. Increase in the concentration of thin and thick paste which will reduce the amount of thick paste for the same cold thru-put. Dr. Wissel believes, on the strength of the Pölitz experience, that the thin paste should contain 41 per cent solids while the thick paste could be operated with 53 per cent concentration without any difficulties.

3. It should be attempted to develop heat exchangers for the 700 atm. HOLD as has been done for years in Leuna for 200 atm., where some of the intake gases were heat exchanged with the HOLD in jacketed coils. The HOLD heat exchanger, in particular paste against HOLD (Josenhans suggestion) has not yet been technically perfected and the heat of distillation gas mixture should be utilized as much as possible.

The saturated steam cooler already provided in Blechhammer for the cooling of the HOLD is an evasion of problem not yet solved technically. Such a cooler generates 3,000,000 kcal/h of steam, which actually increases the efficiency of the Blechhammer preheater from 52 per cent to 68 per cent.

II. A fifth converter is added to the stall. It has been found with the Gelsenberg stalls, that the outlet temperature of the preheater, originally kept at 425°C, could be lowered to 390° without "extinguishing" the reaction. In that way the return flow formed inside the converter will raise the temperature at the end of the converter by about 40° which will extraordinarily hasten the reaching of the reaction temperature. It has thus been shown in Gelsenberg and Pölitz that with the total heat of reaction of about 50 - 60 per cent 3,000,000 kcal/h will be set free in the first converter. However for safety reasons the intake converter temperature was kept at 400° instead of 390°. The reduction of the peak temperature in the preheater from 425 to 400° will mean considerable reduction of load. With the same number of hairpins the circulation gas intake temperature may be reduced in the Blechhammer gas from 600° to 540°, with a corresponding lowering of the tube wall temperatures.

The fifth converter will represent a gain also, when considered merely from a heat economy standpoint:

1. In Gelsenberg (gas heat exchange).

The smaller amount of cold gas necessitated by the lower converter intake temperature has hardly any action upon the gas heat exchanger, and the amount of heat corresponding to 25° of temperature difference will be considered as a net gain:

With 36 te/h of paste and

36,600 m3/h of gas intake and

70% heat exchanger efficiency, there will be

850,000 kcal/h of heat gained.

2. In Blechhammer and Pölitz (thin paste heat exchanger).

In this case the cold gas is absent and the heat exchanger production is slightly lower, so that the heat corresponding to a temperature difference of 25° would be only 80 per cent. The heat gain for Blechhammer with its high thru-put will be 1,600,000 kcal/h.

Our conclusions are based on the Gelsenberg production for gasoline + middle oil while the conditions at Blechhammer with the high thru-put and with the production of gasoline + fuel oil may be somewhat different.

III. Cold paste method.

One part of the paste is not passed through the preheater but entered directly into the reaction space, and this cold paste is also heated to temperature by the return flow inside the converter. This cold paste process was first tried out in Scholven and has been found very satisfactory in Gelsenberg for over one year. The fears formerly entertained that too rapid an increase in temperature of the paste would be harmful have not been confirmed in Gelsenberg. It may however be noticed that a small increase in the excess of heavy oil (asphalts) has been observed. No experience is yet available for the fuel oil process, where the increase in the asphalt to be expected will affect the amount of the residue utilization. The coal paste may also be slightly preheated, say to 200°, which will increase the amount to be used in operations. Operationally this method offers no difficulties because with larger thru-puts a subdivision of the paste injection is anyway necessary.

The reduced amount of cold gas will produce a corresponding saving in power of the circulation gas pump as well as in cooling water in the mixture coolers.

In Figure 1 is given a scheme of the present conditions (upper picture) of the scheme as compared with the intended improvements (lower picture). The figures in circles refer to the individual measures.

Figure 2 shows the corresponding temperature diagram. The circulation gas temperature may therefore be strongly lowered and yet one may save 10 hairpins. Should the full number of hairpins be placed in the preheater and the possible saving disregarded, the circulation gas temperature and the temperature of the hairpins will be found much reduced. The reduction in the heat requirements by 7,000,000 kcal/h (with 70 per cent efficiency) is worthy of notice; the resistance of the stall is also reduced by reducing the number of hairpins.

An exact investigation will be carried out jointly with Blechhammer in which the method suggested may be realized.

Recalculation has shown that in the course of some 15 months of operation in Gelsenberg, Pölitz and Blechhammer about 20 converter shells had to be obtained. At present a delivery plan is being developed. Nor does the delivery of the liners offer any difficulties, and one may even consider to disregard the use of special steels and use temporarily the S2 material as has already been done in Leuna and Welheim.

B. <u>Chemical measures.</u>

Later on chemical measures have been discussed which have been introduced since operations started and were intended to prevent the formation of the crust.

In the composition of the Gelsenberg crust (see Table 2) the principal constituent is FeS with small amounts of W, Mo, V and Cr, which are produced from the material of the tubes, and the amounts of which become less at greater distances from the tube walls. These metals are presented in much smaller amounts in the Pölitz crust. The inner tube wall was found in Gelsenberg to be strongly attacked and brittle to a depth of ½ to 1 mm. A diffusion in the solid phase may possibly also have taken place. The constituents Ti, Al, Ca and C, which have been introduced by the coal or the catalyst, increased in amount inside the crust from the outside in. Occasionally the Fe: Ti proportion in the crust is in the Fe: Ti ratio of the coal ash and the catalyst, which may be a starting point for deductions on which of these substances are primarily responsible for the formation of the crust.

The Fe catalysts appear to play the principal role there. During coal hydrogenation at 300 atm. with Enox (?) and chlorine such crusts have so far not been observed or else were around 1 mm thick in the crust. Neither Leuna nor Wesseling (basic iron and Bayer mass) have so far observed such depositions. On the other hand Ludwigshafen has observed formation of FeS crust even when $FeSO_4$ alone was used (extraction test).

It may be that iron, in particular $FeSO_4$, or the joint action of $FeSO_4$ and Na_2S, are the principal reasons for the preheater incrustation. One may consider changing the way the catalyst is added, by testing, on the one hand, the addition of catalysts to the coal, and on the other hand, the addition of the catalysts only behind the preheater in the converter intake. Pölitz is going to test the advisability of adding Na_2S or the iron catalyst directly into the converter. The chemical effects of such measures cannot be foreseen. Another means would be the use say of Fe - Grude as a substitute for the present catalyst. Ludwigshafen is performing tests to answer these questions.

Other means to reduce the load on the preheater would be to reduce the amount of gas in the preheater. For instance Ludwigshafen has reduced the amount of gas during the extraction tests to 0.55 m^3/kg of paste. It remains to be proven how far the amount of gas can be reduced without affecting the operations in the converter and the progress of the reaction, as well as whether some of the gas may be introduced behind the preheater, and how much of it. Wesseling reports on the effect of reducing the amount of gas on raising the stall temperature. Reducing the amount of gas at the same HOLD temperature results in lowering the quality of the distillation.

Lowering the preheater inlet temperature would be possible if more reactive substances, such as SO_2, could be introduced into the first converter. 1 kg SO_2 produces 820 heat units and consumes 1.1 m^3 of hydrogen, and could only be used for raising the peak heat, without at the same time making use of the catalytic action of the hydrogen sulfide formed.

Lowering the pressure as means of reducing the load on the preheaters would result in disadvantages from a chemical standpoint. Reducing the pressure by 50 atm. will increase the asphalt content by about 1 per cent. A greater amount of washing (to maintain the hydrogen partial pressure) would result in greater hydrogen losses.

The present pressures are:

	The pressure side of circulation pump	Stall inlet
Gelsenberg	700 atm.	670 atm.
Pölitz	650 "	630 "
Welheim	700 "	660 "

C. Materials.

Two accidents in the Gelsenberg hydrogenation plant, where hairpins of N10 material have burst after two years of operation, have created fears regarding the operational safety of these hairpin preheaters.

Damage to N10 parts has been repeatedly observed in the past years, but could so far always be explained by structural defects, the composition of the material or the strength affected by annealing. The new cases differ from the former in that such faults have not been found. One should rather state that the original good qualities have gradually deteriorated in the course of operations. In other words the material has not stood up under the strains of the operation. Operations evidently were not carried out with the usually employed safety factors. Tests have shown that the material was not destroyed, merely changed, and that these changes could be rectified again by a subsequent annealing. One has dealt here presumably with segregations at the grain boundaries under the combined influence of high temperatures, high pressures and of compressed hydrogen. When finally the tensile strength and the resistance to creep strength of the grain boundary substance has dropped below a certain value, the wall bursts in one brittle break; a fraction of a mm on the inner fibers caused the separation of the grain through the piece in a notched bar effect. In certain parts of the tubes at the highest temperatures this zone is hardened by the absorption of nitrogen.

Nothing has been said about the two burst tubes having previously been of optimum quality and that one must therefore consider the immediate possibility of the bursting of other tubes. It may well be that the other tubes would show much longer life. From the available results of investigation of test tubes, small differences in the temperature and pressure results in a considerable difference in life; reducing the temperature by 10° and the pressure by 10 per cent nearly doubles their life. Even if the situation with respect to safety of operations appears dangerous, it is not catastrophic. We must create the necessary safety reserves. This is possible to a certain extent by changing conditions of operation but also by changing the material. We may count on that, when the temperature of the inner wall does not exceed 520°, and the tubes have been annealed to the upper hardness values (about 260 - 300 Brinell), their life would be increased to a sufficient extent. Tubes which have already suffered through the effects of operation may be restored by a new annealing. A regular removal of any crusts formed for the first time after about one year of operations) will avoid the production of unsafe high temperatures.

A change of the composition of the material which would make it less sensitive to the effects of long time of operations by increasing the hydrogen-time resistance against the resistance to creep strength is at present being studied. A higher life would then be achieved in spite of a lower calculated safety factor. High alloyed austenitic chromium-manganese or chrome-vanadium steels would presumably produce a perfect resistance, but cannot be used with the present raw material situation.

Sternberg/MC/jw

8-8-1946

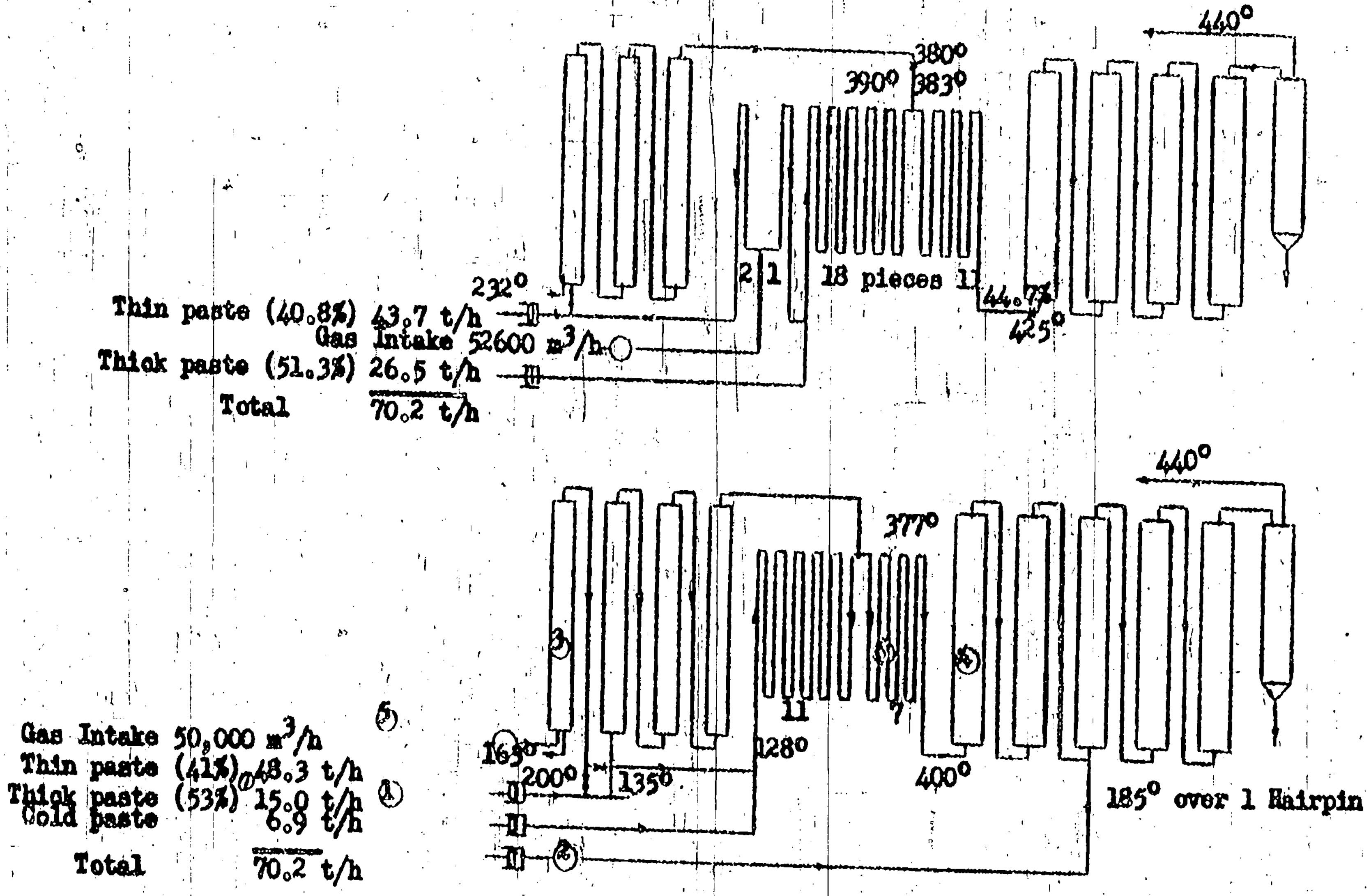

440°
380°
390° 383°
232°
2 1
18 pieces 11
44.7%
425°
Thin paste (40.8%) 43.7 t/h
Gas Intake 52600 m³/h
Thick paste (51.3%) 26.5 t/h
Total 70.2 t/h
440°
377°
3
6
4
11
7
5
Gas Intake 50,000 m³/h
165°
Thin paste (41%) 48.3 t/h
200°
135°
128°
400°
1
185° over 1 Hairpin
Thick paste (53%) 15.0 t/h
Cold paste 6.9 t/h
2
Total 70.2 t/h

Fig. 1

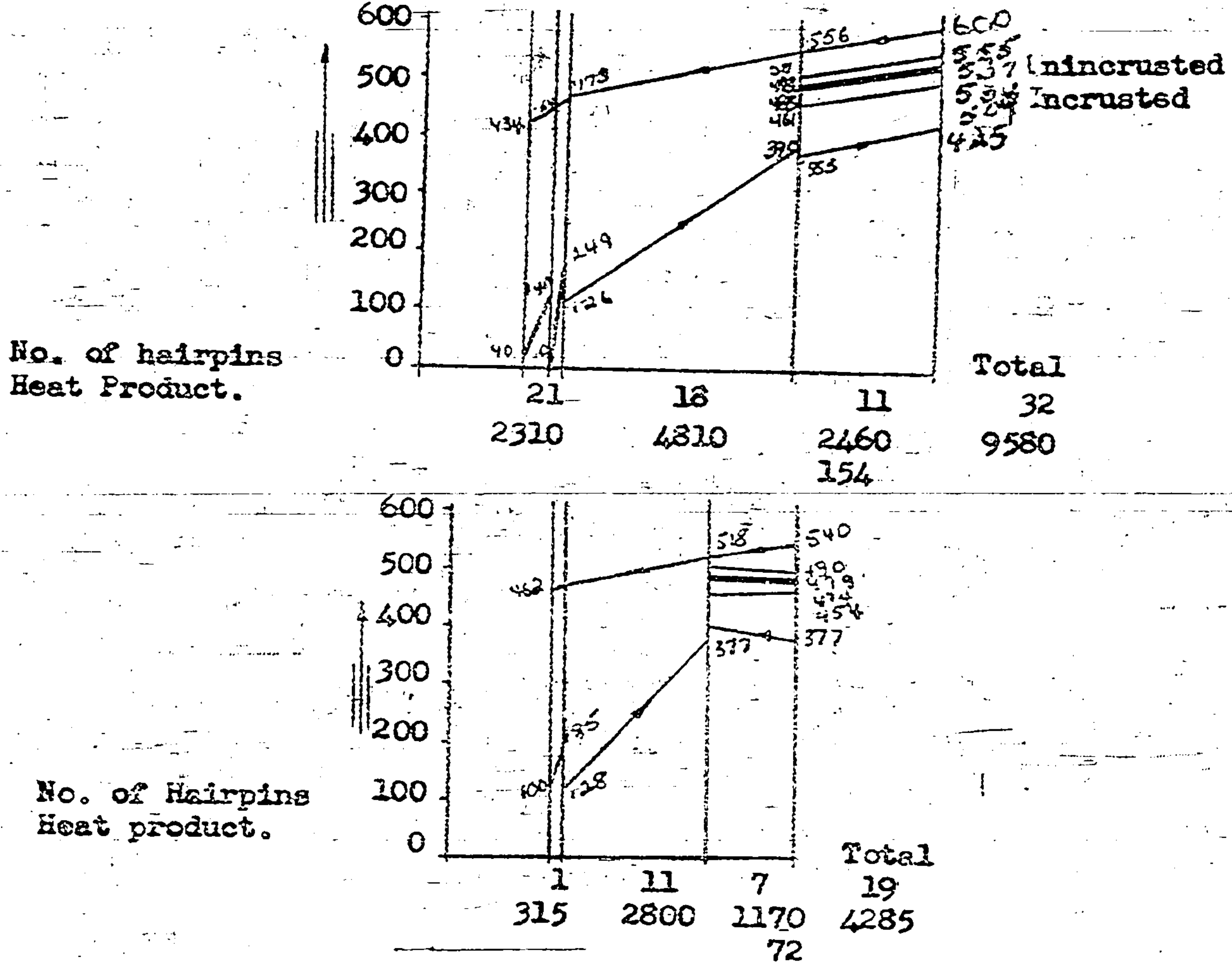

600
500
400
300
200
100
0
434
173
556
600
555
537
533
521
425
379
383
249
149
126
40
0
Unincrusted
Incrusted
No. of hairpins
Heat Product.
21
2310
18
4810
11
2460
154
Total
32
9580
600
500
400
300
200
100
0
462
518
540
490
479
474
456
377
377
135
128
100
No. of Hairpins
Heat product.
1
315
11
2800
7
1170
72
Total
19
4285

Fig. 2

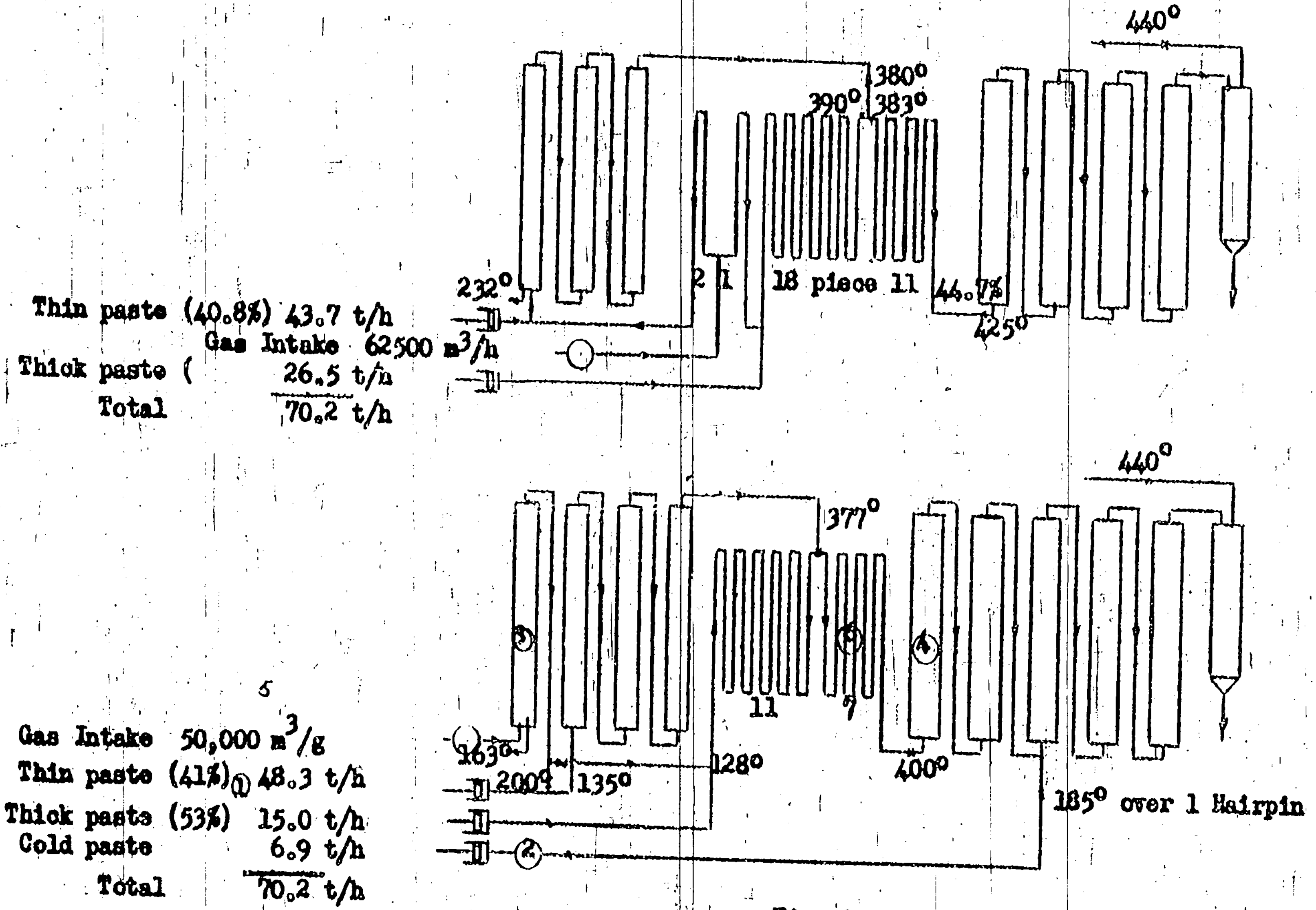
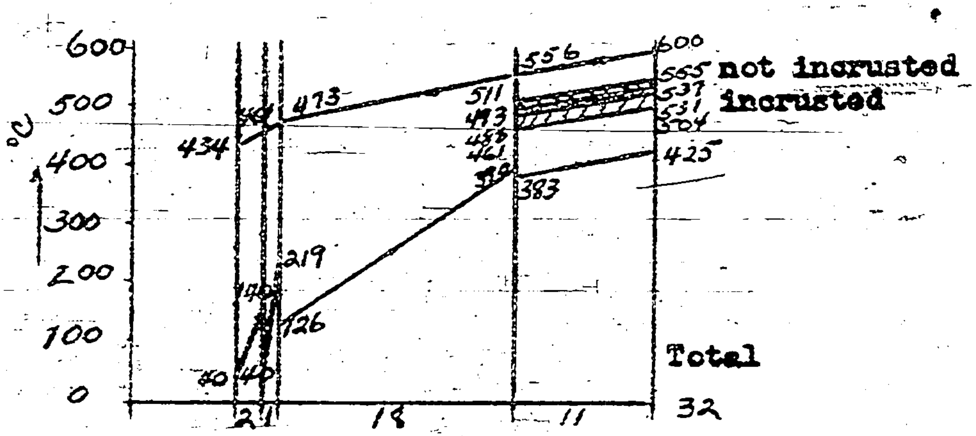
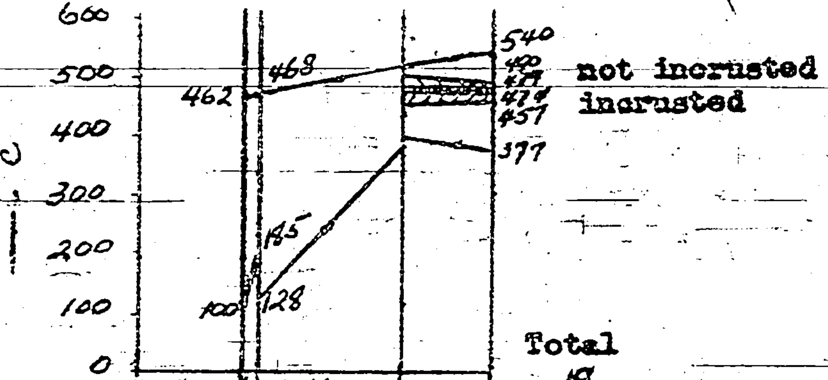

440°
380°
390°
383°
232°
2
1
18 piece 11
44.7%
425°
Thin paste (40.8%) 43.7 t/h
Gas Intake 62500 m³/h
Thick paste (26.5 t/h
Total 70.2 t/h
440°
377°
5
11
163°
200°
135°
128°
400°
185° over 1 Hairpin
Gas Intake 50,000 m³/g
Thin paste (41%) ① 48.3 t/h
Thick paste (53%) 15.0 t/h
Cold paste 6.9 t/h
Total 70.2 t/h
②

Fig. 3



					Total
Number of Hairpins		2 1	18	11	32
Heat Output	10^3 Cal/h	2,310	4,810	2,460	9,580
Δp	ata			15.4	



					Total
Number of Hairpins		1	11	7	19
Heat Output	10^3 Cal/h	315	2,800	1,170	4,285
Δp	ata			7.2	

Fig. 4

T.O.M. Reel 130
pp. 175-178
Date unknown

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-84

TESTING OF MATERIALS (STEEL)

By Dr. Küntscher

PRINCIPAL PROBLEMS

1). Attack by Hydrogen.

Is manifested by numerous fine cracks. Material partially destroyed. Mechanism: H_2 diffuses into the steel and reacts with the carbides (decarburization):

$$\text{Fe carbide} + H_2 \rightarrow CH_4 + \text{Fe}$$

To overcome it: alloying with Cr, which was the cause of development of Cr steels. 2.5% Cr must be present to make the steel hydrogen-resistant. The complex Cr-Fe-C is not replaced with H_2. Other elements also added to increase strength. The annealing state is important, the material must be free from strains.

2). Attack by Sulfur.

The narrow heat exchanger tubes were originally sulfurized in a few weeks, plugged up with FeS.

Resistance to H_2S is obtained by high alloying, but material then becomes difficult to work. For this reason it is preferable to produce a high-alloy outer layer by depositing zink.

Hot dipping (Feueverzinkung) produces a thin layer of zink which vaporizes at 450°. Protection was only effective for 1/4 year. Zink plating in vaporized zink was for this reason introduced, with the material exposed at 870° for 40 hours to the vapors of zink (vapor pressure of Z at 920° 1 atm., at 870° 3/4 atm.), when a disfusion layer is formed, actually an alloy of Fe and Zn (on 2 1/2% Cr steel). Vapor coated zink tubes can be treated for a very long time with H_2S without formation of crust.

High-Cr - Ni steels (such as V2A, 18% Cr, 9% Ni resist H_2S well below 500°, but they become embrittled. (separation of C). They are not S-resistant at high temperatures. Hot strength.

Testing of different high alloy Cr-steels at high temperatures and at high pressures

There is a rapid increase in permanent elongation at first, and fatigue tests are therefore run for from 1000 hours to 1 year. N8 is stable for 1200 hours and less (3% Cr. 0.5% Mo. 0.5% W, small amounts of V)

Tests on creep resistance is run on different tubes, at high temperatures and under high pressures. A rate of flow of 0.5% of increase in diameter per year is still permissible.

N8: 500-600 hrs.	
500° C	0.1%
550° C	0.4%
600° C	2.1%

Unalloyed steel is satisfactory for cold pipe lines, i.e. S2, with 0.25% C. N03 with 1% Cr, 1.3 Mo for hot steam screws at 520° C. N5 and N8 are used as H_2 resistant steels. N6 and N7 are not used. N10 is now used for preheater tubes at 700 atm.

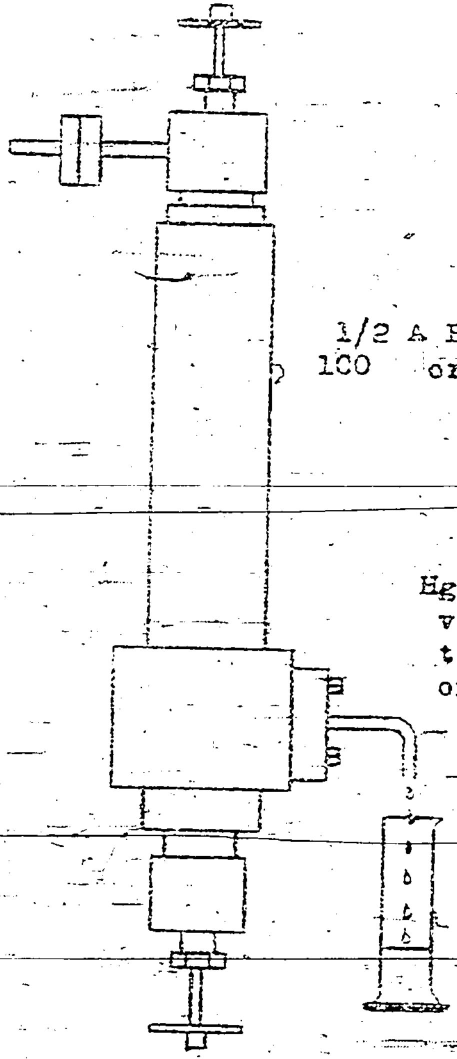
The different steels are subjected to numerous tests at the smelter and by the receiving department of the I. G. Each individual piece is tested to prevent any mixups. After their installation in the stall a rapid "Tupflprobe" test is made.

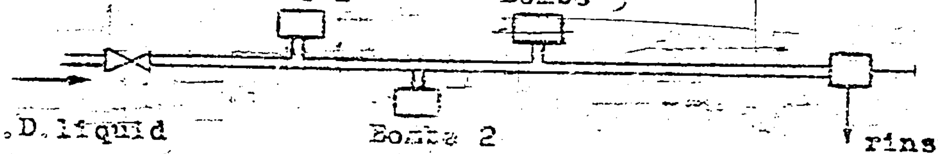
Literature on "Tupflprobe":

Zeitschrift für Metallwirtschaft, vol. 16, 1937, pp. 439-444, 551-552.

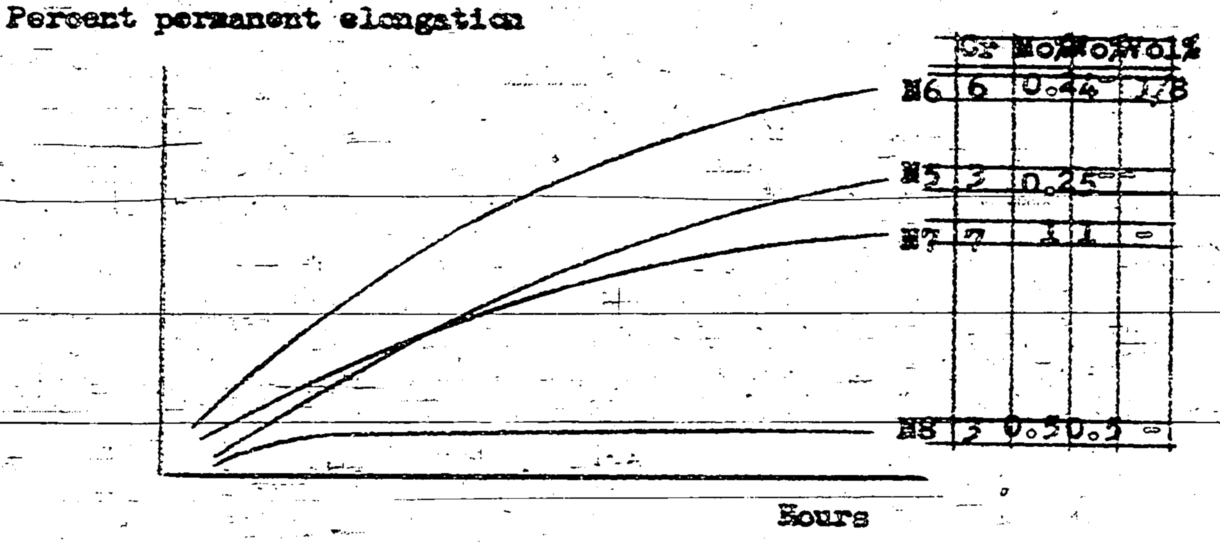
Sternberg/ /jw

Collector





Several bombs connected to one collector



	Cr	Mo%	V%	Wol%
N6	6	0.44	-	1.8
N5	3	0.25	-	-
N7	7	1	1	-
N8	3	0.5	0.3	-

T.O.M. Reel 130, pp. 176-179

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-85

ACCIDENT PREVENTION

Dr. Hähnel. (Date not given)

The purpose of accident prevention is not merely the protection of people, but is also of economic importance.

Accidents are more frequently caused by mechanical than by chemical factors.

The danger of accidents is higher in hydrogenation because of the fire hazard, poison, high operating temperature and high pressure.

Chemical factors.

Combustibility and formation of explosive vapor and air mixtures.

Electric discharge with spark formation.

These are to be considered when gasoline, or similar liquids come in contact with air currents, for instance when containers are drained or let down. In the absence of grounding, sudden discharges with spark formation may be produced from electric charges. Charges are avoided by a proper grounding of all paths of fluids, i.e. in the emptying of tank cars.

(drawing, not available)

When emptying, both vessels become charged and both must be grounded by conductors to the level of ground water. The stream of liquid must pass through a pipe which is also grounded.
(Frictional electricity, drop effect). When funnels and screens are used, they again must be grounded. The metal connections must be clean.

When gums are dissolved in gasoline, even dipping or removing woolen or silken rags may be dangerous.

Pure gases do not become electrically charged, but the presence of minute amounts of solids is sufficient to produce a charge!

No one should ever wash their hands in gasoline. When necessary to wash hands in gasoline, some soapy water must be added, or the hands wet with the gasoline.

Production of sparks by hammering should be avoided in the neighborhood of flammable gases. Tools must be made of bronze, beryllium-nickel alloy (hard, for chisels) or beryllium-copper (for hammers).

No one should do welding in clothes saturated with oil.

Tanks with protective gases may become fire hazards when discarded from operations, should any FeS have formed. Oxidation may result upon exposure to air, and a bursting into flames. It is very dangerous when there are inflammable vapors or liquids around. A tank must be filled to the top with water before admitting air.

Harm from substances occuring in the hydrogenation may also manifest itself by itching, rash formation and poisoning.

Gasoline, middle oil are occasionally used to clean hands, machines and floor. The results may be skin diseases, objectionable odor in the room. Substitutes must be used. The floor must be cleaned with Nerad oil (produced by I.G.) or with Siliron; Machines with Siliron or with Henkel P 3 hand soap.

Phenols irritate the skin and the mucous membranes, goggles must always be used because eyes are very sensitive. Distillation and catchpot water may contain phenols. Other substances of like properties: NH_3 (high rates of diffusion, mucous membranes irritated) and H_2S (in low concentrations irritating to the eyes, powerful poison for nerves, can not be smelled in high concentrations).

Protection against H_2S:

Gas masks with insertions ("S" for H_2S, "R" for H_2S and hydrocarbons) have but a limited efficiency with very poisonous gases. At concentrations of over 2%, H_2S begins to pass through the insertion in a short time. These gas masks are therefore of only limited use as protection. For that reason, everywhere where H_2S is present (alkazid, hydrogenation of HOLD expansion, H.D. washing, emptying of converters, measurement of level of tanks) one must have during repair work:

1). Compressed air masks (compressed air connections!)
2). Oxygen equipment.

Injection of heart remedies, i.e. "lobelin".

Deadly poisoning may occur also with N_2, CO_2, hydrocarbons and Hg vapors: with N_2 or CO_2 connections. The latter are built similar to the air connections "(bayonet connection)". On all such connections the contents must be indicated by color and tag. In Leuna the N_2 and CO_2 identification tags must first be lifted before connections can be made. The compressed air pipe line must first be blown out, to prevent water from entering the gas masks. When vessels are to be blown with air, they must be at a lower pressure than the compressed air.

When the immersion of a gas line breaks through, no one is permitted to come near until water has been replenished (the valve must be then horizontal), i.e. in the dipping of exhaust or fuel gas.

Goggles must always be worn when pipe lines are opened, because some may come out even after exhausting the pressure ("concealed pressure"), should the line have been plugged (deposition of rust, FeS, catalyst dust, paraffin, naphthaline, salt).

/3

T.O.M. Reel No. 163 U. S. Bureau of Mines T-86
Hydro. Demon. Plant Div.
pp. 221-226

October 16, 1942

STEELS USED IN HYDROGENATION

Of all the different properties required of the steels used in hydrogenation we shall treat here only the most important ones, namely resistance to hydrogen, creep strength and resistance to hydrogen sulfide.

In the earliest experiments the apparatus was made of unalloyed steels in which the inner strains were overcome by careful heat treatment which was the subject of strict inspection requirements. However such material was more or less decarbonized and embrittled at temperatures of about 350° - under special conditions even at 300° - so that it would repeatedly break like cast iron with no previous deformation. Work with this material under critical temperature condition was only possible by using special construction details.

The temperature limit of the attack by hydrogen was raised to 425 - 450° by the introduction of the N4 steel, a chromium nickel alloy with about 0.3 - 0.4% C, 1.15% Cr and 2.5 - 3% Ni when this steel was properly worked and had the proper structure. The upper limit of stability would sink otherwise to 400° and the steel did not offer the required safety in operations. A large increase in alloying additions was made by changing over to the V2A steel which has become in the meantime widely used and which contained 18% chromium, 8 - 9% nickel and about 0.12% C; it was stable against attack of hydrogen and had good strength, and it was not attacked by hydrogen sulfide at the normal operation temperatures. However this steel became very expensive, and in addition presented great difficulties at first in the production of thick-walled seamless tubes. Moreover, if the material was raised to temperature of 500 - 600°C and placed in a corroding medium, among which the acid factory air had to be counted, there resulted breakdown of the grain, a phenomenon which caused the material to fall apart as a powder under very slight strains. This breakdown was caused by carbon which unquestionably had become dissolved during heat treatment (quenching from some 1100 - 1200° in ice water) to be deposited at 500 - 600° in the form of chromium carbides at the grain boundary with a resulting local lowering of the chromium content and reduction of the corrosion resistance. The combination of carbon with titanium, tantalum, or columbium permits the production of V2A which is resistant to breaking down of the grain; however, the high nickel and chromium content has limited for a long time the use of these materials only to parts under particularly high strains. Nickel is basically unsuited by lowering the resistance to hydrogen and by being attacked by sulfur and, as a result, chromium which has been found beneficial was combined with molybdenum which, in turn, improves mechanical properties more, even when added in small amounts, than does nickel (0.5% Mo corresponds to about 2% Ni) and is moreover known to be particularly active as a catalyst.

The first steel made on that basis was Krupp's P459, to which we have given the designation N5 and which contained about 0.15 - 0.2% C, 6% Cr, 0.5% Mo and 0.1 - 0.2% V. This material was resistent to hydrogen up to 600°, and had sufficient creep strength to meet the strains to pressure and temperature requirements of that day. The N6 material is even today used in large amounts in Leuna. Experience with high pressure boilers and in the aviation industry has shown that with increasing chromium content in the chromium-molybdenum steels a maximum tensile strength was obtained with about 1% after which it became lower, and steels with a lower Cr content than in N6 have been tested with the formulation of N8, (0.18% C, 3% Cr, 0.5% W, 0.5 Mo, 0.1V) which had a sufficient hydrogen resistance and a markedly higher creep resistance (18 kg/mm² at 450° against 15 kg/mm² of N6), a sufficient resistance to hydrogen, and were in addition cheaper. Experiments with small scale equipment have shown that increasing the pressure to 700 atm. resulted in marked improvements in hydrogenation, but these higher pressures permitted also the use of higher temperatures, and the demands on the creep resistance had to be further raised and brought to the N10 material containing 0.17 - 0.22% C, 2.5 - 3% Cr, 0.35 - 0.5% Mo, 0.35 - 0.5% W and 0.7 - 0.86% V. This material was developed from N8 with an increased vanadium content. It can, however, only be of service after the material before hardening was heated to very high temperatures - about 1050°C - in order to produce a maximum solution of vanadium carbide which will become very finely sub-divided in a subsequent precipitation by annealing at about 700° and cause a great hot strength through the damming of glide planes. N10 is a highly developed material, with the strength in the heat-treated state amounting to 90- 100 kg/mm², with good toughness which is about twice that in the soft-annealed state and which therefore requires the greatest care in heat treatment and working.

The development of steels for converter shells, flanges and bolts proceeded over the same path as with the tube material, from selected carbon steel, through chromium-nickel steels to chromium-molybdenum steels with the addition of some nickel chiefly for metallurgical reasons in case of the converter steels.

The converter steel N1: 3% Cr, 0.25% Mo, maximum 0.8% Ni.

Steel for bolts and flanges under highest strains, K5: 1% Cr, 1% Mo.

The tube bundles of the heat exchangers are made of N5 which contains 3% Cr and 0.25% Mo and the converter liners and heat exchanger parts were made of V2A or with 17% chromium steel. During this development the apparatus was protected against the attack by sulfur.

Hydrogen sulfide attacks most of the industrial metals and alloys especially at high temperatures, as was known from the experience of the petroleum industry. During hydrogenation, products were treated with very high sulfur content, or else with low sulfur content but at high temperatures as, for instance, in the electric heating of the preheaters and difficulties were experienced through decomposition and deposition of sulfide crust. The problem of sulfur resistant material became particularly important after the introduction of sulfided catalysts, with the feed occasionally also sulfided in order to increase the permanency of the catalysts.

Many tests were made in special small-scale furnaces to test the effects of hydrogen sulfide contents of up to 1.5 - 2% at temperatures from 20 - 25 ev using several hundreds of steels with an iron base and with the addition of chromium, nickel, tungsten, molybdenum, aluminum, silicon and manganese, also testing with different compositions and varying the methods of production, and also coating with light metals like tungsten (sic), molybdenum, silver and others. The lowest alloyed steel with sufficient productive properties against hydrogen sulfide contained 13% Cr but was then difficult to manufacture into high pressure tubes.

Further tests were made with samples of brass tested together with [illegible], and which showed no marked attacks by sulfur, and the possibility of using copper-tin alloys of the most variable composition, in most cases specially prepared, was also tested. It was found that among the technically useful brasses, alloys containing 58 - 63% copper with the balance of zinc were resistant, while brasses with 70% copper were slightly attacked and brasses with 80% copper were strongly attacked. One sample was of particular interest. It was not cast from the molten state but was obtained by turning from regulus obtained in a crucible. This sample was unaffected at the upper end but completely converted into sulfide at the bottom, which was explained by subsequent analyses to a segregation during solidification. The upper end contained 58% copper, while the lower end contained 95% copper, and this one sample gave information on the whole range of alloys. Copper is attacked by hydrogen sulfide even at low temperatures, and the high stability of brass was the result of its zinc content, prompted making experiments to obtain useful alloys even with the less resistant nickel and iron by the addition of zinc. The first alloys prepared with such zinc additions seemed almost entirely unpromising because of the failure to introduce zinc into the melts and maintain it there. The boiling point of zinc is 907°C, way below the melting point of nickel (1452°C) or of iron (1528°C) and the vapor pressure of zinc is equal to 54 atm. at 1500°C. However, "anything may happen under high pressure" and a Tammann tubular carbon furnace was installed with a suitable high pressure container, and the melting carried out under 60 atm. in nitrogen or permitted to solidify, thus producing for the first time iron-zinc alloys with a zinc content as high as 60%. These samples behaved in experiments on attack with sulfur similar to the copper-zinc alloys, while nickel containing 10% zinc formed a sulfide crust 3.3 mm thick at 25 atm, which was reduced to 0.03 mm with 20% zinc. 15% zinc was sufficient with iron to produce complete sulfur resistance. These nickel and iron alloys are difficult to process industrially in spite of their great stability, because they are extraordinarily brittle and no forming is possible even by casting.

In hot galvanization of steels an iron-zinc alloy is formed, and galvanized iron samples were tested and have also been found to be unattacked by hydrogen sulfide. These successful small-scale experiments were then immediately jumped and in the beginning of 1930 Stall 505 was installed with a heat exchanger with hot-dipped bundles of tubes made of N6, which have been found successful. The hot-dipping of tubes 18 m long for heat exchangers is industrially difficult to perform and Leuna has developed, on the strength of these results, the galvanizing in the vapor phase which has since been used for all heat exchanger bundles of tubes and has permitted recently to replace the difficultly obtainable high-grade chromium-nickel alloys in the linings of the converters.

This was approximately the conditions existing before the outbreak of the war. From this time on scarcity of molybdenum, tungsten and chromium necessitated a saving of these metals and the use of larger amounts of vanadium, manganese and silicon as alloy materials. The table below is a comparison of conditions in the middle of 1939 against the middle of 1942.

Purpose	Middle of 1939		Intended, beginning April, 1942	
	Markings	Analysis	Markings	Analysis
Gaskets, bundles of tubes for heat exchangers, foundation, shells for Wickelöfen	N5	2.5-3 Cr; 0.25 Mo; >0.12 C.	N5A N5B N5C	<0.12C; >2.5 Cr; max. 0.1 V. <0.12 C; >2.5 Cr. 0.12-0.18 C; >2.5 Cr; 0.1-0.2 V.
Tubes for pipelines and preheaters for 300 and 700 atm.	N8	3 Cr; 0.5 Mo; 0.5 W; 0.1 V; 0.15-0.20 C.	N8A N9	2.5-3 Cr; 0.2-0.3 W; 0.2-0.25 C. 3.0-3.5 Cr; 0.2-0.3 Mo 0.45-0.55 V; 0.19-0.24 C.
	N10	2.7 Cr; 0.4 Mo; 0.4 W; 0.8 V; 0.19-0.24 C.	N10	Unaltered but in an annealed condition strongly limited.
	K2	1 Cr; 0.2 Mo; 0.6-0.9 Mn; 0.23-0.28 C.	K2M	1.5 Mn
Flanges and bolts.	K3	1 Cr; 0.3 Mo.	K1M K4MS K3CV	0.8-1.5 Mn; about 1 Si. 1.5 Mn; 0.15 V; with Si alloy. 1 Mn; 1.3 Cr; 0.25 V.
	K5	1 Cr; 1 Mo.	K7	1.5 Cr; 1.2 V; max. 1 Mn.
Converter shells and covers.	N1	3 Cr; ~~0.25 Mo~~; max. 0.8 Ni.	N1A for wall thickness 120 mm	a) 2.5-2.8 Cr; max. 1.0 Mn; 0.8 Ni; b) 2.2-2.5 Cr; max. 1.0 Mn; 0.15 V (0.5 Ni from scrap permissible)
			N1 for wall thickness 120 mm	2.2-2.5 Cr; up to 0.22 Mo; max. 0.8 Ni; max. 1.0 Mn.

Comparison between the requirements in alloy pieces for the high pressure stalls for the hydrogenation with a 250,000 year/te production of automobile gasoline from coal. The following savings will be the result of using the 5/1/42 requirements against the 5/1/41 requirements:

Savings:

Chromium		10%	= 37,000 kg.
Molybdenum		45%	= 16,000 kg.

Increased Requirements:

Nickel		11%	= 7,500 kg.
Vanadium		30%	= 4,800 kg.
Manganese	about	100%	= 95,000 kg.

For a DHD installation for the production of 200,000 year/te of DHD gasoline the values for the same time periods are as follows:

Savings:

Chromium		41%	= 13,300 kg.
Nickel		100%	= 320 kg.
Molybdenum		75%	= 3,460 kg.

Increased Requirements:

Vanadium		200%	= 1,830 kg.
Manganese	about	33%	= 1,500 kg.

/S/ Dinkler

Sternberg/MC/jw
8-9-1946

T.O.M. Reel No. 145
Item No. 7

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-87

Lu 1. 22 May 1944

HOT OIL LET-DOWN DISTILLATION

Summary: Processes described in DRP 735 469 for the distillation of pitch with super heated steam was tested for its adaptability for the distillation of coal residue.

We have succeeded in driving off 75 to 82% of the let-down oil (the difference between HOLD and distillation residue, assuming no loss) with little splitting, as distillate, containing little insolubles and asphalt. Vacuum distillation would give us 25% less yield. In addition, a high asphalt containing distillation residue of high viscosity was obtained, which is suitable for a briquetting medium, but which might also be extracted or further distilled in a ball kiln.

It seems apparent that the, very sensative to temperature, let-down has a tendency to coke in the mixing section, even at high flow velocities, if the temperatures indicated in the Patent Claims of 600°C for the steam and 500°C for the mixture are appreciably exceeded. Conditions under which an almost oil-free distillation residue, similar to the residue of ball kiln, could be obtained have therefore not been found.

Further experiments in distillation and in the testing of the pasting oil quality of the distillate are in preparation.

DRP 735 469 of the Rütgers Works describes a process according to which the distillation of low volatile oils without appreciable decomposition is made possible by heating it in fractions of a second with consequent volatilization without cracking, by mixing it with an inert gas or steam serving as heat exchange medium. In the described examples, high temperature coal pitch, brown coal tar pitch, or petroleum bitumen, preheated to 370 - 380°C, are sprayed thru a nozzle into a 600°C stream of steam, where for one part by weight of pitch 1.1 - 1.4 part by weight of steam are used. From the specific heats and the mean composition of these residues a mean mixture temperature of 495°C may be calculated for these examples. The mixture of pitch and steam flowed through a mixing section approximately 20 cm long with a velocity of about 5 m/sec, so that the mixture remained at working temperature for about 0.04 seconds. Then it entered sidewise into an expansion chamber, where it was brought to a temperature of about 400°C. Here the vapors going off at the top were separated from the unvaporized residue. With a loss of 1 - 2%, 30-40% unvaporized hard pitch was obtained, which we estimate consists of about 40 - 60% insolubles and a high-asphaltic oil, as well as a high viscosity oil. The oil yield is therefore higher than with other distillation processes, for example, vacuum. By mixing the distillate and residue of coal tar residue, a pitch of original quality was again obtained, an indication that, in reality, no decomposition took place.

It seemed advisable to test this process for its suitability for working up residues, because it seems to open up the possibility to obtain, by distillation of the let-down, a return oil low in insolubles and asphalts, in the use of which an increase in the coal thru-put, with the same pumping energy and concentration of solids in the paste, and a decrease in the gasification by eliminating the return of high condensed asphalts to high pressure, may be expected. The question is still open, if it is possible to extract so much oil from the distillation residue that a kiln distillation would not appear a paying proposition, or if it should be used in the ball kiln with a higher oil content or as a briquetting medium for non-baking coal.

RESULTS OF EXPERIMENTS

The conditions for the experiments are given in Table I.

It was to be expected from the start that the hydrogenation let-downs are more easily decomposed at high temperatures, and therefore more readily lead to equipment trouble, than tar residues, which have already passed through high temperatures at low pressures. Therefore, contrary to the examples in the Patent Application, higher velocities in the mixing section and therefor shorter periods at working temperatures, were used. This required that the mixture stream be introduced from top to bottom in the separator (catch pot) to prevent sticking of the residue on the opposite wall of this vessel.

Let-down from the coal hydrogenation at Pölitz, properties of which are given in Table 3, was used as feed.

In Experiment 1 pure heavy let-down oil and P 1598 was run alternately with a relatively high thru-put (8.5 - 9.0 kg/h), where the proportion of oil to steam was held to that given in the examples in the Patent Application. Deviating from these, 0.5 m^3 of gas, at standard conditions, per kg of feed oil was pre-heated with it and run thru the nozzle for the protection of the heating coils. This required an increase in the steam temperature to 624° C. to obtain a mixture temperature of about 490°C. This experiment, running for several hours could not be balanced because of repeated failure of the paste pumps which were unsuitable for working without pressure. These interruptions may have been principally responsible for the wide spread coking up of the mixing section, which was disclosed after the experiment.

In Experiment 2 a somewhat reduced steam consumption was experienced, possibly because the mixing section was already coked-up in the early stages, since here also the cold paste pumps worked erratically. Since the heat-up temperature of the let-down was at the same time reduced by 11° to 379°C, a mixture temperature of only 477°C was obtained. The experiment was discontinued after ten (10) hours in the regular manner. The mixing section was again fully coked up, as was disclosed in dismantling.

According to the balance (Table 2), about 40% of the let-down was obtained as distillation residue, which appeared coky, because the separator, even at the bottom, was held at 400°C thru-out the entire experiment by electrical heating. Because of this, the balance shows considerable renewed formation of insolubles. The resulting distillate (Table 4) was, as expected, low in benzol insolubles (1.3%) and in asphalt (2.2%).

As the comparison of the specific gravity of its vacuum fractions and its middle oil contents with the corresponding values of the feed oil show, a very light cracking occurred. If the losses, which here are comparatively high because of ineffective condensation in the equipment, an oil yield of 75% from the oil of the let-down is calculated, while in vacuum distillation only a 36% yield was possible. The effect of the process described in the Patent Application was therefore proved. Due to the intense heating of the separator sludge the residue was largely coked (see Table 5).

In Experiment 3 the quantity of steam was to be doubled in order to increase the oil yield. This can be obtained only by reducing the feed oil injection with a corresponding gas reduction, since at the beginning of the experiment the steam temperature rose to 688° because of carelessness of the operator, which led to a sudden coking-up of the mixing section and thereby to a reduction of the steam consumption by 50%. This shows that the steam temperature in this process cannot be increased at will. In the following twenty (20) hours experiment with a mixture temperature of 525°C, the coking increase' somewhat further.

The increase in the quantity of steam and the mixture temperature has increased the distillate-oil yield to 82.5% of the let-down oil (again assumed to be free of loss) (see Table 2). As the specific gravity of the oil (Table 4) shows, more difficult boiling constituents were carried over than in experiment 2, as well as some asphalts, according to the analysis, 15% of the asphalt of the let-down was found in the distillate. The insoluble content was about the same as in the preceding experiment. The new formation of middle oil may have increased somewhat. Accordingly, a working temperature of about 500°C may not be appreciably exceeded for the oils from hydrogenation let-downs in order to avoid splitting. Since the separator was not heated at the bottom this time, a very viscious residue with a softening point of 160°C, suitable as a briquetting medium for non-baking coals, according to tests made by Dr. Bähr, was obtained. The proportion of oil consists of 75% s-asphalt (Table 5). According to the balance, the new formation of benzol insolubles was considerably smaller than in experiment 2, the new formation of Tetralin-kresol-insolubles was inconsequential.

Experiment No. 4 was made under identical conditions, but lasting only three and one-half hours, including the running of the oil, in order to determine the start of incrustation of the mixing section. The incrustation here was as great as in the preceding experiments. The coking up of the mixing section to a narrow channel appears, therefore, to occur at the very start of the process under the chosen conditions. The coke contained 32% ash. Therefore, 67% of the let-down was volatilized, the rest was coked. Since the separator was held to only 300°C this time, the distillation residue contained only 45% insolubles. In order to drive off sufficient volatile matter, a mean separator temperature of 400° C indicated in the Patent must be held to.

Experiment No. 5. Further experiments were particularly to serve the purpose of avoiding the coking up of the mixture section. For this purpose the mixing section was narrowed from 24 to 10 mm diameter, which increased the stream velocity about 5 times (120 m/sec). At the same time the quantity of gas was further reduced to 0.125 m3/kg of let-down, so that the let-down-gas-mixture emerged from the nozzle with relatively slow velocity compared to the steam. Herewith was to be avoided, that the let-down be shot against the tube wall of the mixing section opposite the nozzle opening, where it would stick and coke. It was shown that with this small quantity of gas a short interruption in the gas supply led to a damage of the mixing section and the passage between preheater and nozzle, although the mixture temperature was this time only a little above 500°C.

The following Experiment 6 showed that it was possible to run for an extended period under these conditions. It ran undisturbed for almost twenty eight (28) hours and ended thru a sudden stopping up of the mixing section and the nozzle, which was caused by a momentary lowering of the gas pressure and the consequent gas consumption due to a bombing alarm. Compared to experiment 3, the lowering of the mixture temperature by 21° to 504°C caused a lowering of the oil yield by about 5% to 77% of let-down oil. Because less heavy oil was driven off a somewhat lighter distillate was produced. Its content of insolubles and asphalt remained practically unchanged. As expected, the residue had a low insoluble content (54%) and its oil contained less asphalt. Accordingly, the residue had a somewhat lower softening point at 140°C. The economical working also showed itself in the balance in a smaller new formation of insolubles. This time also the asphalt remained at 80%. The increase in separator temperature from 377°C to 388°C in Experiment 6 had therefore no appreciable influence on the results.

Nearly all balances showed a deficit in the ash balance. Presumably the iron sulfide is largely decomposed in the distillation by the super heated steam, so that in the ashing of the insolubles no further sulfate formation ($CaSO_4$) can occur.

After the sensability of the equipment against variations in the gas consumption had made itself apparent, the gas was omitted in Experiment 7. In order to lessen the increasing danger of the closing of the nozzle by this procedure, the let-down was run in at a lower temperature (350°C) and the steam temperature increased. After two (2) hours the cold paste press service was interrupted for several minutes with a consequent stopping-up of the nozzle.

The next Experiment 8 was again run with gas. The conditions differed from those in Experiment No. 6 by a lower paste pre-heating, consequent higher steam temperature (627 against 575°C) and higher mixture temperature (518 against 504°C). While Experiment No. 6 was successfully concluded after twenty eight (28 hours) only thru external influences, it was here possible to run only 13 hours. A gradual stopping-up of the mixing section occurred and eventually also the nozzle was almost closed. The temperature indicated in the Patent Application, 600°C for steam and 500°C for the mixture, could, accordingly, not be appreciably exceeded in the distillation of the sensitive hydrogenation letdown even if, as here, the stream velocity in the mixing section is increased more than twenty (20) times compared to the patent examples.

Since, due to the stopping-up of the mixing section, less steam was run at times, the resulting balances of this experiment are somewhat less favorable than those of Experiment No. 6. In particular, an increase in the new formation of benzol insolubles appears, which leads us to presume that from this point of view also a mixture temperature of above 500 - 510°C should be avoided.

Arrangement of Experiment
(Rebuilt Pressure Distillation Lu 522)

In an electrically heated gas preheater, heated gas is mixed with the let-down supplied by the cold paste press. The the mixture goes to the pre-heater in a 10 mm tube, upward and downward coil, 10 x 24 x 6,000 mm in electrically heated air space, from there to the coil furnace, upward and downward coil, 10 x 24 x 6,000 mm in electrically heated air space, then thru an electrically heated passage to the mixture nozzle. Steam heating in steam coil hanging in electrically heated air space, then downward thru a 10 mm tube to the mixing section.

Mixing Section, 24 mm tube fitted into the separator (catch pot) cover from the top. The mixing nozzle, 4 mm tube, at an angle of 45° to the longitudinal axis of the tube and bent in the direction of the tube flow, extends to the center of the tube in the mixing section.

Separator (catch pot) 265 mm diameter, 1300 m high, electrically heated, with interchangeable liner of 71 liters capacity. Vapor out at the top thru the cover.

Further course of the distillate: Thru a water cooler into a separating column for separation of oil and steam. The oil is drawn off at the bottom thru a goose-neck, steam discharged at the column head, again thru a long water cooler into a condensate vessel (light oil vessel), from there thru a partly water cooled line into atmosphere (Über Dach).

Description of Experiment

Experiment No. 1. 3/9/44.

400 li/hr of gas at standard conditions thru pre-heater. Temperature in the gas preheater 9 mv, in the pre-heater 12 mv, in the coil furnace, 19.5 mv.

10 kg/steam/hr thru steam inlet, steam coil 34 mv.

Separator inside, 20 mv.

(NOTE: Detailed description of the several experiments follows here in the original report which, however, does not appear essential to our purpose at this time).

KCBraun/pkk/jw

TABLE 1

CONDITIONS OF EXPERIMENTS

Experiment No. Date 1944	1 3/9 & 10	2 3/12	3 4/11 & 12	4 4/15	5 4/21	6 4/23 & 24	7 4/27	8 4/28 & 29
Duration of Experiment in Hrs.	8	10	20	2	2	27.5	2	13
Thruput:								
P 1598 kg/h	8.5	9.0	4.0	4.0	4.0	4.0	4.0	4.0
Standard gas li/h	4,000	4,000	2,000	2,000	500	500	0	500
Steam kg/h	10.0	8.0	8.0	8.0	8.0	8.0	8.0	7.35
Temperatures:								
S4 Coil Furnace °C	390	379	382	382	386	379	350	348
S4 Steam Coil °C	624	624	624	624	579	575	624	627
Separator °C	410	410	377	302	340	391	388	388
Mixture Temperature Calculated °C		477	525	525	508	504	527	518
Stream Velocity								
In the Nozzle m/sec		229	110	110	37	36	0.1	35
In the Steam Coil m/sec.		22	22	22	120	120	124	114
In the Mixing Section m/sec		25	23	23	113	113	112	107

Braun/pkl/jw

TABLE 2

BALANCE RESULTS

(Oil Yield Calculated Without Loss)

Experiment No.		2	3	6	8
Distillate yield from let-down free of insolubles	%	59.2	65.1	60.8	57.7
From oil in Let-down	%	75.3	82.5	77.0	73.4
Yield of asphalt free oil in the let-down	%	94.5	104.9	94.3	84.5
New formation of Middle oil in the let-down oil	%	3.5*	Aprx 15	2.7*	1.2
New formation of Insolubles					
Benzol in Let-down oil	%	19.2	9.9	5.6	11.3
Kresol in Let-down oil	%		3.8	2.7	1.8
Asphalt Decomposition	%	92.5	50.3	18.9	15.0
Asphalt in Distillate on Asphalt in let-down	%	7.5	15.2	16.2	18.5
Ash out/in	%	80	79.5	64.9	110.6

* Minimum Value

Braun/pkl/jw

TABLE 3

PROPERTIES OF THE FEED OILS

		Original Test	Experiment 4 5
Specific Gravity/60°C		1.100	1.110
Water	%	0	0
Benzol Insolubles	%	21.2	21.3
Ash in Insolubles	%	53.1	49.5
Tetralin-Kresol-Insolubles	%	17	17.5
Ash therein	%	58.9	56.6
a-Asphalt in Oil	%	22.0	17.0
Start of boiling	°C	250	248
Wt. Engler - 325°C		2.2	4.3
350°C		20.7	-
Vacuum Curve at mm Hg		15	
152 - 225°C	%	18.0	-
Sp. Gr. /40°C	%	1.030	-
275°C	%	42.8	-
Sp. Gr. /60°C		1.073	-
325°C	%	55.2	-
Sp. Gr./90°C		1.092	-
Residue	%	100.0	-
Composition		Oil	Insolubles
C	%	90.00	43.84
H	%	5.64	1.69
O	%	2.32	-
N	%	0.96	0.53
S - total	%	0.98	5.67
S - volatile	%	-	3.69
Disp. H/100 C		5.93	-

Braun/pkl/aw

Newman

T.O.M. Reel No. 130
pp. 846-873
Braun/jw

T-88

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

Leuna Werke, 23 Jan. 1944

Abstract of Report on the Automatic Regulation of the Liquid and Vapor-Phase Hydrogenation Stalls at Leuna.

By Dipl. Ing. Weis

Liquid Level Reg. in the HOLD Vessels:

The hot oil let-down from the hot catch pot passes through a so called let-down vessel, for the purpose of degassing, from which it is pumped for further processing by a steam pump "DP".

The regulation of the liquid level in the hot oil let-down vessel is shown in Figure 1. The level is measured in the usual way by introducing nitrogen as bubble-gas into the vessel below the liquid level. The pressure of this gas in the top of the vessel is indicated on a pressure gauge in the form of a single-leg manometer, which controls the steam to the pump by means of a compressed-air operated diaphragm valve actuated by an impact plate "P" (Prall platte) and so keeps a constant level in the vessel.

Liquid Level Regulation in the Hot Catch Pot:

The level regulator for the hot catch pot is an electro-pneumatic regulator, working on the "open-shut" principle, shown in Figure 2. Compared to the purely electrical regulator with electrically driven regulating device, the electric-pneumatic regulator has the great advantage, that, besides the accuracy of the electrical measurement and the independence of its location, it enables the rapid, continuous control of the regulating device by diaphragm actuation.

The level in the catch pot is measured by introducing circulating gas as bubble gas, which indicates the pressure on a U-tube type balanced pressure gauge "W". "W", in turn, actuates an electrical circuit operating 2 electric valves V_1 and V_2, which, in the manner of 3-way cocks, connect one side of the diaphragm valve S_1 either to the atmosphere or to 5 atm. compressed air. If S_1 is open to the atmosphere, the 2 atm. pressure in S_2 closes the needle valve (Patronenventil) "D", but if the rising level switches S_1 to 5 atm. air the needle valve opens. The needle valve stem is also provided with a hand wheel for emergency hand operation.

Since it occasionally happens that one valve will not handle the volume of let-down, an appropriate device is provided, which opens a second valve when the level in the catchpot reaches a predetermined maximum height. To prevent this second valve becoming cold in normal operation, the 2 valves are interchanged every 15 minutes. Other side of diaphragm S_2 is connected to 2 atm. compressed air.

Holding the Bubble Gas Constant in the Liquid Level Measurements:

The bubble gas is automatically held constant by means of a so-called filter throttle (orifice), shown in Fig. 3. Essentially, this consists of a filter or screen inserted in a high pressure tube, arranged vertically, and a capillary throttling orifice. (For arrangement see Fig. 3). This simple device has proved so satisfactory in continued operation that it has been decided to eliminate the continuous registering of the bubble gas, whereby 5 pressure gauges and the valve groups that go with them are eliminated for each coal stall. Only one pressure gauge will be used for the 6 bubble gas measurements, which can be used selectively for the control of any of the 6 bubble gas volumes.

Automatic De-sanding of Converter I:

The automatic regulation of this operation is shown schematically in Fig. 4. A resistance thermometer "W" is inserted in the line from Converter I to the de-sanding valve. As soon as "W" falls below a predetermined temperature, it actuates a photo-electric compensator, starting a motor successively opening the let-down valve (in line from catch pot) and the de-sanding valve. After 2 seconds, both of these valves are closed. 30 seconds later, the motor is also stopped, if the temperature of "W" has exceeded a predetermined value. If it has not, the motor runs on and initiates a new control period. The course of de-sanding is through the de-sanding valve and the let-down valve to the let-down vessel.

Liquid Level Regulation In Cold Catch Pot:

The cold catch pot regulator is shown schematically in Fig. 5. The level is measured electrically, an indicating device serving as an alarm instrument. The terminal voltage, proportional to the level, is amplified by a photo-electric compensator. The photoelectrically controlled compensator current acts on the field coil "F" of an electric-pneumatic relay and this delivers a control pressure directly proportional to the catch pot level. This control pressure is not directly used to operate the diaphragm valve, but acts on the coil spring of the pilot control "V". The impact plate "P" attached to the pilot control lever actuates the diaphragm valve "MV" by controlling the air to the diaphragm through the nozzle "D". The arrangement shown in Fig. 5 makes it possible for the nozzle "D" and with it the valve stem "S_1" to follow the position of the impact plate "P" with an accuracy of ± 0.1 to 0.15 mm, and, since the total lift of the valve MV is 25 mm, a setting accuracy of ± 1 to 2% may be attained in continuous operation, even with difficult moving valve stems.

Cold Gas Regulators for Holding a Constant Converter Temperature:

The usual hydrogenation converter temperatures are near the peak of the heat-of-reaction curve, that is, only a slight increase above the permissible temperature will cause the converter to "run away". This fact added difficulties to the problem at hand. The introduction of the resistance thermometer at particularly important points offered a forty-fold deflection compared to the usual thermo-element.

The same electro-pneumatic regulator used for regulating the liquid level in the catch pots can be used for regulating the converter temperatures, by simply replacing the electrical level indicator by an electrical temperature indicator in the form of a Wheatstone bridge. Accuracies in converter control of ± 1° to 2°C can be obtained with these regulators in continuous operation.

As shown in Fig. 6, each coal stall has 2 cold gas regulators K_1 and K_2. The controlling resistance thermometers are installed at points 144 W and 244 W in the lines to and from Converter II. If need be, the resistance thermometers 02W and 0102 W could be switched onto the regulators. In order to avoid oscillation of the regulator, the nearest cold gas injection should be automatically controlled so as to keep the "running time" as short as possible. The short cold gas line in Converter I and the intermediate cold gas line in Converter II are automatically controlled, but the cold gas lines are so arranged that any one of the 3 may be switched onto the regulator. In case a regulator fails, the cold gas injection can be controlled by hand. Only half of the total cold gas is controlled by the regulator, while the basic load is controlled by a hand valve set to a constant volume and added either to the cold gas line controlled by the regulator or to another line. This method requires that the operator be constantly aware of the degree of opening of the regulating valve. Registering the regulated temperature on a multi-thermograph gives us a better picture of the operating efficiency of the regulator. Temperature regulators S_1 and S_2 are also mounted on the control panel, with which the operator can change the converter temperature to suit the let-down quantity with changes of the load on the stall.

The construction of the cold gas regulators of the vapor-phase stalls is exactly the same, except that resistance thermometers 101 W and 301 W are used as controlling indicators, while the automatically regulated cold gas is added between Converters I and II and Converters III and IV.

Liquid Level Regulator for Intermediate Catch Pot:

The satisfactory solution of this problem was contingent upon the development of a continuous working (with intermediate positions) diaphragm actuation for needle valves (Patronenventile). These needle valves have hard-metal nozzles of 12 mm dia. The lift required to open the valve is, therefor, only d/4 = 3 mm. But a setting accuracy of 1 to 2% is necessary for good regulation. Consequently, such diaphragm actuation would have to set the valve stem to an accuracy of ± 0.03 to 0.06 mm. This was not possible with the direct actuated "open-shut" regulators, as used for the level regulation in the hot catch pot, in spite of the pneumatic pilot control. Only a lever arrangement could help us here. In the arrangement shown in Fig. 7, air pressure opens the valve while the counter spring closes it. The valve cone (needle) "K" of the needle valve "PV" is fastened to the valve stem by a spring with 2 mm play, similar to the valve used on the hot catch pot. The balanced pressure gauge "W", indicating the level in the intermediate catch pot, actuates a needle nozzle "N", which operates the pilot control "VS". This arrangement permits the valve to be operated with a setting accuracy of ± 1 to 2%. A handwheel on the valve stem permits hand operation in case of emergency.

Other Considerations:

The pneumatic actuation has only one disadvantage compared to the electric, that is, in case of air failure the valve does not retain its position but assumes one of its end positions. Therefor, the following rules should be followed:

1). In particularly important positions the actuation should be such that the valve will assume the least dangerous position. For example, our cold gas valves open on air failure, thus preventing the converters from "running away".

2). An emergency air compressor should be provided. This compressor may be started automatically on failure of the regular air, supply, by a manometer or pressure gauge. Allow about 2 M^3/h per regulator.

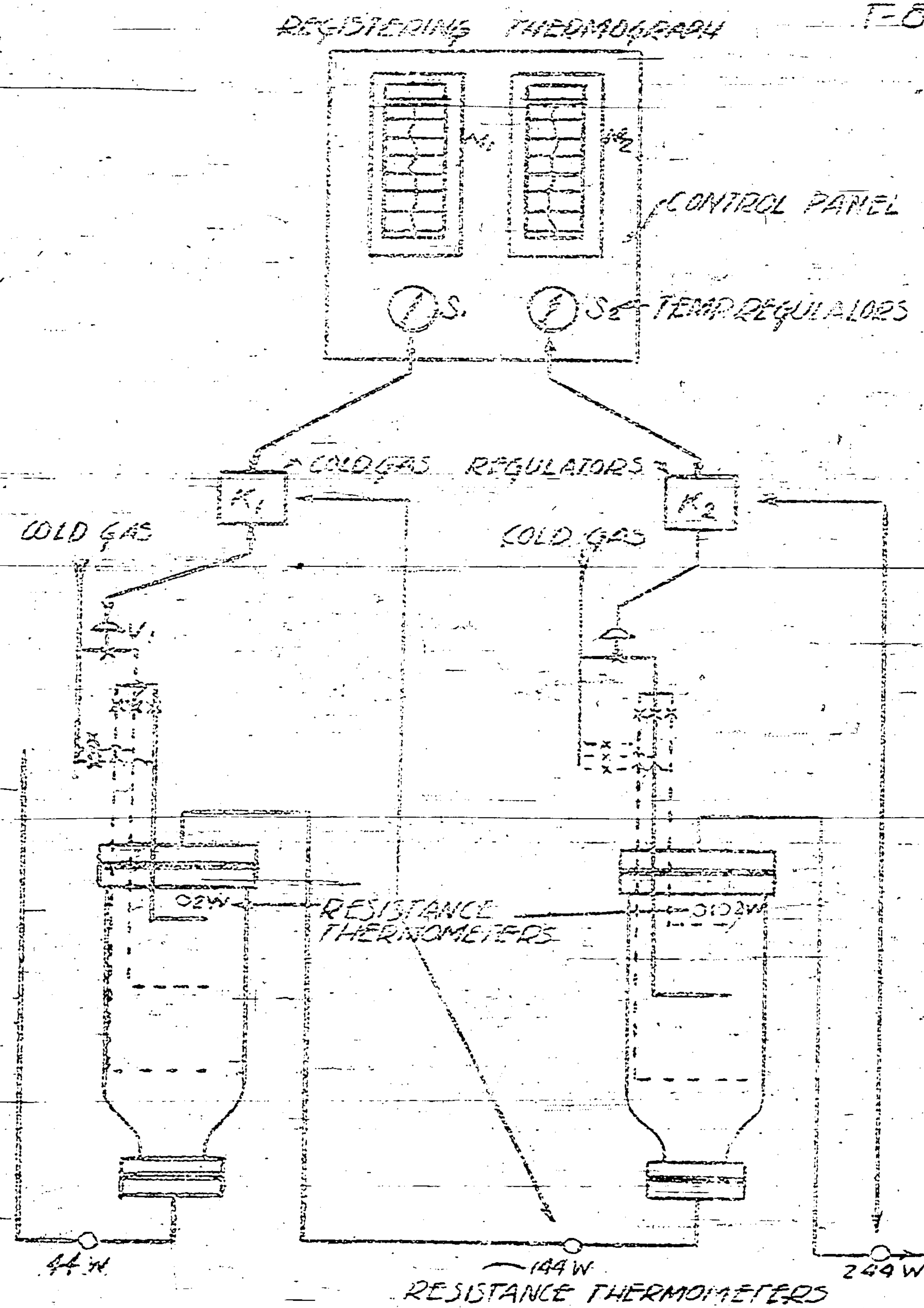


FIG. 6
COLD GAS REGULATION

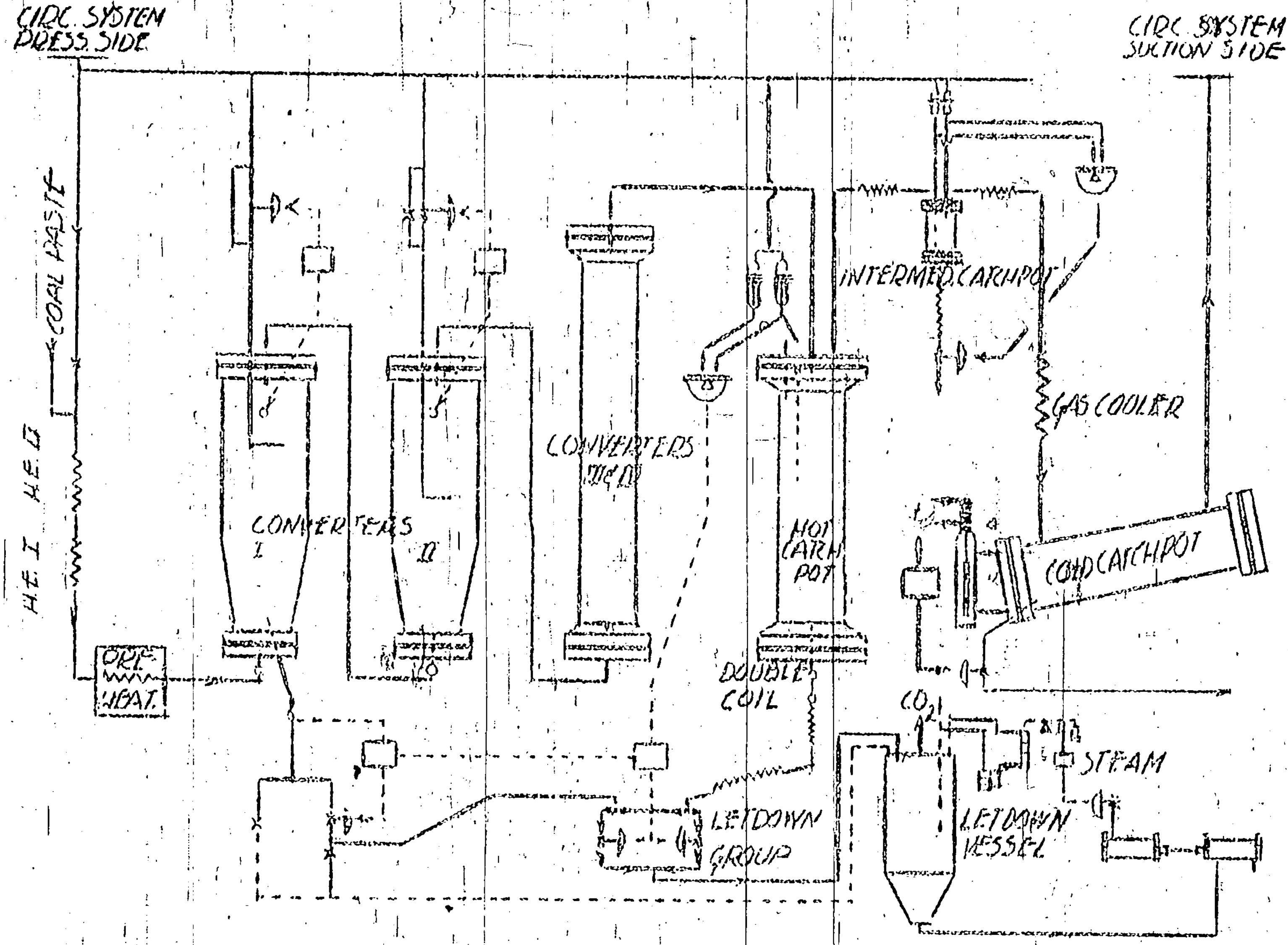


FIG. 10 SUMMARY

U. S. BUREAU OF MINES
HYDROGENATION DEMONSTRATION PLANT DIVISION

This drawing was inadvertantly omitted from T-88. "Abstract of Report on the Automatic Regulation of the Liquid and Vapor-Phase Hydrogenation Stalls at Leuna,

Please attach to Copy in Your Possession

Nauman

T-88

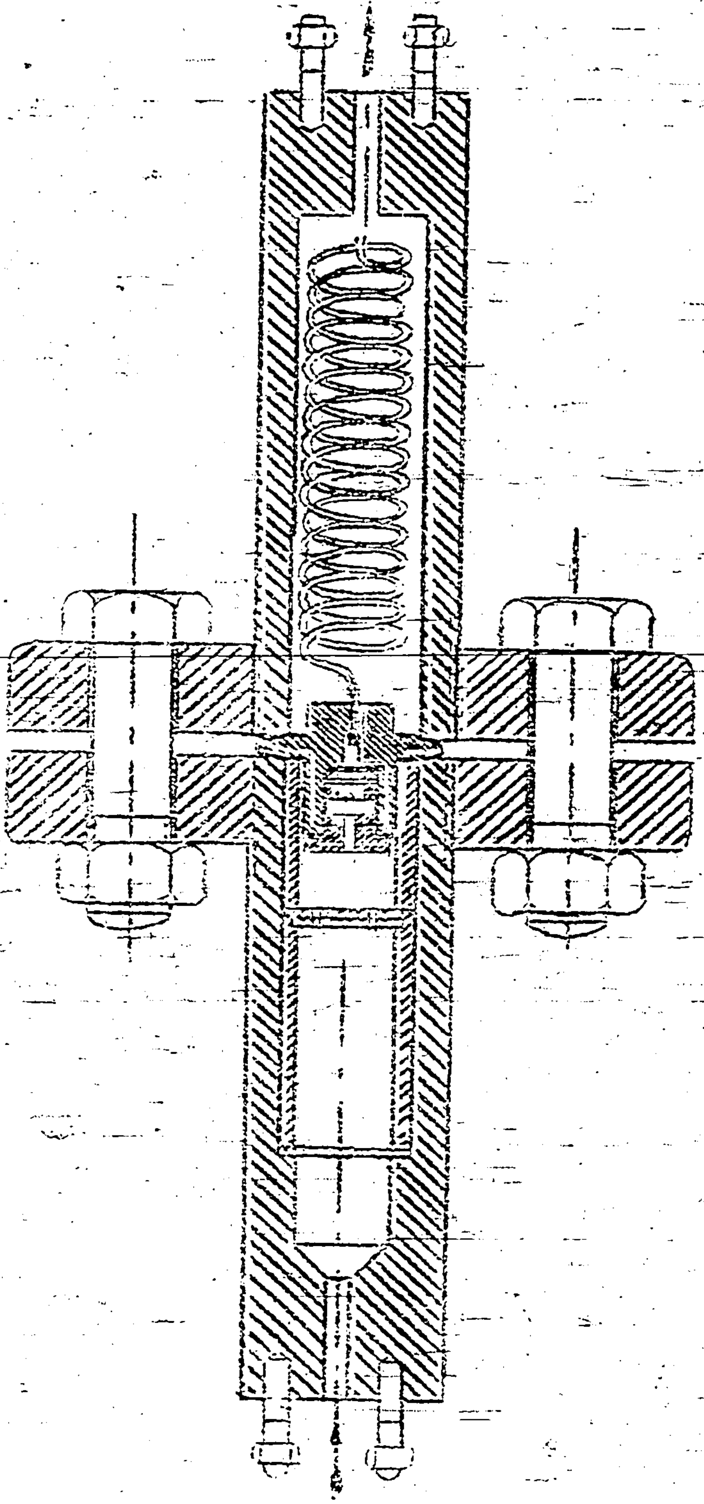


FIG 3
Filter orifice (throttle)

W/

T.O.M. Reel 170
Frames 534-547

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-89

LIQUID AND VAPOR PHASE OPERATIONS

DISCUSSION AT PÖLITZ March 27-29, 1944.

Topics:

Part 1 - Liquid Phase

Fifth Converter
Comparison of Pölitz with Gelsenberg
Lutzkendorf Liquid Phase.

Part 2 - Vapor Phase

Introduction of 8376 and 5058
Four-Converter Saturation Stall in Pölitz.
6434 Stall in Gelsenberg and Pölitz
8376 Operations in Zeitz

PART 1: LIQUID PHASE.

a). Fifth Converter.

Following a suggestion of Ludwigshafen, Pölitz has introduced a fifth converter (12 m converter) in its coal stall 16. The stall has been in operation for 240 days, and a comparison of its performance with that of the normal stalls 13 and 14 is shown in the table 1. Even now, in spite of the poor heat exchange, the throughput of the stall 16 is 1.5-2 to/h larger than of the four converter stalls. The 5-th converter produces at present about 35% of the usual converter production. The intake temperature of the first converter is 12-15° below that of the first converter of a four-converter stall. As one could expect, the consumption of cold gas in the first converter of the five-converter stall is less than in the four-converter stalls. The pressure difference in the system has been increased by the introduction of the fifth converter by 1 - 2 atm. The five-converter stall offers no operational difficulties, and the original opposite observation (difficulties of temperature control) is no longer correct in the light of the experience gained since.

We may summarize as follows about the installation of a fifth converter: first of all, the preheater must be capable of operating with an increased throughput, which necessitates sufficient reserve production capacity of the coal paste unit, pumps, etc. Should heat exchanger and preheating deteriorate after longer operations, (approach to the maximum allowable tube wall temperature of 520°), the throughput will gradually become reduced to the normal throughput of a four converter stall, as the first converter increasingly assumes the functions of a preheater. According to our latest observations, the first converter delivers under such conditions at least 20°. In addition, Pölitz has observed also the following advantages from the addition of the fifth converter: the five-converter stall is more elastic in its operation regarding sudden deterioration in quality of the coal and pasting oil, than the four-converter stall. Variations in the utilization caused by such disturbances are greatly reduced in the five-converter stall. Pölitz plans to equip two other stalls with a fifth converter (including the new stall 17. (18 m. converters)).

b). Comparison of Pölitz and Gelsenberg.

Dr. Klinkhardt (Gelsenberg) and the gentlemen from Pölitz compared their experiences in the liquid phase at the two places. Table II contains the results of the discussion in an accessible form.

The following is to be added to the individual points:

1). Hydrogenation coal. With respect to ash, conditions are more favorable in Gelsenberg (4% ash) than in Pölitz (5,6% ash). The ash content and the proportion of C were formerly higher in Pölitz (6% ash and 82% C, against the present 81%). At present the coal in Pölitz is a blend of coals from Beuthen, Heinitz, Jupiter, Charlotte and Donnersmark. The C and N proportions are more favorable in Gelsenberg, who use Ruhr coal. An 83% C coal from Ruhr produces the same hydrogenation results as the 81% C from the Upper Silesian fields, and the coals appear readily comparable (Gelsenberg 83 - 83,5% C in pure coal.

2). Coal Grinding Installation and Pasting.

(one short paragraph, dealing with coal grinding in Gelsenberg could not be read).

Pölitz operates with Büttner driers (impact mill, Schleudermühle), drier Multikica (?), vibrating screen, rolling stand). The Koncentra mill must carry a large proportion of the grinding. According to the information exchanged on screen analysis, the Pölitz grinding was the finest, although some course particles were present (vibrating screen). Pölitz has recently placed a greater load upon grinding by increasing the throughput, and the grinding has deteriorated. Pölitz and Gelsenberg wish again to exchange information on screen analysis (offer of Ludwigshafen). There were no disagreements on the screen analysis methods.

Details of Pölitz coal grinding:

3 Büttner driers (1 new), a fourth drier is intended. The intake coal contains 9% H_2O, the outlet coal 2.5%. The circulation gas enters at 140°, leaves at 101-107°. The circulation gas contains 3% O_2 and 16% CO_2. The observation has been recorded that the arms of the Büttner drier broke frequently.

After drying, the coal with about 20% coarser than 1.0-1.2 mm is carried at a temperature of 95° with an air blast through Fuller pumps. The coarse residue of the vibrating screens is fed into the roller stands (abt. 20% 1.2 mm). Four combinations are at present in use, with 2 new ones in the course of construction (for the new coal stalls).

The difference between the two installations is illustrated in the different amounts of the "spritzkorn" screened out in front of the paste pumps:

Gelsenberg, 6 stalls	400 kg/day
Pölitz, 4 stalls	29.000 kg/day

These coarsest particles tell us however nothing about the fineness of the grind, but the drying of the grind seems to be more effective than in the Bruckner driers.

3). Catalysts.

Pölitz uses more $FeSO_4 \cdot 7H_2O$ and Bayer mass (losses after drying)

	Pölitz	Gelsenberg
$FeSO_4 \cdot 7H_2O$, %	1.0	1.2
Bayer mass, %	2.9	1.8
Sulfigran, %	0.3	0.3

Pölitz has found a poorer utilization and hydrogenation when the iron sulfate was reduced from 2.8 to 1.2%, while Gelsenberg has omitted $FeSO_4 \cdot 7H_2O$ altogether for two months and found the results to be unaffected (probably because of the higher temperature, 25.5 mv.).

4). Crust formation in preheaters.

The thickness of the crust increases in Pölitz towards the end of the preheater. Dr. Wissel has expressed in January a suspicion that the Bayer mass was the cause of the incrustation, but this has been found not to be correct (coal catalysts in the tar liquid phase). The theory developed in Ludwigshafen several years ago that $FeSO_4$ is responsible for the crust is now accepted by Dr. Wissel as being the most probable. To find an explanation, Pölitz is going to introduce $FeSO_4$ directly into the converter.

5). Pasting Oil.

Both works add tar oil in about the same proportion of 10-20%. The Pölitz pasting oil contains less solids (5-6%, against 9% in Gelsenberg), but seems nevertheless to be somewhat more viscous than the Gelsenberg oil (less middle oil and vacuum residue). The ash content is higher in Gelsenberg than in Pölitz because of the greater amount of coal utilization (60 against 30%).

6). Pressure.

Pölitz operates at 690 atm. Gelsenberg at 710. An increase of 20 atm. has no effect in Gelsenberg. The pressure appears to exert a more pronounced action only in the much lower pressure regions.

7). Synthesis gas.

Gelsenberg operates with somewhat more synthesis gas than Pölitz, 55,000 - 60,000, against 45,000-50,000 m3/h.

8). Temperature.

Gelsenberg has trouble in manufacturing its heavy oil and operates at 25.5 mv. or about 4° higher than Pölitz (25.3 mv.). Gelsenberg has observed sudden rises in the 3rd and 4th converters. This is successfully overcome by lowering the solids in HOLD to 21 - 23%. Pölitz has therefore mastered the rise in the 3rd and 4th converters.

9). HOLD.

Pölitz produces 1.11 te HOLD/te coal, Gelsenberg 0.95 te. No exact agreement may be expected between the difference in the process (heat exchanging in Pölitz) and the different amounts of ash. The Pölitz HOLD has about the same amount of solids as in Gelsenberg, but is otherwise heavier (% - 325° and the vacuum residue).

10). Catchpot Product.

Gelsenberg produces 47% by weight at - 330°, Pölitz 40% - 325°.

11). Production and Gasification.

The production in Pölitz is somewhat higher with 0.24 (0.26 technically) than in Gelsenberg (0.23). As a result, probably, of the high temperature, gasification in Gelsenberg, 26 - 27%, is distinctly higher than in Pölitz (24 - 25%).

12). Coal Phase Off-Water.

The off-water at Gelsenberg and Pölitz contain 36 g NH_3/ li and 29 g CO_2 per liter.

13). HOLD.

Pölitz uses oil scrubbing for the removal of gasoline. Gelsenberg sends the gas directly into the converters. The gas contains 60-80 g gasoline gas/m3. The Pölitz HOLD gas contains after scrubbing 18.3% hydrocarbons (C = 1.66) and 70% H_2.

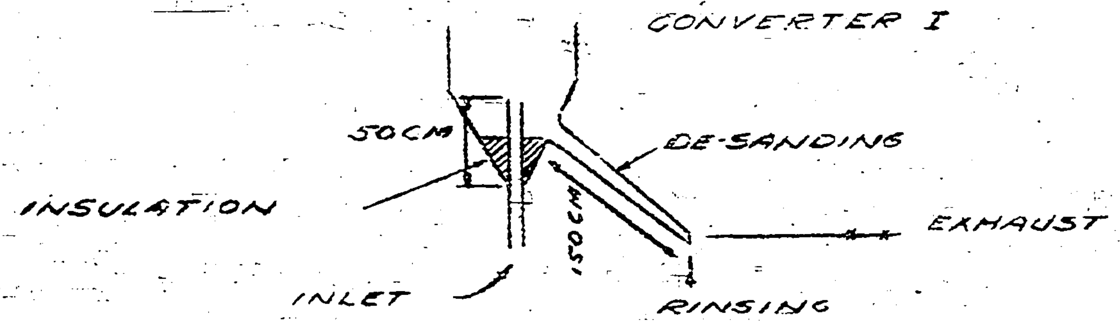
c. Pölitz Liquid Phase. General.

The fifth coal stall (17) will be put in operation in June 1944.

The catchpot product distillation operates with the addition of small amounts of 10% NaOH to overcome corrosion. A better separation of water is brought about by the addition of about 20% of gasoline. The coal catch pot product from the "ant egg" is mixed with the tar catchpot product, tar oil and gasoline, and the NH_4Cl is removed by washing. NaCl is injected into the suction pipeline of the distillation.

Pölitz has built in an arrangement (installation of exhaust dampers) to permit sampling between the preheater and the converter I, as well as between the individual converters of the coal and tar stalls. This permits also the analysis of the exhausted gases. The progress of the coal and asphalt utilization can be followed from the results obtained. The results are placed into the hands of Ludwigshafen, and Ludwigshafen in turn will furnish information on the determination of solids.

The de-sanding of the first converter of the coal stall is operated every three minutes by hand. The sketch below shows the construction:

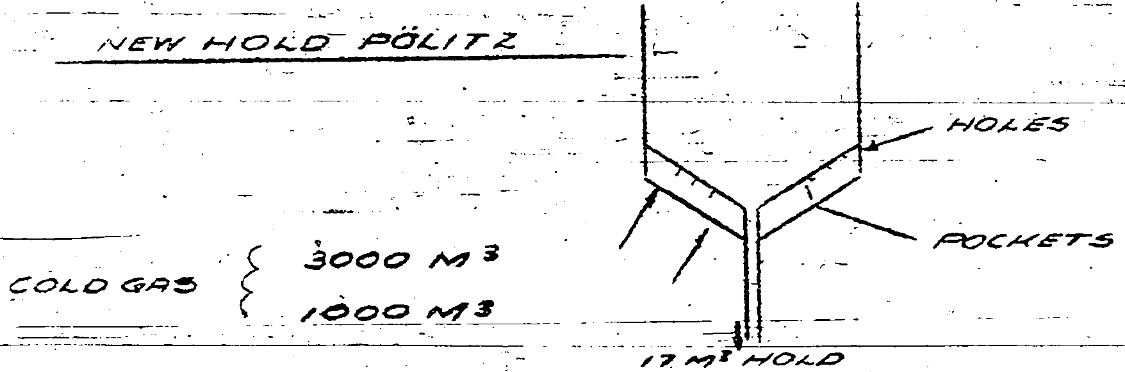


This arrangement is based on the experience in Leuna and Wesseling.

d). Lützkendorf Liquid Phase.

Dr. Wieland informed that the liquid phase catchpot at Lützkendorf had recently been coked three times. The Lützkendorf injection consists of 30% petroleum asphalt, 20% coal tar, and 50% return flow. The catalyst (Fe-grude) forms 0.4 - 0.5% of the fresh oil, at times only 0.3%. Experience has shown that when the amount of tar is reduced to below 20% of the injection, the catalyst efficiency begins to drop. The HOLD has 26-28% solids, 1.5-1.8% asphalt, and is colored olive color. Lützkendorf has no average recorder. For unexplained reasons, a gummy HOLD is occasionally produced. (plastic bitumens).

Pölitz also had coking in the hot catchpot, but carries the HOLD to only about 18-20% solids, and it contains practically no asphalt. With 22% solids there are deposition of the catalyst (0.7-1.0% Fe-grude, calculated to the amount injected, or about three times as much as in Lützkendorf). Pölitz is at present testing a new hot catchpot construction (on stall III (2 round pockets of sikromal with 5 rows of 1.5 mm holes). New Pölitz hot catchpot:



In the presence of 3000 + 3000 m3 of cold gas, only gas is drawn off. with 3000 + 1000 m3 only liquid is drawn off. No conclusions can as yet be made about the success of the new design.

In Lutzkendorf as well as in Pölitz the exhaust valves of the HOLD have much wear. Lutzkendorf has made some progress in this respect by introducing an intermediate catchpot, in which the large lumps are drawn off. Pölitz has inserted screening gaskets on which the larger pieces become ground.

(Pölitz has a similar arrangement in the prehydrogenation to prevent the platelets of FeS reaching the heat exchangers, with the holes of the screens somewhat smaller than the diameters of the small tubes of the heat exchangers).

Table I

5th Converter in Pölitz coal stall.

		Stall 16 No. of conv.	Stall 13 No. of conv.	Stall 14 No. of conv.
Temperatures:				
max. hairpin temp. 1)		505°		475°
13 heat exch. outlet		18.6 mV		19.8 mV
Preheat. outlet	143	27.0 mV		22.0 mV
		→ some cold gas		→ some cold gas
	144	21.7 mV	22.3 (corr. 22.8)	22.6 mV
Converter I	101	- -	23.8 (Wid.El)	24.0 "
	102	23.7 mV	24.3	23.9 "
	103	24.8 "	24.7	24.6 "
	104	25.0 "	25.2	24.4 "
	105	24.8 "	25.2	25.3 "
	106	25.3 "		25.3 "
	107	25.3 "		- -
	114	18.8 " (?)		
	115	24.9 "		
	244	24.2 "		
Converter II		25.3	25.1 25.3	25.3 mV
	344	23.9		
Converter III		25.3	25.2 25.1	25.3 "
Converter IV		25.1-25.2	25.0 25.2	25.1 "
Converter V		25.1		
		→ cold gas		→ cold gas
hot catchpot				
hot inner element		23.2 mV		- -
16		23.2 "	22.7	
hot c. outlet	644	21.4	20.7 (544)	
17 a			20.7	
Cooler		85 90°		
Days of Operation		240		120

1) Max. limit 520°

Table 1, Cont.

	Stall 16 No. of Conv.	Stall 13 No. of Conv.	Stall 14 No. of Conv.
Intake Gas	28,000 m3/h	28,000 m3/h	-
Paste Gas	2,000 "	2,000 "	-
Gas Outlet	50.500 "	-	-
Cold Gas Convert. I	7.300 "	6.700 "	-
" " " II	7.700 "	6,200 "	-
" " " III	4,100 "	4,400 "	-
" " " IV	2,200 "	2,300 "	-
" " " V	-	-	-
Agitating Gas	3,000 "	-	-
between Conv. V and Hot Catchpot	6,200 "	-	-
Pressure differ.	39 atm.	-	-
Initial Press.	15 atm.	-	-
Conv. V	2-3 atm.	-	-
Part. Press. H_2	537 atm.	-	-
Injection:			
Thin paste (42% F)	21,000 Li/h	21,000 Li/h	21,500 Li/h
Thick paste (53% F)	15,000 "	13,000 "	13,000 "
Pure coal	16.7-17 te/h	15 te/h	15.6 te/h
Water	2,500 Li/h	-	-
Output:			
HOLD	15.0 te/h	-	14.5 te/h
Catchpot Prod.	21.0 "	-	18.0 "
K value, heat ex. I	-	127	-
" " II	-	250	-
" " III	-	43	-

Table II

Comparison of Vapor Phase, Pölitz and Gelsenberg

Subject	Pölitz	Gelsenberg
Coal: % Ash	5.6	4.0
% C/ pure coal	81.1 (formerly 82)	abt. 83 - 83.5
% O	12	
% H/100 C	3.8	4.9
Fineness of grinding % thru 10,000 mesh		45 - 50
Catalyst: % $FeSO_4\ 7H_2O$	1.8	1.2
% Bayer mass	2.9	1.8
% Na_2S	0.3	0.3
Pasting oil: % Solids	5 - 6	9
% Ash in Solids	30	60
Spec. Gr./100°	1.09	1.115
% S-Asphalt	8 - 10	8.5
% -325°	2	7
Vac. res. +325°	28 (15 mm)	20 (11 mm)
Tar oil addition to pasting oil	10% at times 20%	13%
Spritzcor/day	29,000 kg	400 kg
Total pressure, atm.	690	610
Intake Gas m3/h/Stall	45 - 50000	55 - 60000
Heat exchange	—	
K Value, after 270 days	150	—
Pure coal thrput	ca. 0.43	0.375
Pure coal, te/h, stall	15 - 15.6	13.5 1)
Temperature:		
mv. max. temp.		
Converter I	25.2	25.5
Converter II	25.3	25.5
Converter III	25.2	25.2 - 25.3
Converter IV	25.2	24.9
Top of hot catchpot	22.7	22.5

1) Max. load, 16 te dry coal = 15.3 te p.coal/h. Temperature lower with smaller load.

Table II. Cont.

Subject	Pölitz	Gelsenberg
HOLD		
te HOLD/te pure coal	1.11	0.95
spec. gr./100°	1.20	1.2
% solids	20-22	21-23
% ash in solids	40-45	63
% asphalt	17-19	17-18
% -325°	1.5	7
Vac. res., + 325°	58-60	30-35
Catchpot		
Spec. Gr/20°	1.02	1.003
G. Engler. % - 325°	40	(-330°) 47
Production (x techn. factor)	0.24 (0.26)	0.23
% gasol. + m.o. in product	- -	91-92
gasificat.	24-25	26-27
Liquid phase, off water		
g NH_3/li	similar to Gelsenberg	36
g CO_2/li		29
HOLD		
use	oil washing	for CO_2 washing during conversion
Gaseous gasoline g/m^3	- -	60-80
after wash:		
% hydrocarb.	18.3	
Average C	1.66	
% H_2	70	

Table III

700 atm Crude oil Stall		
Subject	Lützkendorf	Pölitz (Stall 12)
Preheater	26 short hairpins	22 normal hairpins (15 m)
Converters	2 converters (12 m)	3 Converters (18 m)
Injection	30% petroleum asphalt +20% coal tar oil +50% return flow	petrol. resid. + HOLD 1:1 1)
Amount	10 m3/h	5.0 m3/h heat exchanged 5.0 m3/h preheated 6 m3 Cold catchpot return flow + cat. 12 m3 Hot circuit in preheating
Catalyst	Iron grude 0.4 - 0.5% fresh oil	Iron grude 1.4 - 2.0%/fresh oil
Temperature:		
of flue gas	max. 543°	- -
tube walls	- -	455-480° after 127 days of operation. 2)
144	22.4 mV	- -
Converter I	22.4 25.0 mV	25.4 25.4 mV
Converter II	24.8 24.9 mV	25.0 25.0 mV
Converter III	- -	24.4 24.4 mV
HOLD outl.		
above		22.7
17a		18.8
HOLD:		
% solids	26 - 28	18 - 20
% asphalt	1.5 - 1.8	trace
Color	olive	- -
Catchpot:	50 Vol. % - 350°	42-45 Vol.% - 350°
Production:	- -	0.26
Fresh gas: % H_2	91.2	96
% N_2	4.0	--
% CH_4	4.8 3)	--
Circul. gas % H_2	75	85 4)

1) data uncertain
2) Thermocouple tied on
3) from the Fisher unit
4) never below 520 atm.

T.O.M. Reel 201.
Item 27
Frames 624 - 630.

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-90

July 26, 1940

Comparison of Costs of 7019, 5058 and 6434 Stalls

In a cost investigation made recently, a vapor phase 7019 stall was estimated to cost some RM 200,000 more than the average costs of 5058 and 6434 stalls.

The preheaters play a major role in the increase in costs, and the present investigation is to a great extent limited to the differences in preheating.

Table I gives the data necessary for the preheater computations taken from the Nordstern flow scheme, together with the corresponding values for one three-converter 7019 stall. Six such 7019 stalls produce the same amount of gasoline as 3 three-converter 5058 stalls + 3 two-converter 6434 stalls, namely 36 te/h, and it means therefore, that the 7019 preheating is comparable with the combination of the two above systems. It may, however, be mentioned in passing, that the comparison is bound to come out unfavorable to 7019, if 2 three-converter 6434 stalls be provided instead of the 3 two-converter 6434 stalls.*)

Table II contains the heats of reactions which have been determined in the Scholven 5058 and 6434 stalls; the values found in Nordstern were similar, but have not as yet been determined accurately. We may therefore assume, that

the heat of reaction for the gasoline production over the 7019

catalyst is equal to 1 kg gasoline over 5058 + 6434 catalysts

and from the value obtained, 625 kcal/kg gasoline, we may calculate 147 kcal/1 kg injection.**) for the heat of the reaction over the 7019 catalyst.

Table II also gives the catalyst temperatures, as obtained during regular operations with 5058 and 6434, while for 7019 the results obtained operating with the highest pressures.

The following operating data already recorded in tables I and II will greatly affect the size of the preheater:

	5058	6434	7019
1) Gasoline concentration in the catchpot,%	30	65	25
or for injection/te gasoline	2.4	1.7	4.25
2) Temperature jump in the catalyst	40	15	15
3) Outlet temperature in the preheater	420	405	495°C

---

*) Gasoline produced from 5058 + 6434: 0.3 kg/li
Gasoline produced from 7019 0.25 kg/li

**) Confirmed in Scholven to be 150 kcal/kg injection

All of these three measures act unfavorably on the design of the 7019 preheater. The combined action is shown in Table III. The 5058 stall works self sustaining, because of the high temperature jump in the catalyst as well as because of the high heat of the reaction, as a result of which an electric preheater is sufficient. 6434 and 7019 require gas heated preheaters. Computations show that the 7019 requires several times the surface of the 6434 preheater (350%) caused by the greater heat value (see above) and the smaller average temperature difference of the feed and the circulation gas, and because the upper limit of the flue gas inlet temperature with respect to the product and the high pressure feed will be 600°, while the outlet temperature of the circulation gas, in consideration to the blower, must be at 500° C. Should the necessary heating surface be referred to the same production of gasoline, a four-fold increase in the preheater surface will be required.

We have counted in the past on a small increase in the 7019 preheater with circulation gas temperatures below 560°, and this required too large a preheater, especially to serve a four-converter stall and still larger throughputs.

For the sake of completeness, table IV shows the heat flow diagrams and the heat balances; they again show, that the 7019 requires about 4 times greater amount of heat per tonne gasoline, than when 5058 + 6434 are used.

Summary.

A larger 7019 preheater than 5058 + 6434 is required for the following three reasons:

1) A larger return flow with 7019

2) Smaller temperature jump in the catalyst

3) Higher outlet temperature from the preheater.

The table below shows the increased cost of the 7019 preheater in comparison with an average costs of the 5058 and 6434 preheaters.

	5058	6434	7019
Number of hairpins	4	8	16
Material	N10	N8	N8V
Cost of 1 hairpin	40,000	65,000	170,000
Complete preheater (incl. blowers with 5058 and 6434)	170,000	330,000	440,000
Excess price of a 7019 preheater against the average of 5058 + 6434 prah)			190,000
Excess of cost of a 7019 preheater over the 5058 or 6434 preheaters, caused by higher quality tube and connection material			40,000

Total excess cost of a 7019 preheater 230,000

The 7019 preheater requires also a higher expenditure of heat, namely 177,000 kcal/te gasoline, against the heat requirement per te of gasoline made with 5058 + 6434.

This additional heat requirement may be reduced only by the installation of third heat exchanger, and while this will result in a small reduction in preheater requirements, the difference in the installation costs will be increased to 320,000 RM.

Table I.

PROPORTIONAL LOADS OF THE NORDSTERN STALL
ACCORDING TO FLOW SCHEME, CONSTRUCTION STEP 3 e.

		5058	6434	7019
Number of stalls		3 x 3	3 x 2	1 x 3
Catalyst volume	m3	72	48	24
Injection of A middle oil	t/h	35.7	-	6.7
Injection, coal gasoline	t/h	6.3	-	0.8
Injection, B return flow	t/h	10.7	24.0	18.0
Injection, C return flow	t/h	-	11.7	-
Total injection	t/h	52.7	35.7	25.15
Throughput	m3/m3	0.9 (s=0.83)	0.58 (s=0.85)	1.23 (s=0.85)
Gasoline formed	t/h	15.6	21.2	6.0
Gasoline production	t/m3	0.22	0.44	0.25
Catchpot prod. formed	t/h	51.6	32.9	24
Gasoline concentration in catchpot product	%	30	68	25
Thruput/te gasoline	te/te	3.4	1.7	1.28

2.40

Table II.

HEATS OF REACTIONS

1. Found in Scholven stalls for 5058 and 6434.

	5058	6434
Kcal/te Injection	350	140 (?)
kg gasoline formed/kg injection (table 1)	0.3	0.6
kcal/kg gasoline formed	1160	233
Percent gasoline production	42.5	57.5
kcal/kg gasoline formed	625	

2. Heat of reaction per kg. of gasoline over 7019 should be the same as calculated over 5058 + 6434.

	7019
kcal/kg gasoline formed	625
kcal/kg injection	147

Temperatures

	5058	6434	7019
Inlet, converter I, ° C	375	405	495
Outlet, last converter, ° C	415	420	510
Temperature jump in the catalyst, ° C	40	15	15

Table III

SIZES OF PREHEATERS OF THE STALLS

	5058	6434	7015
Stall equipment	3 conv.; 2 heat exch; 1 el. preheater	2 conv., 2 heat exch., 1 gas preheater	3 conv., 2 heat exch., 1 gas preheater
Thruput thru stall t/h	17.6	11.9	25.5
Gas inlet m3/h	50,000	20,000	40,000
Heat value kcal/h	17,200	14,200	30,600
Temperature diagram	Electric preheater in operation Preheater inlet = converter inlet		
Heat to be supplied kcal/h	0	700,000	1,300,000
Aver. temp. differ. °C		120	70
7019 preheater surface, assuming 6434 preheater surface = 100 m² m²		100	$\frac{100\text{x}1300000}{70000}\,\frac{120}{70} = 350$
do, referred to the gasoline production of the 6434 stall m²		100	$35\text{x}\,\frac{7}{6} = 408$

Table IV

HEAT FLOW DIAGRAM AND HEAT BALANCE OF VAPOR PHASE STALLS

		5058	6434	7019
Heat flow diagram for 1 stall				
heat of reaction	kcal/h	6,000,000	1,750,000	3,700,000
heat exchanger heating	kcal/h	5,800,000	4,850,000	13,100,000
heating in preheater	kcal/h	0	700,000	1,400,000
Radiation	kcal/h	500,000	400,000	600,000
Cooler losses	kcal/h	5,500,000	2,050,000	4,500,000
Heat to be added per 1 te gasoline	kcal/te gas.	0	100,000	234,000
Do. for 5058 + 6434		57,000		

Sternberg/jw

T.O.M. Reel 130
PP. 762-771
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U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-91

Abstract of Report on Advances in Measuring, Regulation, and Automatic Control of Operations in High Pressure Plants

Lu - 17 Oct. 1942

Summary

A. Temperature Measurements.

- 1). Increase in accuracy of measurements.
  - a) - By counter-connecting a constant tension (potential.)
  - b) - Using resistance thermometers.
- 2). Increase in speed of measurements.
- 3). Automatic temperature control.

B. Pressure and Differential-Pressure Measurements.

- 1). Pressure measurement.
  - a) - Increase in life (spring manometer)
  - b) - Increase in accuracy (piston manometer)
- 2). Differential Pressure Measurement.

C. Liquid Level Measurement.

- 1). Oppau level measurement.
  Leuna level measurement.

A. TEMPERATURES.

A number of disadvantages are inherent in the simple method of determining temperatures in high pressure converters, consisting of a thermoelement and a high-ohm milliampmeter. The most important of these are the long time required to adjust the instrument and the dependence of the instrument-recording on the resistance of the thermoelement and its equalizing lines. Also, the rather coarse divisions of the scale, intervals of 0.5 mv, corresponding approximately to 10°C, leaves much to be desired, since, at best, it permits only an estimate of the tenths mv's, which does not give us an accurate measurement to 2° C. But even this imperfect measuring accuracy can be achieved only by proper calibration thru an increase in the measuring accuracy near the preferred values at the expense of the mean error.

1). Increase in Accuracy of Measurement.

If a part of the tension delivered by the thermoelement is suppressed by an accurately constant counter-tension of known value, only the difference reaches the mv meter, whose measuring range can now be chosen correspondingly smaller. In this manner, the measuring accuracy may be increased by one decimal, so that the tenths millivolts, which could only be estimated in the primitive method, can be read with assurance and the temperatures accurately measured to 0.5° C.

The counter-tension, on whose constancy the greatest demands must be made, because it may not fluctuate more than a few hundredths mv's, can be taken from a lead collector (Bleisammler) by careful attention. More appropriate, however, is a source of constant tension fed from the A.C. circuit, which, with the aid of a transformer, equalizing tube, hydrogen ferride lamp and stabilivolt lamp, delivers a highly sensitive constant tension, even against line fluctuations, of which a correspondingly smaller portion can be used as counter-tension.

Platinum resistance thermometers have been installed at all important points. They constitute an improvement in measuring accuracy, compared to the former method, of the same magnitude as the use of counter-tension.

2). Increase in Speed of Measurements:

To eliminate the weaknesses of the primitive measuring method, the long adjusting time and dependence on the resistance of the thermoelement, a currentless measuring process or compensation (photolectric) method was introduced. The principle is this, that in a resistance of known value a drop in tension is produced, with the aid of a current, equal to the unknown tension to be measured. The equality of the two tensions may be recognized by the fact that no current flows thru a highly sensitive galvanometer measuring their difference.

In connection with the photoelectric cell compensator attention is again called to the possibility of partially suppressing the thermal tension by a counter-acting constant emergency tension. The same apparatus can deliver this tension. It is only necessary to replace the thermoelement by a standard element, whose tension at no current is reliably constant over a long period. The combination of these two devices, that is, the use of the counter-tension and the photoelectric cell compensator, represents the most recent measuring method, which is able to meet all operating requirements.

3). Automatic Indication of Dangerously High Temperatures:

Because of the large number of thermoelements and the scarcity of operating personnel, the converter temperatures are often read too infrequently. The interval between readings may be so great that under unfavorable conditions the converter temp. may have reached excessive figures, because in a period of only 2 minutes the temp. at any measuring point may have increased by 1 mv, that is, about 20° C. A further increase in the adjusting speed of the recording instrument would not help much because the 6 seconds required represent the limit of the operators effort. This problem was solved by a device which contacts one converter element after another at regular intervals of 5 seconds and notifies the operator of any excess temp. by accoustical and optical alarm signals. This device consists of a revolving time switch with 24 measuring points, which contacts each successive element at intervals of 5 seconds. A photoelectric cell compensator with a small measuring range, (2 mv), and a small regulator serving as alarm apparatus are added to this device. As previously explained, the thermal tension is suppressed by a counter-tension to about 1 mv. If the indicator on the small regulator passes the predetermined danger point an accoustical alarm is set off and signal light goes on. The revolving switch is held at the critical point so that the operator can read the indicating instrument. He can, at the same time, contact any other element at will for control purposes. By pushing a button the time switch may again be set in motion.

B. PRESSURE AND DIFFERENTIAL PRESSURE MEASUREMENTS

1). Pressure Measurement

a). - Spring Manometer

Until recently the life of high pressure manometers was very low. Leaks or even breaking of the Bourdon springs were frequent. The introduction of the so called safety spring brought considerable improvement. The new spring is longer than the regular Bourdon spring and is spirally wound for mounting in the manometer housing. Because of the small mechanical load, its life is much longer.

b). - Piston Manometer:

Because of the importance of after-calibration of the spring manometer, piston manometers were developed by Oppau, whose power is derived from springs, Fig. 4, Betr. Kontrolle - 1284, (not available), shows such an instrument with a measuring range up to 1000 atm. Counter-weights up to 650 atm. permit a much more accurate measuring of absolute pressure than is possible with other apparatus. For example, by using a measuring range of 650-750 atm, an operating pressure of 700 atm. can be measured within a fraction of 1 atm.

2). Differential Pressure Measurement:

Fig. 5, Betr. Kontr. 1275, (not available), shows a piston differential manometer. The general introduction of this reliable instrument permits us to measure the pressure drop in all high pressure stalls daily from point to point, so that irregularities caused by clogging of preheater tubes or closing of heat exchangers can be corrected by proper measures.

D. LIQUID LEVEL MEASUREMENT

(For later developments in this field see T-88).

T.O.M. Reel 130
pp. 772-784
Braun/jw

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-92

Abstract of Report on The Aid of Physical Control of Operations in the Development and Operation of Hydrogenation Works

By P. Gmelin, Oppau

(See also T-88 and T-91)

In 1932, C. Bosch, in his Nobel-Lecture based on 20 years development in synthetic ammonia, has already pointed out the indispensability of physical operations-control-instruments for undisturbed, regular, and therefor profitable, operations of high pressure plants.

Hydrogenation plants could, at first, use the Oppau instruments developed for the ammonia process, among which may be mentioned the universal quantity recorders for pressures to 1000 atm. and almost all ring-gauges using fluid, gas, or vaporous media, which are connected to our internationally standardized nozzles and diaphragms (Blenden) as differential pressure recorders.

Also redesigned were the gas density recorders based on the Bunsen law of discharge, which are indispensable for the calculation of gas quantities from the ring-gauge diagrams.

For feeding of coal paste a stroke-speed recorder was developed for the piston pumps, which records the coal paste delivery in mean values every 3 minutes. A similar instrument was built for the "Eckardt" piston oil meters.

The automatic belt feeder scale developed by Oppau for fertilizers was redesigned for a capacity of 30 T/h for uniform feeding of pulverized coal to the pasting oil. A smaller type is used for feeding catalyst.

Since the absolute gas pressures are necessary for the accurate calculation of quantities or partial pressures, they must also be recorded as accurately as possible. The necessary accuracy and pressure safety is attained by improved steel coil spring manometers as well as by oil lubricated, counterweighted or spring-loaded, pistons. Constructed as differential pressure recorders, these pressure recorders permitted precision measurements at the high absolute pressures of hydrogenation plants, even for small differential pressures of a few atm. and a rigid control of the resistances to flow, particularly in clogging at critical points in the high pressure equipment. In connection with these, pneumatically controlled relays may be used, in which the differential of 2 steel coil springs is transferred to a recorder-drum by means of a compressed air nozzle over an oil-filled U-tube manometer with float.

Just as important was the adaptation of the temperature measurements to the increased demands of hydrogenation converters, which demanded a measuring accuracy of ± 1-2°C at 400-500°C, as well as the least possible delay in recording. These demands could be met by the introduction of a photoelectrically regulated counter-tension with the aid of a photo-electric cell compensator.

For the Hy-Works Pölitz and Gelsenberg, Oppau developed an automatic temperature control system, in which a motor operated revolving switch contacts 60 temperature measuring points in 2 minutes, in order to record small, though already dangerous, temperature rises, for example, from 450 to 460°C. (See T-91 for further details of this multi-switch).

Particularly complex was the introduction of automatic physical gas analysis recorders, provided with an alarm and acting as safety device. Our old gas density recorder was redesigned for alternate connection of 2 gas mixtures. This double density recorder takes alternate density samples of the inlet and outlet gas of the reaction converters. The increase in density due to vaporization gives the management a clear picture of the course of the reaction on the same diagram.

Our heat-of-reaction apparatus, with which the temperature rise occurring in a small catalytic reaction is measured by a thermo-column or a resistance-thermometer, also proved to be a useful safety-gauge for registering traces of oxygen in various gas mixtures or of carbo-hydrates, such as butan in air.

Pölitz also uses the magnetic oxygen-recorder developed at Oppau for recording O_2-content down to 0.01% in any gas mixture. This recording is applicable to any O_2-content of multiple gas mixtures, without the aid of troublesome specific reactions, by using the exceptionally high magnetic susceptibility of O_2, compared with all other gases (except NO), in the following manner:

The O_2-containing gas mixture is passed between the poles of a powerful electro-magnet over a differential resistance thermometer, which is not influenced without a magnetic field or without the presence of O_2, and which has no current flowing thru its bridge connections. If O_2 is present, it will be drawn to the points of greatest field strength, due to its high susceptibility in the purposely unhomogenously created magnetic field, that is, a magnetic wind is created, cooling the resistance thermometer on one side, thereby causing a deflection, which is recorded.

This magnetic O_2-recorder is being rebuilt for a currentless permanent magnet, instead of the electro-magnet, which consumes 100 watts at constant current strength.

For recording the smallest dangerous traces of H_2S and, in certain gas mixtures, of higher contents of CO, O_2 and organic gases, such as the chemically difficult to hold CH_4, for certain catalysts, for example in splitting plants, other methods had to be found. These were first tried out for the determination of 0-250 and 0-15 respectively mg/m^3 H_2S in the rich, poor and hy-gases. The determination succeeded by means of recording the change in conductivity, either of bromine water or of Cd-chloride solution, which appears when the gas mixture to be analyzed is passed through it. Fig. 6 (not available) shows the small device schematically, together with the reaction equations used. The sensitivity equals 10^{-6}% for one division of the scale in the first case, in the second case 10^{-5}% H_2S by volume. The second process may also be used in the presence of unsaturated hydrocarbons, while the first is disturbed by hydrocyanic acid, NO, NH_3 and unsaturated hydrocarbons.

The flue gas analyzer, based on the recording of its heat conduction properties, could be used for recording some % N_2, CO_2 and H_2S, partly by the addition of a little absorbing medium.

The infra-red recorder may be used wherever gases are to be analyzed, which have absorption bands in the infra-red spectrum. It has, therefore, many uses, and is particularly used for recording of 0-5% NH_4 and of the smallest traces of CO dangerous to personnel or catalysts in the room air or pure gas mixtures, respectively.

In its simplest form, shown schematically in Fig. 10 (not available) the apparatus consists of 2 Cr-Ni-Coils heated to a red glow, whose radiation heats the gas to be determined in the mixture, for example CH_4, in 2 chambers, through rock salt windows, which permit heat rays to pass through them. If the gas mixture to be analyzed for CH_4 is passed through a socalled analyzing chamber arranged in front of the right-hand socalled measuring chamber, the pure CH_4, corresponding to the CH_4-content of the analyzing chamber, in the measuring chamber is heated less than that in the socalled comparative measuring chamber superimposed on the left. In order to measure the extremely small temperature difference between the 2 measuring chambers without being disturbed by unavoidable external temperature fluctuations, both groups of rays transmitted are intermittently interrupted by a screen, causing an alternate heating of the gas layers, which can be very accurately measured by a diaphragm condenser separating the 2 chambers filled with CH_4.

The hollows in the diaphragms, only a few thousands mm thick, change the electrical capacity of the condenser and cause alternate tensions, which are recorded on an mv meter after amplification by 2 electronic tubes and rectification. Since the absorption is caused only by the rays, which correspond to the characteristic vibrations of the gas to be measured in the measuring chambers, changing contents of the mixture are without influence on other gases, as long as their infra-red vibrations do not overlap those of the gas to be measured. However, this difficulty could be overcome by superimposing a filter chamber. It should be noted, that the indications for each gas are specific, and it is not necessary to isolate the infra-red bands by spectral decomposition. These instruments are very reliable, accurate, and have many uses. Oppau has developed an infra-red spectrograph for use in its own physical laboratory, which will automatically record an infra-red absorption spectrum with constant dispersion of 25 or 50 Ma each My, as desired, between 1 and 14 My wave length, in such a manner that the ordinate directly indicates the % absorption.

The use of P_H recordings by means of antimony electrodes to control the alkali liquor, may be mentioned, as well as the frequent use of automatic de-sanding for the prevention of Kaviar-formation in the converters, and many others.

Fig. 14 shows in tabular form the extent of the use of operating control devices in one of the larger Hy-works. Fig. 15 represents a synopsis of the total use of automatic analyzing devices and the principal pressure and differential pressure recorders in a Hy-works. Fig. 16 shows a liquid phase stall with the most important control devices of all kinds.

T.O.M. Reel 130
pp. 623-627
Braun/jw

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-93

Abstract of
Remarks About Materials in Hydrogenation and Their Supply by Steelworks.

Materials Testing Division, LU 23 Oct. 1942. By Dr. Ing. Class.

Characteristic of the questions raised by the material demands of hydrogenation works and their supply by steel works are the special conditions imposed by the industry. Among these are the high total pressure, the partial hydrogen pressure, and the high temperature, all of which differ materially from the high pressure construction previously developed for the production of ~~the~~ nitrogen. Also, the cheapest possible materials, for example, low alloy steels, which could be elaborated in a rational manner, had to be used. War conditions also demanded that the alloy content of steels be held to a minimum. Unusually large pieces posed the question of workability of the materials and the methods of fabrication. This is particularly applicable to the jackets of high pressure vessels, for which large units were desired, as well as to seamless tubes. The number of suppliers, who could satisfy the special requirements, had to be increased in the course of time, to assure a sound basis for the safe and continued expansion of hydrogenation works. In recent years, French works, particularly Schneider-Creusot, and a number of works from the East have been drawn upon. To equip the steel works for our demands was made possible by many experiments, close familiarity with production processes and fabrication methods, and thorough testing of the finished products by the most modern methods. Among others, the assurance of avoiding the mistake of one material for another because of the dangers implied therein, requires careful consideration.

First to be mentioned of the construction elements is in the seamless tube of alloyed steel. Close cooperation between steel works and tube mill on questions of billet preparation, rolling of tubes, as well as heat treatment and control methods is essential. Besides the high pressure tubes proper, the long heat exchanger tubes particularly required the solution of extraordinary fabrication difficulties.

The large jackets and the parts belonging to them placed special demands on metallurgy, forging, pressing, rolling and heat treating, since veritable giants of the forging press and ingots of over 100 tons of alloyed material were involved. It was a notable step forward when the former liner-tube of the high pressure converter was abandoned. The recently developed method of building vessels of multiple parts, particularly high pressure vessels with walls of spirally wound strips, offered other new problems. Very large and long core tubes of alloyed material were to be built without forging presses and other expensive equipment, yet with great precision in dimensions.

In connection with high pressure tubes and vessels the great progress made in welding should be mentioned. High pressure tubes and jackets of rolled plates up to 130 mm thick and nearly 100 kg/mm^2 cold strength are continuously welded. I. G. workshops led the field in butt fusion-welding of large cross-sections of alloyed materials. The successful welding of special alloy tube steels of heavy wall thickness made the construction of large tubular apparatus and the laying of long pipelines without flange connections possible.

The development of high pressure machines and the absolute control of the materials for their constituent parts represents a special field. Unusual demands are made by parts which are subject to pulsating inner pressure, such as pump bodies for 700 atm., decompression machine cylinders and, in part, also the last stages of compressors. These required forgings as free as possible of material-loosening, flaking or flaws in structure.

If the particular demands on use-characteristics are summarized, we may distinguish between mechanical and chemical requirements. Of the sum total of chemical effects on materials, the influence of high pressure hydrogen at high temperature and that of hydrogen-sulfide are most important. The effect of chlorine and ammonia deserve only secondary consideration. Besides complete imperviousness, by avoiding disturbing local flaws, the demands on the mechanical properties are characterized by high strength, particularly at high temperatures, and good ductility without particular tendency to brittleness under heat. Knowledge of heat resistance was very meager before hydrogenation. However, many experiments have been made in the past 15 years, which pointed to the fatigue-elastic strength (Dauerstandfestigkeit) as the characteristic evaluation. The fatigue elastic strength or creep strength of steels has been steadily increased in the course of time. It was repeatedly shown that distinctly long period experiments can not be dispensed with in determining the time-dependence of the breaking strength (ultimate strength) and the resistance to deformation. The breaks on long-period loading at high temperature may be characterized as deformation-poor grain-limit breaks. It was shown that the effect of high pressure hydrogen must also be considered in the durability, so that in an apparent hydrogen attack, seemingly more of a physical than a chemical nature below the pressure-dependent decarbonization temperature, the time elastic strength (Zeitstandfestigkeit) is below that under purely mechanical loading, that is, without the effect of high-pressure hydrogen. (See also T-98)

We were enabled to combat hydrogen-sulfide attacks, partly by the use of proper corrosion-resistant materials, partly by a division of the problem in such a manner that the basic material has the required mechanical properties and is hydrogen-resistant, while the sulfide-formation is suppressed by surface protection. Among materials with high heat resistance at distinctly favorable time-elastic strength, simple heat treatment and high corrosion resistance 18-8-Cr-Ni steel deserves first mention. These special alloys were first used in hydrogenation at continuous high temperatures, which requirements exceed those of the grain-decay stability in welding. When 700 atm. preheaters were first built, 18-8-Cr-Ni steels with tungsten and titanium addition proved very valuable. The further developed low chromium steels with the alloy components of N6 and N8 materials (chromium, molybdenum, tungsten, vanadium) were of great significance. However, the limiting temperature of 560°C at which these steels can be used, ~~it~~ is lower than that of the 18-8-Cr-Ni steels or the austenitic Cr-Mn steels. Besides, the properties of these low alloy steels are dependent on a very elaborate heat treatment. Steels deriving their special properties from columbium or titanium additions are being tested, but are not yet ready for general use.

Wear in tube bends, due to coal paste or high hydrogen pressure at high temperature, with, in part, simultaneous corrosion, was successfully combated by suitable special materials. In other places, wear, due to strong whirls or eddies, was countered with hard alloy liners (tungsten-carbide). For the mass production of highly stressed hydrogen and sulfur resistant valve cones (disks), which required great hardness, the autogenous hardening process, not considered feasible for high alloy chrome steel by the steel works at the time, was introduced.

The historical development of high-pressure hydrogen-resistant steels and the protection against hydrogen-sulfide attacks by galvanizing is discussed in Dr. Dinkler's report of 16 Oct. 1942, and is, therefore, not taken up here. (See T-96)

T.O.M. Reel 130 U. S. Bureau of Mines T-94
pp. 628-635

Hydro. Demon. Plant Div.

The Present Status of Investigations of Attacks by Hydrogen Upon Non-Loaded Test Pieces, As affected by Hydrogen Pressure, the Duration of the Experiment and the Hardening State of the Material.

Leuna, April 4, 1944

Earlier experiments on resistance of steels to hydrogen used in the ammonia works and the hydrogenation plant, performed 1926 - 1932, established the fact that all steels containing 3% chromium and over, even with no additions of Mo, W or V, were resistant to hydrogen up to + 600° C. These tests were run on unstressed test pieces and under pressure of 200 atm of hydrogen and lasted 144 hours. A conclusion whether the material was affected by hydrogen or not was even then primarily drawn from the contraction. Any reduction in contraction indicated the effects of hydrogen.

The experiments were extended in 1938 - 9 to 650 and 700 atm pressure, and the length of the test increased to 200 hours. These experiments were performed at 560° C on N10, the peak preheater material for the hydrogenation preheater hairpins. In one particular case the composition of the N10 material was: 0.17% C, 2.86% Cr, 0.30% Mo, 0.33% W and 0.94% V. and the tests were prolonged to 1000 hours at 560° C. All these tests showed a satisfactory resistance of N10 to hydrogen at 560° C. The small differences in contraction of the rods only 5.5 mm thick before and after the hydrogen treatment were considered normal variations of results.

These results are in agreement with information found in literature. The most important work in this field is that of F. K. Naumann: "Bestandigkeit von Stahl gegen Wasserstoff unter hohen Druck", Stahl und Eisen, 1938, p. 1239, and has been performed in the testing laboratories of the firm Fr. Krupp, in Essen. Fig 1 is a reproduction of the experiment results with a steel containing 0.25% C and 3% Cr under 200 atm and after 100 hours at above 600° C. It shows that the steel was resistant under such conditions, and they show also, that the max. effect is at a lower temperature when the pressure is raised to 700 atm. However, the difference at the lower temperatures is not large. Chromium steels with 1% Cr and over are affected but very little differently at different temperatures at 200 and 400 atm., but this difference disappears entirely at high pressures. The temperature at which hydrogen was found to begin to attack was found to be independent of pressure for the steels investigated if they contained at least 2% Cr (with 0.10-0.15% C, 0.4% Mo, or 0.23% C and no Mo) was above the temperature in the preheater tube walls in the hydrogenation works.

Our own earlier results as well as the data in literature left us therefore no suspicions regarding the resistance to hydrogen and it was assumed that all our "H_2-resistant" steels, such as N6, N8, N9 and N10, could be safely exposed to temperatures of the preheater tube walls during the hydrogenation at 700 atm.

Breaks which have occured in the hairpins of the Gelsenberg A. G. N10 have caused us to run numerous additional tests on hydrogen resistance as affected by the length of the test, the hydrogen pressure and the hardening of the pieces. Most of the work was done with the peak heating material, N10.

These tests have shown that a knowledge of the chemical composition of the steels was not sufficient to judge the hydrogen resistance of the material. Analysis naturally gives some general information, but there are individual test pieces which exhibited an extraordinarily poor resistance to hydrogen, without the analysis giving any reasons for suspecting it. A direct determination only can give information on the resistance to the attack by hydrogen.

Extending the test time to 1000 hours and longer has shown that 200 hours were not sufficient for judgement, that the majority of test pieces showed a reduction in contraction only after 400 - 600 hours, and some only after 1000 hours. Such is not only the case with the normally alloyed N10, but also with higher alloys. We have investigated the resistance to hydrogen of 8 alloys similar to N10 with about 6.5% Cr, and have found either no changes in 1000 hours test, or only a small reduction in the contraction which might have been explained by a variation of results. Test pieces of one of these steels have been subjected to further 2000 hour testing, making a total of 3000 hours in hydrogen under 700 atm., and a 64% reduction in the contraction from the original value was observed, or definitely a large reduction. We have accordingly come to the conclusion based on our past experience, that from perlitic-ferritic Cr steels with up to 6.5% Cr, such as alone may be considered in the manufacture of hairpins, no perfect hydrogen resistance may be expected. The destruction of grain boundaries is merely a matter of time. We shall discuss later the mechanism of this destruction.

Testing the relationship between the pressure of hydrogen and its effects upon steel in use in the 325 atm. hydrogenation is done by subjecting various samples, which develop a strong reduction in contraction at 560° and 700 atm, also to tests at the same temperature, but at 225 atm. sheet 2 shows the results obtained in such tests on one sample which was tested for effects of hydrogen in relationship to the hardening and annealing temperatures. All samples show a great difference in behavior at 700 and 225 atm even after 200 hour tests, and the difference becomes much greater after 1000 hours. We expected no great effect of pressure neither from our own tests nor from the tests of F. K. Naumann of Krupp. Tests on the effects of hydrogen at 325 atm upon the N9 steels are at present contemplated.

The effect of hardening upon the action by hydrogen was investigated next, as mentioned above. Fig 2, sheet 1 shows the results obtained in one of our studies along this line. It shows the reduction in contraction plotted against the annealing temperature after different hardening and with different quenching media used (oil and air). The tests have shown that hydrogen had less effect with lower and with higher annealing temperatures, and a greater effect at intermediate temperatures of 700--750°. The drawing shows further, that overheating and over-annealing (1150°/3 hours) caused greater attacks by hydrogen than obtained in 1 hour at the usual temperature of 1050° C. Moreover, the increase in the effect with oil annealed samples is striking. The curve shown in the figure is the normal curve for N10 and has been reproduced in a large number of cases. Fig. 3 shows the same experiments with a sample the resistance to hydrogen of which was very poor, but the analysis of the sample gave no reasons to expect it. The curve is similar up to two points to that obtained with samples at 800°C, Fig. 2, but the effects are in general greater.

It is however impossible to draw any conclusion on the behavior of the material in hairpins. One needs, rather to know the combined effects of hydrogen and the hot creep resistance to evaluate a material for high pressure work. Additional information on this will be given upon the conclusion of the present tests. We may however already state now that the hot creep resistance of oil-quenched steel is markedly lower than of the air-quenched. There is in addition the poorer hydrogen resistance of that material, as already stated. The distinct advantages of the air hardened N10 become also clearly manifest in the high pressure tests, as could be anticipated. When oil-hardened N10 is used, great attention must be paid to permissible peak temperatures.

The most important observation made in these studies, aside from the great effect of hydrogen under high pressure, is the slowness with which the reaction proceeds. Hydrogen diffusion rate in iron is very great, and this slow rate of reaction is therefore difficult to explain, were we to assume that the hydrogen which diffuses attacks the carbides directly. On the other hand, the following considerations lead to a very graphic picture of the process, and we will accept it as a guide in our future studies.

The rate of diffusion of hydrogen in the intergranular space is commonly assumed to be about 100 times greater than through the crystallites. The partial pressure of hydrogen is correspondingly greater in the grain boundaries. The grain boundary material exhibits no distinct crystallographic structure, and there are many porous spots in it, in which the decomposition products formed by the interaction of hydrogen upon the carbides, oxides, etc., may be formed and occluded. We shall therefore first discuss the interaction of hydrogen at the grain boundaries, and any possible action of hydrogen upon the crystal lattice will be left for the present out of consideration.

This first interaction of hydrogen with steel will be completed in a short time. Its effect upon the mechanical properties will therefore depend upon the amount of reactive carbides and other reactive constituents present in the grain boundaries. This conception may explain why some steels show a marked deterioration in properties after a few hours of interaction of hydrogen, while others do not.

This view point will further explain the relationship between the attack by hydrogen and the degree of hardening of the material.

We now imagine, that after this first step in the interaction is completed, a second one will begin, which proceeds at the characteristic slow rate found in the experiments. Iron carbide and other carbides are found in the alloy steels in finely subdivided form distributed throughout the crystallites. There is in addition some definite, though small, amount of carbon in solution in the crystallites, in some kind of equilibrium with the carbides. As the grain boundary substance become more or less decarburized, a certain, even though small, drop in concentration will be produced between the crystallites and and the grain boundary material. Carbon can therefore diffuse from the crystallites into the grain boundary material. This slow migration of carbon must occur at operating temperatures, and since the latter is very low for the diffusion of carbon, the process will require a long time at the existing difference of concentrations. As time progresses, more and more carbon is brought to the grain boundary to form hydrocarbons with the hydrogen which diffuses in, and which slowly magnifies the destruction phenomena wrought by hydrogen.

The carbon migrated from the crystallites into the grain boundaries will be missing from the equilibrium and must be resupplied from the carbides. This process, which is also a diffusion process, will also require a long time. This conception explains the formation of the white seams at the destroyed grain boundaries, and their hardness in the alloy steels may be as great as of the unattacked material, when the hardness of the ferrite is caused to a greater extent by the dissolved alloy constituents and the dissolved carbides, than by the visibly separated carbides. Fig. 4, sheet (*) 3 shows a carbon steel attacked by hydrogen. It shows clearly the partial decomposition of the carbide constuent of the pearlite along the grain boundary producing steadily widening seams of ferrite. Fig. 5 shows the same process in N10. The microhardness of the white seam along the grain boundaries is the same as of the crystallites which still contain carbides.

The rate of diffusion of carbon is the lower in the iron carbide, and especially so in the special carbides, the more carbide-formers are present, and a steel, in agreement with this hypothesis, must be the more resistant to hydrogen, the more it contains of such alloy constituents, since they will require more time for the later diffusion. Furthermore, that pearlitic steel is the most resistant to hydrogen, which has the least amount of unstable carbides in the grain boundary, and the least dissolved carbon in the ferrite. An absolute resistance can only be expected when the solvent power of the ferrite for carbon is equal to 0. In addition, a steel must behave particularly favorably with respect to hot strength, i.e. block the slip planes with intermetallic compounds instead of carbides, as it happens in columbium alloys, and which will permit the reduction of the carbide content.

A few experiments are being run at present along these lines.

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WMSternberg

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*The very fine micrographs, sheet 3, not reproduced in the translation.

LIMITS OF DURABILITY OF
Cr-Mo Steels

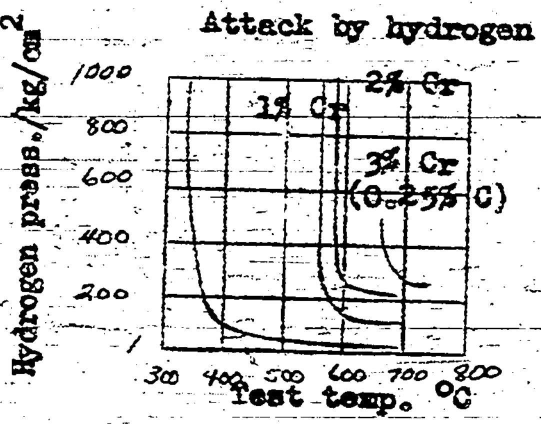
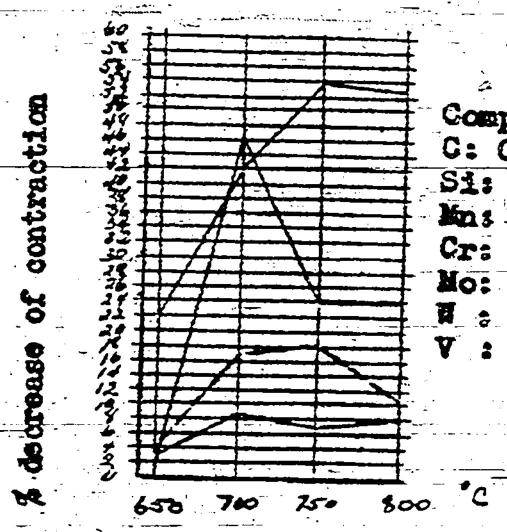


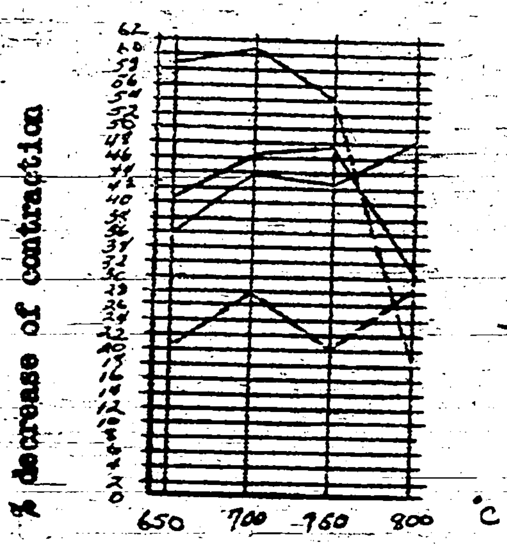
Fig. 1



Comp.
C: 0.185
Si: 0.35
Mn: 0.27
Cr: 2.73
Mo: 0.39
W : 0.31
V : 0.74

Anneal. temp. 6 hrs.
H_2O tests with non-stressed
N10 rods
700 atm. 560°C, 1000 hrs.

Fig. 2



Comp.
C : 0.190
Si: 0.25
Mn: 0.29
Cr: 3.05
Mo: 0.41
W : 0.23
V : 0.76

Anneal. temp. 6 hrs.
H_2O tests with non-stressed
N10 rods
700 atm. 560°C, 1000 hrs.

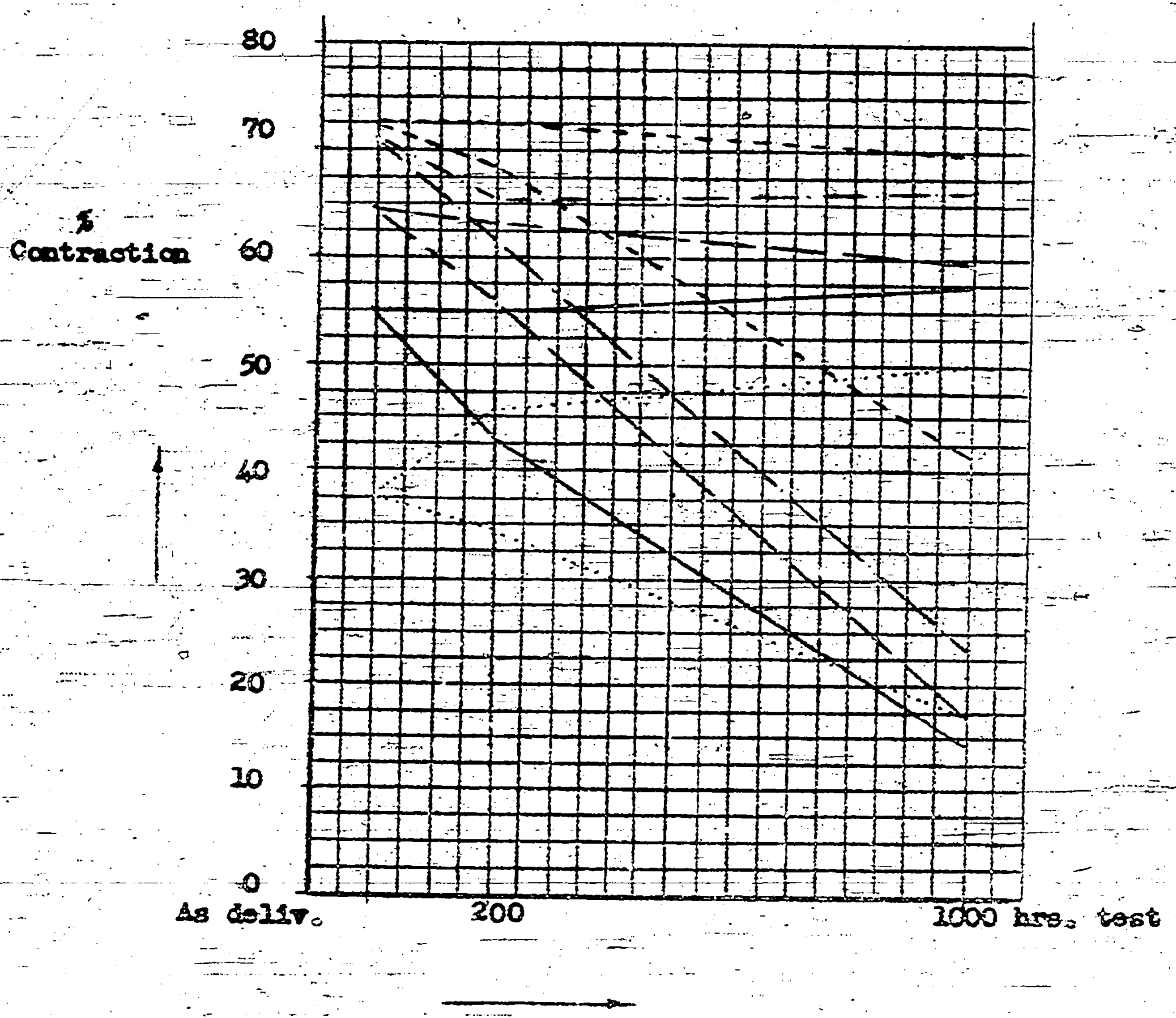
Fig. 3

TESTS ON ATTACK BY HYDROGEN WITH N10 STEEL AT 560°C

C: 0.19; Cr: 3.05; Mo: 0.41; W: 0.23; V: 0.76%

═══ = 225 atm.
——— = 700 atm.

═══ = Hardened 1050°, 1 hr/air, anneal 650°, 6 hrs. furnace
══ ══ = " " " " 700° " "
=·=·= = " " " " 750° " "
= = = = = " " " " 800° " "
······ = " 1150, 3 hr/air " 650° " "



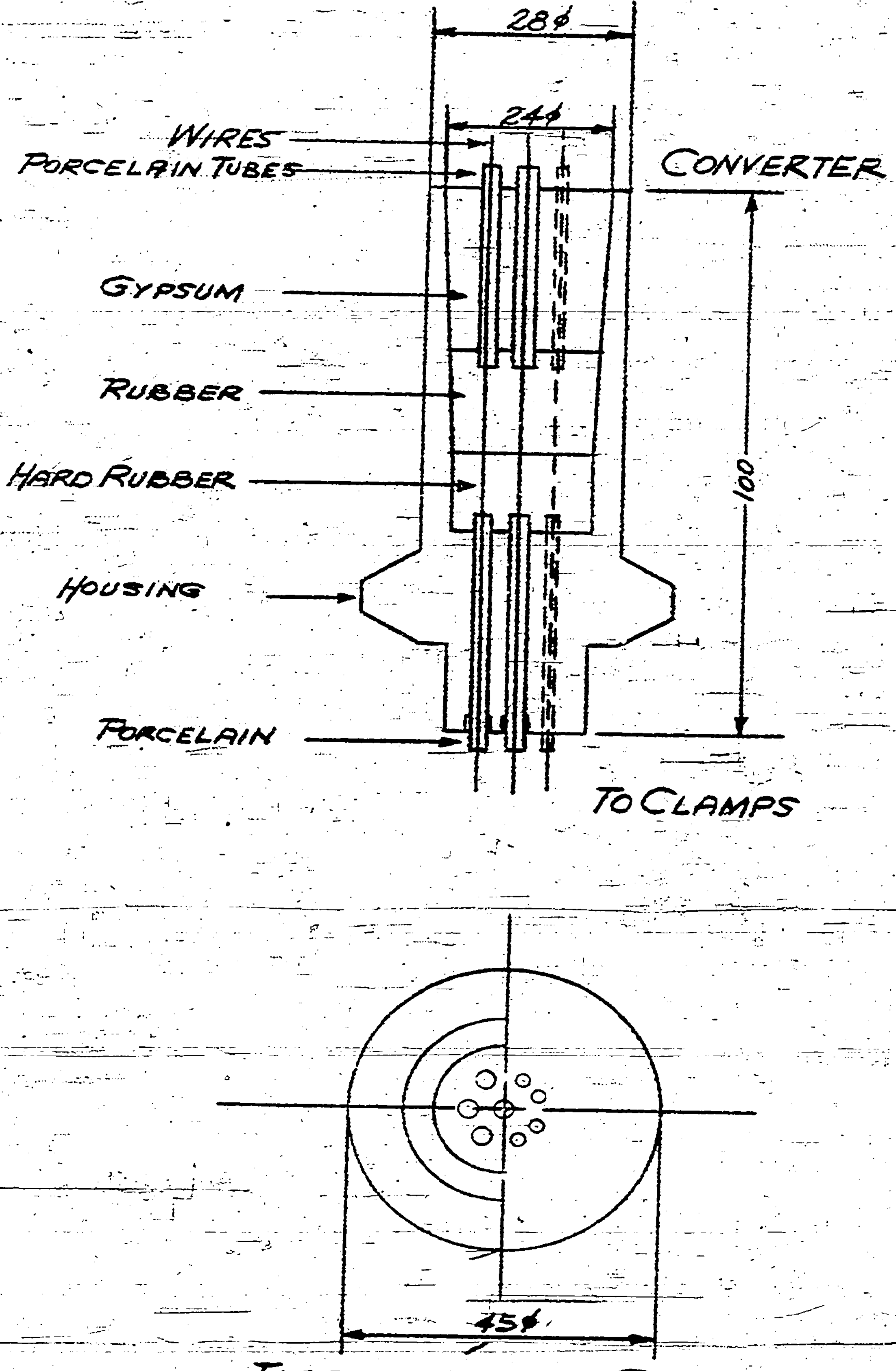
T.O.M. Reel 192 U. S. Bureau of Mines T-95
Item 13
KCBraun Hydro. Demon. Plant Div.

Pressure-tight Closure for Thermoelements

Leuna Werke, 14 June 1937

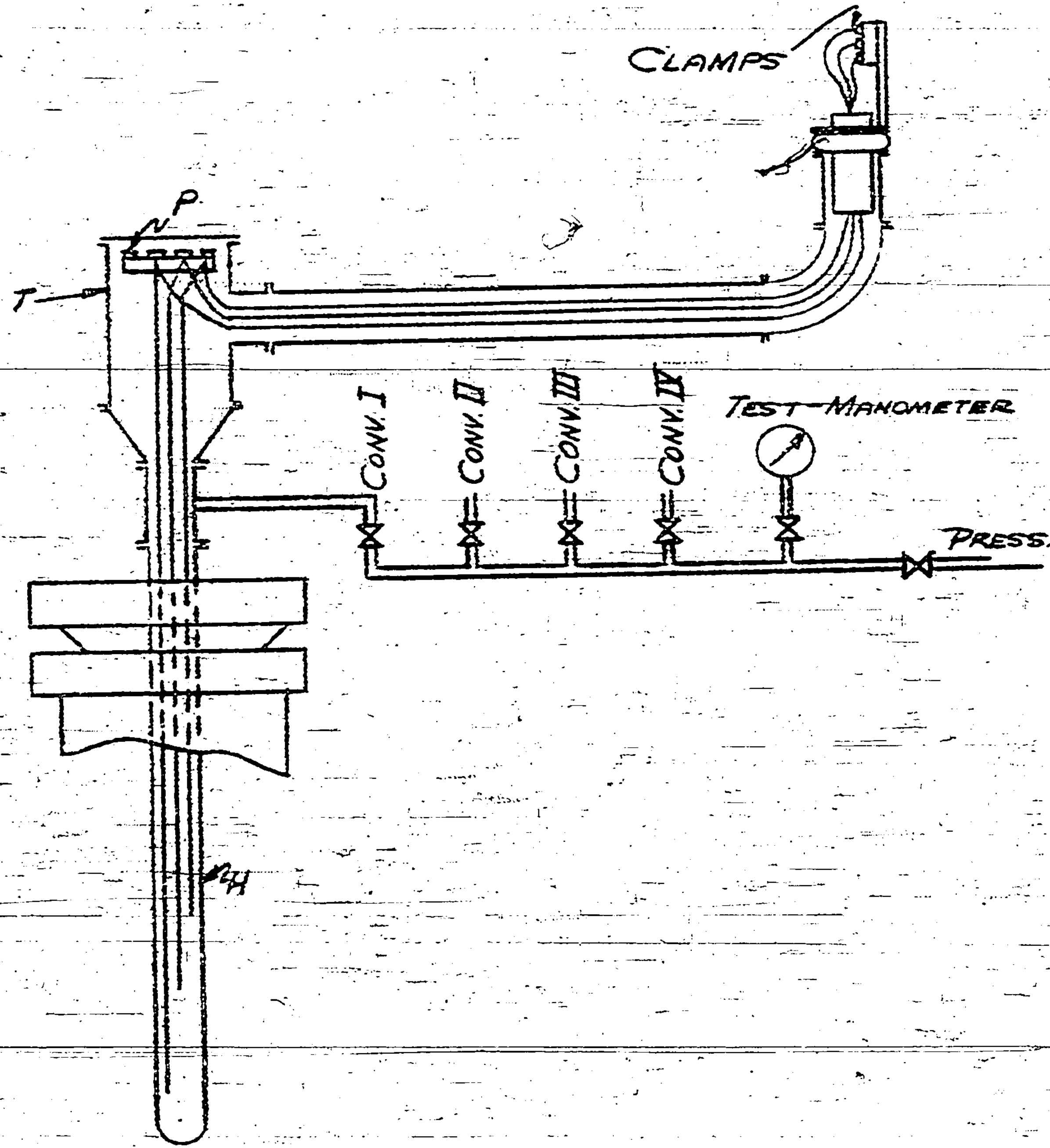
For measuring temperatures on the inside of high pressure hydrogenation equipment, the thermoelements are arranged in a pressure-tight housing. Should the housing ever leak, due to failure of the material or to the grinding action of high sand content of the coal paste, the stall is liable to be set on fire. If, in an installation protected in this manner, an element-housing should leak, the pressure-tight closure at one end of the housing prevents an escape of the gas and product and the stall can continue to run without danger. In the development of the closure, particular value was attached to a compact construction. Sketch Br. Sk. Me 201/1101 shows the final form of the closure. In a sealing ring for a 30 mm high pressure tube, 4 steel and 4 constantan wires are insulated and arranged pressure-tight. Each of the 3 fillers has a different function. The hard-rubber insert takes the surface pressure, the rubber stopper provides a seal, and the cast gypsum provides protection against heat should hot gas or product reach the closure in case of a leaky housing. The use of soft rubber is limited to places where the continuous temperature does not exceed 70°C. Therefore, the closure must be mounted within 1-1.5 m of the converter cover. The pressure-tight thermo-housings must be lengthened correspondingly. Another method of installation is shown in Sketch Br. Sk. Me 201/1100. On the end of the thermo-housing "H" is a "T"-45/30 mm. In this "T" a clamp-plate "P" is mounted on the clamps of which the transition from the porcelain tube insulated wires to the rubber insulated feeding lines to the pressure tight closure takes place. The closures themselves are arranged on the crown of the stall, easily accessible alongside of each other. One of the disturbances of the measuring installations with pressure-tight closures first appearing was that the water in the thermohousing, which may have been there before the closing or due to rain, would vaporize and the vapor settle on the clamp plate or the closure, damaging the insulation. Opening the pressure-relief valve of the housing to let water escape brought no improvement. Evacuating the thermo-housing before starting a stall has proved very successful. Before the start of a stall the common pressure relief line of the thermohousings for the 4 converters is connected to the suction of a small water spray pump, which sucks every bit of vapor from the housings before it can reach the clamp plates or the closures.

After four days of operation the water spray pump may again be disconnected, since every bit of moisture has been removed from the housings. During normal operation each closure is shut off from the common pressure relief line by a valve. At regular intervals of 3 to 6 days the operator checks the housing for tightness by switching one after another on to the relief line provided with a manometer. It has been shown that even in a perfect housing a little hydrogen will accumulate which has been diffused through the wall of the housing. By regular control and pressure relief the pressure of the diffused hydrogen in the thermohousings will not exceed 5-10 atm. so that no damage to the iron wires of the thermoelement by hydrogen attack has occurred even after 9 months operation. No fire due to leakage of thermohousings has occurred since the introduction of the pressure-tight closure. In all cases, the converter could continue operating without interruption after leaks in one of the two thermohousings were indicated.



THERMOELEMENT - CLOSURE

Br. Sk. Me 201/1101



Br. Sk. Me 201/1100

T.O.M. Reel 130
pp. 591-596
Transl.-K.C.Braun

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-96

Lu 558, 16 Oct. 1942

Abstract of Report on Construction Materials for Hydrogenation.

(By Dinkler)

Of the various properties demanded of construction materials for hydrogenation only the most important, namely hydrogen-resistance, hydrogen-sulfide-resistance, and fatigue elastic strength (Dauerstandfestigkeit) will be dealt with.

For the first experiments the equipment was built almost exclusively of carbon steels for which especial care was used in melting and more rigid acceptance tests were applied. However, this material was usually decarbonized and became brittle within a few days at 250 to 350°C due to hydrogen under pressure, so that it would break without deformation, similar to cast iron. Working with this material in the critical high temperature range was, therefore, possible only by applying special tricks of the trade.

By using N_4 material, a chrome-nickel steel of about 0.3-0.4% C, 1-1.5% Cr, and 2.5 to 3% Ni, the temperature limit against hydrogen attack was increased to 425-450° C, provided the material structure and workability were favorable. Otherwise the resistance limit would drop to 400°C and, therefor, did not offer the required operating safety. This was followed by a big increase in alloy content, using the V_2A steel with 18% Cr, 8-9% Ni, and about 0.12% C, which, besides having good heat resistance and resistance against hydrogen attacks, was not attacked by hydrogen-sulfide at normal operating temperatures. But this steel was very expensive and offered great difficulties in the fabrication of thickwalled seamless tubes. In addition, on exposure to corrosive media, to which our acid containing works-atmosphere belongs, grain decomposition would ensue, a condition in which the material breaks into powder under small stresses. This destruction is due to the fact that the carbon, forcibly kept in solution by quenching in ice water from 1100-1200°C, is segregated at 500-600°C on the grain boundaries in the form of chrome-carbides, which causes a local chrome-deficiency and lowering of corrosionresistances. By binding the carbon to titanium, tantalum or columbium, it is possible to produce a V_2A steel resistant to grain decomposition. Since nickel is basically unsuitable, because without the addition of other compensating metals it reduces the resistance to hydrogen and is also attacked by sulfur, the favorable chromium was combined with molybdenum, which improves the mechanical properties in a manner similar to nickel, (0.5% Mo corresponds to about 2% Ni at 20°C, while at higher temperatures Ni has no effect but Mo increases the heat resistance appreciably) and is also an effective catalyst.

The first steel of this sort was Krupp P 469, our designation N6, with about 0.15-0.2% C, 6% Cr, 0.5 Mo and 0.1-0.2% V. This steel was hydrogen-resistant at 600°C and had sufficient fatigue elastic strength for the usual pressures and temperatures. N6 is still used at Leuna in large quantities.

Because experience in high pressure vessel construction had shown that in Cr-Mo steels the heat resistance decreases with chromium contents above about 1%, lower chromium steels than N6 were tried. These led to N8, which, with 0.18% C, 3% Cr, 0.5% W, 0.5 Mo and 0.1% V, had considerably higher fatigue elastic strength, about 18 Kg/mm^2 at 450°C against 15 Kg/mm^2 for N6, with about the same simple annealing, and was somewhat cheaper, besides.

After experiments had indicated considerable advantages in increasing the pressure to 700 atm, with correspondingly higher temperatures, the demands on the fatigue elastic strength were again raised. This led to N10 steel, with 0.18-0.22% C, 2.5-3% Cr, 0.35-0.5 Mo, 0.35-0.5W, and 0.7-0.85% V. The difference between N8 and N10 is the higher vanadium content of the latter, which, however, can be effectual only if heated to about 1050° C before hardening to obtain an extensive dissolution of the vanadium carbides, which, on later reheating to about 700°C, segregate, finely dispersed, and, by blocking the planes of slippage, increase the heat resistance. N10 is a distinctly high grade material, (its heat treated strength at 90-100 Kg/mm^2 is, with good ductility, about twice as high as soft annealed,) which requires extreme care in heat treating and working.

The development of steels for converter jackets, flanges and bolts followed the same course as the tube materials, from the selected carbon steel to Cr-Ni steel, to Cr-Mo steel, which, for converter jackets, contains some Ni for metallurgical reasons.

Converter steel Ni:-3% Cr, 0.25% Mo, max. 0.8% Ni.

Highest strength flange and bolt steel K5:-1% Cr, 1% Mo.

N5 was used for the bundle tubes of heat exchangers, while converter liners and individual parts of heat exchangers were of V2A and 17% chrome steel respectively, though the latter has since been replaced by the less brittle 13% chrome steel.

Experiences in the petroleum industry clearly showed the destructive effect of hydrogen-sulfide on most metals and alloys, particularly at high temperatures. In high pressure hydrogenation, also, disturbances occurred due to deposition of sulfide crusts in the working of products containing sulfur, as for instance, in electric preheaters. But the problem of sulfur resistant materials assumed particular importance on the introduction of catalysts containing sulfides, because the products were now largely sulfured in order to increase the life of the catalysts.

In extensive experiments in a special converter, several hundred materials were tested with products containing 1.5-2% hydrogen sulfide at temperatures of 20 and 25 (millivolts). These materials were all of a ferrous base with additions of chromium, nickel, wolfram, molybdenum, aluminum, silicon and manganese. In addition, inserts of the most varied compositions and methods of fabrication, as well as light metals, wolfram, molybdenum, silver and other metals were tested. The lowest alloy steel with the best hydrogen-sulfide resistance proved to be the 13% chrome-steel, which, however, was very difficult to work into high-pressure tubes at the time.

In further tests a brass sample was installed in conjunction with catalyst experiments. Since this showed no appreciable sulfur attack, copper-zinc alloys of the most varied compositions were systematically tested for their usability. These tests showed the alloy 58-63% copper, the rest zinc, to be hydrogen-sulfide proof, while brass with 70% copper was weakly and tombac with 80% copper very strongly attacked. Of particular interest was one test, in which the metal was not cast after melting, but in which the sample was turned from the regulus solidified in the crucible. This sample was not attacked at its upper end but was completely converted into sulfide at the lower end, which, in a later analysis, could be attributed to segregation in solidification. The analysis indicated 68% copper at the upper end and 95% of the lower, so that the whole alloy range was contained in this one sample. Since copper is largely destroyed by hydrogen-sulfide, even at low temperatures, the good resistance of brass must have been due to the zinc content. It seemed proper, therefore, to try to obtain usable alloys by zinc additions, even with the low resistant nickel and iron. The first of such experimental melts seemed almost hopeless, because it was almost impossible to mix and hold the zinc in the melt. The boiling point of zinc at 907°C is far below the melting point of nickel at 1452°C and iron at 1528°C, and at 1500°C the vapor pressure of zinc is about 54 atm. But since "anything goes" in high pressure operations, a Tamann type coal tube furnace was built into a suitable high-pressure vessel and the melt then made at about 60 atm. nitrogen pressure and allowed to solidify, whereby iron-zinc alloys up to 50% zinc content were obtained. These samples acted very similar to the copper-zinc alloys in the sulfur attack experiments. Whereas with nickel-containing 10% zinc the sulfide crust at 25 MV was still 3.3 mm, it decreased to 0.03 mm with 25% zinc. With iron an addition of 15% zinc was enough to obtain complete sulfur-resistance. However, these nickel and iron-zinc alloys are not technically useful, in spite of their high resistance, because they are extraordinarily brittle and shaping is impossible even by casting.

Since in hot galvanizing of steels iron-zinc alloys are formed on their surface, galvanized iron samples were tested, and these too were not attacked by hydrogen-sulfide. After these successful small-scale experiments, a heat exchanger with hot galvanized bundle-tubes of N6 was installed in stall 505 early in 1930, with good results.

However, hot galvanizing 18 m long heat exchanger tubes is very difficult, and Leuna developed the vapor galvanizing, based on our results, which is now used on all heat exchanger bundle tubes, and which more recently has replaced converter inserts of chrome-nickel steel.

The end of these developments corresponded approximately to the beginning of the war. Since then, the scarcity of molybdenum, wolfram and chromium compelled us to save these metals and more extensively use vanadium, manganese and silicon as alloying metals. The following table shows a comparison of the most important construction materials between the middle of 1939 and the middle of 1942:

PURPOSE FOR WHICH USED	MIDDLE 1939 DESIGNATION	ANALYSIS	MIDDLE 1942 DESIGNATION	ANALYSIS
Lens-gaskets,			N5A	<0.12C, >2.5 Cr, Minim. 0.1 V.
Bundle-tubes			N5B	<0.12C, >2.5 Cr.
for heat exchangers,	N5	2.5-3 Cr, 0.25 Mo, 0.12C	N5C	0.12-0.18C, >2.5 Cr 0.1-0.2 V.
Core-tubes for Nickelofen			N1K	0.15-0.20C, 2.0-2.3 Cr, Max. 0.15 V.
Tubes for	N8	3 Cr, 0.5 Mo, 0.5W, 0.1 V, 0.15-0.20 C	N8A	2.5-3 Cr, 0.2-0.3 V, 0.2-25 C.
lines and			N9	2.5-2.8 Cr, 0.2-0.3 Mo, 0.55-0.65 V, 0.19-0.24 C.
Preheaters,	N10		N10	Unchanged but very restricted in use.
300 & 700 atm.	K2	1 Cr, 0.2 Mo, 0.6-0.9 Mn, 0.23-0.28 C	K2M	1.5 Mn
Flanges &	K3	1 Cr, 0.3 Mo	K1M	0.8-1.5 Mn, abt. 1 Si
Bolts			K4MS	1.5 Mn with Si.
			K3CV	1 Mn, 1.2 Cr, 0.25 V.
	K5	1 Cr, 1 Mo	K7	4.5 Cr, <1.2 V, Max. 1 Mn.
Converter Jackets and Covers	N1	3 Cr, 0.25 Mo, Max. 0.8 Ni	N_1A	Wall Thickness Mn Cr Ni >80 0.8 2.3 0.8 >200 0.8 2.6 0.8 <200 0.8 3.0 1.0

Based on these material changes, the following relations exist in a comparison of alloy parts requirements for the high pressure stalls of a coal hydrogenation works producing 250,000 T/Ann. auto-gasoline, between May 1, 1941, and May 1, 1942:

				Total Requirements - Kg.	
				1941	1942
Saving:					
Chromium	10%	=	37,000 Kg.	367,000	330,000
Molybdenum	45%	=	16,000 Kg.	35,000	19,000
Additional Requirements:					
Nickel	11%	=	7,500 Kg.	68,000	75,500
Vanadium	30%	=	4,800 Kg.	15,700	90,500
Manganese, abt.	100%	=	95,000 Kg.	90,000	185,000
				18,200,000	18,200,000

For a DHD-plant for producing 200,000 T/Ann. DHD (aviation) gasoline, the following values are applicable for the same time period:

Saving:					
Chromium	41%	=	13,300 Kg.	32,300	19,000
Nickel	100%	=	320 Kg.	320	
Molybdenum	75%	=	3,460 Kg.	4,650	1,190
Additional Requirements:					
Vanadium	200%	=	1,830 Kg.	920	2,750
Manganese, abt.	33%	=	1,500 Kg.	4,500	6,000
Iron				1,280,000	1,280,000

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Newman

T. O. M. Reel 130
pp. 597-611
Trsl. - KCBraun
8/28/46

U. S. Bureau of Mines
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T-98-A

Abstract of Lecture on High-Pressure Steels.
(See also T-93 and T-96)

By Dr. Dinkler, Spring 1944

Since my subject will be held to very general terms, I shall begin by giving a short summary of my remarks. First, I shall touch on the reasons which led to the preferential use of steel and its alloys, then, I shall give a summary of the most important high pressure steels and discuss the concepts of "Dauerstandfestigkeit" and "Zeitstandfestigkeit".

(The author here discusses elementary principles of the molecular structure and physical properties of steel and its alloys, which can be found in any American textbook on related subjects and is, therefore, not reproduced here. Some of his subject matter is also reproduced in T-93 and T-96. Certain diagrams referred to by the author are either not available or are not sufficiently explained and these, also, are omitted.)

The quenching at high temperature often leads to such hardness that the material may become as brittle as glass. Quenching is, therefore, usually followed by reheating to about 500° C, which appreciably increases the ductility with only a slight decrease in hardness. The combination of hardening and reheating is designated as heat treating, which is essential for attaining higher strength in alloy steels; since a soft annealed alloy steel has barely greater strength than plain carbon steel. There is another form of hardening, socalled tempering, on which the high strength of duralumin is based, for example. It may be explained by the fact that Al can hold larger quantities of Cu and Mn in suspension at high than at low temperature. If such alloys are quenched at high temperatures, these constituents remain in solution and are segregated on reheating to 200° C in finely dispersed form, causing hardness by blocking the planes of slippage. This tempering may occur in steels in addition to normal hardening and plays an important role in N10, to be discussed later.

At the beginning of high-pressure experiments only plain carbon steels similar to St 35, 0.2% C, were available. These, however, were destroyed by hydrogen attacks at pressures of 200 atm. and temperatures above 300° C. In this process atomic hydrogen enters the tube walls and combines with the carbon tofform CH_4 and with the oxide pollutions to form H_2O. These larger molecules can no longer diffuse out and their pressure causes loosening of the structure and partly the formation of blisters. But plain carbon steel would also fail at high pressures and temperatures because of its low strength, since higher loads can be taken up only to a certain degree by thicker walls, because the outer layers of extremely thick walls are practically unstressed. According to Mises the strain on the inner tube wall is:

$$S = P \frac{K^2\sqrt{3}}{K^2 - 1} \quad \text{where } K = \frac{(da = O.D)}{(di = I.D)} \text{ and } P = \text{Pressure}$$

and the following table indicates the stresses for various wall thicknesses:

di mm	da mm	Pressure Atm.	Si Kg/mm^2	S permissible at 500° C St 35	N10
100	190	700	16.7	2.5	20
100	500	700	12.6	2.5	20
1	500	700	12.1	2.5	20
1	1000	700	12.1	2.5	20

(Note: - The German text omits "P" in the formula above and has "da" interchanged with "di" in the table.)

For the experiments at 1000 atm. and 400° C, N4 was then introduced; it is only conditionally hydrogen-resistant. In 1928, N8 (Cr-Mo) was developed and it proved to be quite satisfactory in its hydrogen-resistance and heat strains. Mo increases the strength similar to Ni, but is much more effective, so that 2.5% Ni may be replaced by 0.5% Mo. In very heavy wall thicknesses, such as converter jackets, however, a certain amount of Ni is indispensible, because of more satisfactory heat treating with it. Cr-Ni steel 200 mm dia, rim hardness 220, core hardness 215, corresponds to Cr-Mo steel 200 mm dia., rim hardness 250, core hardness 210.

I shall now discuss the concepts "Dauerstandfestigkeit" and "Zeitstandfestigkeit". Generally, we try to select construction materials, which will permanently satisfy operating requirements. We, therefore, figure on "Dauerfestigkeit". Where this may lead to unwieldy dimensions, we base our calculations on "Zeitfestigkeit", which, according to the time chosen, is considerably higher than the "Dauerfestigkeit", and the most heavily stressed parts must be frequently replaced. The concepts "Dauer-& Zeitfestigkeit" apply to varying stresses in bending or torsion, as well as to static stresses, such as in steam boilers and high pressure vessels. The "Dauerfestigkeit" can readily be determined with varying stresses, since it is dependent merely on the number of repeated stresses and not on the time in which they are applied, while with static loads the continuous experiment "Dauerversuch) must extend over several years. To determine the true "Dauerstandfestigkeit" in a much shortened experiment the test specimen are stressed at test temperature with a static load and the elongation is measured continuously with precision instruments.

If, within a period of 25-35 hrs., the speed of elongation does not exceed 0.001%/h and the permanent elongation after 45 hrs. is not over 0.2%, the stress in Kg/mm² is designated "Dauerstandfestigkeit".

In this process, however, it is assumed that the elongation measured within the time of the experiment really ceases. The dependence of strength on duration of loading is more clearly shown for steel above 300° C, while, up to this temperature, the yield paint determined in the short experiment or the ultimate strength may be used as a basis for calculations.

It has been shown that the dependence on time of the strength of steels of varying composition at equal temperatures may vary considerably and a seemingly poor steel may give better performance over an extended period. For this reason, experiments have been under way for years to determine the true "Dauerstandfestigkeit" by a continuation of loading to the breaking point, or the "Zeitstandfestigkeit" for fixed periods.

A comparison of experiments to determine the "Zeitstandfestigkeit" in 10,000 hrs. and the "Dauerstandfestigkeit" in the shortened experiment, shows that V2A behaves much better than the shortened experiment would indicate, while K5 (0.2 C; 1 Cr, 1 Mo, 0.07 V) is poorer. N 10 shows the same values in both experiments. The good behavior of N 10 after 10,000 hrs. is limited by its tendency to brittleness under high stresses.

The high strength of N-10 is based, besides the effect of normal heat treating, on a tempering similar to duralumin. By holding at 1050° C for one hour, the vanadium-carbides go into solution, remain in solution in rapid air or oil cooling, segregate microscopically finely dispersed on reheating to 650° C., and so lead to high added heat resistance by blocking the planes of slippage (Gleitebenen).

Besides the load limits, the designer must also know the time-elongation limits, that is, the loads causing no greater elongation than 0.2%, since this value is permissible in all cases.

V2AED with the addition of 1% W would seem to behave similar to N 10, and appear to be the ideal material.

("Dauerstandfestigkeit" has been variously interpreted as "creep strength", "fatigue strength" or "fatigue elastic strength", that is, the maximum stress to which the material may be subjected within its elastic limit, or just beyond, when applied a large number of times. "Dauerfestigkeit" is defined in German textbooks as "the maximum stress any material is able to resist without breaking, when applied 10,000,000 times". "Standfestigkeit" is defined as "The maximum stress at which no further deformation, or one limited to 0.001%/h, takes place after a certain time; it coincides approximately with the elastic limit". This latter seems to correspond to the "Dauerstandfestigkeit" defined by the author. "Zeitstandfestigkeit" has been interpreted as "time-elastic strength", which comes closest to the literal translation. From the author's explanation, it appears to correspond to the "Dauerstandfestigkeit" with some correction factor for upward revision where the material is intended for use with higher stresses because of temporary use or periodic replacement, allowing higher stresses.)

T.O.M. Reel 129
pp. 134-141
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U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-99

Abstract of Discussion on Spiral-Wound High-Pressure Jackets. (Wickelmantel)

Lu, 25 May, 1939.

In order to proceed with the design, dimensions of the core-tube, liner-tube, cover, etc., must be determined.

The dimensions of the jackets are as follows, for the indicated number of currently proposed jackets:

A) Jackets for Hydrogenation:

a) 1 Converter 1000 mm I.D. x 18 m lg. @ 325 atm, 300° C. Wall temperature.

b) 1 Converter 1200 mm I.D. x 18 m lg. @ 325 atm, 300° C. Wall temperature.

c) 1 Heat Exchanger 600 mm I.D. x 18 m lg. @ 325 atm, 300° C. Wall temperature.

d) 1 Washer 1000 mm I.D. x 12 m lg. @ 700 atm, 20° C. Wall temperature.

B) Jackets for Tanol:

a) 1-2 Converters, 1200 mm I.D. x 18 m lg. @ 325 atm, 300° C. Wall temperature.

b) 1-2 Converters, 1000 mm I.D. x 18 m lg. @ 325 atm, 300° C. Wall temperature.

c) 2 Heat Exchangers, 800 mm I.D. x 12 m lg. @ 325 atm, 300° C. Wall temperature

d) 2 Classifiers, 800 mm I.D. x 12 m lg. @ 325 atm, 20° C., Wall temperature.

e) 5 Catch Pots, 800 mm I.D. x 6 m lg. @ 325 atm, 20° C., Wall Temperature.

It is proposed to wind and fully complete the jackets for Tanol at Oppau, while the jackets for hydrogenation will be made by Krupp.

The design details include:

1) Wall thickness and material.
2) Closures, covers, cover drilling.
3) Core-tubes.
4) Liner-tubes.
5) Inserts, etc.

To 1) Wall Thickness:

Details of stress calculations were not discussed. The basis for these will be determined by Oppau after completion of the tests conducted by the Materials Testing Laboratory Stuttgart, Prof. Dr. Siebel.

The following data are included in this:

a) Modulus of elasticity of the wound section in axial direction for the purpose of determining the proportion of axial load taken by the core-tube, liner-tube and wound section.

b) The transfer of the axial forces from the closure attached to the core-tube to the wound section.

c) Heat transfer capacity of the wound section for calculating the heat stresses.

d) Initial tension due to the shrinking effect of the hot wound layers.

e) Determination of dimensions, shape and material of the winding strips.

f) Determination of dimensions, shape and material of the core-tubes.

Where any of these spiral wound vessels are to be used for other than I.G. works, the Siebel Committee for determining general rules for the calculation of wound vessels, is to be consulted.

To 2) Closures:

Two basic designs are possible.

a) Shrinking on flanges with studs, as in solid jackets.

b) An inner closure with inner-thread ring attached to the core-tube and pressure bolts.

To a). This construction has the advantage of greater freedom of movement with respect to cover holes and particularly cold gas inlets. It has the disadvantage of increased weight and consequent cost of the jackets.

To b) With solid wall jackets it would be particularly disadvantageous, if, in using an inner closure, the jackets, whose dimensions are barely within the limit of possible construction, would have to be enlarged an amount corresponding to the dimensions of the closures in order to obtain the same reaction space, which would be largely impossible.

With wound jackets the lengthening of the jackets offers no difficulty whatever. The disadvantages of the difficult cold gas inlet arrangement may be overcome by using a cold gas distribution ring on the inside of the jacket. Since, at present, it is not possible to reduce the diameter at the end of wound jackets, particular attention must be paid to keeping the closure weights at a minimum. These considerations led to the decision to study the construction with inner closure first of all.

However, the possibility of using shrunk-on flanges with studs must be examined also, because in special cases, for example the use of a special interchangeable liner-tube (apart from the core-tube), this construction might be particularly suitable.

A 500 mm wound jacket made in Oppau is to be used as a test piece for this purpose, so that one end is to be provided with an inner closure and the other end a stud bolt closure. It is intended to try to wind the flange also of strips.

To 3) Core Tubes:

The following wall thicknesses of the core tubes may be chosen for the initial design:

a) Hydrogenation Converters, 1000 mm I.D.) 25 mm N5
) finished outside
Hydrogenation Converters, 1200 mm I.D.) rough inside

b) Hydrogenation Converter Heat Exchanger, 600 mm I.D.(15-20 mm,N5
(finished outside
(rough inside

c) Tanol-Heat Exchanger, 800 mm I.D., 20 mm, S.M. St, finished outside and inside.

d) Tanol-Catch Pot, 800 mm I.D., 20 mm, S.M. St, finished outside rough inside.

e) Tanol-Classifier, 800 mm I.D., 20 mm, S.M. St, finished
outside rough inside.

f) Tanol-Converter.. 1000) mm, I.D., 25 mm, S.M. St, finished
1200) mm outside and inside

To 4) Liner Tubes:

While the hydrogenation jackets require no special liner tube for protection against chemical action, since the core-tube is constructed of hydrogen-resistant material, the Tanol converters and heat exchangers must be provided with an interchangeable copper-clad iron liner tube. The copper lining itself does not provide complete protection, because it becomes brittle and tears in practice, so that, eventually, the steel liner-tube below it is attacked by H_2 and CO, and it must, therefore, be made interchangeable. The idea, to eliminate the steel liner-tube by making the core-tube of copper plated hydrogen-resistant material, was rejected as unsafe, because of the possibility of gradual destruction of the copper plating.

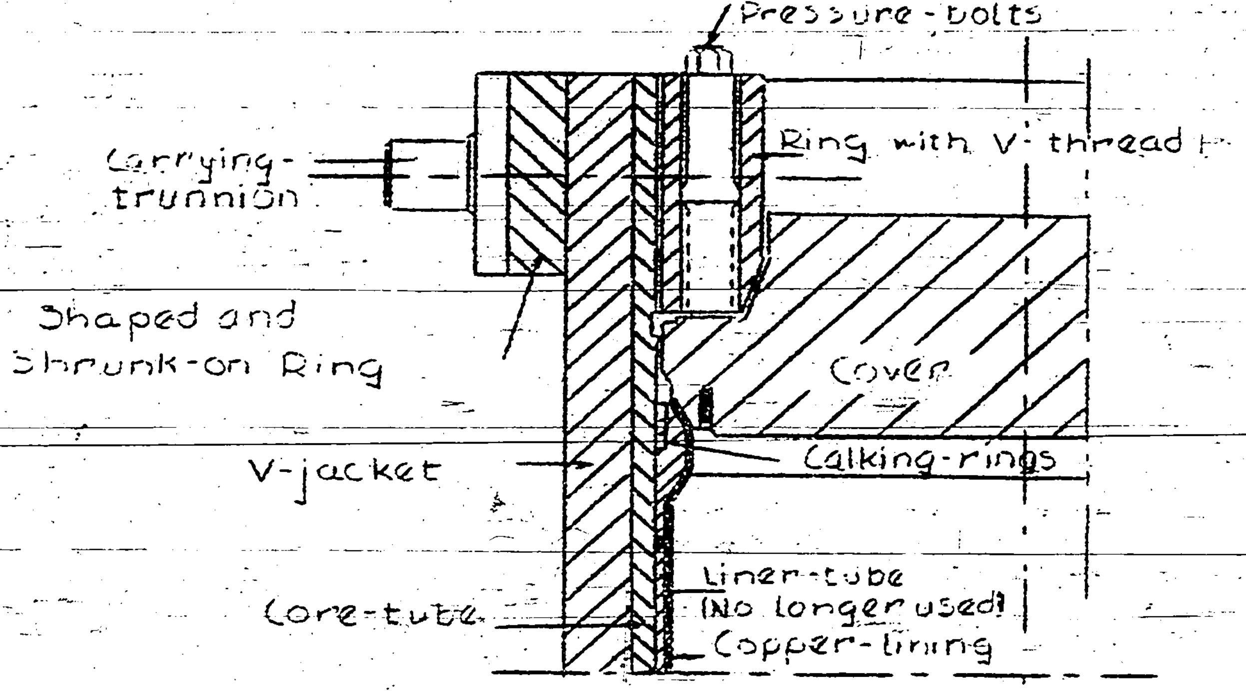
The requirement of interchangeability of the steel liner-tube requires a construction differing from that of the hydrogenation jackets. (See appendix)

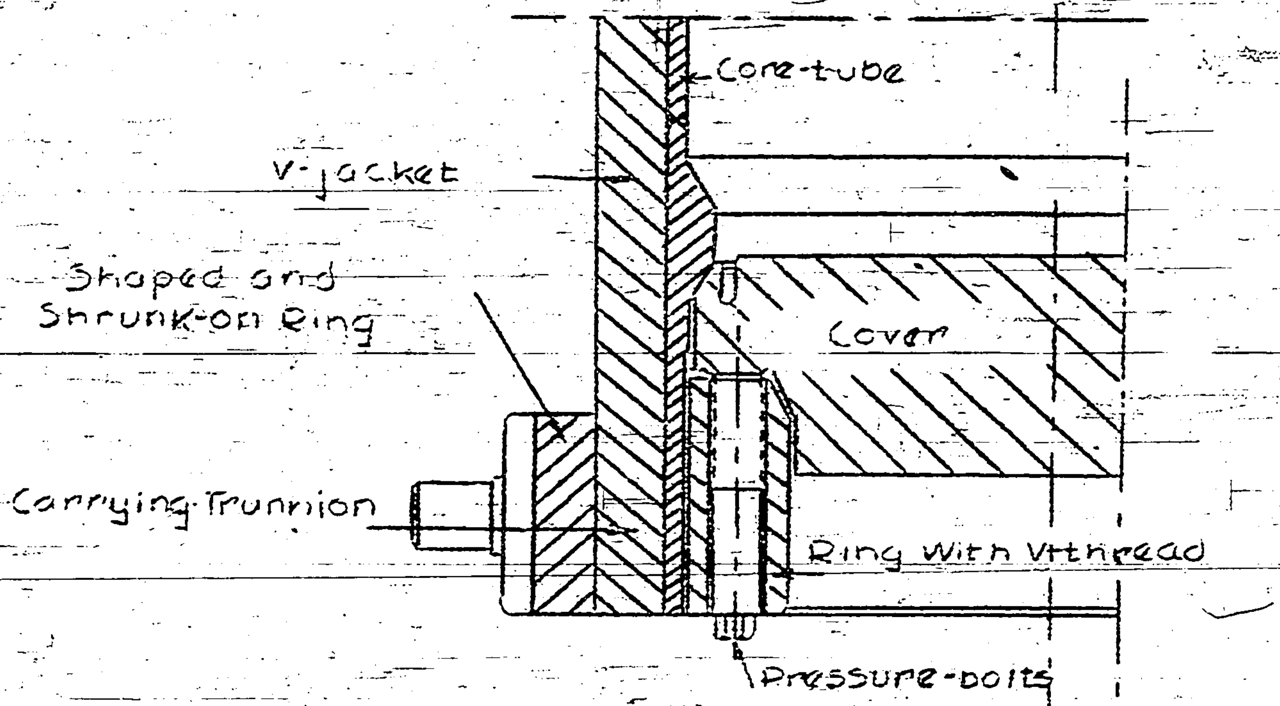
To avoid making the core-tube of one full-length piece, 12 to 18 m long, it is made of shorter pieces, about 6 m long, finished overall and driven or lightly shrunk into the liner-tube. Because the shaped winding strips forming the jacket wall take the axial loads, welding the individual pieces of the core-tube to one another should not be absolutely necessary, since distortion of the liner tube-core tube combination must be avoided. At most, a light tack welding would be permissible.

It is assumed that, after removal of the liner-tube for replacement, the jacket will not be distorted due to inherent stresses.

T-99

Basic Construction of Wickel-jackets with liner tube.





Basic Construction of Wickel-jacket without Liner-tube.

T.O.M. Reel 5
pp. 548-555

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-100

Phenols from Coal Hydrogenation Oils

By Dr. Bemmann, Ammonia Works Merseburg.

The report below deals with the production of phenols from hydrogenation oils. We mean by phenols the carbolic acid, the cresols and the xylenols, while the "hydrogenation oils" are those used in hydrogenation, in particular oils produced in low temperature coking of brown coal, as well as the oils produced during the hydrogenation proper.

Permit me first a few remarks on the growing importance of phenols.

Up to about 10 years ago, conditions in Germany were such, that the demands on phenols could be satisfied by the then available means for the production of synthetic phenol as well as by dephenolating the tar oil fractions. Since then the field of application of phenols has been increased by the development of the older fields as well by the introduction of new and very important uses of phenols, to such an extent, that the older sources of phenols have long ago ceased to satisfy the requirements and new ways must continually be discovered. Such a new source is offered in the phenol-containing off waters of coke oven plants, low temperature coal distillation, and hydrogenation works, which can furnish appreciable amounts of it. However, even these new, and necessarily limited, sources are insufficient to satisfy the ever increasing demands. It becomes therefore necessary to obtain additional amounts, using methods permitting adjusting the production to the demands, that is such, which are not rigidly coupled with any other manufacturing process. Such methods may be found in an extension of the existing methods of carbolic acid manufacture. However, the raw material necessary for it, benzol is not available in unlimited quantities, and is being used as a motor fuel; moreover, the homologues of phenol, the cresols and xylenols, can not be obtained in this way. On the other hand, the ever increasing amounts of low temperature carbonization tars are produced in Germany in ever increasing amounts, and certain hydrogenization products contain such amounts of already formed phenols, that their recovery could with one stroke relieve the phenol scarcity. This was the reason why within the last years suitable methods have been developed for the recovery of phenols from this kind of oils, and introduced industrially.

Before discussing the individual processes, I wish to go more deeply into phenol removal from the different oils, and take the low temperature carbonization tars first. They are not suited in in their usual commercial form to the extraction of phenol, because they form emulsions with the extraction fluids which can not be broken. On the other hand, light fractions of the tars can frequently be used. Such fractions, with boiling points between 200 and 300°, are fluid and of sufficiently low gravity to permit a rapid settling of the extracting liquid. They moreover contain a higher proportion of the lower boiling phenols than does the tar, and definite amounts of phenols are obtained by using smaller amounts of the liquids, which correspondingly reduces the size of the equipment. Most of the low temperature coke plants deliver their product to the hydrogenation plants as obtained, i.e. not distilled. It would be too expensive to separate all the tar into fractions. However, certain amounts of fractionation is done in most coke plants during the fractional condensation of the tar. It would take us too far to describe in detail the operating details. We will limit ourselves to saying, that most of the product is obtained as a high boiling viscous tar, while a small part of the total production forms an oil similar to the middle oil and as a benzol-containing light oil. The different products are in part remixed at the coke plant, while some of the mixing is done at the hydrogenation plant. There are no difficulties in principle in the separation of phenol from the lighter products before mixing with the thick tar. The boiling point range of the different fractions differs only slightly, and the thick tar contains some of the lighter oil and therefore still contains some of the phenols.

The principal amounts of the phenols is, however, to be found with the light fraction in an enriched form, and, depending on the nature of the coal carbonized at low temperature, as well as on the conditions of condensation, they may contain 5 to 15% low boiling phenols together with varying amounts of higher boiling acid oils.

The proportion of phenol to cresols varies, and depends principally on the nature of the coal. Thus, most brown coal tars carry considerable amounts of phenol, but they are practically absent from the soft coal low temperature tars. Carbolic acid is evidently produced from soft coal only at high temperature cracking through decomposition of the higher-molecular weight oxigenated products, while the temperatures used in the low temperature carbonization of soft coals 500 to 600° is insufficiently high for their formation.

The thin oils and light oils produced in the low temperature carbonization may well be used for the production of phenols by one of the methods to be described presently. They are quickly and readily separated from the extraction media, especially if treated as formed, i.e. before aging and without having been long in contact with air. There are, however, products, especially among those produced by the older low-temperature distillation methods, which produce inconvenient emulsions with the extraction media, and are therefore unsuited to be dephenolized. Preliminary tests must therefore be run for the different products to tell whether the products of the different coke plants are suitable for extraction.

In addition to different emulsifiers, the various carbonic acids of the tars may introduce difficulties, by being more strongly acidic than the phenols, and when extracted with alkaline solutions will therefore dissolve first and make the recovery of the lye more difficult.

The principal amounts of phenols produced in low temperature coking may therefore be obtained from light oils and the thin tars, but they will fail to include the phenols present in the thick tar. These, however, may also be frequently recovered, if the phenols extraction is made at the tar hydrogenation works. In most hydrogenation works operating with low temperature tars, the total tar delivered, i.e. the mixture of the thick tar, the thin tar and the light oil, are broken down in special installations into a distillate and a residue because the low-boiling tar constituents are preferentially hydrogenated in the vapor phase, while the higher boiling fractions are better suited to the liquid phase treatment. The fractions are cut at 310-315°, much sharper than the cut between the heavy tar, light tar and light oil at the coke plants. The distillate will accordingly contain all the low boiling phenols present in the tar; it will contain in addition newly formed phenols from the high boiling oxygen-containing tar constituents, because the reaction product of the liquid phase stalls is distilled in the same unit with the crude tar. The distillate obtained in these installations does therefore form not merely a very suitable material for the phenol recovery, but will furnish a wider source of raw materials than the lighter-- first condensates since the latter are not produced in all the low temperature coking plants.

In addition to the tars, some other oils, directly produced in the coal hydrogenation, may be used as a source of phenols. These are the oils produced in the so-called liquid phase, and are intermediate products in the manufacture of fuel oils. They are but imperfectly saturated with hydrogen, and contain, in addition to nitrogen and sulfur compounds, also considerable amounts of oxygenated compounds, with low boiling phenols amongst them. To produce satisfactory fuel oils, the liquid phase oils must be further hydrogenated in the vapor phase. To do this, they must first be separated into distillate and residue, similar to the hydrogenation of tar oil. The distillate is similar to the tar distillate with respect to phenol content, mobility and specific gravity, but is still better adapted to the phenol recovery, and for the following reasons:

1: The liquid phase oil had been treated previously with hydrogen, even if but imperfectly, and is therefore less contaminated with such materials which may interfere with extraction e.g. emulsifiers and carbonic acids.

2. In comparison with coal, the liquid phase hydrogenation oil is a much richer phenol source than tar. Möhrle and Bauerfeld

(Z.Ang. Chem., vol. 52, 1939, p. 183) have shown that in the pressure hydrogenation of soft coal 73 times greater amount of phenol-cresol mixture is obtained, than in the high temperature coking operations. The relationship between low temperature tars and hydrogenation phenols is similar, although not as strongly pronounced. Thus, direct hydrogenation of brown coal produced 10 to 20 times as much phenols as in the low temperature coking.

Coal hydrogenation oils will therefore not merely produce phenols more easily, but also in appreciably greater amounts.

I wish to describe briefly a process of phenol recovery suitable to hydrogenation oils.

There are many suggestions for the extraction of phenols from tars and similar products, and the patent literature is very voluminous in this field. In comparison with that, the number of processes which can be carried out industrially is but small. Of the older processes we may mention the extraction of tars or tar oils with concentrated sodium hydroxide and with aqueous alcohol (Fresol process). Neither of the processes are very selective and are more suitable to oil refining than to phenol extraction. The extract obtained is similar to cresol, and so strongly contaminated with non-phenolic constituents, that pure acid oils can only be produced after extensive further purification.

We have tried to develop a process in Leuna, which would permit a direct continuous extraction of the pure acid oil from the oils obtained. The oils produced were to be readily soluble in a dilute sodium hydroxide solution, indicating maximum freedom from neutral oils. In addition, the oils have a rather wide boiling point range, and contain the valuable low-boiling phenols as well as varying amounts of the higher boiling acid compounds, and the process should permit the separation of the valuable phenols, i.e. the extraction medium was required to possess a maximum selectivity. The following three processes were carried out in Leuna:

1. The hot water process.
2. The sodium sulfide process.
3. The counter-current sodium hydroxide process.

The Hot Water Process

In this process the extraction is done with water at such temperature conditions, under which the solubility of phenol is rather large. The separation is primarily based on the different solubilities at different temperatures.
Fig. 1 shows the method of operation. Water is saturated at a temperature of 250° C. The required operating pressure calculated from the existing pressure relationships of oil and water is about 50 atm. The best proportion of water to oil is 2 : 1. To make the

process economical, the heat transfer must be good. The unit is, therefore, similar to a heat exchanger. Nothing else is of great importance. The mixing is done in a flow mixer. In addition to pumps, only one preheater each, for oil and for water, a cooler for oil and water, and a catchpot for high and low temperatures are required. The water is circulated, the recovery of phenol is based on the increase in solubility of 23 grams/li, 35 gr/li at 250° and 12 gr/li at 25°.

Before crude oil can be used as a source of phenol, it must first be distilled with the separation into a low boiling fraction and a high boiling fraction, and the considerable neutral oil-content removed. While the process has been found satisfactory from the standpoint of operations, it leaves much to be desired with respect to the purity of the phenol. At 250° water is much less selective than at room temperature. Its ability to dissolve neutral oils increases with rising temperature relatively more strongly than of phenols.

The Sulfide Process

This process is based on the solubility of phenols in solutions of sodium hydrosulfide, with the evolution of hydrogen sulfide, and on the possibility of separating phenols from such solutions by treating with H_2S. Phenol containing oils again are extracted in a mixer, but in this case with a solution of sodium sulfide at about 100° (Fig. 2), the phenol-free oil is separated after settling in a separator, and the solution containing phenols is finally treated with gaseous H_2S at 50° in towers, in which the dissolved phenol separates as crude phenol. The alkali is regenerated during the gas treatment and is returned in the process. The hydrogen sulfide required is blown from a gasometer by means of a blower into the tower. The unabsorbed gas, after passing the tower is combined with the H_2S liberated during solution and is returned to the gasometer. The alkali as well as the gas form thus closed cycles. Only the losses of the gas and of the alkali, caused by leaks in the apparatus and the solubility in the products, must be replaced.

The crude phenol is practically free from neutral oils and merely requires being fractionated by distillation. It contains appreciably more lowboiling phenols than obtained with the same raw material in the previously described hot water process. This is due to the fact that the weakly alkaline sodium sulfide solution dissolves selectively the more acidic low-boiling phenols. Should the proportion of the low-boiling phenols in the solution to be extracted to the high boiling acid oils be 1 : 4, the crude phenol obtained by the sulfide extraction method will contain them in proportion of 1 : 2. The process therefore satisfies rather fully the requirements set up in the beginning. It possesses one fault, however, consisting in the use of the strongly toxic hydrogen sulfide in a concentrated form, as well as the corrosive action upon construction materials of the hot sulfide solution.

Counter-Current Sulfide Process

The process may be called a step-like counter-current sodium hydroxide extraction and is a development of the known method of extracting phenols at room temperature with a solution of sodium hydroxide, saturating the solutions of the phenolates with CO_2, which causes a separation of the dissolved phenols, and re-causticizing the sodium carbonate solution with lime. The regenerated lye may be then returned into the extraction process.

The later developments consisted in carrying out the extraction counter-currently. It has been found the extraction can preferably be carried out in a cascade counter-current, instead of an extraction column. Three steps were in most cases sufficient. (Fig 3). There is some saving in the sodium hydroxide consumption in comparison with a single step extraction, caused by the selective solubility of stronger-acid low-boiling phenols in sodium hydroxide, while the high boiling weaker acid oils remain undissolved. The selectivity is noticeable even among the low boiling phenols, in that carbolic acid is preferentially dissolved in comparison with the cresols and xylenols. The selective action of sodium hydroxide used in counter-current becomes particularly manifest when samples of the lye are withdrawn from every step of the extraction, acidified, and any phenol separated tested. It will be found that the individual samples have an entirely different composition. (Fig. 4).

If the different extraction steps be examined in the direction of flow of the lye, an exchange of the weaker acidic for the stronger acidic phenols will be observed, i.e. of high-boiling for the low-boiling phenols.

This process permits the production of phenols practically free from neutral oils, as long as the sodium hydroxide solution is not over 10% in strength. It is not recommended to use concentrated sodium hydroxide solutions because of the difficulties of caustisizing them. Phenol oils are absolutely free from neutral oils, are soluble to a clear solution in dilute alkalies, and the concentrated solution may be directly returned to the extraction process.

Should the oil freed from phenol, contain noticeable amounts of acid gases, such as CO_2 or H_2S they are better removed prior to the extraction, i.e. by passing some inert gas. Otherwise, being more strongly acid than the phenol, they would be preferentially extracted by the alkali, limiting the solvent power of the latter for the phenols. Moreover, the presence of sodium sulfide makes the caustification of the alkali solution more difficult.

The stepwise sodium hydroxide counter-current process is run at ordinary temperature and pressure. The energy consumption is limited to the relatively low requirements of the power for the pumps. There are no difficulties caused by corrosion. The extraction apparatus proper consists therefore of thin-walled sheet containers, and the usual centrifugal pumps, and is therefore inexpensive and requires but little iron. The as yet unsatisfactory step is the, at present, complicated and expensive regeneration of the carbonate solution by caustification with lime. Possibly the American suggestion (Pat. declaration K 147,049, to the Koppers Co.) to decompose the carbonate solution by electrolysis is a better solution of the problem of regeneration.

One must bear in mind when considering the effect of phenol removal that the further step in the use of tar or hydrogenation oils consists in hydrogenation in the vapor phase over a fixed bed catalyst. Any contamination of the product is therefore harmful, especially with non-volatile inorganic materials, because they have a tendency to settle on the walls of the equipment, which will lead to plugging up and to making the catalyst inactive. Oils from which phenols have been removed with alkali must be carefully freed from entrained alkali by settling or centrifuging. Occasionally these measures do not prove entirely sufficient, i.e. when the oils contain some inorganic salts in dissolved form, such as phenolates. The oils must be carefully washed with water in cases like that, or redistilled. The reduced amount of phenols in the oil may in itself affect hydrogenation. The hydrogen requirements of the phenol-free oils may be smaller than of the phenol-containing, because of the absence of the much hydrogen-consuming phenols. The heat of the reaction of the phenol-free oils is reduced, which at times may prove beneficial. The presence of little phenol may be beneficial for the action of some catalysts. There is also one disadvantage, which consists in that the phenol-free oils produce gasoline of somewhat lower antiknock value.

I shall discuss now the distillation of phenols obtained by one of the above processes. The crude oils contain, in addition to the valuable low-boiling phenols also some small amount of water, gasoline, high-boiling acid oils as well as traces of alkalies in oils prepared by leaching with sodium hydroxide. These materials are removed by distillation, when water and gasoline distil first, the low-boiling phenols with the main part of the distillate, while the high boiling organic acids and the alkalies remain in the residue. The principal fraction is a mixture of the different homologues and is used as such, or else broken down into carbolic acid, cresols and a mixture of xylenols by a repeated fractionating distillation. The separation of the low-boiling phenols may also be accomplished during the distillation of the crude oil. However, such a distillation requires well working distillation columns. The distillation is usually done in batches in a vacuum still, but the separation of the crude oil into the low-boiling, principal fraction and the residue may also be performed in continuous pipe stills. Strong corrosion is frequently met in phenol oil distillations, principally caused by the high-boiling residues. Corrosion occurs principally in that part of the apparatus, where the temperature as well as the velocities of flow are high. The corroding substance is probably not the alkali, but certain high-boiling strongly acid organic compounds. Thus, Kruber and Schmieden have found in coal tar (Ber. d.d.ch. Ges., fol. 72, 1939, 0. 653) that 4-oxy hydrinden and 7-oxy cumarone, both strongly acid compounds, when condensing with separation of hydrogen, form substances of high molecular weight, which cause much corrosion of the tar stills. An American work (Ind.Eng.Chem., News edition, vol. 16, p. 361) finds that low temperature tars, rather than coke oven tars, have a great corrosive action, attributed by them to substances they called "resinols". These or similar substances are probably also present in the residue from phenol oils in a more concentrated form, but at present practically nothing is known of the nature of these high boiling constituents of the phenol oils.

The quality of the phenols obtained from low temperature coking processes or from liquid phase hydrogenation oils is, as obtained, somewhat lower than from coke-oven tar and from gasoline refining, which is primarily due to their high content in sulfur-containing compounds. However, their purity is entirely satisfactory for a number of uses. For higher requirements relatively cheap and inexpensive refining processes have been developed which permit the production of permanent-color materials of good odor and in good yields from these products.

We may summarize by saying that the problem of production of phenols from low temperature coking oils and from liquid phase hydrogenation oils has in the main been solved, even though some questions remain unanswered. I have reference here to the corrosion problems mentioned above, also to the unknown nature of the high boiling acid oils, the clarification of which may give valuable information for their industrial application. It may be mentioned in this connection, that there still is no simple and accurate analytical methods for the determination and separation of the low-boiling homologues of phenol.

A number of schemes for the recovery of phenol oil from low temperature tars have already been developed. In actual operation there is at present only the de-phenolization of the light-tar distillates in the so-called Koppers process, a phenol recovery process for phenol-containing off waters, in which a solution is obtained only partially saturated with phenolate. A better utilization of this solution is achieved by extracting it with a phenol-containing light oil fraction, saturating it in this way completely with phenol.

The development has progressed further with liquid phase hydrogenation oils. An industrial installation has been in operation in Leuna for about 1 year, the results are so satisfactory, that the installation, originally built to make use of only a part of the oil produced, is to be replaced as soon as possible by a larger one, in which the total oil produced will be treated.

I hope to have shown, that we possess ways and means to obtain phenols in almost any amounts from hydrogenation oils, the production of which is tremendously great in Germany, and which will be still further increased to enable us to satisfy our requirements in liquid fuel. This large source of phenols is at present only partially utilized. We therefore are lucky to possess reserves of this important raw material, which will readily cover a further increase in phenol requirements.

Trld-
W. M. Sternberg

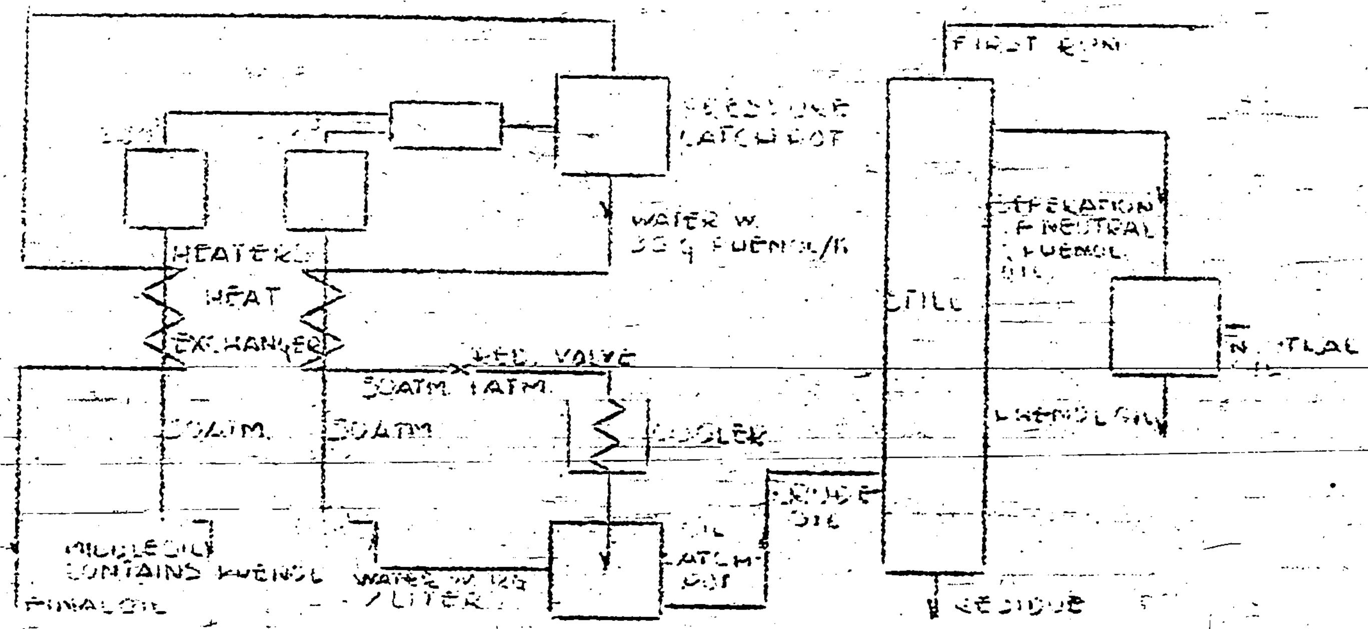


FIG. 1 PHENOL RECOVERY WITH HOT WATER.

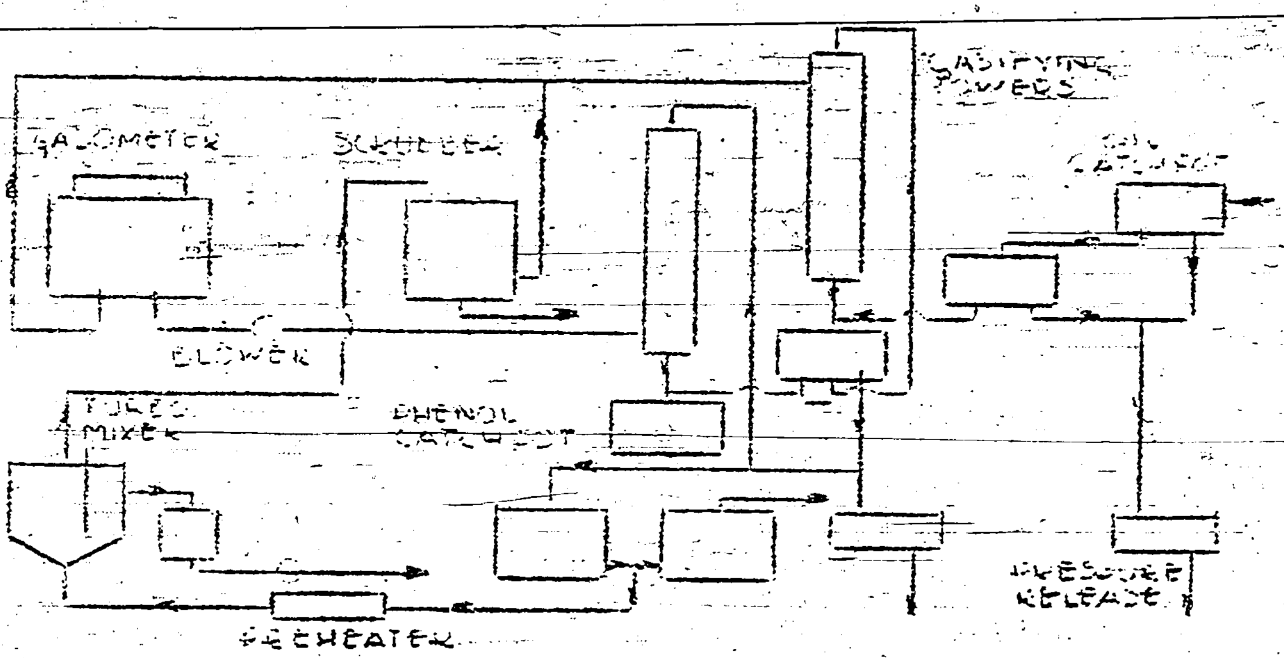


FIG. 2 PHENOL RECOVERY WITH [illegible]

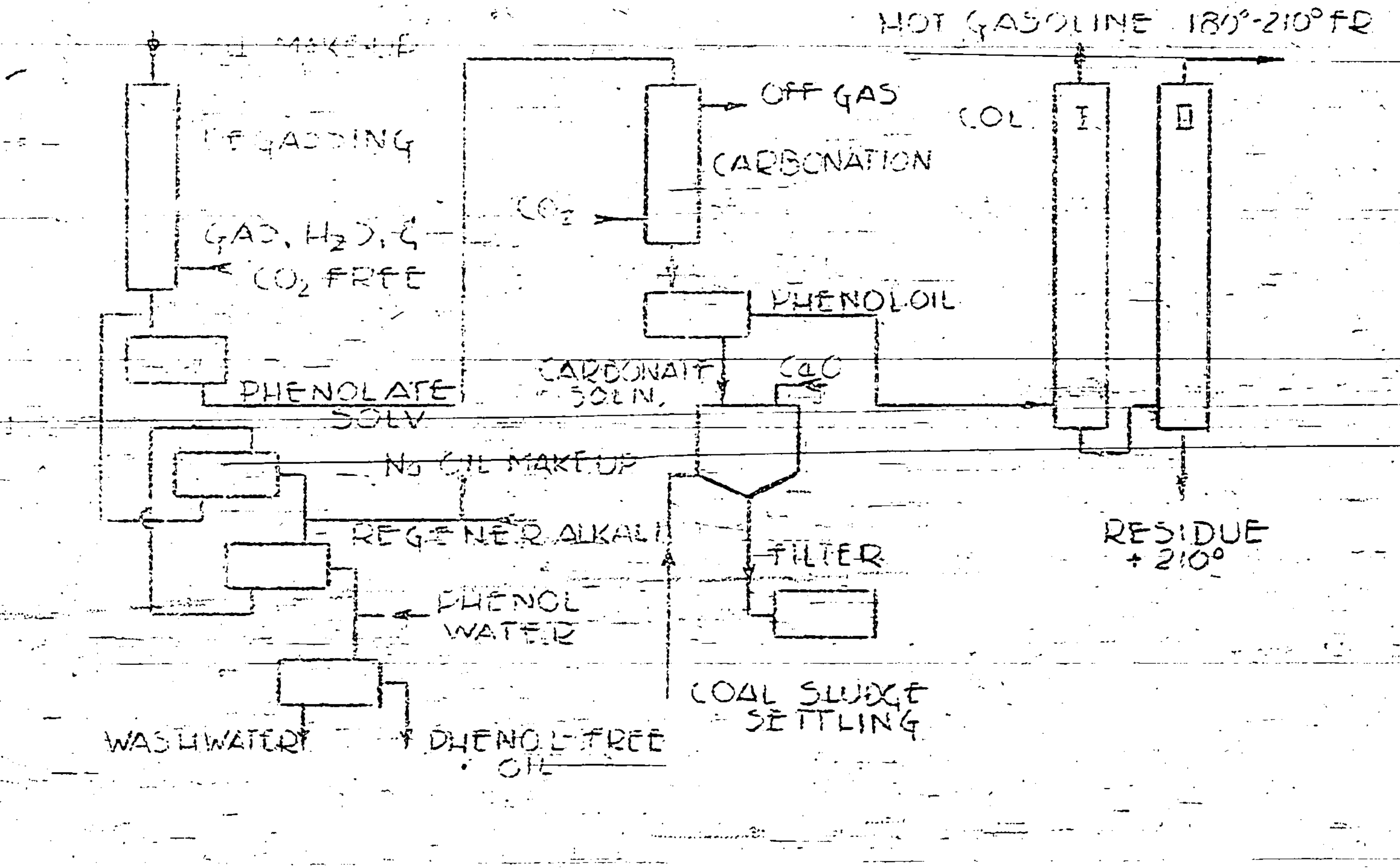


FIG. 3 STEPWISE PHENOL EXTRACTION WITH NaOH

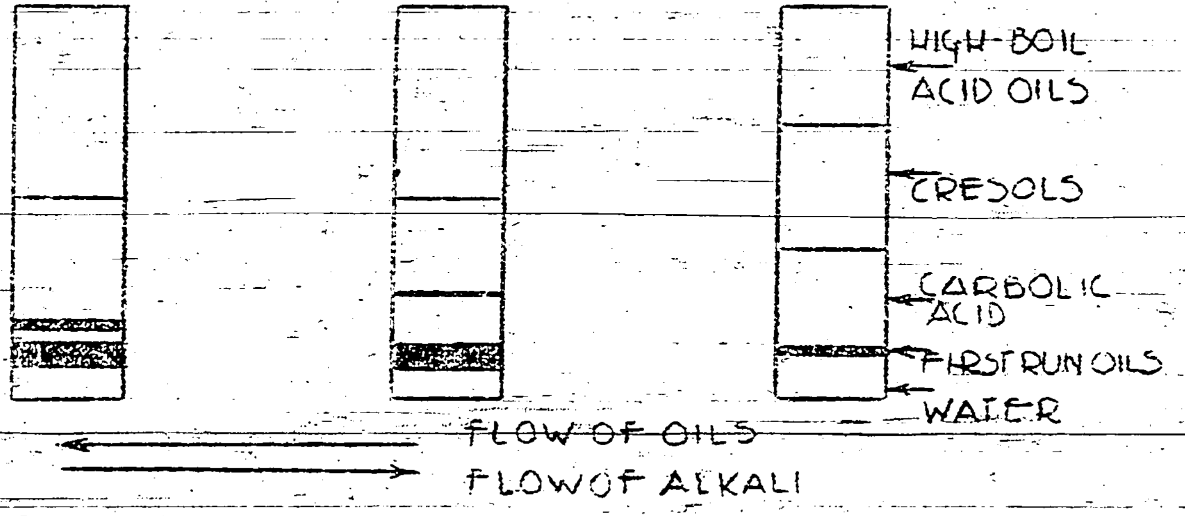


FIG. 4. COMPOSITION OF PHENOLS IN SEPERATE STEPS.

T.O.M. Reel 5
pp. 182-188
Bag #2747-21
Target #30/4.08

U.S. Bureau of Mines

Hydro Demon. Plant Div.

T-101
Trld/Braun/jw
9/18/46

Abstract of Report on Sludge Plant Operation

Gelsenberg Benzin A.G.-Dr.Hu.
Gelsenkirchen-Horst, 17 July 1940

The processing of the hydrogenation residue, consisting of a mixture of oil, undigested coal, and ash, is often considered a necessary evil, and does, therefore, not receive the care it demands. The fact is often overlooked, that the efficiency of a hydrogenation plant is largely dependent upon an intelligent processing of the residue. A poor treatment of the residue immediately leads to great losses. Let us consider that with a gasoline yield of 300,000 T/ann, 540,000 T. of sludge is produced, corresponding to 410,000 T. of oil. At RM. 80/T of oil the value of the oil contained in the residue amounts to RM 32,000,000. A loss of only 0.1%, therefore, means a loss of RM. 32,000/ann. It must not be overlooked, also, that all these products are very unstable substances, which easily decompose on improper treatment, particularly their exposure to air.

Therefore, all experiences, to date, were considered in the construction of our plant. Residue processing plants were already in operation at Scholven and Leuna. The experiences at Leuna could be used only in a very restricted sense, because brown coal sludge is of a chemically different composition and behaves differently in processing. Wide comparison, however, could be made with Scholven, although it was to be expected that our sludge would behave more favorably because of the higher pressure in the liquid phase, 700 atm. compared to 325 atm. Above all, we were to prevent the residue processing, particularly in the kiln department (Schwelerei), from becoming a production bottle-neck, as is often the case at Scholven. A centrifuge department with 60 continuously operating Laval-Centrifuges and a kiln department with 12 ball kilns was provided for our plant.

No basic changes were to be expected in the centrifuge department, because in so highly developed and complicated machines as the centrifuges changes can only be made in close cooperation with the maker. He, however, turned down our request for immediate cooperation because of the pressure of other contracts and because of too high costs. On the other hand, it would have meant too much of a risk to use other centrifuges. However, we have since then induced this firm to make certain changes. Above all, we are trying to increase the load on the lower section of the centrifuge by changes in the product feed. We are also trying to obtain a better separation by increasing the speed of rotation. The mean particle size of the centrifuge solids is - 1.5 micron, which indicates the enormous difficulty in separating such fine particles, considering the fact that the difference in specific gravity between them and oil is small and that all the particles are completely covered with oil.

Certain changes were made on the auxiliary equipment. We have replaced the scale containers by Eckardt meters. After making a correction they have proved to be satisfactory and save space and capital investment. The several storage and mixing vessels have been considerably enlarged, whereby we obtain a more uniform centrifuge mixture, the most important requirement for satisfactory centrifuge operation besides a constant pressure, and can more readily overcome smaller disturbances. Furthermore, we have subdivided the individual lubricating oil circulating lines to the centrifuges, so that the cause of any lubricating trouble may be more easily located.

The centrifuges were placed into service on the 2 August 1939 and 150173 tons of centrifuge mixture have been processed to the 1 July 1940. At present 15 machines are in continuous operation. As was to be expected, an increase to 12% in the solids in the centrifuge or pasting oils occurred, due to very fine particles. At first, the solids content of the centrifuge oil was only 7-8%. In April 1940 we had a sudden increase in the use of lubricating oil when the centrifuge mixture temperature was increased to 175° C., which, however, was corrected by a complete overhauling of the individual machines. Frequent disturbances occurred in the centrifuge department due to clogging of the nozzles and centrifuge screens, although no changes were made in the pressure. Nor could a change in the product be proved analytically. We are working on the clarification of these incidents. Similar phenomena frequently occur also in starting up a new stall. It was a surprise to find that the wear of the centrifuges is greater here than in Scholven. One cause of this is the strongly abrasive effect of the pyrites contained in the residue. This was particularly noticeable when we received hardened steel scraper knives instead of such of Widia by mistake. There were completely ground off after 4 days. Even the Widia knives showed a certain wear after a longer period of operation. We were likewise forced to build up the spirals of the centrifuge screens with welded Ticit. The best load on the centrifuges has been shown to be 3.2 T/h mixture containing 16.5% solids. By using smaller nozzles (1.7 mm dia.) we increased the solids content of the centrifuge residue to 40% and reduced the proportion of centrifuge oil to centrifuge residue from 5:1 to 3:1. Apart from the changes in the centrifuges, changes in operation may also be expected by the use of other thinning oils or ~~to~~ double centrifuging. The expectation to replace the centrifuges with filters in the near future may be frustrated by the viscosity of the products and the fine particles, besides the great cost.

The most important task in centrifuging is to keep the oil losses to a minimum. Scholven had constant difficulties in trying to avoid the baking on of the product in the kilns and produce an oil-free discharge, with consequent considerable oil losses. We were less bothered by these snags, possibly because of the higher pressure of 700 atm. in the liquid phase. But even here much care was required to keep operations trouble-free.

We have found out that a satisfactory kiln operation depends on many details. Among others, the entry of the feed into the kiln is of particular importance. Minor changes in it will cause trouble. In our case, the injection tube projects 20 mm into the kiln and the product is directed against the walls of the drum as a fine spray in a direction opposite to its rotation. Shortly ahead of the discharge nozzle high pressure steam is introduced for dispersion. The nozzle itself has been made slit-shaped and the injection tube was reinforced by ribs to prevent distortion. The outer holes in the separating wall, as used at Scholven, were enlarged and made slit-shaped. We also provide the best possible insulation of the kiln steam lines to insure the entry of steam at a temperature at least as high as the kiln temperature. The Schilde burners used at Scholven have been replaced by Selas burners, which permit a more uniform heating of the kiln drum because of their construction features. We have lowered the kiln temperature from 30 mv to 27 mv by which we spare not only the product but also the kiln drum. As a safety measure for the preheater in case of trouble we have provided a rinsing oil line. Thermo-technically the kiln works as expected but the heating of the preheater could still be done more uniformly.

To increase the life of the kilns and reduce the cost of repairs, we have provided a better heat-resistant material for the kiln drums. On 10 drums we use 124 and on 2 drums TH31R. To protect the most highly stressed kiln part, immediately behind the separating wall, we have reinforced these parts with welded-on metal. These welds have the advantage of serving as a catch for the milling elements as well as a protection for the kiln. Scholven has had good results with a cross-shaped milling element. But the wear on the kilns or the milling elements was too great, depending upon the corresponding hardness. We adopted this shape of the elements but chose different kinds of steels to determine the most suitable material. The milling elements furnished by Krupp have proved very satisfactory compared to those furnished by Gevelsberg. It must not be overlooked, however, that the hole in the center of the Gevelsberg elements was enlarged, which may have caused the greater wear. Elements of manganese steel are still being tried out. Independently of these, we tried another experiment and used cast hollow balls. With these the kilns worked even better, presumably due to their greater freedom of movement and the greater space taken up in the kiln for equal weight. The kiln wall is also better preserved by these elements. However, these hollow balls showed a much greater wear, 84 operating days. We, therefore, are trying out a new material, Sius, which is supposed to have greater impact strength.

A further important question was, if it was proper to discharge the residue wet or dry, because it was largely suspected that the wet discharge was the main cause of the high oil content of the kiln residue. We, therefore, have provided a double discharge on 4 kilns, but achieved such good results with the wet discharge that we eliminated the dry discharge, because it is much more troublesome. The oil content of our kiln residue is approximately 1%. We have reinforced the discharge trough and scraper. Due to this, we have had no trouble with the discharge equipment. For loading the residue we have provided a belt conveyor but may possibly shift to chute loading. The great wear may be partly explained by the fact that while operating only one kiln in winter the belts were covered with ice causing breaks in the material. A clarification plant for the waste water must be installed without fail, because, due to the high dust content of the waste water in the traps, the sewers have been repeatedly clogged up.

In the condensation we have joined groups of 4 kilns behind the precooler. A part of the circulating phenol water is used for cooling the rinsing oil to prevent the formation of boiler scale at the high temperature. The automatic regulators have proved very satisfactory. The kiln gas is fed into the fuel gas line by a blower. All pressure and temperature gauges and the most important valves have been mounted on one control panel for groups of 2 kilns each.

The installation was put into operation on the 8 August 1939 and was intermittently operated to January 1940 because of lack of product. To July 1940 a total of 23553 tons of centrifuge residue was processed. We have increased the kiln production from 2.6 T/h in Scholven to 3.2 T/h. According to our latest experiments the production may be increased to at least 3.5 T/h. An experiment to add hot-oil-let-down to the centrifuge residue showed that the kiln yield remains practically the same with an addition of up to 10%. However, the kiln must be watched very carefully with such a mixture. The present oil yield is 78%. The expectation to burn the kiln residue in the boilers met with great difficulties, due to the low melting point of the ash. We, therefore, have already tried to utilize the kiln residue in a sintering plant, with satisfactory results.

Two tanks were damaged in the intermediate tank storage due to the explosive evaporation of water. In one case this was caused by a leak in the cooling jacket of the circulating pump. The artificial weakening of the cover seams agreed upon with the Industrial Safety Commission probably protected the tank jacket but could not prevent a deformation of the cover. Bursting disks are, therefore, built into the tank covers for safety, and the temperature in all tanks held below 100° C.

In conclusion, it may be said that the residue processing operations have met the demands made on them.

TOM Reel 77
Pp. 32-33

U. S. Bureau of Mines
Hydro. Demon. Plant Div.

T-102

DISTILLATION OF COAL HOLD

Pölitz, November 27, 1943

The coal HOLD has been distilled since beginning of July, 1943. The distillation could be carried out in practice, with 42.9% distillate produced. The softening point of the residue was 78.7° ave. A comparison of losses of pure oil showed in centrifuging of the HOLD and the kilning operations with vacuum distillation, see below, showed a loss of 4.2% in centrifuging and 15.7% in distillation, basing the computations in the latter case on laboratory results of kilning operations. We have found a 63% yield when kilning the residue without catalyst, 67.5% yield in the presence of catalyst, if the oil produced is calculated to that worked. When computing the pure oil produced in centrifuging and kilning, the corresponding daily production figures and analytical results were used. In the latter case, the boiling point curve of the centrifuged pure oil has not been considered in the computation of the thinning oil, because the boiling point curve of the centrifuged pure oil was not any different, which leads to the conclusion that the two are present in the same proportion as the total oil.

RESULTS OF ANALYSIS FROM UNIT 276

Product:	Coal HOLD	Distillate	Residue
Solids	21.2%	0.2%	33.9%
Specific gravity	1.135/180°	1.033/50°	1.280/100°
Ash in solids	54.8%	- -	46.1%
Solidifying point	- -	10°	- -
Softening point	- -	- -	78.7°
Kindling temp.	- -	148°	- -
Engler Viscosity	- -	30.4°	130° 230°
			140° 129°
			150° 49°

	Solid-free distillate		Solid-free residue
Spec. Grav.	1.023/50°		1.101/100°
Asphalt (15.35 in HOLD)	1.5%		29.1%
Boiling point curve:	760 mm	11 mm	11 mm
10%	289°	150°	258°
20%	316	175	290
30%	340	195	319
40%	358	209	- -
50%	- -	220	- -

Computations for comparison:

Case A: Distillation process:

Input:
246 m^3 coal HOLD = 279.9 te, 58.7 te solids, 32.3 te ash,
33.9 te asphalt

Yield:
Distillate, 116.3 m^3 = 120.1 te, 0.3 te solids, 0.28 te ash,
30.7 te asphalt

Residue, 129.7 m^3 = 159.6 te, with 54.1 te solids, 24.9 te ash,
30.7 te asphalt.

The residue was kilned with a 63.0% yield of pure oil (in the lab.)
accordingly, the oil in the residue was 159.6 te residue
54.1 te solids
105.5 te oil, of which
66.5 te are recovered in kilning.

Pure oil balance: Pure oil introduced 221.0 te
Pure oil recovered 186.3 te
Loss 34.7 = 15.7%

Case B: Centrifuging and kilning:

Input as above,

Produced 194.8 m^3 centrifuge oil with 27.5% solids, 27.4% asphalt.
51.2 m^3 centrifuge residue = 66.4 te, 25.2 te solids,
6.4 te asphalt.

66.4 te sent to the kiln, with no catalyst, yielded 31.7 te pure oil.

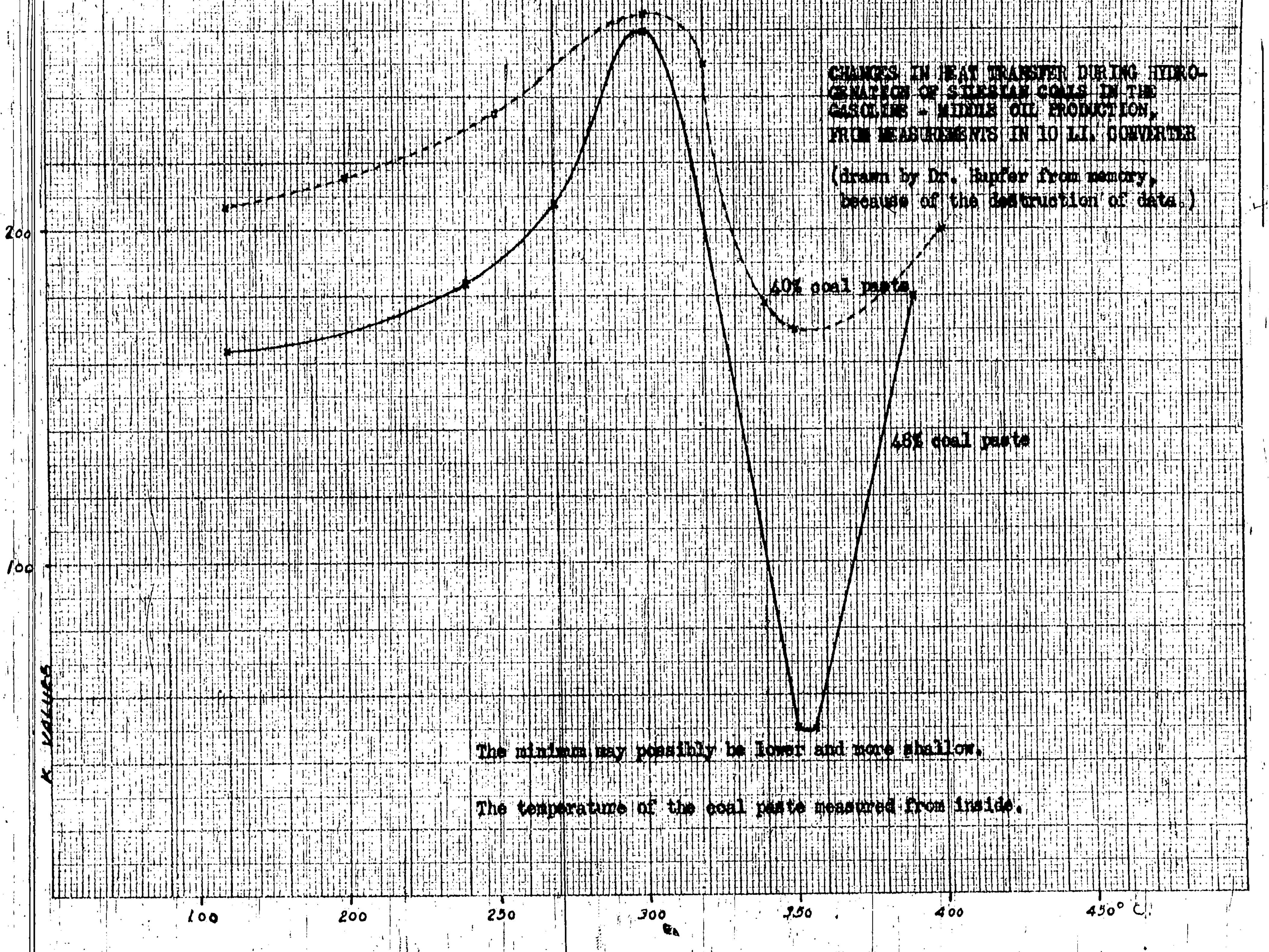
Pure oil introduced: 227.0 te
" " recovered: 185.8 te
31.7 te from centrifuge residue
Total 217.5 te
19.5 te = 4.2%

Sternberg/jw

Frame 108
T103 – T.O.M Reel 145,

CHANGES IN HEAT TRANSFER DURING HYDROGENATION OF SILESIAN COALS IN THE GASOLINE - MIDDLE OIL PRODUCTION, FROM MEASUREMENTS IN 10 LI. CONVERTER

(drawn by Dr. Hupfer from memory, because of the destruction of data.)



The minimum may possibly be lower and more shallow.

The temperature of the coal paste measured from inside.