CO REMOVAL UNIT AT OPPAU

The raw gas for the catalytic processes is freed from CO_2 at 368 psi., compressed to about 3235 psi. and passed to the final purification stage consisting of the CO removal unit. The CO removal for the hydrogen-nitrogen gas ("Sti-gas") for the NH_3 synthesis and the hydrogen ("C-gas" or "Hy-gas") for the hydrogenation is carried out separately.

Hydrogen-nitrogen.

The gas (3235 psi.) is passed through empty or coke filled separators in order to remove oil and water. The CO removal unit consists of the following equipment:

for hydrogen-nitrogen

5	copper solution	wash towers,	2.6 ft.	diam.,	39.4 ft. length
7-8	"	" "	" ,	1.6 ft. " ,	39.4 ft. "
4	NH_3	" "	" ,	1.6 ft. " ,	39.4 ft. "

for hydrogen

1-2	copper solution	wash towers,	1.6 ft.	diam.,	39.4 ft. length
1	NaOH	" "	" ,	1.6 ft. " ,	39.4 ft. "

The connections for the gas and solution lines have a diameter of 2.28 in. for the 2.6 ft. tower, 1.77 in. for the 1.6 ft. Cu solution tower and 3.54 in. for the 1.6 ft. ammonia tower.

Gas flow is regulated on the feed gas side which results in a pressure drop of 59-88 psi.; if instead the flow of purified gas would be regulated, the pressure drop would be 118-177 psi., since the flow would have to be throttled more strongly because pressure variations in the ammonia plant are noticeable at the wash towers resulting in a change in the distribution of the copper solution according to the flow conditions of each tower.

The gas capacity for the 1.6 ft. towers is 106,000-159,000 cu.ft./hr. and for the 2.6 ft. towers 353,000-495,000 cu.ft./hr. The towers are packed with iron rolls of 1.77 in. or 1.97 in. length. After the gas has been washed, it passes through a solution separator and a safety bottle. Metering of the gas is carried out after purification to avoid corrosion and clogging of the orifice meters.

Oxygen is removed by the copper solution to a large extent; the raw hydrogen-nitrogen gas contains 0.02-0.03% O_2 whereas the purified gas contains only 0.0006-0.0008% O_2. The CO concentration decreases from 3.6-5.9% in the raw gas to 0.01-0.02% in the purified gas.

Hydrogen.

The same principles apply as for the hydrogen-nitrogen gas mixture. The capacity of the wash towers (1.6 ft. diam., 39.4 ft. length) amounts to 70,600-106,000 cu.ft./hour. The composition of the raw hydrogen gas is about as follows:

1.5 - 2% CO_2
6 - 7% CO
89% H_2
1.2% N_2

After passing through the copper solution tower, the gas is freed from CO_2 in a caustic washer (1.6 ft. diam., 39.4 ft. length). The gas is subsequently dried with silica gel at high pressure. The composition of the completely purified hydrogen is as follows:

98% H_2
0.01% CO
0.2% CH_4
1.6% N_2
85-142 mg. NH_3/1000 cu.ft.

Prior to the treatment with silica gel, the gas contains 850-1420 mg. NH_3/1000 cu.ft., originating from the copper solution.

A CO concentration of 0.1% CO is satisfactory for normal hydrogenation purposes.

Copper Solution.

Dr. Krauch found that copper salt solutions of weak acids (formic acid, acetic acid, carbonic acid) do not corrode iron. For commercial purposes, ammoniacal copper carbonate solution has been selected; $(Cu\langle^{NH_3}_{NH_3})_2CO_3$. The complex $(Cu\langle^{NH_3}_{NH_3})$ acts as a monovalent positive ion and it can add CO, since only 2 of the possible 4 coordinate valences are used up. Two-valent Cu compounds do not add CO.

The fresh solution contains in 1 liter solution:

5	mols	NH_3	= 8.6% by vol. NH_3
2.8	"	CO_2	= 11.1% " " CO_2
0.2	"	Cu^{++}	=
1.4	"	Cu^{+}	= 10.2% " " Cu

The copper is present as carbonate and the solution contains an excess of NH_3 and CO_2.

In spite of the fact that it does not add CO, the two-valent copper complex is necessary to prevent formation of metallic copper.

$$2\ Cu^{+} \rightleftharpoons Cu_{metal} + Cu^{++}$$
$$Cu_2{}^{+}O \rightleftharpoons Cu_{metal} + Cu^{++}O$$
(complex) (complex)

The reactions with dissolved CO can be represented as follows:

increase in pressure, cold

(1) $(Cu\langle^{NH_3}_{NH_3})_2\ CO_3 + CO \rightleftharpoons (Cu\langle^{NH_3}_{NH_3})_2\ CO_3$

decrease in pressure, heat — CO

During this reaction the solution heats up from 25°C to 35°C (77°F - 95°F).

(2) The excess of NH_3 and CO_2 reacts as follows:

$$2NH_3 + H_2O + CO_2 \underset{\text{vacuum, heat}}{\overset{\text{pressure, heat}}{\rightleftharpoons}} (NH_4)_2\ CO_3$$

$$NH_3 + H_2O + CO_2 \rightleftharpoons (NH_4)H\ CO_3$$

(3) The oxygen present in the gas oxidizes the cuprous salt to the cupric salt:

$$2\ Cu_2^{++}O + O_2 = 4\ Cu^{++}O$$
(complex) (complex)

(4) In the wash tower and, to a larger extent, in the pressure reducing vessel at 4.3 psig. and 122°F (50°C) the following reaction takes place:

$$2\ Cu^{++}O + CO \longrightarrow Cu_2^{++}O + CO_2$$

(5) The formation of metallic copper

$$Cu_2^{++}O + CO = 2\ Cu_{metal} + CO_2$$

is avoided by the addition of air to the solution after cooling. This corresponds to the reaction shown under (3) and restores the equilibrium between mono- and two-valent copper.

Equipment and Operating Practice.

The solution is injected at the top of the tower using a piston pump operating against the gas pressure of 3235 psi. The liquid level in the tower is controlled by means of high-pressure gauge glasses and an automatic alarm indicates lowering of the level below a predetermined height.

The solution capacity of the tower is as follows:

for the 2.6 ft. towers - 13,200 - 17,200 gals./hour
for the 1.6 ft. towers - 4,760 - 6,080 gals./hour

The average solution requirements for 1000 cu.ft. of hydrogen-nitrogen gas are 34 gals. of solution for 2.6 ft. towers and 38 gals. of solution for 1.6 ft. towers.

70-75% of the fresh solution required is brought to the necessary pressure by means of pressure recovery engines, the remainder by twin-piston pumps. There are available

2 pressure recovery engines, 39,600 gals/hour each
6 pressure pumps, 9,600-10,600 gals/hour each

The total quantity of circulating solution amounts to about 95,000 gals. The temperature of the fresh solution should not be lower than 57°F. (14°C) since otherwise ammonium bicarbonate separates out. On the average a temperature of 73-77°F (23-25°C) is used; higher temperatures should be avoided since otherwise solution consumption would be increased. The solution is regenerated by releasing the pressure, heating and evacuating. Blowing with inert gases as practiced in some plants to save evacuation has not been found satisfactory.

In general, the copper solution is brought to a pressure of about 4.4 - 5.9 psig. so that the gas taken up is mostly released in this stage. Slight heating (113-122°F, 45-50°C) helps the release of gas; the residual gas, mainly CO_2, is removed by evacuation of the solution. After removal of NH_3 the released gas is added to the gas entering the hydrogen converter. The distribution and composition of the released gas is approximately as follows:

	Gas Yield, (% of total gas recovered)	Composition of Gas % CO	% CO_2	% H_2/N_2
Pressure released to 4.4 psig.	about 40%	85-90	8-13	Remainder
Heating to 122°F (50°C)	" 35%	70-75	15-20	"
Evacuation	" 25%	20-30	65-75	"

At present Oppau produces about 5,300,000-6,350,000 cu.ft. per day of gas which is recycled to the hydrogen converters; the gas has the following composition:

50% CO
23% CO_2
20% H_2*)
7% N_2*)

*)At low pressures the solubility ratio of H_2 and N_2 in the solution is 0.0084:0.0058.

At Oppau 0.425-0.567 Kw.-hr. (1450-1935 B.t.u.) (high and low pressure steam, electric power) are needed for 1000 cu. ft. of pure gas.

Plant Control.

The quantity of the gases is controlled by orifice meters and ring balances, the density is automatically recorded and all pressure recorders are equipped with optical and acoustic alarms.

The O_2 content of the copper solution is determined by the thermocolorimeter of Ernst. Light of the same intensity passes through a selected blue filter and through a cell through which fresh solution flows continuously; the light then falls on 2 thermopiles. When the O_2 content of the solution increases, i.e. when the content of cupric ion increases, the blue solution becomes darker and the millivoltmeter connected to the thermopiles gives a corresponding indication. A CO recorder (Pfundt) indicates the CO concentration in the purified hydrogen-nitrogen gas. In this apparatus the CO in the gas is burned to CO_2 in a combustion tube containing I_2O_5. Following the absorption of the liberated I_2 by means of silver wool at about 250°C (482°F) the CO_2 is absorbed in aqueous $BaCO_3$ solution. Soluble barium bicarbonate is formed which changes the conductivity of the contents of the absorption vessel; the changes in conductivity are automatically recorded with an accuracy of 0.001% CO.

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